Rapid Thermal Processing of Silicon Solar Cells -Passivation and Diffusion

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То

my grandmother for faith

my parents for setting me on the path toward my dream and encouragement

my elder sister for her love, patience and sacrifice

my other sister and brothers for their love and support

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1 Introduction

Today the demand for energy is increasing steadily and rapidly. However, the conventional sources of energy such as fossil and nuclear fuels are limited. Moreover, the associated negative effects on the environment such as the green house effect, the hole in the ozone layer, acid rain and smog can no longer be neglected. Therefore, the development of renewable energy is necessary.

The conversion of sunlight into electricity using photovoltaics (PV) is a very attractive way to produce renewable energy. Photovoltaic systems are environment friendly, use abundant material (especially in the case of silicon solar cells), require no fuel, can be used everywhere, are reliable, almost maintenance-free, flexible in scale from miliwatt to megawatt and aesthetically pleasing. In spite of these various advantages, PV competes with the conventional energy since the production cost of PV electricity is still higher compared to the traditional methods. Therefore, the aim of most of the research is to increase the competitiveness of photovoltaics. The cost of industrial solar cell modules is at present around 3.5 Euro/W_p. This cost can be reduced to near or below 1 Euro/W_p, which is the present target price [1] by

- High volume of production (\geq 500 MW_p/year)
- Reduced material costs
- High throughput processing
- Improved efficiencies

In this thesis, to contribute to the achievement of these goals, cost effective Czochralski (Cz) crystalline silicon materials and process technologies such as rapid thermal processing, plasmaenhanced chemical vapor deposition (PECVD) and spin-on dopants are investigated.

Cz silicon materials represent 40 % in the world-wide solar cell production and are three times cheaper than FZ wafers. Also, Cz silicon materials can be treated at high temperatures and can yield high efficiencies well above 20 % [2].

Rapid thermal processing (RTP) uses tungsten-halogen lamps in the range of ultraviolet and infrared wavelengths as heating sources. RTP is a promising technique to replace the classical thermal process which only uses infrared radiation. RTP can achieve high throughputs due to short annealing times of a few seconds and high ramping rates of over 100 °C/s, and opens the possibility of simultaneous diffusion of both sides of a silicon wafer. In addition, the low thermal budget, and the low power consumption are some of the attractive properties of RTP.

Surface passivation is crucial for high-efficiency solar cells. Silicon nitride (SiN_x) deposited by PECVD is a very attractive technique to fabricate passivation and antireflection layers. The deposition at low temperatures, the high deposition rate, the very good passivation quality and the adjustable refractive index are the reasons, why SiN_x layers are increasingly used for solar cells.

Using spin-on dopants, allows to adjust easily the doping concentration and junction depth of the emitter. Spin-on dopants also give the possibility of simultaneous diffusion. Furthermore, spin-on dopants used in conjunction with RTP only require low thermal budgets.

This thesis is organized in the following way:

In chapter 2 the device physics of solar cells is presented. From the fundamental device equations, a p-n junction cell is described. From this simple model the ideal form of the dark and illuminated characteristics of silicon solar cells are obtained.

In chapter 3 the basic recombination mechanisms in bulk and at the silicon surface are described. The photoconductance decay method used in this thesis to measure the effective lifetime is presented. The method for measuring the injection level dependence of the effective lifetime is discussed.

In chapter 4 rapid thermal processing is introduced. The general properties and mechanisms of RTP are compared to those of the classical conventional furnace. The different methods for the temperature measurement are presented and the problems associated with such measurements in RTP are discussed in detail.

In chapter 5 the fundamentals of the Cz-metastable defects are introduced. Various models and theories for the Cz-metastable defect are also discussed. The effects of RTP-process parameters on the stable lifetime after degradation are systematically investigated using the 'design of experiment (DOE)' method. The influence of two sequent high temperature processes for diffusion and for oxidation in the fabrication of solar cells on the stable lifetime is investigated. Finally, the optimized and non-optimized processes are applied to the fabrication of solar cells.

In chapter 6 the fundamental properties of silicon oxides (SiO₂) fabricated using classical thermal oxidation and rapid thermal oxidation and of silicon nitrides (SiN_x) using PECVD are discussed. The surface passivation qualities of a single layer and a double layer SiO₂/SiN_x stack composed of the thermally grown SiO₂ and SiN_x by PECVD are investigated on pure p-type and on emitters. Furthermore, silicon solar cells passivated with such SiO₂/SiN_x stacks are also analyzed.

In chapter 7 a cost-effective diffusion with spin-on dopants (SODs) is presented. Various phosphorus SODs, boron SODs and mixed p-type SODs are used in this work. The electric properties and the doping concentrations as a function of depth are investigated. Phosphorus SODs for emitters and boron SODs for back surface fields are used for the fabrication of silicon solar cells.

2 Device physics of silicon solar cells

Semiconductor solar cells are based in most cases on a simple p-n junction. In this chapter using the basic equations, especially, the current-density and continuity equation, the minority carrier transport mechanism and current density of the p-n junction in the cell are described in the dark and under illumination. From these results the performance parameters of a solar cell are derived and characterized.

2.1 The p-n junction model

2.1.1 Basic equations

The basic equations describe the behavior of charge carriers in semiconductors under the influence of an electric field and/or light, both cause deviations from thermal equilibrium conditions. In the following they are simplified to one dimension particular to the p-n junction.

A. Poisson's equation

The poisson's equation correlates the gradient of the electric field E with the space charge density ρ . In one dimension it is given by

$$-\frac{d^2\varphi}{dx^2} = \frac{dE}{dx} = \frac{\rho}{\varepsilon \varepsilon_o}$$
(2.1)

where ϕ is the electric potential, ϵ_o is the permittivity of free space, and ϵ is the material's permittivity.

When we consider the contributions to the charge density in a semiconductor, electrons in the conduction band contribute a negative charge, whereas holes in the valence band lead to a positive charge. If a donor atom N_D is ionized a positive charge is obtained while an ionized acceptor atom N_A results in a negative charge. Hence,

$$\frac{dE}{dx} = \frac{q}{\varepsilon \varepsilon_o} \left(p - n + N_D^+ - N_A^- \right)$$
(2.2)

where p and n are the densities of holes and electrons, and $N_D{}^+$ and $N_A{}^-$ are the densities of ionized donors and acceptors.

B. Current-density equations

Electrons and holes can contribute to current flow by drift and diffusion processes. Therefore, the total electron current density I_n and the hole current density I_p become

$$I_n = q \left(n \mu_n E + D_n \frac{dn}{dx} \right)$$
(2.3)

$$I_p = q \left(p \mu_p E - D_p \frac{dp}{dx} \right) \tag{2.4}$$

The first term in Eq. (2.3) and (2.4) describes the drift current driven by the electric field E and the second term is the diffusion current driven by a concentration gradient. The mobilities $\mu_{n/p}$ and diffusion constants $D_{n/p}$ are related through the Einstein relationships ($D_n = (kT/q)/\mu_n$; $D_p = (kT/q)/\mu_p$).

C. Continuity equations

The gradient of the current density I is related to the recombination and generation rates of charge carriers by the continuity equation. The electron and hole continuity equation are given by

$$\frac{1}{q}\frac{dI_n(x)}{dx} = U - G \tag{2.5}$$

$$\frac{1}{q}\frac{dI_p(x)}{dx} = -(U-G) \tag{2.6}$$

where G is the net generation rate and U is the net recombination rate by external processes such as illumination by light.

2.1.2 The p-n junction at equilibrium

If isolated pieces of a n-type and a p-type semiconductor are brought together in a conceptual experiment, the Fermi levels of n-type and p-type become identical. It would be expected that electrons and hole will flow from the region of high concentration to the region of low concentration. This causes band bending of the conduction band-edge energy E_c and the valence band energy E_v . Electrons leaving the n-type part induce a positively charged region. Similarly, holes leaving the p-type side lead to a negatively charged region. The resulting electric field produces a drift forces that opposes the diffusion force (see Figure 2.1 (left)). The diffusion and drift forces are equal at equilibrium conditions.

In the quasi-neutral regions that lie outside the space-charge region the donor and acceptor charges are compensated by electrons and holes, so the space-charge density is zero. The majority carriers are the dominant carrier type ($n_{no} >> p_{no}$ and $p_{po} >> n_{po}$) (see Figure 2.1 (right)) and their concentrations n_{no} and p_{po} in the quasi-neutral regions at room temperature are given by the density of ionized dopants



Figure 2.1 (left) Energy band bending of the p-n junction and (right) the electron and hole concentrations at thermal equilibrium.

$$n_{no} \approx N_D, \quad p_{Do} \approx N_A$$
 (2.7)

At thermal equilibrium the free carrier concentration of electrons and holes are given by the Boltzmann expression

$$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right), \qquad p = N_v \exp\left(-\frac{E_F - E_v}{kT}\right)$$
(2.8)

where N_c and N_v are the effective densities of states of the conduction band and of the valence band, respectively. The intrinsic carrier concentration, n_i can be described as

$$n_i^2 = n p = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$
(2.9)

Where E_g is the energy band gap (E_c-E_v) between the conduction and valence band. The band distance $qV_D = E_g-E_1-E_2$ and the diffusion voltage V_D is described with n_i as

$$V_D = \frac{kT}{q} \ln\left(\frac{N_D N_A}{n_i^2}\right)$$
(2.10)

For example, if $N_D = N_A = 10^{16} \text{ cm}^{-3}$, the diffusion voltage is 0.69 eV at room temperature in silicon while if $N_A = 10^{16} \text{ cm}^{-3}$ and $N_D = 10^{20} \text{ cm}^{-3}$ comparable to the real solar cells, V_D is 0.93 V at room temperature in silicon.

The space-charge region is depleted of mobile charge carriers (Figure 2.1 (left)). Therefore, the space-charge density is given by

$$\rho(x) = -qN_A \qquad (-W_p \le x \le 0) \qquad (2.11)$$

$$\rho(x) = qN_D \qquad (0 \le x \le W_n) \qquad (2.12)$$

2.1.3 The p-n junction at non-equilibrium

The p-n junction is not at equilibrium if an voltage V is applied over the junction. The minority carrier concentration is changed due to an applied voltage and then the net carrier density at the edge of the depletion region is not same as shown in Figure 2.2. The recombination rate of minority carriers is then proportional to the excess minority carrier concentration Δn on the p side and Δp on the n side.

From the current density equation Eq. (2.3) and (2.4) the current density I_p on the n-type side and I_n on the p-type quasi-neutral region is:

$$I_n = qD_n \frac{dn}{dx} \quad , \qquad \qquad I_p = -qD_p \frac{dp}{dx} \tag{2.13}$$

The minority carrier recombination rate U is given by

$$U = \frac{\Delta n}{\tau_n}, \qquad \qquad U = \frac{\Delta p}{\tau_p} \tag{2.14}$$

where τ_n and τ_p are the minority carrier lifetimes of electrons and holes, respectively. The excess carrier concentration Δn of electrons equals the total concentration n_p minus the equilibrium concentration n_{po} . Using Eq. (2.13) and (2.14) the continuity equation, Eq. (2.5) and (2.6) can be modified to

$$\frac{d^2 \Delta p}{dx^2} = \frac{\Delta p}{L_p^2}, \qquad \qquad \frac{d^2 \Delta n}{dx^2} = \frac{\Delta n}{L_n^2}$$
(2.15)

where the diffusion length L is defined as

$$L = \sqrt{D\tau} \tag{2.16}$$

The hole and electron concentration in the n-doped depletion region and in the p-doped depletion region can be described with solution of Eq. (2.15) as



Figure 2.2 (left) Electron and hole carrier concentration if a forward bias voltage is applied to the p-n junction in the dark. (right) Electron and hole carrier concentration though a p-n junction under illumination.

$$n(x_p) = n_{po}(e^{qV/kT} - 1)e^{-x_p/L_p}$$
(2.17)

$$p(x_n) = p_{no}(e^{qV/kT} - 1)e^{-x_n/L_n}$$
(2.18)

This carrier distribution of electrons and holes is plotted in Figure 2.2 (left). Using Eq. (2.17) and Eq. (2.18) in Eq. (2.13) the current density of electrons in the p side and holes in the n side is given by

$$I_{p}(x_{n}) = \frac{qD_{p}p_{no}}{L_{n}}(e^{qV/kT} - 1)e^{-x_{n}/L_{n}}$$
(2.19)

$$I_n(x_p) = \frac{qD_n n_{po}}{L_p} (e^{qV/kT} - 1) e^{-x_p/L_p}$$
(2.20)

The total current density is the sum of I_n and I_p at all point in the depletion region. Since,

$$I(x) = I_o \left(e^{qV/kT} - 1 \right)$$
(2.21)

where I_o is the saturation current density. From $p_{no} = n_i^2 / N_D$, respectively, $n_{po} = n_i^2 / N_A I_o$ is given by

$$I_o = \left(\frac{qD_n n_i^2}{L_n N_A} + \frac{qD_p n_i^2}{L_p N_D}\right)$$
(2.22)

2.1.4 The p-n junction under illumination

When light falls on the materials, electron-hole pairs are created. In real solar cells, the generation rate of the electron-hole pairs is not homogenous through the device since the sunlight is distributed widely from UV to IR with a varying absorption probability. Here, we will assume for mathematical simplicity that the generation rate of electron-hole pairs by illumination is uniform throughout the device. This is given in experiments where an illuminating source with very long wavelength light corresponding to the energy of the bandgap¹ is used [3].

In the continuity equation Eq. (2.5) and (2.6) the generation rate G is not zero, but constant. Using Eq. (2.15) the continuity equation is given on the n-type side and on the p-type side as

$$\frac{d^2 \Delta p}{dx^2} = \frac{\Delta p}{L_p^2} - \frac{G}{D_p}, \qquad \qquad \frac{d^2 \Delta n}{dx^2} = \frac{\Delta n}{L_n^2} - \frac{G}{D_n}$$
(2.23)

The corresponding current density in n-type side and in p-type side is

$$I_{p}(x_{n}) = \frac{qD_{p}p_{no}}{L_{p}}(e^{qV/kT} - 1)e^{-x_{n}/L_{n}} - qGL_{n}e^{(-x_{n}/L_{n})}$$
(2.24)

$$I_n(x_p) = \frac{qD_n n_{po}}{L_n} (e^{qV/kT} - 1) e^{-x_p/L_p} - qGL_p e^{(-x_p/L_p)}$$
(2.25)

It should be noted that the effective recombination in the depletion region is neglected. Generation produces current in the depletion which is given by

$$I_d = qGW \tag{2.26}$$

where W is the width of the depletion region (W = $W_p + W_n$). Therefore, the total current density is given by

$$I = I_o \left(e^{qV/kT} - 1 \right) - qG(L_n + L_p + W)$$
(2.27)

The total current density can be split up into dark current density and illuminated current density I_L . Therefore,

$$I = I_o \left(e^{qV/kT} - 1 \right) - I_L \tag{2.28}$$

where $I_{\mbox{\tiny L}}$ has the value

$$I_{L} = qG(L_{n} + L_{p} + W)$$
(2.29)

 $^{^1}$ The bandgap for silicon is 1.1 eV and then the corresponding wavelength is 1.13 $\mu m.$

Eq. (2.29) shows that the current generated by illumination in solar cells is produced by the diffusion flow of minority carrier to the edge of the depletion region an both sides of the junction and by generation in the depletion region. The solar cell characteristics under illumination will be presented in the following section.

2.2 Solar cell characteristics

2.2.1 Solar cell parameters

For the practical analysis of the solar cell performance the dark and illuminated current-voltage (I-V) characteristics are shown in Figure 2.3. The dark I-V curve is shifted down by a light-generated current I_L resulting in the illuminated I-V characteristics.

Four parameters of solar cells are used to characterize illuminated solar cells: the short-circuit current I_{sc} , the open-circuit voltage V_{oc} , the fill factor FF, and the efficiency η .

Short-circuit current I_{sc} is defined as the current when there is no voltage applied to the solar cell (terminals are short circuited). I_{sc} is ideal when it is equal to the light-generated current I_L . The maximal I_{sc} in silicon solar cells under illumination with AM1.5² of 45.56 mA/cm². It is only obtained without any recombination in the cell (surfaces and volume), perfect light trapping, no shadowing and reflection losses at the front surface.

The open-circuit voltage V_{oc} is defined as the voltage when terminals are open in the solar cell. By setting the total current I to zero in Eq. (2.28), the relation between the open-circuit voltage V_{oc} , the saturation current density I_o and the light generated current I_L is

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{I_L}{I_o} + 1\right)$$
(2.30)

 V_{oc} is related to I_L and I_o . For a high V_{oc} a low I_o is absolutely necessary. A low I_o can be obtained when the diffusion lengths of minority carriers (L_n and L_p) are long and the doping concentrations of the regions (N_A and N_D) are high (see Eq. ((2.22)).

The maximum power P_{mp} is given by the product $V_{mp}I_{mp}$. Where V_{mp} and I_{mp} are voltage and current at the maximum power point, respectively. The fill factor, FF, is defined as

$$FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}$$
(2.31)

It is the ratio of the two rectangular areas in Figure 2.3. The FF lies in the range of 0.7-0.85.

² AM is the abbreviation of Air Mass. The 'air mass' is the degree to which the atmosphere affects the sunlight received at the earth's surface and is defined as $1/\cos\theta$. θ is an angle between sunlight and a horizont of the earth's surface. AMO is the solar spectrum outside the earth's atmosphere and AM1.5 is (sun at about 48.2 ° above the horizon) represents the conditions for most industrial countries.

The efficiency of the cell is the ratio of output power P_{mp} at the maximum power point to the incident illumination power P_{in} :

$$\eta = \frac{V_{mp}I_{mp}}{P_{in}} = \frac{V_{oc}I_{sc}FF}{P_{in}}$$
(2.32)

The highest efficiency attained for single crystal silicon is around 23-24 % for laboratory cells while for commercial cells the efficiency lies in the range of 14-16 % [4].



Figure 2.3 Typical dark and illuminated I-V curves of solar cell.

2.2.2 Illuminated current-voltage (I-V) characteristics

In real solar cells a series resistance R_s and a parallel (shunt) resistance R_p is present. Accounting for series and parallel resistances, the illuminated I-V characteristic Eq. (2.28) becomes

$$I(V) = I_o \left[\exp\left(\frac{q(V - I(V)R_s)}{kT}\right) - 1 \right] + \frac{V - I(V)R_s}{R_p}$$
(2.33)

where V is the voltage at the cell terminals. The series resistance of a solar cells is determined by the metal grids, the contact resistance and the base and emitter sheet resistance. The parallel resistance can arise from imperfections on the device surfaces as well as leakage currents across the edges of the cell.

Figure 2.4 shows the influence of the series and parallel resistance on the illuminated and dark I-V characteristics according to Eq. (2.33) and Eq. (2.34) in the next section. The series and parallel resistances influence significantly fill factor, open circuit voltage, and short circuit current density. Small shunt resistances reduce V_{oc} and very large series resistances can limit I_{sc} .



Figure 2.4 Influence of series resistance R_s and parallel resistance R_p on the I-V characteristic: (a) Illuminate R_s varied; (b) illuminated, R_p varied; (c) dark, R_s varied; (d) dark, R_p varied [5].

2.2.3 Dark current-voltage (I-V) characteristics

Until now it has been assumed that there is no recombination loss in the depletion region. However, in real solar cells depletion-region recombination represents a substantial loss mechanism. For simplicity a single-level recombination center is assumed to be located in the depletion region and the recombination rate should be constant throughout the space-charge region. This recombination current in the depletion region is added to Eq. (2.33) and thus the two-diode model becomes:

$$I(V) = I_{01} \left[\exp\left(\frac{q(V - I(V)R_s)}{n_1kT}\right) - 1 \right] + I_{02} \left[\exp\left(\frac{q(V - I(V)R_s)}{n_2kT}\right) - 1 \right] + \frac{V - I(V)R_s}{R_p}$$
(2.34)

The ideality factors n_1 and n_2 in Eq. (2.34) can become 1 and 2, respectively. As shown in Figure 2.5 (left) the I-V curve can be fitted using the two diodes equivalent circuit. In practice, most measured I-V curves of solar cells can be approximated by several exponential regions in the dark forward I-V characteristic revealing the presence of several dark current components. A wide range of experimentally observed I-V curves can be fitted by varying J_{01} , J_{02} , n_1 , n_2 , R_p , and R_s as shown in Figure 2.5.



Figure 2.5 (left) Equivalent circuit of a solar cell described by the two-diode model. (light) Typical dark I-V characteristics of solar cell. From the measured dark I-V curve as varying the applied voltage the dark parameters, R_p , I_{o2} , I_{o1} , and R_s can be determined.

3 Recombination mechanisms

Recombination is a loss process of light-induced charge carriers resulting in a lower efficiency of solar cells. We present the three main recombination processes in silicon: radiative, Auger, and Shockley-Read-Hall recombination in the bulk and at the surface. Methods for the measurement of the effective lifetime which includes all the recombination processes occurring in the silicon wafer are described.

3.1 General theory

The illumination of light on a semiconductor material produces electron-hole pairs. Therefore, the concentrations of carriers in illuminated material will be in excess of their values in the dark. These excess concentration decay back to their equilibrium values if the illumination is switched off. This decay process is known as recombination. The recombination rate of minority carriers, U_R is then proportional to the excess minority carrier concentration $\Delta n=n-n_0$ in p-type material and $\Delta p=p-p_0$ in n-type material and is given by

$$\frac{\partial \Delta n}{\partial t} = U_R = \frac{\Delta n}{\tau} \tag{3.1}$$

where τ is the carrier lifetime. The total recombination U_R can be calculated with sums of different recombination channels, U_i :

$$U_R = \sum U_i \tag{3.2}$$

In experiments the carrier lifetime is measured. The total carrier lifetime τ of the material can be determined from the recombination rate:

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i} = \sum \frac{U_i}{\Delta n}$$
(3.3)

In the following section, three main recombination mechanisms, which determine the carrier lifetime will be discussed: Radiative (τ_{rad}), Auger (τ_{Auger}), and Shockley-Read-Hall (τ_{SRH}) recombination.

3.2 Radiative recombination

Radiative recombination is just the reverse of the absorption process. During radiative recombination electron-hole pairs recombine directly from band to band with energy dissipation over photons as shown in Figure 3.1 (left). Therefore, the total radiative radiation rate, U_{rad} is

proportional to the concentration of free electrons n and free holes p. In thermal equilibrium $(np=n_i^2)$, this recombination rate is balanced by an equal generation rate. Therefore, the net recombination rate is given by the total recombination rate minus the equilibrium generation rate:

$$U_{rad} = B(np - n_o p_o) = B(np - n_i^2)$$
(3.4)

where B is the coefficient of radiative recombination. B has the value of about 2×10^{-15} cm³s⁻¹ for silicon and 3×10^{-10} cm³s⁻¹ for GaAs [6]. The radiative recombination is more significant in direct semiconductors than in indirect semiconductors.

For the radiative recombination with $\Delta n = \Delta p$, the lifetime is determined from Eq. (3.3)

$$\tau_{rad} = \frac{1}{B(n_o + p_o) + B\Delta n}$$
(3.5)

Eq. (3.5) can be described under low injection and high injection conditions³,

$$\tau_{rad}^{low} = \frac{1}{BN_{dot}} \qquad and \qquad \tau_{rad}^{high} = \frac{1}{B\Delta n}$$
(3.6)

where N_{dot} is the density of donors (N_D) in n-type or acceptors (N_A) in p-type. It can be shown by Eq. (3.6) that under low injection the radiative lifetime is constant while in high injection the radiative lifetime is decreased with increasing injection level.



Figure 3.1 (Left) Schematic of radiation recombination mechanism. (Right) Schematic of Auger recombination. For high concentration the Coulomb enhancement factors g_{eeh} and g_{ehh} should be considered.

³ The condition of low injection is $\Delta n \ll n_o + p_o$ or $\Delta n \ll N_{dot}$ while the condition of high injection is $\Delta n \gg n_o + p_o$ or $\Delta n \gg N_{dot}$.

3.3 Auger recombination

3.3.1 Traditional Auger recombination

Auger recombination is related to three particles interaction. The electron recombining with the hole gives the excess energy to a third free electron in the conduction band (eeh process) or a third free hole in the valence band (ehh process) instead of emitting a photon as depicted in Figure 2.1 (right). This third electron or hole returns to its original energy by emitting phonons. The total Auger recombination rate is described with $U_{eeh}=C_nn^2p$ and $U_{ehh}=C_pnp^2$. The net Auger recombination is given by

$$U_{Au} = C_n \left(n^2 p - n_o^2 p_o \right) + C_p \left(n p^2 - n_o p_o^2 \right)$$
(3.7)

The Auger lifetime in p-type and n-type material under low injection and high injection conditions can be determined:

$$\tau_{Au}^{low, p} = \frac{1}{C_p N_A^2}$$
 and $\tau_{Au}^{high, p} = \frac{1}{(C_n + C_p)\Delta p^2} = \frac{1}{C_a \Delta p^2}$ (for p -type) (3.8)

$$\tau_{Au}^{high,n} = \frac{1}{C_n N_D^2}$$
 and $\tau_{Au}^{high,n} = \frac{1}{(C_n + C_p)\Delta n^2} = \frac{1}{C_a \Delta n^2}$ (for $n - type$) (3.9)

where C_a is the ambipolar Auger coefficient. C_n and C_p for silicon with high doping concentration (>5×10¹⁸ cm⁻³) are determined to be 2.8×10⁻³¹ cm⁶s⁻¹ and 0.99×10⁻³¹ cm⁶s⁻¹, respectively [7]. And then, the ambipolar Auger coefficient be obtained as 3.79×10⁻³¹ cm⁶s⁻¹.

The Auger lifetime is proportional to the inverse of the carrier density squared and depends stronger on the injection level than on the radiative lifetime. Therefore, the Auger recombination dominates the recombination in silicon for high injection levels, e. g., for concentrator solar cells or for heavily doped emitter.

3.3.2 Coulombic enhanced Auger recombination

For non-interacting between the mobile charge carriers the distribution of electrons and holes is uniform in space. In contrast, since electrons and holes interact via Coulomb forces, the electron density in the vicinity of a hole is increased while it is decreased in the vicinity of another electron. A similar enhancement mechanism is occurred for ehh process. Therefore, the Coulombic enhancement lifetime should be described with the enhancement factors g_{eeh} and g_{ehh} . The electron-hole correlation factor can be described by contributions of bound states (i.e. excitons) and of scattering states. Under low injection bound states dominate the electron-hole correlation factor in silicon while under high injection the bound state vanish [8]. In the following, the Coulombic enhanced Auger lifetime is considered under low injection (N_D, or N_A>\Deltan), high injection and intermediate conditions.

A. Low injection

At N_D or $N_A > 1 \times 10^{18}$ cm⁻³, free-carrier screening is very strong, preventing the formational bound states (excitons) [8]. Therefore the Auger lifetime can be described by the traditional Auger recombination as in Eq. (3.8) and (3.9).

At N_D or $N_A < 1 \times 10^{18}$ cm⁻³, free-carrier screening is weak. Therefore, excitons are present and the Coulombic enhancement lifetime can be described with the enhancement factors g_{eeh} and g_{ehh} :

$$\tau_{CEAu}^{low,n} = \frac{1}{g_{eeh}C_n N_D^2} = \frac{1}{C_n^* N_D^2} \quad and \quad \tau_{CEAu}^{low,p} = \frac{1}{g_{ehh}C_p N_A^2} = \frac{1}{C_p^* N_A^2} \quad (3.10)$$

The enhancement factors g_{eeh} and g_{ehh} under low injection conditions can be described as [9]:

$$g_{eeh} = 1 + 44 \left\{ 1 - \tanh\left[\left(\frac{n}{n^*}\right)^{0.34}\right] \right\} \qquad g_{ehh} = 1 + 44 \left\{ 1 - \tanh\left[\left(\frac{p}{p^*}\right)^{0.29}\right] \right\}$$
(3.11)

where $n^*=p^*=5\times 10^{16} \text{ cm}^{-3}$.

B. High injection

Under high injection, the density of electrons and holes is the same (n=p), and C_n and C_p cannot be distinguished by lifetime measurements. Therefore, the Auger lifetime under high injection can be described from Eq. (3.8) and (3.9) as:

$$\tau_{Au}^{high} = \frac{1}{\left(C_p + C_n\right)\Delta n^2} \equiv \frac{1}{C_a\Delta n^2}$$
(3.12)

Typical values quoted for the ambipolar Auger coefficient, C_a are in the range from 1×10^{30} - 2×10^{30} cm⁻⁶s⁻¹ [9]. C_a under high injection condition can be described with an injection level [10]:

$$C_{a} = 3 \times 10^{-27} \,\Delta p^{-0.2} = 3 \times 10^{-27} \,\Delta n^{-0.2} \tag{3.13}$$

C. Intermediate injection

Under intermediate injection the carrier density is similar to the dopant density. This range is very important for solar cells since their base is lowly doped (normally 10^{16} cm⁻³) and the injection level is in this range at V_{oc} conditions. The density of electron and hole is not the same (n≠p) since the bound states are present even though their concentration is lower than those under low injection. Therefore, the Auger lifetime needs to be rewritten from (3.7) as:

$$\tau_{CEAu} = \frac{n - n_o}{C_n^* (n^2 p - n_o^2 p_o) + C_p^* (n p^2 - n_o p_o^2)}$$
(3.14)

where C_n^* and C_p^* are defined as

$$C_n^* = g_{eeh} C_n \left(\frac{n_o}{n_o + \Delta n} \right) + \frac{C_a}{2} \left(\frac{\Delta n}{n_o + \Delta n} \right)$$
(3.15)

$$C_{p}^{*} = g_{ehh}C_{p}\left(\frac{p_{o}}{p_{o} + \Delta p}\right) + \frac{C_{a}}{2}\left(\frac{\Delta p}{p_{o} + \Delta p}\right)$$
(3.16)

The Auger coefficient C_n , C_p and C_a are the same values as quoted in traditional Auger recombination ($C_n = 2.8 \times 10^{-30} \text{ cm}^{-6} \text{s}^{-1}$, $C_p = 9.9 \times 10^{-32} \text{ cm}^{-6} \text{s}^{-1}$, and $C_a = 1.66 \times 10^{-30} \text{ cm}^{-6} \text{s}^{-1}$). In the following section Figure 3.3 shows the dependence of radiative and Auger lifetime on doping concentration and injection level.

3.4 Shockley-Read-Hall recombination

3.4.1 Shockley-Read-Hall recombination in bulk

Defect levels can be created within the energy bandgap by impurities or crystallographic imperfections. Figure 3.2 (left) shows the four dynamic processes of a SRH mechanism: (1) electron emission, (2) electron capture, (3) hole capture, (4) hole emission.

The SRH recombination rate, U_{SRH} for a single level is given by

$$U_{SRH} = \frac{(np - n_i^2)\upsilon_{th} N_t}{\sigma_p^{-1} (n + n_1) + \sigma_n^{-1} (p + p_1)}$$
(3.17)

where v_{th} and N_t are the thermal velocity of charge carriers ($\approx 10^7$ cm/s at 300 K) and the density of recombination centers, while σ_n and σ_p are the electron and hole capture cross sections, respectively. n_1 and p_1 are statistical factors for the specific defect and are defined as:

$$n_1 \equiv N_C \exp\left(\frac{E_t - E_C}{kt}\right), \qquad p_1 \equiv N_V \exp\left(\frac{E_V - E_t}{kt}\right)$$
(3.18)



Figure 3.2 (Left) Schematic of Shockley-Read recombination mechanism in bulk: (1) electron emission, (2) electron-capture, (3) hole capture, (4) hole emission. (Right) Schematic SRH recombination at the surface.

It follows from Eq. (3.3) that the SRH lifetime, τ_{SRH} can be expressed as

$$\tau_{SRH} = \frac{\tau_{no}(p_o + p_1 + \Delta n) + \tau_{po}(n_o + n_1 + \Delta n)}{(p_o + n_o + \Delta n)}$$
(3.19)

Where τ_{no} and τ_{po} are the minority-carrier lifetimes for electrons and holes, respectively, and are defined as:

$$\tau_{po} \equiv \frac{1}{N_t \,\sigma_p \,\upsilon_{th}} , \qquad \tau_{no} \equiv \frac{1}{N_t \,\sigma_n \,\upsilon_{th}}$$
(3.20)

The total bulk lifetime consists of the radiative lifetime (τ_{rad}), the Auger lifetime (τ_{Auger}), and Shockley-Read-Hall lifetime (τ_{SRH}) in bulk. Figure 3.3 shows the maximal bulk recombination as a function of the doped concentration (left) and of the excess carrier density (right). For the chosen SRH lifetime the maximum bulk lifetime is dominated by recombination via defect levels for doping concentration under 10¹⁵ cm⁻³ and over 10¹⁵ cm⁻³ the influence of the radiative and Auger recombination on the $\tau_{b, max}$ begins and over 10¹⁶ cm⁻³ $\tau_{b, max}$ is decreased drastically by an impact of the CE-Auger recombination (Figure 3.3 (left)).

In addition, in the low injection range under 10^{15} cm⁻³ the $\tau_{b, max}$ is not influenced by SRH and CE-Auger recombinations, while in the high injection range over 10^{16} cm⁻³ the $\tau_{b, max}$ is nearly proportional to the inverse of the carrier density squared just like the CE-Auger lifetime.



Figure 3.3 (Left) Maximal bulk recombination under low injection at 300 K as a function of the doped concentration. (Right) Maximal bulk recombination as function of the excess carrier density, Δn [6].

3.4.2 Shockley-Read-Hall recombination at surfaces

Besides SRH bulk recombination there is also SRH surface recombination at bare surfaces or interface recombination at Si-insulator interfaces. The large number of defects create states within the bandgap as shown in Figure 3.2 (light). Therefore, the recombination occurs very efficiently at surfaces via the same mechanism of SRH recombination in the bulk (see section 3.4.1). The rate of the surface SRH recombination U_s for a single defect type at the surface is given by

$$U_{s} = \frac{n_{s}p_{s} - n_{i}^{2}}{\frac{n_{s} + n_{1}}{S_{po}} + \frac{p_{s} + p_{1}}{S_{no}}}$$
(3.21)

where n_s and p_s are the concentrations of electrons and holes at the surface while S_{no} and S_{po} are surface recombination velocities of electrons and holes, respectively. S_{no} and S_{po} are given by

$$S_{no} \equiv \sigma_n v_{th} N_{ts}$$
 and $S_{po} \equiv \sigma_p v_{th} N_{ts}$ (3.22)

where σ_n and σ_p are the electron and hole capture cross sections, respectively. N_{ts} is the density of surface states per unit area and v_{th} is the thermal velocity of charge carriers. It should be noted that N_{ts} has the unit of cm⁻², as opposed to the unit cm⁻³ in the case of bulk recombination. Therefore, U_s has the dimension of cm⁻²s⁻¹. Similar to the definition of the recombination lifetime Eq. (3.3), a surface recombination velocity (SRV) S at the semiconductor surface can be defined as

$$U_s \equiv S \Delta n_s \tag{3.23}$$

where Δn_s is the excess minority-carrier concentration at the surface.

The total rate of surface recombination can be obtained by integration over the entire bandgap using the energy-dependent trap density $D_{it}(E)$ and capture cross sections σ_p and σ_n :

$$U_{s} = \int_{E_{v}}^{E_{c}} \frac{v_{th}(n_{s}p_{s}-n_{i}^{2})}{\sigma_{p}^{-1}(E_{t})(n_{s}+n_{1})+\sigma_{n}^{-1}(E_{t})(p_{s}+p_{1})} D_{it}(E_{t}) dE_{t}$$
(3.24)

3.4.3 Reducing the surface recombination rate

Reducing the recombination rate at a semiconductor surface can be considered with two fundamental mechanisms resulting from Eq (3.23) and (3.24) [11].

A. Optimisation of the properties of the surface states

As seen in Eq. (3.24) the surface recombination can be reduced by decreasing the defect density, D_{it} . D_{it} can be drastically reduced using passivation methods such as growing silicon oxides or depositing silicon nitrides or by combination of both techniques such as oxides/nitrides stacks (see chapter 6).

B. Reduction of the surface concentration of electrons and holes

As seen in Eq. (3.23) the recombination rate at the surface is related to excess concentration of minority carriers at the surface. Therefore, the recombination can be minimized by a reduction of one carrier type at the surface. Using high-low junction (p⁺p or n⁺n) the minority carriers are reduced at the surface. This technology, known as back surface field (BSF), is widely used at the rear surface of solar cells. Another method is the field effect passivation. The fixed charges in a passivation layer repel the minority carriers or the extremely large fixed charges bend the energy band resulting in an inverting layer at the surface [12]. Alternatively, low recombination rates at the rear surface of solar cells can be obtained using floating junctions [13], [14] where n-type dopants are diffused shallowly into the rear surface.

3.5 The effective lifetime

An effective lifetime is measured experimentally which includes all the recombination processes occurring in the silicon wafer, i. e., radiative recombination (τ_{rad}), Auger recombination (τ_{Auger}), Shockley-Read-Hall recombination (τ_{SRH}) in bulk and at the surface (τ_s). Therefore, the effective lifetime is described as

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}} + \frac{1}{\tau_s}$$
(3.25)

Thus, the effective lifetime can be described as sum the lifetime in bulk (τ_b) and at the surface (τ_s):

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s}$$
(3.26)

For the determination of the effective lifetime photoconductance decay (PCD) is a widely used technique. Electron-hole pairs are created by light pulse, and the decay of the excess minority carrier concentrations Δn or Δp is monitored as a function of time via the conductance of the wafer.

Let us consider a p-type semiconductor as shown in Figure 3.4. The wafer has a thickness of W, minority carrier bulk lifetime τ_b , minority carrier diffusion coefficient D, and the surface recombination velocities S₁ and S₂ at the two surfaces. The excess minority carrier concentration $\Delta n(x,t) = n(x,t) - n_o$ is obtained from a solution of the one-dimensional continuity equation

$$\frac{\partial \Delta n(x,t)}{\partial t} = D \frac{\partial^2 \Delta n(x,t)}{\partial x^2} - \frac{\Delta n(x,t)}{\tau_b} + G(x,t)$$
(3.27)

Generally during transient measurements, the carrier decay is monitored after the excitation source is turned off. Therefore, G(x, t) is 0 during the measurement. The boundary conditions

$$\frac{\partial \Delta n(x,t)}{\partial x} = S_1 \frac{\Delta n(0,t)}{D} \qquad \qquad at \quad x = 0$$
(3.28)

$$\frac{\partial \Delta n(x,t)}{\partial x} = -S_2 \frac{\Delta n(W,t)}{D} \qquad at \quad x = W$$
(3.29)



Figure 3.4 Homogeneous p-type sample geometry under optical excitation with a light pulse.

gives the general solution [15]

$$\Delta n(x,t) = \sum_{m=1}^{\infty} A_m(x) \exp\left(-\frac{t}{\tau_m}\right)$$
(3.30)

Where the coefficient A_m (x) is related to the initial conditions $\Delta n(x,0)$ and the decay time constant τ_m is given by

$$\frac{1}{\tau_m} = \frac{1}{\tau_b} + D_n \gamma_m^2 \tag{3.31}$$

with γ_m being the mth root of

$$\tan\left(W\gamma_{m}\right) = \frac{D_{n}\gamma_{m}\left(S_{1}+S_{2}\right)}{\left(D_{n}\gamma_{m}\right)^{2}-S_{1}S_{2}}$$
(3.32)

In Eq. (3.32) the positive eigenvalue γ_m is not dependent on τ_b , but on the SRV S₁ and S₂. Therefore, the decay time τ_m is described as a sum of a constant bulk term and a surface term which depend on the wafer geometry. In addition, Eq. (3.32) shows that γ_m is monotonous growing with m ($\gamma_{m+1} > \gamma_m$). Consequently, the decay time τ_m is decreasing rapidly with increasing m and thus all modes m>1 are not relevant after an initial decay. In the dominant fundamental mode lifetime τ_1 dominates the asymptotical decay. τ_1 is denoted as τ_{eff} and is given by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \qquad \text{with} \qquad \frac{1}{\tau_s} \equiv D_n \gamma_1^2 \qquad (3.33)$$

If both surfaces are passivated identical ($S_1=S_2=S$), Eq. (3.32) can be described simplifying :

$$\tan\left(\frac{W\gamma_1}{2}\right) = \frac{S}{D_n\gamma_1} \tag{3.34}$$

Two limiting cases are interesting. For low surface recombination velocity Eq. (3.33) simplifies to

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{W} \qquad \qquad for \quad \frac{SW}{D_n} < \frac{1}{4} \tag{3.35}$$

For example, for a wafer thickness, W of 300 μ m and a diffusion coefficient D_n of 30 cm²/s, Eq. (3.35) is valid for S < 250 cm/s.

On the other hand, for high surface recombination velocity, Eq. (3.33) simplifies to

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + D_n \left(\frac{\pi}{W}\right)^2 \qquad \qquad for \quad \frac{SW}{D_n} > 100 \qquad (3.36)$$

For W=300 μ m and D_n=30 cm²/s, Eq. (3.36) is valid for S>10⁵ cm/s.

The general effective lifetime can be described with the combination of Eq. (3.35) and Eq. (3.36):

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \left(\frac{2S}{W} + D_n \left(\frac{\pi}{W}\right)^2\right)$$
(3.37)

The relative deviation of Eq. (3.37) from the exact solution for τ_{eff} is below 5 % for all cases of S [16].

In this work mirocrowave-detected photo conductance decay (MW-PCD) is used to measure the effective lifetime. The theory and methods for MW-PCD are detaily expalined in Appendix B.1.

4 Rapid thermal processing

Rapid thermal processing is based on incoherent light sources in the range of Vacuum ultra violet (VUV) and infrared (IR) for the fabrication of solar cells and semiconductor devices while in classical furnaces only IR radiation sources are used. Low-cost, minimum overall thermal budget, low-power consumption, and high throughput are some of the attractive features of rapid thermal processing. Firstly, we describe three types with different radiative heating sources. Secondly, rapid thermal processing and classical furnace are compared and the mechanism of the high heating and cooling rates which is the main advantage of RTP is described. Finally, the RTP set-up used in this work is presented and methods for measuring the accurate temperature are described.

4.1 Fundamental properties of radiant heating systems

Short time annealing techniques vary over a wide range of methods for the energy transfer from heating source to sample. For example, visible and infrared laser light, incoherent light, electron and ion beams, and black body radiation are used as a heating source. The most important difference between these heat sources is the time scale in which the energy is delivered and how it compares with the thermal response time t of silicon

$$t = s^2 k^{-1} (4.1)$$

where s is the thermal diffusion length or the sample dimension and k is the thermal diffusivity. k varies between 0.8 cm²/s at 25 °C and 0.1 cm²/s at 1400 °C. The thermal response time t varies from about micro to milliseconds depending on the value of k and the absorption depth of the radiation which depends on the crystallinity and doping of the semiconductor and the wavelength of the radiation. In the case of k=0.2 cm²/s and s=10 μ m, t is 5×10⁻⁶ s. On the other hand, for s=375 μ m and k=0.2 cm²/s, t is 7×10⁻³ s [17].

Basically, all of the thermal processes can be divided into three groups according to the process time with reference to the thermal response time: (A) adiabatic processing, (B) thermal flux processing and (C) isothermal heating processing [17], [18]. The temperature-depth profiles of the three groups are shown in Figure 4.1.

• (A) Adiabatic processing: In the adiabatic processing case, a high-power laser beam is used for a time 10-100 ns, which is less than the thermal response time of silicon⁴. The temperature is increased extremely rapid and the sample melts. Therefore, the adiabatic processing is not suitable for VLSI applications even though the heating is confined to the silicon surface region. Pulsed laser, e-beam, and ion beam are used as an adiabatic source (Figure 4.1 right (a)).

 $^{^4}$ Thermal response time of silicon is about $10^{-5}\text{--}10^{-2}$ s.

- **(B) Thermal flux processing:** Thermal flux processing heats the silicon for times of 10⁻⁴- 10⁻² s, comparable to the thermal response time of the silicon. Thermal flux processes include raster scanned point (or line) CW laser and e-beam energy sources. The main disadvantage of this method is that although defects are removed from the center of the scanning spots, thermal stresses can be introduced at the boundary of the scanning line causing new defects.
- (c) Isothermal flux processing: the pulse duration of isothermal flux is 1-100 s. It is obvious that only isothermal heating give rise to uniform lateral and depth temperature profiles throughout the wafer as shown in Figure 4.1 (c), thus minimizing yield loss due to the disruption of layers and circuits. In this time regime, the anneal time is clearly longer than the thermal response time of the silicon wafer. In addition, a faster wafer throughput compared to scanned beams is obviously attainable and the energy sources themselves are much more energy efficient than pulsed or scanned lasers. Light sources for isothermal flux processing are halogen lamp, resistance black body, plasma and e-beam.



Figure 4.1 Schematic figure showing (left) time duration of various short time annealing processes and (right) spatial temperature distribution in RTP processes: (a) adiabatic, (b) thermal flux, and (c) isothermal. The diagrams in the first, second and third column show the isothermal lines, temperature-depth profiles and total temperature distribution, respectively [17].

4.2 Characteristics of RTP

4.2.1 Fundamental difference between CTP and RTP

There are several fundamental differences between rapid thermal processing and classical thermal processing (CTP or conventional furnace processing: CFP). The main advantages of RTP as compared to CTP, i. e., low costs, along with minimum overall thermal budget low-power

consumption, and high throughput, makes this technique popular not only for solar cells but also for application in other areas such as integrated circuit technology.

The low thermal mass feature of RTP leads to high heating and cooling rates. As discussed in the following section, the photon spectrums of the two energy sources are also different as shown in Figure 4.2. A summary of the main differences between RTP and furnace processing are given in Table 4.1.

RTP	СТР
Cold-wall	Hot wall
Single-wafer	Multi-wafer
Low thermal mass	High thermal mass
Small process volume	Large process volume
Short high temperature cycles	Long thermal cycles
Single-process tools	Multiprocessing
Photon spectrum (from VUV to IR)	Photon spectrum (IR)

Table 4.1 Fundamenta	I differences between	RTP and CTP [18].
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4.2.2 Role of photoeffects in RTP

As mentioned earlier, both classical furnace processing and rapid thermal processing use thermal sources. The black-body radiation spectra depends on the source temperature. In case of classical furnace processing, the substrate temperature and the furnace temperature are identical. The radiation spectrum of a furnace (for processing temperature of about 1000-1300 °C) consists of photons in the infrared and longer wavelength regions. Thus, radiation in the infrared region results in thermal reactions where the molecules in ground state are raised to higher vibration levels and dissociation occurs when sufficient energy is concentrated in the bonds to be broken.

On the other hand, in case of RTP, although the substrate temperature is relatively low (as in the case of furnace processing) the filament temperature is higher. For example, the typical temperature of tungsten halogen lamps are 3000 °C and the silicon wafer is 600-1200 °C. As shown in Figure 4.2, the spectrum of the incoherent sources of light consists of photons from vacuum ultra violet (VUV) to infrared (IR) region. Photons of appropriate wavelength (from VUV to visible) induce a transition from the ground state to a quantized electronically excited state in the case of atoms and to a quantized rotational and vibrational level of an upper electronic state in case of small molecules [19]. As a result, photochemical reactions and photophysical effects differ from thermal reactions resulting in lower temperature processing. Therefore, RTP based on radiation spectra from VUV to visible region can provide lower temperature processing as compared to CTP based on IR.



Figure 4.2 Relative energy intensity of a tungsten-halogen lamp and black body radiation at 800 K. Left y-axis shows the scalar of tungsten-halogen lamp for RTP and and right y-axis shows the black-body radiation for classical [20].

4.2.3 Emissivity of Radiation

The basis for understanding the physics of energy transfer in a rapid thermal processing is to recognize that it consists of a number of thermally radiating bodies at different temperatures. For example, the lamps may be at 2000-3000 °C (filament) or ~6000 °C (arc lamp) or ~3000 °C (tungsten halogen lamps), the slice wafer at temperatures between 20-1400 °C and the chamber walls between 20 °C and 600 °C depending on system design and wafer temperature [21].

The radiation emitted by hot objects has a well-defined spectral distribution. In the simple case of black bodies, the power emissivity at wavelength λ is only a function of temperature, and given by Planck's radiation law:

$$\varepsilon(\lambda) = \frac{2\pi h c^2 \ \lambda^{-5}}{\exp\left(\frac{hc}{k} \frac{1}{\lambda T}\right) - 1} = \frac{c_1 \ \lambda^{-5}}{\exp(c_2 \ / \ \lambda T) - 1}$$
(4.2)

Where, c_1 and c_2 are $3.7403 \times 10^2 \ \mu\text{W} \ (\mu\text{m})^2$ and $14384 \ \mu\text{m}$ K, respectively. λ is in μm and T is in K. The power distribution for a black body at various temperatures is shown in Figure 4.3 (left). There are two important features: As the temperature of the source increases, the radiant energy output at all wavelengths increases respectively as shown in Figure 4.3 (left). In addition, the output at shorter wavelengths increases very rapidly with temperature so that the wavelength range containing the bulk of the radiation energy shifts from 6 μm at 200 °C to 1.2 μm at 2000 °C [21]. The total power radiated from a black body at temperature T is given
by the integral under the appropriate curve of Figure 4.3 (right), numerically equal to that given by Stefan-Boltzmann's law, $P = 5.67 \times 10^{-12} \text{ T}^4 \text{ W/cm}^2$.



Figure 4.3 (left) Spectral distribution of the power radiated from a black body as a function of black body temperature. The dotted line shows how the peak power is emitted at progressively shorter wavelengths as temperature increases. (right) Spectral distribution of thermal radiation at 1000 °C (a) a black body, (b) a grey body of emissivity 0.7, (c) a body with spectrally-dependent emissivity varying between 0.7 and 0.95 (e.g., silicon coated with a 1 µm thick layer of SiO₂) [21].

The real components of a system are not perfect black bodies: they emit less radiation at each wavelength than a black body. The simplest approximation to real emission behavior is to assume the emissivity by a constant factor e. For example, if the total emissivity of a black body is 1, a grey body has a emissivity of 0.7 which corresponds to a bare silicon wafer, and a silicon coated with SiO_2 with a thickness of 1 µm has a emissivity of 0.95 at the same temperature as illustrated in Figure 4.3 (right). This grey body approximation is not adequate under all conditions. In silicon, deviations from grey-body behavior occur when the silicon surface are modulated by the presence of layers of differing refractive index. It should be recognized that the temperature measured with pyrometer is strongly depended on the emissivity in the chamber. We will discuss this topic in section 4.4.2.

4.3 Structure of the RTP used in this work

Figure 4.4 shows a cross sectional drawing of a single wafer RTP furnace (SHS 100 from STEAG-RTP) operated in atmosphere. The reactor is coated with gold for high reflection and is cooled with water. A quartz chamber is mounted in the reactor. Silicon wafers are heated by incoherent irradiation of 21 tungsten halogen lamps of 1.5 kW each which are placed above (10 lamps) and below (11 lamps) in the reactor. The inlet for process gases, N₂, O₂ or Ar is on the rear side of the quartz chamber. The gas leaves the reactor block by holes at the front side. For better gas flow homogeneity gas distribution plates are installed on the wafer tray. The wafer tray is placed inside the quartz chamber. The wafer is positioned on three pins on the wafer tray. Wafers sizes of up to 4 inches and 10×10 cm² can be processed. The pyrometer is placed below the wafer. The pyrometer measures temperatures through a window in the quartz chamber and monitors the silicon temperature continuously. The pyrometer in our RTP is operated at a single wavelength of 2.7 µm. Figure 4.5 shows the schematic of the RTP set-up used in this work.



Figure 4.4 Schematic drawing of the RTP furnace used in this work.



Figure 4.5 (left) Photograph of the RTP furnace at Fraunhofer ISE used in this work (right) the quartz chamber and wafer tray of the reactor.

4.4 Temperature measurements

4.4.1 Thermocouple

The generally accepted method for measuring the absolute temperature of a silicon wafer is by means of a properly embedded and corrected thermocouple (TC). Thermocouples are based on the principle that if different metals are jointed at one end, a predictable voltage will be generated which is proportional to the temperature difference between the measuring junction and the reference junction (connection to the measuring device). In an effort to optimize the performance, numerous combinations of metals have been characterized to determine their output voltages vs. temperature transfer function. The selection of the optimum thermocouple type (metals used in their construction) is based on the application temperature, atmosphere and required length of service. In this work the 'type S' thermocouple was used. This thermocouple consists of Platinum + Rhodium (10%) for positive polarity and Platinum for negative polarity and is suitable to measure the temperature in the range of 800-1400 °C. The temperature precision is ± 4 °C. The thermocouple must be mounted into the interior of the silicon. Therefore, it is very cumbersome and inconvenient for routine monitoring. It must be noted that the thermocouple must be small so that the temperature is determined by the wafer and not by the heat capacity and properties of the thermocouple.

4.4.2 Pyrometer

Optical pyrometery, which deduces the wafer's temperature from the intensity of the thermal radiation that it emits, is commonly used for RTP wafer temperature measurements. Optical pyrometers can be used as non-contact wafer temperature sensing devices. Pyrometer response time can be as short as 1-10 ms.

The pyrometer is calibrated to convert the detected intensity signal into a temperature: for a given emissivity and wavelength a unique value is obtained as can be seen from the black-body curves of Figure 4.3 (left). The temperature sensitivity to emissivity can be determined from these curves. If the pyrometer emissivity is set at ε_0 , whereas the actual wafer value is ε , then the pyrometer will register a temperature T₀ (not equal to the true temperature T) given as:

$$\varepsilon_o \,\varepsilon_\lambda(T_o) = \varepsilon \,\varepsilon_\lambda(T) \tag{4.3}$$

where ε_{λ} (T) is the black-body spectrum as given in Eq. (4.2), at wavelength λ . This equation cannot be solved analytically for T though to a good approximation the solution is:

$$\frac{1}{T} - \frac{1}{T_o} = \frac{\lambda}{c_2} \ln \frac{\varepsilon}{\varepsilon_o}$$
(4.4)

where c_2 refers to the Plank's second radiation constant (14384 µm K) in Eq. (4.2). It should be noted that this equation is exact if $c_2/\lambda T >> 1$ which implies $\lambda T << 14384$ µm K.

For example, at real temperatures of 800 °C the spectral emissivity of a flat silicon wafer is 0.6662 at a wavelength of 1 μ m. The registered temperature would also be 820 °C. However, the wafer deposited two-layers on silicon with 0.2 μ m of oxide and 0.2 μ m of polysilicon film has the emissivity of 0.178⁵. A pyrometer calibrated on flat silicon would report a temperature of only 704 °C instead of an actual temperature of 800 °C. The same emissivity error is magnified at higher temperatures. The error would be 153 °C at 1100 °C [22].

Other approaches note that the intensity of the radiation entering the pyrometer is typically affected by the structure of the RTP chamber. The radiation emitted by the wafer is reflected between it and the chamber wall several times before it enters the pyrometer. This phenomenon increases with the wafer's apparent emissivity. The sum of the radiation directly entering the pyrometer plus the radiation that multiple-reflected from the chamber wall and wafer surface gives an effective emissivity, ϵ_{eff} , of:

$$\varepsilon_{eff} = \frac{\varepsilon_o}{1 - R_c \left(1 - \varepsilon_o\right)} \tag{4.5}$$

where R_c is the reflectivity of the chamber wall, and ε_o is the emissivity of the wafer. As the reflectivity of the chamber wall rises, ε_{eff} increases toward 1, and the value of the wafer's free-space emissivity becomes progressively less important. At 800 °C, if the chamber reflectivity is 0.9, then the effective emissivity of plain silicon at a wavelength of 1 µm is 0.951, and for the coated wafer discussed above, it is 0.685. If these values are substituted in Eq. (4.4), the temperature error at 1100 °C is only 42 °C. A highly reflecting chamber wall reduces the impact emissivity variations. As the wafer emissivity decreases, a reflecting chamber wall is less effective. The reactor used in this work is coated with gold to increase the reflectivity of the chamber wall R_c .

4.4.3 Calibration

For the calibration of the pyrometer of the equipment thermocouple (TC) wafers are recommended. Thermocouple equipped wafers offer the possibility to determine temperature conditions in the reactor chamber under process conditions. For the calibration in this work a S-type thermocouple was used and attached to the wafer in the following way: Ceramic adhesive powder is mixed with water. The TC ball is dipped into the ceramic adhesive. In the middle of the backside of the cleaned wafer a cavity is drilled on requested spots. Then the wafer is cleaned with air gun and isopropanol moistened line free cloth to remove Si dust thoroughly. The TC ball is placed into the drilled cavity and is fixed with a tiny drop of ceramic adhesive brought into the cavity or onto the thermocouple ball immediately before. The TC equipped wafer should be dried at least for 4 hours at 200 °C or for 24 hours at room temperature. The

 $^{^5}$ the emissivity of a flat silicon wafer is relative constant and independent on the wavelength. However, The variation of emissivity of two-layer coated silicon wafer with 0.2 μ m SiO₂ and 0.2 mm polysilicon film is fluctuated between 0.178 and 1.0 and strongly dependent on wavelengths. For example, the emissivity at 0.75 μ m, 1 μ m and 2 μ m is 0.35, 0.18 and 0.25, whereas that at 0.65 μ m, 0.85 μ m, and 1.8 μ m is 0.75, 1.0 and 0.95, respectively.

prepared wafer is mounted into RTP-system. Both wires of TC are connected with sockets by screws. The sockets are placed on the inside of the door as shown in Figure 4.4 and connected with the compensation cable and the TC amplifier. The process recipes for calibration is chosen, in which the lamp power is increased by controlled ramping-up rate of 1 W pro second up to 1050 °C. The wafer temperature is measured by thermocouple during calibration and the thermovoltage of the TC and the pyrometer signal are simultaneously stored. From the stored TC and pyrometer data the temperature can be defined, at which the first valuable emissivity signal appears. In longer isothermal periods the difference between actual TC and pyrometer measurements is less than 5 -10 °C.

Figure 4.6 shows the impact of the rear surface on the calibration. The wafer deposited Al on the rear surface can not be calibrated since Al layer absorb the heating radiation and the emissivity is changed. The difference of the temperature between polished and shiny etched surface is about 10 °C at the same pyrometer signal.



Figure 4.6 Calibration curves from the different materials. Calibration depends strongly on the rear surface. The wafer deposited with Al on the rear side can not be calibrated since the emissivity of both sides is not identical caused by a high absorption of Al. The difference of temperatures between 900 °C and 1050 °C often used in the solar cell fabrication results in about \pm 10 °C for the same pyrometer signal depending on the surface properties.

5 Czochralski (Cz) silicon-specific defects during RTP

Cz silicon material is of major importance not only for solar cells but also for semiconductor device fabrication. The main impurity in Cz silicon in comparison to FZ silicon is oxygen caused by the fabrication process. In this paragraph firstly Cz crystal growth is introduced. Secondly we discuss the Cz silicon-specific metastable defect, which causes the lifetime degradation by illumination and is reversible annealing at above 200 °C. Thirdly the main experiments for the development of an optimized process using RTP are given. Also other importance effects on lifetime are shown. Finally, the results of this work are applied in solar cell processing in order to investigate the influence of optimized processes on solar cell performance.

5.1 Czochralski silicon

5.1.1 Chemical refining of silicon

Silicon is the second most abundant element in the earth's crust (28 %). Silicon is found mainly as silicon dioxide in quartz and sand (silica). Before silicon can be used for solar cells or semiconductor applications, the raw material, i.e., quartz and silica must be refined. Firstly, the silica material is melted with carbon in an electric furnace at temperatures of about 2000 °C in order to produce metallurgical-grade silicon as Eq. (5.1).

$$SiO_2 + 2C \xrightarrow{2000^\circ C} Si + 2CO \uparrow$$
 (5.1)

In the second step metallurgical silicon powder reacts chemically with gaseous hydrogen chloride. This chemical reaction according to the formula (5.2) gives rise to trichlorosilane and hydrogen. Since trichlorosilane is melting at temperatures of 300 °C, it is very easy to dissociate it from hydrogen.

$$Si + 3HCl \xrightarrow{300^{\circ}C} SiHCl_3 + H_2^{\uparrow}$$
 (5.2)

Pure solid silicon can be obtained by the reaction of trichrosilane liquid with hydrogen at high temperatures by chemical vapor deposition (CVD):

$$2SiHCl_3 + 2H_2 \rightarrow 2Si + 6HCl \tag{5.3}$$

The polycrystalline silicon produced by the above described refining process is called electronic grade silicon. This silicon is used to produce a single crystal silicon such as Cz and FZ silicon or direct fabrication of silicon-film such as edge defined film growth (EFG); block-casked mc-Si and silicon sheet from powder (SSP) growth [4, chapter 7].

5.1.2 Czochralski crystal growth

At present, about 99 % of all semiconductor devices are produced on monocrystalline silicon. About 95 % of all silicon single crystals are grown according to the Czochralski (Cz) technique and the rest by the float zone (FZ) technique [23]. This shows that single crystal silicon is one of the most important materials today and in the nearer future.

The technique originates and takes its other name, from pioneering work by Jan Czochralski in 1917 [24] who published a method for measuring the maximum crystallization rates of metals. Firstly he pulled metal wires vertically from melts with increasing velocity until they tore off from the melt. In this experiments, single-crystalline wires occurred and he recognized that with this pulling technique, single crystals could be grown successfully if single-crystal seeds are used. Figure 5.1 (a) shows the Cz-Si single-crystal puller for the growth by Czochralski.

Figure 5.1 (b)-(e) shows the principle of Cz silicon single crystal. The technique consists of a crucible which contains the charge material (Figure 5.1 (b)) to be crystallized surrounded by a heater capable of melting the charge. A seed holder with a chuck attached to its lower end is mounted co-axially above the crucible. A seed crystal is attached to the chuck and the seed holder is lowered until the end of the seed crystal is dipped into the melt (Figure 5.1(c)). The melt temperature is carefully adjusted until a meniscus is supported by the end of the seed (Figure 5.1 (d)). Once a thermal steady state has been achieved, the pull rod is slowly lifted and rotated and crystallization onto the end of the seed occurs (Figure 5.1 (e)). Lifting rates vary with the material, the size of the crystal and the amount of dopant in the melt and are in the range of a few tenths of a mm per hour up to tens of cm per hour. Crystal rotation rates usually range from a few revolutions per minute up to a maximum of a few hundred [25, Part 2a, p101].



Figure 5.1 (a) Schematic of a modern Cz-Si single-crystal puller for the growth of large crystals [24]. (b-e) Process schematic for the manufacture of the Cz silicon crystal growth.

Figure 5.2 shows a LBIC (light beam induced current) map of a Cz-Si solar cell with a typical swirl-like pattern's distribution and inhomogeneous diffusion length of the Cz material as a result of the crystal growth technique. Usually, in Cz growth there are more impurities possible in the melt as comparable to FZ growth since in the Cz process silicon materials are melted in crucibles whereas FZ materials grow crucible-free. Therefore, the most frequent impurities of Cz come from the crucible and the melt.

Quartz (silica) is an excellent crucible material to reduce impurities in Cz-Si. However, silica is the also the main source for oxygen. The solved oxygen evaporates easily from the melt in form of silicon monooxide, SiO. The strong evaporation of SiO prevents the supersaturation of the melt with oxygen.

The whole crystal growth assembly is located within an envelope containing a noble gas (argon) to reduce oxygen content in Cz material (see in Figure 5.1 a). The gas is used to purge the crystal puller in order to remove quickly the large quantities of SiO that evaporate permanently from the silicon melt. Without purging, soon SiO and SiO₂ would form on the surface of the melt and the growth of a single-crystal would be impossible. Normally, more than 99 % of the oxygen induced into the melt by silica dissolution evaporate at the free melt surface. Using this method the oxygen content in Cz-Si can be limited to 10^{18} cm⁻³. However, in comparison to FZ silicon the main impurity in Cz is oxygen [23].



Figure 5.2 Diffusion length topography of a boron-doped Cz silicon solar cell. Cz material shows the lateral inhomogeneous distribution of diffusion length. Clearly the lateral form is caused by crystal proceeding.

5.2 Cz-Si specific metastable defects

Czochraski (Cz) solar cells have a share of 40 % of the world-wide solar cell production. The cost per Cz wafer is about three times lower than that of FZ, which allows to reach the highest solar cell efficiency. Cz wafers can be treated at high temperature (>1000 °C) and show high efficiencies well above 20 % on solar cells [2]. Unfortunately, an initial degradation at the Cz solar cell efficiency by illumination or carrier injection was observed [2] [26] [27]. The efficiency degrades by 3-4 % relativity within 10 hours illumination using of 1 Ω cm boron doped material. No further degradation is observed afterwards. Spectral response measurement has shown that the degradation of efficiency can be attributed to reduction of carrier lifetime and bulk diffusion length, respectively.



Figure 5.3 Relative loss of open circuit voltage (V_{oc}) of Cz-Si solar cells for different base resistivites and different illumination intensities. The slight degradation of the cell without additional illumination (■) may be due to several repeated measurements of the IV-curve [28].

Figure 5.3 shows the relative open-circuit voltage (V_{oc}) degradation of solar cells for different base resistivities and illumination intensities. The degradation follows an exponential law and depends on the illumination intensity. However the degradation is only observed for low resistivity materials while cells produced from high resistivity materials do not degrade.

The degraded efficiency and initial lifetime, respectively, can be completely recovered using an annealing temperature at about 200 °C in room ambient as shown in Figure 5.4 (a). Figure 5.4 (b) shows the result of a multistep experiment where a cell was alternately illuminated with a intensity of 100 mW/cm² for 30 h and annealed at 200 °C for 20 min. Consequently, the lifetime degradation/recovery cycle is fully reversible independently of the number illumination and annealing cycles.

Recently, several attempts were undertaken to understand and explain the fundamental Cz-Si specific metastable defects [29]. Observations described in the literature on the light-induced degradation of Cz-Si are summarized in the following points.



Figure 5.4 (Left) Relative increase of open-circuit voltage (V_{oc}) due to the anneal of Cz solar cells at different temperature. The initial V_{oc} , respectively, efficiency can be recovered by an annealing step at 200 °C in room ambient [28]. (Right) Measured open-circuit voltage circle after annealing at 200 °C, 20 min and illumination in suntester at 1-sun, 30 h.

5.2.1 Influence of Boron and interstitial oxygen

A shown above the Cz-specific metastable defect is activated by illumination of 1-sun for 30 h and deactivated during annealing above 200 °C. In 1995, Knobloch et al. [2] showed that the lifetime degradation is not directly caused by illumination photons but by excess charge carriers, because the degradation is also induced by a forward bias voltage without any additional illumination. Recently, Glunz et al. [30] have performed experiments with boron and gallium doped silicon material of various resistivities and of different concentration of interstitial oxygen. Figure 5.5 shows very well the strong correlation between the light-induced lifetime degradation in Cz silicon and the boron as well as the oxygen concentration. The conclusions from Figure 5.5 are presented in the following points.

- A strong degradation was observed for the materials which have quite high boron doping concentration and a significant concentration of interstitial oxygen (#1 and #2).
- A slight degradation was observed for materials which have significant lower boron doped concentration, even though the oxygen concentration is high. (#3)
- No degradation was observed for materials with a high boron concentration but with a very low oxygen concentration (#4)
- No degradation was observed for gallium doped materials although they have a quite high oxygen concentration (#8-10)



Figure 5.5 measured effective lifetime of boron and gallium doped silicon materials with different resistivity and concentration of interstitial oxygen before illumination and after illumination [30].

These observations justify that boron and oxygen are the main components of the metastable defect underlying the Cz-specific lifetime degradation. Therefore, the potential of materials avoiding higher oxygen or boron content is clearly demonstrated for highly efficient solar cell by a stable efficiency of 22.7 % for MCz silicon (magnetic Czochralski silicon with low oxygen concentration) and 22.5 % for boron-free gallium-doped Cz silicon [30].

In the following years several studies have been attempted for a physical model which can explain the light-induced degradation and the recovering by annealing above 200 °C of the Cz silicon materials. Reiss et al. [31] suggested the light-induced Cz-specific metastable defect may be caused by the thermal dissociation reaction of FeB pairs at room temperature. Interstitial iron Fe_i is about 10 times more effective as a recombination center than FeB and reduces the minority carrier lifetime more strongly. However, this model could not explain the light-induced degradation of high efficiency solar cells which contained very low iron content.

A few papers [29] [32] [33] have suggested a model assigning the origin of the metastable defect to the B_iO_i pair complex. This model seems to fit well to the experimental results. Kimerling et al. [33] have observed that the production of B_iO_i increases linearly with boron concentration [B_s] and at high [B_s] above 2×10^{16} cm⁻³ the B_iO_i generation rate decays as a function of [B_s]². The forming of the defect C_iO_i -complex rate decays linearly with increasing [B_s] and increases slightly [C_s] in material of high [O_i]. Defects from B_iO_i pairs disappeared after annealing at around 175 °C. At the same time, a new majority carrier trapping from B_iC_s emerges. The fractional conversion of [B_iO_i] to [B_iC_s] increases linearly with [C_s]. These oxygen-

boron pairs act as deep-level defects which completely dissociate at temperatures above 200 °C and are identified as Cz metastable defects. This model explains the observed bulk lifetime increase with decreasing boron doping concentration (#1 in Figure 5.5) because a decrease of $[B_s]$ leads to a decrease of the B_iO_i pair concentration.

This model was very attractive and made possible to explain the phenomenon of Cz metastable defects. There is a lot of oxygen (>10¹⁷ cm³) available in Cz silicon material for the trapping of mobile interstitial boron. In addition, the formation of the [B_iO_i] is energetically possible, because the chemical bonding energy (~192 kcal/mole) between boron and oxygen is slightly higher than that (~188 kcal/mole) between silicon and oxygen [32]. This [B_iO_i] complex dissociates by emitting an interstitial boron [B_i] at around 170 °C. The [B_i] is then trapped to form the [B_iC_s] complex because this level from [B_iC_s] complex appears upon the disappearance of the defect of [B_iO_i]. [B_i] dissociated from [B_iC_s] complex by illumination associated with [O_i]. Therefore, the defect level is activated. The annealing behavior was controlled by dissociation and recombination of this defect.

Little is known concerning the composition of this metastable defects which correspond to the energy levels and capture cross sections of the deep level defects. By DLTS measurements [32] [33] [34] it was determined that the energy level of the [B_iO_i] and [B_iC_s] complex in Cz silicon material was $E_t = E_c - 0.27$ eV and $E_t = E_v + 0.29$ eV by DLTS. On the other hand, Schmidt and Cuevas [35] have used quasi-static photoconductance lifetime measurements. The most probable value for the energy level is close to in the range between $E_v + 0.35$ eV and $E_c - 0.45$ eV. From this observation they concluded that the [B_iO_i] pair complex is not a candidate for the light-induced degradation. A new boron-oxygen complex like [BO_{i5}] was suggested. Glunz and Rein [36] [37] support this exclusion. They observed $\Delta E = 0.35...0.41$ eV and $\Delta E = 0.008 \pm 0.003$ eV as the energy level of the defect in its active state and as that in its passive state using temperature-dependent lifetime spectroscopy (TDLS). This deep and shallow energy levels are in good agreement with the fact that the defect shows a very strong and weak recombination activity, respectively.

More recently, Ohshita et al. [38] found that B_i does not exist stable near the O_i, but exists stable near Si_s as [B_i-Si_s-O_i] complex. It creates a deep energy level in the band gap. However, the [B_i-Si_s-O_i] complex is not stable, since the binding energy of the B_i to the [Si_s-O_i] is relatively small. This explains the experimental results that the light-induced defect disappeared by annealing above 200 °C. On the other hand, Schmidt et al. [39] showed that the energy level of light-induced degradation is 0.4 eV and the energy level after the annihilation of the defect is 1.8 eV. They suggested a [B_s-O_{2i}] complex. Oxygen dimer, O_{2i} can diffuse extremely fast in silicon and [B_s-O_{2i}] complex acts a highly effective recombination center. On the other hand, Rein and Glunz [APL, 2003] determined by TDLS and IDLS⁶ measurement that the Cz specific defect is localized in the upper band-gap half at E_c – 0.41 eV and has an electron/hole capture cross section ratio k = $\sigma_n/\sigma_p = 9.3$.

⁶ TDLS and IDLS are an abbreviation of temperature- and injection dependent lifetime spectroscopy, respectively.

5.2.2 Influence of process steps

As already mentioned in section 5.2.1, the bulk lifetime can be reduced significantly if standard Cz-Si (boron-doped and oxygen-contaminated) has to be used, and can not only be increased temporarily. Recently, it was shown that it is possible to increase the stable lifetime after degradation, τ_d , permanently by a high temperature step (1050 °C, 55 min) in a conventional furnace [40]. Therefore, the process parameter strongly influence the carrier lifetime. For example, the initial lifetime can be either decreased by 6.3 % by processing with unfavorable process parameters or increased up to 425 % by processing with favorable parameters. This improved lifetime is mainly caused by the reduction of the concentration of metastable defects.

On the other hand, the permanent reduction of light-induced recombination centers was also found after short annealing at 820 °C for 8 s using phosphorous pregettered Cz silicon materials in a belt furnace processing [41]. The stable bulk lifetime were enhanced by a factor of up to 2.4.

In this work the influence of process parameters on the bulk lifetime after the light-induced degradation is investigated for RTP (Rapid Thermal Processing) which is suitable for industrial silicon solar cells. RTP is very a short process (~ few seconds) which is introduced to reduce the thermal budget in solar cells processing (see chapter 4). The important five process parameters are varied and observed which parameter has the significant influence on the stable lifetime without any external gettering (e.g. phosphorus gettering).

Primary research for the light-induced degradation of Cz silicon materials and solar cells is summarized in Table 5.1. The light-induced metastable defect of boron doped Cz materials was first found in 1973 by Fischer. Despite this early finding the numerous studies attempted to understand and to explain its fundamental characteristic have started only a few years ago. However, this metastable defect is not fully understood at the present time. Further studies should pursue these possibilities.

Researcher	contents	Energy level of defect (E_t)
Fisher (1973) [26]	First paper about the light-induced degradation and recovery	
Kimerling (1989) [33]	[B _i O _i] pair model	$E_{c} - 0.27 \text{ eV}$
Knobloch (1995) [42]	Light-induced degradation in high efficiency Cz solar cells	
Reiss (1996) [31]	FeB pair model	$E_v + 0.4 \text{ eV}$
Schmidt (1997) [29]	$[B_iO_i]$ pair model. Analysis of correlation with oxygen and boron.	
Glunz (1998) [28]	First paper on a reduction of defect concentration due to an optimized process by conventional tube furnace and analysis of correlation with oxygen and boron	
Glunz (1999) [30]	No degradation for gallium doped Cz-Si and MCz solar cells	
Schmidt (1999) [35]	[BO _{i5}] pair model	E _v +0.5 eV ~ E _c − 0.45 eV
Rein(2000) [43]	Influence of process parameters on lifetime of B-and Ga-doped Cz-Si	
Nagel (2000) [41]	Reduction of light-induced degradation due to the optimized process by belt furnace (included phosphorus gettering)	
Glunz (2001) [44]		$\Delta E_v \leq 0.48 \text{ eV}$
Rein (2001) [37]	Analysis of defect generation and annihilation	
Lee (2001) [45]	Reduction of light-induced degradation due to the optimised process by rapid thermal Processing (this work)	
Ohshita (2002)[38]	[B _i -Si _s -O _i] model	
Schmidt (2002) [39]	[B _s -O _{i2}] model	$E_{gen} = 0.4 \text{ eV}$
Rein and Glunz (2003) [46]	$k = \sigma_n / \sigma_p = 9.3$	$E_c - 0.41 eV$

Table 5.1 Papers on the light-induced degradation of Cz silicon materials and solar cells and related issues.

5.3 Influence of high-temperature steps on the carrier lifetime in Cz silicon

5.3.1 Selection of a barrier layer to avoid external contamination

It is well known that the ambient (furnace, gas) or the surfaces of the sample might act as sources of external contamination during RTP which can lead to deep energy levels in the band gap of silicon. They could act as recombination centers and thus degrade the lifetime [47] [48]. Therefore, a barrier layer is needed in order to protect the bulk sample against external contamination. This is especially important since in the present study the effect of high-temperature cycles on the carrier lifetime should be analysed.

High-lifetime p-type FZ wafers of 1.25 Ω cm resistivity were used for this experiment. The wafers are 4 inches in diameter and 250 μ m thick. For lifetime measurements the samples are passivated on both sides with a 60 nm thick SiN_x layer which has been optimised with respect to low surface recombination velocities (S < 10 cm/s) [49]. Using this excellent passivation layer, lifetimes are measured by microwave-detected photo conductance decay (MW-PCD) with an additional bias light of 0.5 suns (see Appendix B.1). Since this technique is a differential measurement method the measured values are strictly speaking differential effective lifetimes.

After RCA cleaning SiN_x is deposited by means of PECVD at low temperature (350 °C) or a SiO₂ layer is grown at 1050 °C in a conventional tube furnace. Subsequently, the SiN_x or SiO₂ covered samples are processed at a plateau temperature of 950 °C for 100 s. After the RTP process SiN_x and SiO₂ are removed using plasma etching and the sample surfaces are passivated with SiN_x for the final lifetime measurement.

Figure 5.6 shows the effective lifetime of different layers (1) before, (2) directly after RTP and (3) after etching the barrier layer and depositing a new SiN_x passivation layer. The values given in Figure 5.6 are the average values and 5 points measured on each wafer. It is obvious that the passivation quality is severely decreased by the RTP step. If the barrier layer is replaced by a new SiN_x passivation layer, high effective lifetimes can be recovered. This shows that all barrier layers protect the wafers from contamination effectively. The best result is obtained for the SiN_x covered wafer where the lifetime level can be kept on a very high level. The slight lower lifetime after etching may be due to the rougher surface because the SiN_x passivated wafer is etched by plasma while the SiO₂ passivated wafer is etched by chemical etching. A second result is that the thick oxide can protect the wafer better than the thinner one. Especially, the spatial lifetime deviation is much stronger if the wafer is protected only with a thin oxide (i. e. τ_{eff} varies from 30 µs to 419 µs across the wafer).

In this work the STEAG-RTP system SHS 100 as shown in chapter 4 is used in which the wafer is processed in a quartz chamber. In order to assess the influence of external contamination from the surrounding quartz chamber, lifetime measurements before and after intense cleaning of the quartz chamber are carried out. The quartz chamber is cleaned in 65 % HNO₃ for 10 minutes and etched in 5 % HF for 2-5 minutes at room temperature. Subsequently, the quartz chamber is rinsed with DI-water and purged with nitrogen.



Figure 5.6 Comparison of the effective lifetime of FZ-Si wafer before and after RTP covered by three different barrier layers. \blacksquare : Before RTP with SiN_x or SiO₂ passivation as barrier layer; \Box : After RTP with SiN_x or SiO₂ passivation as barrier layer; \bullet : After removal of SiN_x or SiO₂ and new SiN_x passivation.

Table 5.2 shows the effective lifetime before and after a quartz chamber cleaning. After the quartz chamber cleaning τ_{eff} of the oxidised wafer improves by 51.4 % from 354.1 µs to 536 µs, whereas τ_{eff} of the SiN_x coated wafer is not influenced by the cleaning. This shows that the reduction of lifetime of SiO₂ coated samples during the RTP process is likely to be caused mainly by external contamination. In contrast, the SiN_x coated wafers exhibit the same high lifetime before and after the quartz chamber cleaning. This underlines the excellent barrier quality of SiN_x although it is thinner than the SiO₂ layers and is deposited at low temperatures (350 °C).

Barrier Layer	$ au_{eff}$		
	Before quartz chamber cleaning	After quartz chamber cleaning	Deviation
SiN _x 60 nm	612.7	634	+3.5 %
SiO ₂ 180 nm	354.1	536	+51.4 %

Table 5.2 Comparison	of effective	lifetime	of p-type	e FZ silicon	sample	before	and
after quartz chamber cle	aning.						

5.3.2 Optimization of process parameters

Rapid thermal processing (RTP) has many advantages over conventional thermal processing, such as a low thermal budget due to very high heating and cooling rates, of the order of 100 °C/s, and a short process time (see chapter 4). However, defects can be introduced during RTP not only by external contamination from furnace and gas supply [47], but also by internal impurities such as the dopant, oxygen, and other residual impurities [50]. Also the defects can be affected by the process chosen.

In this work we have used 'design of experiment (DOE)' in order to analyze the influence of process parameters on the lifetime systematically. Five process parameters are analyzed: plateau temperature ($T_{plateau}$), plateau time ($t_{plateau}$), heating rate (R_{up}), cooling rate (R_{down}) and cooling point temperature ($T_{cooling pt}$). Table 5.3 indicates the total list of variable factors and Figure 5.4 represents response value for DOE and the temperature cycle with varied parameters. The 17 different parameter sets for the 2⁽⁵⁻¹⁾ experimental design are represented in Table 5.4. Each column of the design contains '-' or '+' to indicate the setting of the respective process parameters. '-' and '+' indicate low and high value of each parameters. a17 and a18 are the center-point runs which is the midpoint between '-' and '+'. This is to support and to check for nonlinear types of interactions.

Boron-doped Cz-Si wafers with a resistivity of 1.06 Ω cm, 350 µm thickness and 5×5 cm² in size are used for this experiment. The oxygen content [O_i] of this Cz material is 5×10¹⁷ cm⁻³ and the stable effective lifetime after degradation by illumination is 15 µs as measured on SiN_x passivated reference samples.

	abbreviation of factor name	Full factor name	dimension	low (-) value	high (+) value
variable	T _{plateau}	Plateau temperature	°C	850	1050
	t _{plateau}	Plateau time	S	30	120
	R _{down}	Rate of ramping-down	°C/s	1	50
	R_{up}	Rate of ramping-up	°C/s	10	100
	T _{cooing Pt.}	Temperature of cooling point	°C	750	820
Response value	τ	Effective lifetime	μs		

Table 5.3 Total lists of variable factors and	l response value fo	or Design of	experiment (DOE)
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Figure 5.7 Schematic illumination the ramped temperature transient RTP thermal cycles. A profile consists of varied ramping up (R_{up}), plateau temperature ($T_{plateau}$), plateau time ($t_{plateau}$), raping down (R_{down}) and cooling point temperature ($T_{cooling pt}$)

Table 5.4 Scheme of 17 different processes in RTP for $2^{(5-1)}$ design of experiments. The columns are the groups of components and the rows are the individual runs. – and + refer to the low (minimal) and high (maximal) value of each variable parameters, respectively. 0 represents the middle value between the low (–) and the high value (+).

Wafer No.	T _{plateau} [°C]	t _{plateau} [s]	R _{down} [°C∕s]	R _{up} [°C/s]	T _{cooling pt.} [°C]
a1	-	-	-	-	-
a2	-	-	-	+	+
a3	-	-	+	-	+
a4	-	-	+	+	-
a5	-	+	-	-	-
a6	-	+	-	+	+
a7	-	+	+	-	+
a8	-	+	+	+	-
a9	+	-	-	-	-
a10	+	-	-	+	+
a11	+	-	+	-	+
a12	+	-	+	+	-
a13	+	+	-	-	+
a14	+	+	-	+	-
a15	+	+	+	-	-
a16	+	+	+	+	+
a17(c)	0	0	0	0	0
a18(c)	0	0	0	0	0



Figure 5.8 The stable effective lifetime of boron-doped Cz silicon wafer after RTPprocessing according to Table 5.4. The stable effective lifetime of the unprocessed reference wafer is $15 \ \mu s$.

After RCA cleaning, SiN_x is deposited at low temperature by means of PECVD since it can protect better against the contamination from furnace than thermal SiO₂ as already shown in the section 5.3.1. After the RTP process the SiN_x layer is etched off using an optimized plasma etch step [51] and a new SiN_x layer is deposited. Subsequently, the effective lifetime before light-induced degradation, τ_0 is measured directly after a forming gas anneal (FGA) step at 425 °C for 25 min⁷. The wafer is then illuminated with white light of an intensity of 100 mW/cm² (1 sun) for at least 30 h. And finally the stable effective lifetime τ_d is measured.

Figure 5.8 shows the stable effective lifetime (τ_d) after light degradation with respect to 17 different process parameters. The values given in Figure 5.8 are the average values and standard deviation of five points measured on each wafer. The average of the stable effective lifetime of the reference sample which has received the SiN_x barrier layer, the plasma etch step and the deposition of SiN_x passivation layer but no RTP step is 15 µs after light degradation. In the case of an RTP treatment at 850 °C for 120 s plateau time, τ_d is increased drastically by 60 % from 15 µs to 24 µs (a5-a8) almost independent of the ramping conditions.

The wafers (a9-a10, a13-a14) with a slow cooling rate at 1050 °C in RTP have higher stable effective lifetimes than the wafers treated with fast cooling rate (a11-a12, a15-a16). If high cooling rates are applied, the stable effective lifetime is 50 % lower compared to the non-RTP-treated reference sample.

⁷ Forming gas consists of N₂ (95 %) and H₂ (5 %). During FGA the hydrogen passivates defects at the interface such as Si-SiO₂ or Si-SiN_x. Therefore, FGA leads to a large increase in minority carrier lifetime. For example the lifetime for SiO₂ 105 nm passivated wafer is $30 \sim 40 \ \mu s$ and $300 \sim 400 \ \mu s$ before and after annealing, respectively.



Figure 5.9 The pareto chart of standardized effects through $2^{(5-1)}$ design of experiments. For $p \ge 0.05$ an effect is a statistical significance. From the results, It is clear that the plateau temperature, $T_{plateau}$ has a strong influence on the stable effective lifetime. Minus value on the right of pareto chart shows decease the effect lifetime with an increase in the plateau temperature.

These facts can be seen as well in Figure 5.9 which shows the pareto chart of standardized effects through $2^{(5-1)}$ experimental design. The effect estimate value of parameters shows the minus '-'. That means that the effect lifetime decreases with an increase in parameters. For example, the higher plateau temperatures or the faster ramping down process, the lower the effective lifetime. Obviously, the plateau temperature has a strong correlation on the effective lifetime after light-induced degradation. Secondly, the cooling rate (R_{down}) has some effect on the stable effective lifetime which stems from the wafers treated at 1050 °C. The other parameters seem to be negligible, since they are below the statistical significance.

In order to improve the process the correlation between plateau temperature and ramping down rate is investigated. As shown in Figure 5.10 (left) both levels of R_{down} (1 °C/s ad 50 °C/s) have a linear interaction with $T_{plateau}$. Both slow and fast R_{down} have no influence on the effective lifetime in plateau temperature at 850 °C while slow R_{down} results in slightly better effective lifetime at a plateau temperature at 1050 °C. The contour plot in Figure 5.10 (right) supports the same results. It is obvious that for an improved stable effective lifetime after the light-induced degradation, Cz silicon wafers should be processed at low temperatures and with slow ramping down.



Figure 5.10 (Left) Interaction graph between $T_{plateau}$ and R_{down} . This graph shows the effect of increasing $T_{plateau}$ while R_{down} is at the low level (black circle) and while R_{down} is at the high level (triangle). (Right) Contour plot between $T_{plateau}$ and R_{down} . 5 points estimate the effect by comparing the high level for $T_{plateau}$ within each level of R_{down} .

5.3.3 Effect of plateau temperature on the stable effective lifetime

We have shown that the plateau temperature has a very significant effect on the stable lifetime. For a further optimization the parameters of the a5 run are chosen, which have given the best stable effective lifetime (see Figure 5.8). The plateau temperature is varied between 700 °C and 1050 °C while keeping the other parameters fixed.

Figure 5.11 shows the dependence of the stable effective lifetime in Cz-Si on the plateau temperature in the range from 700 °C to 1050 °C for 120 s. The non-RTP-treated reference wafer shows a stable effective lifetime of 15 μ s. All RTP-processed wafers have a lifetime higher than the reference wafer. In Figure 5.11 100 % represents the stable effective lifetime of the non-RTP- treated reference sample. The highest improvement of fairly 80 % (from 15 μ s up to 25.5 μ s) can be observed at 900 °C.

In order to exclude that the significant improvement of the Cz material is caused by hydrogen diffusion from the SiN_x into the silicon bulk, we have repeated the experiment with a 200 nm thick SiO₂ barrier layer. The solid circle denotes stable effective lifetime of a sample covered with a 200 nm thick SiO₂ barrier layer in Figure 5.11. As shown in Figure 5.11 we have achieved the same lifetime improvement. Therefore, we can exclude any external gettering. To our knowledge this is the first time that an improvement of the stable effective lifetime of Cz-Si by an RTP-process without external gettering is demonstrated. On the other hand, after rapid thermal processing at 1050 °C a stable effective lifetime is reduced to 82.3 % compared to this optimum value. But also for this high temperature a strong improvement compared to the initial value is observed.



Figure 5.11 Evolution of the stable effective lifetimes after light-induced degradation as a function of the temperature for SiN_x coated Cz-Si samples (open symbols). The solid circle denotes the stable effective lifetime of a sample with a 200 nm thick SiO_2 barrier layer. The dashed line indicates the stable effective lifetime of the non-RTP-treated reference sample with SiN_x surface passivation.



Figure 5.12 Normalized defect concentration $N_t^*(: = 1/\tau_d - 1/\tau_o)$ of the RTP processed Cz-Si samples (SiN_x coated) for different plateau temperature. The dashed line at 100 % indicates the defect concentration of the non-RTP-processed reference sample.

The defect concentration is determined using the extent of lifetime degradation by measuring the minority carrier lifetime before (τ_o) and after (τ_d) light-induced degradation [28]. A normalized defect concentration N_t^{*} can be determined in the following way:

$$N_{t}^{*} = \sigma_{n} \upsilon_{th} N_{t}$$

$$= \frac{1}{\tau_{d}} - \frac{1}{\tau_{o}} = (\sigma_{res} \upsilon_{th} N_{res} + \sigma_{n} \upsilon_{th} N_{t}) - \sigma_{res} \upsilon_{th} N_{res}$$
(5.4)

where σ_n and σ_{res} are the electron capture cross sections and N_t and N_{res} are the concentration of the metastable defect and the residual defects, respectively, while v_{th} is the thermal velocity. It is possible to calculate N_t^* under the assumption that the metastable defect is completely deactivated after the annealing at 200 °C and is completely activated after an illumination of for 30 h under 100 mW/cm² (1 sun) and all additional defects possibly contained in the material are not affected by the anneal/illumination cycle.

Figure 5.12 shows the normalized defect concentration after rapid thermal annealing. The normalized defect concentration of the non-RTP-treated reference sample is 0.06 μ s⁻¹. N^{*}_t is strongly reduced from 0.06 μ s⁻¹ to 0.037 μ s⁻¹ due to RTP at 900 °C. Thus, it is possible to improve the stable effective lifetime and reduce the normalized defect concentration by rapid thermal processing. This reduction is somewhat smaller for temperatures higher than 950 °C.

In addition, three different Cz silicon materials are processed for varying plateau temperatures with the same process as mentioned above. Table 5.5 shows the properties of the three different boron-doped Cz silicon materials. All Cz silicon wafers have a size $5x5 \text{ cm}^2$ and a thickness $250 \sim 300 \text{ }\mu\text{m}$. Figure 5.13 shows the stable lifetime for three different Cz silicon as a function of varied plateau temperatures. The upper half of Figure 5.13 indicates the measured stable lifetime after RTP and the lower half indicates the improvement in comparison with the initial stable lifetime.

The stable lifetime of all three different Cz materials improves through RTP even though they have different doping and oxygen concentration. Material No12 has a high initial lifetime, however, the best improvement is shown on Baysix material which increases about two times compared to the initial value at the temperature between 780 °C and 860 °C. The improvement ratio of the different Cz materials is not identical, however a similar trend is observed. For plateau temperatures under 950 °C the improvement of the stable lifetime is relatively high. Above 950 °C the improvement of the stable lifetime. For example, for a plateau temperature of 1050 °C the stable lifetime is reduced by about 50 % from 15 μ s to 7 μ s by non-optimized process (see Figure 5.8), while the stable lifetime is increased by 30 % from 15 to 20 μ s or at least 20 % from 15 μ s to 18 μ s using the optimized processes (see Figure 5.11 and Figure 5.13)

It can be concluded that the improvement of the stable lifetime is a general effect and can be observed for Cz materials with different boron and oxygen concentration. The optimal set of process parameter is very important. When the optimized parameters are used, the stable lifetime improves even at high plateau temperatures.

Material ID	ρ [Ω cm]	O _i [10 ¹⁷ /cm ⁻³]	τ_{o} [µs]
No12	0.8 ~ 1.5	7.6~8.0	13
WC4	1.0~1.4	7.9	21
Baysix	1.4	7.8	16

Table 5.5 Properties of the Cz silicon materials used in this work. τ_{o} shows the initial lifetime.



Figure 5.13 Stable effective lifetimes as a function of the RTP plateau temperature with three different Cz silicon materials. The ratio in the lower graph shows the amount of the stable lifetime improvement.

Figure 5.14 shows the dependence of the effective lifetime on the processing temperature in the range of 700 °C to 1050 °C for 120 s for FZ-Si. The reference wafer which has received the SiN_x barrier deposition, the plasma etch step and deposition of the SiN_x passivation layer, but no RTP step, exhibits a lifetime of 700 μ s. This reference value was reached for all RTP-treated FZ wafers with plateau temperature between 700 °C and 900 °C. However, a drastic degradation occurs at temperatures higher than 900 °C. Especially, the effective lifetime at 1050 °C is reduced by 50 % from 700 μ s to 360 μ s. Also, for higher temperatures the standard deviation of the five measurement points on the wafer is higher than the one for lower temperatures. A similar trend has been observed by Eichhammer et al. [47]. The high-purity control FZ material was processed at temperatures in the range of 500-1100 °C for 10 s and μ to 2min. They found that the diffusion length⁸ was not strongly dependent on the processing time. Degradation started around 800 °C. At 1050 °C the diffusion length was decreased more than 40 % from 310 μ m to 125 μ m.

⁸ Diffusion length, L = (D τ)^{1/2} where D and τ are diffusion coefficient and lifetime, respectively. Electron diffusion coefficient in silicon is 28.8 cm²/s for doping concentration of 1.2 × 10¹⁶ cm⁻³ at room temperature (300 K).



Figure 5.14 Effective lifetimes of SiN_x coated FZ-Si samples for different plateau temperatures with the plateau time set to 120 s. The dotted line indicates the reference value which is non-RTP-treated wafer.

Three probable explanations can be found in the literature. The first hypothesis is based on quenched-in defects in silicon [52]. The quenching-induced recombination centers are mainly due to the activation of isolated interstitial 3d metals (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu) and that their diffusivity and solubility increases markedly with atomic number. After a high temperature step the fast diffusing ones (e.g., Co, Ni, Cu) have enough time to precipitate and to form inactive complexes, whereas the slow diffusing one (e.g., Ti, V, Cr, Fe) are frozen in electrically actives sites in the fast quenching step. Therefore, the second group of metals is harmful at much lower concentration to the performance of a solar cells than the first group.

The second hypothesis is based on generation of slip dislocation or warpage caused by temperature non-uniformity on the wafer [53] [54]. It is well known that a wafer processed in the RTP system is not in thermal equilibrium with the cool wall of the system, and as a result temperature non-uniformity on the wafer can easily occur. Yarling et al. [54] observed that warpage and slip dislocation increase with an increase of process temperature and clearly recognizable slip line appears around edges of the wafer whereas no warpage appears in wafers which have been processed in classical furnace.

The third hypothesis is a surface effect. The recombination center distribution as a function of the depth below the surfaces was measured by the surface photovoltage (SPV) method. Low temperatures lead to a lower recombination center concentration than high temperatures. The defect concentration near to the front and rear surfaces is higher than that in the bulk. The more damaged surface induces, the more recombination centers at the surfaces. Thuong et al. [55] observed a large recombination cross section with a lower limit of $\approx 10^{-13}$ cm² after RTP. It is concluded that this defects are not caused by metallic impurities because no metallic impurity

deep levels are known to have such large cross sections. Hence, they assumed that impurityrelated large complexes are the origin of these recombination centers.

The first hypothesis could not fully explain the observations of the present work. We have measured Cz and FZ wafer after RTP at 1050 °C with DLTS (Deep level transient spectroscopy). No effect levels are observed neither in Cz materials nor in FZ materials. This results is not surprising since we used high purity materials and a detection limit of defect concentration in DLTS measurements is 10¹¹ cm⁻³. Even when deep levels from 3d materials are present, their concentrations are not sufficient to explain the low lifetime.

The last two hypotheses are more reasonable to explain that the reduction for high plateau temperatures is similar for both, oxygen-contaminated Cz silicon and oxygen-free FZ silicon material. We have also observed the temperature non-uniformity. The thickness of the SiO₂ layer is higher in the middle of the wafer than on the edge (see Figure 6.9). The candidate for the impurity-related large complex is an oxygen complex [56]. Oxygen is known to form complex defects with vacancies (i.e. A-center) and with metallic impurities. Since surfaces are known to be a source of vacancies, it is likely that the defect observed on the surfaces is correlated to vacancy complexes. Therefore oxygen, by pairing with vacancies, compete with the formation of the defects and would lead to a lower degradation of the lifetime. This is very likely since the degradation of lifetime in FZ silicon material at high temperature is higher than the one with Cz silicon material.

5.4 Optimization of rapid thermal firing (RTF) for screen printed contacts

Screen printing (SP) technologies are used increasingly in industrial solar cells. RTP has been applied for emitter diffusion and for metallic contact formation, i.e., for rapid thermal firing (RTF), in SP solar cells. The firing of screen printed contacts is necessary in order to obtain the desired electrical contact properties after printing and drying of the paste. The firing of contacts by RTP is more attractive for use in production than firing in conveyor belt furnaces since RTP can lead not only to lower processing times and thermal budgets but also every process step of RTP can be regulated easily of thermal cycle and gas atmosphere.

The typical thermal cycle for contact firing by RTP is shown in Figure 5.15. The process consists of different phases. After purging the quartz chamber with the N_2 , the organic binders of the metallization pastes are burned out at low temperature. The time interval 'firing' is the most important process step for the cell performance since the electrical properties of the contact are formed in this phase. Then the quartz chamber is again purged with N_2 . Finally, the irradiation is switched off and the temperature is quenched.

Huljic [57] varied all possible process parameters for the phase 'firing' in order to obtain highquality contacts and high fill factor (FF) values on industrial solar cells. He concluded that plateau temperature, time and oxygen content rate have strong influence on the electrical qualities.



Figure 5.15 Schematic for typical rapid thermal firing (RTF) process showing the different process phases.

Furthermore, the optimal temperature and time depend strongly on cell designs and the kinds of pastes. However, generally the optimal temperature lies in the range of 700 °C and 800 °C. On the other hand, the FF decreases drastically below or above the optimal temperature. A decrease of FF is caused by a high series resistance below an optimal temperature and by more shunts at above the optimal temperatures. Plateau time should be as short as possible for a high FF.

For the following experiment Cz boron doped silicon material of 0.9 Ω cm resistivity with 350 µm thickness and an oxygen concentration [O_i] of 7.6~8.0 x 10¹⁷ cm⁻³ was used. Note that this Cz material has a different characteristic in comparison to the Cz material used in section 5.3. After RCA-cleaning the wafers were passivated with 60 nm SiN_x and were treated in different RTF-processes. The SiN_x layer was removed with plasma etching and then all wafers were passivated again with 60 nm of SiN_x. The stable lifetime was measured using MW-PCD before and after degradation as described in section 5.3.

The important two parameters, i. e. plateau temperature ($T_{plateau}$) and plateau time ($t_{plateau}$) are varied. $T_{plateau}$ was varied between 700 and 950 °C. $t_{plateau}$ was chosen to be 1 s and 10 s, which are used normally for laboratory and for industrial fired contact, respectively.

Figure 5.16 shows the stable lifetime as a function of plateau temperature for 1 s and 10 s. For 1 s the stable lifetime is enhanced drastically up to more than 40 % at temperatures in the range of 850 °C–950 °C while no increase is observed below 820 °C. All Cz materials treated by the RTF-process for 10 s show an increased stable lifetime. The largest increase in the stable time is reached at 850 °C. The improvement of the stable time is decreased slightly with an increase to higher plateau temperatures. These results support the previous observations that the plateau temperature has the most important influence on the stable lifetime after light-induced degradation.



Figure 5.16 The stable lifetime as a function of plateau temperature for 1 s and 10 s RTF time. The heating rate $R_{up} = 90$ °C/s and the colling down rate $R_{down} = 30$ °C/s.

5.5 Influence of two subsequent high-temperature steps

The RTP solar cell process normally contains two high-temperature steps, one for emitter diffusion and the other for oxidation resulting in the emitter passivation or/and AR coating. To evaluate the relevance of process optimizations in the single steps, we have investigated the influence of two subsequent high-temperature steps on the stable lifetime combining an optimized (good) and a non-optimized (bad) process.

Figure 5.17 shows the stable lifetime after the two subsequent processes. The dotted line represents the non-RTP-treated reference wafer. The results are quite interesting: The stable lifetime is reduced from 14 μ s to 9 μ s after one bad RTP-process, whereas the stable lifetime increases from 14 μ s to 22 μ s after one good RTP-process. For the process sequence with two non-optimized (bad-bad) RTP steps the stable lifetime is reduced by 36 % from 14 μ s in the reference wafer to 9 μ s after the first non-optimized (bad) step. No further reduction is observed after the second non-optimized (bad) step. Replacing the second step by an optimized (good) process we observe an increase of stable lifetime up to 19.5 μ s (after a single optimized process the stable lifetime is increased of from 14 μ s to 22 μ s).

From this experiment, it is clear that the last high-temperature step determines the stable lifetime and that the reduced lifetime due to a first non-optimized step can be recovered by an optimized last step.



Figure 5.17 Impact of two subsequent processes on the stable lifetime. bad and good represent a non-optimized step and an optimized step, respectively. The dotted line indicates the stable lifetime of the non-RTP-treated reference sample.

5.6 Effect of improving processes on the RTP solar cells

5.6.1 Solar cell structure and process sequence

In the previous section 5.5 we have shown that the stable lifetime depends strongly on the last high-temperature process. In order to investigate whether these effects influence the solar cell results two different materials were chosen for solar cells : P-type FZ-Si with a resistivity of 1.25 Ω cm and 1 Ω cm Cz-Si corresponding to Baysix in Table 5.5.

Figure 5.18 and Figure 5.19 show the cell structure and the corresponding process steps for the experiments, respectively. Note that the cells are not textured neither with inverted nor random pyramids. After a damage etch of 20 μ m on each side, a 2 μ m thick aluminum layer was evaporated on the rear side. A commercially available phosphorus dopant spin-on source was deposited on the front side and the samples were processed for the simultaneous formation of emitter and BSF in the first high-temperature step. After removing the phosphosilicate glass, two different processes were chosen and carried out as rapid thermal oxidation (RTO) used for emitter passivation [58] [59] which is the second and last high-temperature step in the RTP solar cells process. Two different RTO process schemes have been investigated: The first with a plateau temperature of 900 °C (an optimized process). The front contacts were realized using photolithography and metal evaporation while the back contacts consist of 2 μ m of evaporated AI. All cells were covered by a double layer antireflection coating consisting of TiO₂/MgF followed by a forming gas anneal (FGA) step. Finally, edge isolation has been carried out using a Nd:YAG laser.



Figure 5.18 Schematic design of RTP silicon solar cells. The front surface is plane.



Figure 5.19 Processing sequence for the RTP silicon solar cells. Two different processes are used : one is a process with optimized parameter (900 °C, 2min.) and the other is a process with non optimized parameter (1050 °C, 2min.)

5.6.2 Solar cells results and analysis

A. Cell parameters

The effect of each thermal process on the cell performance before and after degradation is shown in Table 5.6. As expected V_{oc} and J_{sc} measured before light-induced degradation are higher than measured after degradation. Cells processed at 900 °C have a better J_{sc} than those processed at 1050 °C. But it is quite difficult to conclude only from the short circuit current measurement, if this small improvement is caused by the better lifetime due to the optimal process.

Туре	Degradation	Temperature	V _{oc}	J _{sc}	FF	η
		[°C]	[mV]	[mA/cm ²]	[%]	[%]
before Cz — after	900	620.1	35.58	78.1	17.2	
	belore	1050	620.8	34.91	79.9	17.3
	oftor	900	613.9	34.76	78.8	16.8
	arter	1050	612.9	34.22	80.0	16.8
FZ		900	628	35.74	79.3	17.8
		1050	632	35.56	80.6	18.1

Table 5.6 Comparison of solar cells after two different processes in Cz- and FZ-Si before degradation and after degradation with a 1-sun for 30 h.

B. Internal quantum efficiency and reflection

Figure 5.20 shows the reflection and internal quantum efficiency (IQE) of Cz and FZ solar cells after light-induced degradation for both process types. Cells processed at 900 °C show a lower reflection in the wavelengths range below 700 nm and a slightly higher reflection for wavelengths between 700 and 1000 nm as compared to cells processed at 1050 °C. This is due to the thickness of the passivation oxide. The oxide thickness at 900 °C and at 1050 °C for 120 s have been determined to be about 7 nm and 15 nm, respectively. From the V_{oc} -values of the FZ cells it can be concluded that the thicker RTO passivates better than the thinner one.



Figure 5.20 The effect of two different processes on the reflection and internal quantum efficiency of Cz and FZ solar cells.

Notice that the reflection in the wavelength range higher than 1000 nm shows a significant difference between cells processed at 900 °C and at 1050 °C. The reflection above 1000 nm of cells processed at 900 °C is quite high compared to those processed at 1050 °C. A higher amount of the long wavelength light is reflected from the back surface of cells processed at 900 °C. This demonstrates that the RTO process affects the optical quality of the Al-BSF. A different reflection between FZ and Cz material processed at same temperature is caused by a different surface. The surface of Cz material is rough due to etch damage, whereas that of FZ material is smooth like a mirror.

The internal quantum efficiency (IQE) measurements in Figure 5.20 show that all cells processed at 900 °C have a better performance especially in the long-wavelength range than cells processed at 1050 °C. In the short-wavelength range the quantum efficiency of cells processed at 900 °C is slightly higher than the one of cells processed at 1050 °C since the sheet resistance at 900 °C (112 Ω/\Box) is lower than the one at 1050 °C (82 Ω/\Box). The higher concentration can increase the Auger recombination, the front surface recombination velocity, and the bandgap narrowing and thus can result in a decreased short wavelength response. Also in Cz cells the IQE for wavelengths above 800 nm is better for cells processed at 900 °C than for cells processed at 1050 °C. It is certain that the lifetime of the cell at 900 °C is better than that of the cell at 1050 °C, since the long wave IQE response is attributed to bulk diffusion length.

C. Diffusion length

In order to investigate quantitatively this improvement of lifetime, we determined the effective diffusion length L_{eff} from the measured IQE using the following equation [60].

$$IQE^{-1} = 1 + \frac{1}{L_{eff}} \alpha^{-1}$$

$$L_{eff} = L_n \left[\frac{1 + \frac{S_n L_n}{D_n} \tanh \frac{W}{L_n}}{\frac{S_n L_n}{D_n} + \tanh \frac{W}{L_n}} \right]$$
(5.5)

where α^{-1} is a monochromatic absorption length, W is the thickness and D_n is the diffusion constant. L_n and S_n are the diffusion length in the bulk and the recombination velocity at the surface, respectively.



Figure 5.21 Bulk diffusion length vs. back surface recombination velocity for different RTO-processed (left) FZ solar cells and (right) Cz solar cells.

Figure 5.21 (left) shows the L-S plot for the FZ-Si cells. From the determined L_{eff} it is possible to give all possible parameter combinations (L_n , S_n). The asymptotical value of S can be identified with the highest possible value for S_{rear} = 2000 cm/s. This value is in good agreement with the one determined from a PC-1D simulation [61] with a very high assumed bulk diffusion length of 1500 µm. The quite low value of S_{max} also demonstrates the good quality of the Al-BSF.

The L-S plot for the Cz-Si solar cells is given in Figure 5.21 (right). Assuming that the AI-BSF has the same quality in the Cz-Si cells as in the FZ-Si cells we can give a minimal value for L_{bulk} in the Cz-Si cells using the S_{max} as determined in Figure 5.21 (left). The cells processed at 900 °C have a L_{bulk} around 240 µm which corresponds to a τ_{bulk} around 21-22 µs. The cells processed at 1050 °C show a L_{bulk} (τ_{bulk}) around 205 µm (15-16 µs).

The value determined for the cells processed at 900 °C matches excellently with the lifetime measurement shown in Figure 5.17, while the value for the 1050 °C process is slightly higher than the lifetime of the controll sample. The significant difference of L_{bulk} between the process at 900 °C and 1050 °C is a very good proof for the results shown in section 5.5.

Figure 5.22 shows the simulated value of J_{sc} and efficiency for $S_{rear} = 1500$ cm/s calculated with PC-1D. As shown in the Figure 5.22, the difference of J_{sc} and efficiency between the bulk lifetimes of 15 µs and 21 µs is only 0.34 mA/cm² and 0.25 %, respectively. This relative change of current is in good agreement with the differences observed in the measured cells results. In Table 5.7 the measured and simulated cell parameter with Cz and FZ material after degradation are summarized.



Figure 5.22 Simulated J_{sc} and efficiency as a function of the bulk lifetime for $S_{rear} = 1500$ cm/s in RTP- solar cells.

Table 5.7 Measured and simulated characteristics of Cz and FZ boron doped materials processed the plateau temperature of 950 °C and 1050 °C for RTO.

Parameters	Cz		FZ		
	900°C, 2 min.	1050 °C, 2 min	-	900°C, 2 min.	1050 °C, 2 min
Sheet resistivity [Ω/\Box]	112	84		97	82
SiO ₂ [nm]	7	15		7	15
$ au_{eff}$ [µs]	21	15		50.55	52.72
L _{eff} [µm]	233.1	202.5		374.5	382.3
S _{max, meaurement} [cm/s]				2000	2000
S _{max, PC1D} [cm/s]				1500	1500

5.7 Conclusions

The potential of RTP to reduce the metastable defect density in Cz-Si was studied. To avoid external contamination during the RTP process SiN_x was deposited with PECVD. Also two different thermally processed SiO_2 layers on FZ wafers were examined. The SiN_x layer was found to be very effective as a barrier layer even without previous cleaning of the RTP furnace. Using the barrier layer it was possible to keep FZ-Si reference samples on a high lifetime level of 700 µs.

The influence of process parameters on the stable effective lifetime of Cz-Si was investigated using a 'design of experiments (DOE)'. The wafers were SiN_x covered and five process parameters were varied : plateau temperature ($T_{plateau}$), plateau time ($t_{plateau}$), heating rate (R_{up}), cooling rate (R_{down}) and cooling point temperature ($T_{cooling pt}$). Using the design of experiment it was found that the plateau temperature is the most important parameter with respect to the stable effective lifetime.

For all plateau temperatures the light-induced degradation could be strongly reduced. The optimal plateau temperature was approximately 900 °C with a plateau time of 120 s. This led to an improvement of the stable effective lifetime of 1 Ω cm Cz-Si by a factor of 2. To our knowledge this is the first time that an improvement of the stable effective lifetime of Cz-Si by a rapid thermal annealing process without external gettering is demonstrated. Additionally, three different Cz materials were investigated for the same process. An improvement of the stable lifetime could be observed for all three materials with a same trend that up to the temperature of 950 °C the improved stable lifetime is remained and at above 950 °C the improvement of the lifetime is decreasing. The reduced improvement at temperatures higher than 950 °C is also reflected in experiments on FZ-Si. It seems to be correlated with inhomogeneous distribution of temperature on the wafer and impurity-related large complexes.

Also, a Rapid thermal firing (RTF) process was analyzed in terms of lifetime. The plateau temperature and time in phase 'firing' was varied. Even though the plateau time is only 1 s and 10 s, the stable lifetime is improved by about 40 % above temperatures of 850 °C for 1s and at above 800 °C for 10 s plateau time, respectively. Also, the improvement of the stable lifetime was observed at temperatures below 950 °C.

The effect of two subsequent steps on the stable lifetime combining an optimized and a nonoptimized process was studied. The stable lifetime is mainly influenced by the last hightemperature step. For example, the lifetime reduction from 14 μ s to 9 μ s after the nonoptimized process in the first step can be increased up to 20 μ s due to the last optimized process.

Finally, an optimized (900 °C) and a non-optimized (1050 °C) RTO process, being the last high-temperature step in RTP-solar cell process, were performed in order to investigate their influence on solar cells. It could be shown that the difference between optimized and non-optimized process shows the same trend in the solar cell results.
6 Optimal passivation for solar cells

For high efficiency solar cells low surface recombination and high effective lifetimes are both significantly important. Thermal oxide films grown at high temperatures and silicon nitride layers deposited at low temperatures are generally used for the surface passivation of solar cells. Firstly, the oxidation process is described to provide the background of the kinetics of growth and interface properties. Furthermore, two different oxidation technologies are presented. Secondly, the kinetics , characteristics and properties of silicon nitride deposited by PECVD are described. Thirdly, the properties of new passivation layers, SiO_2/SiN_x stacks are shown. Finally, the optimization of the passivation layers is considered for front and rear surface. The optimized passivation layers are investigated on PERC- solar cells and the results are analyzed. A summary and discussion of the future trends are presented in the last section.

6.1 Thermally grown silicon dioxide

Silicon dioxide (SiO₂) has several advantages: it masks against the most common impurities (B, P, As, Sb), is an excellent insulator ($\rho > 10^{16} \Omega$ cm, $E_g > 9$ eV), has a high breakdown field strength (10^7 V cm⁻¹), and shows excellent surface passivation quality, which is stable and reproducible [62].

In solar cells, SiO_2 is used as a passivation and/or an antireflection layer on the front surface and as a passivation and insulator layer on the rear surface. In the following section the general growth mechanism and fundamental properties of SiO_2 are presented.

6.1.1 Growth mechanism

Thermal oxidation is the process of silicon dioxide creation from pure silicon as a result of a chemical reaction of silicon and oxygen. Two different production techniques can be distinguished; dry and wet oxidation. The chemical reactions describing these two thermal oxidation-techniques of silicon in oxygen atmosphere (dry oxidation) or water vapor atmosphere (wet oxidation) are given by

This thermal oxidation process is usually carried out at 900 °C to 1200 °C. Dry oxidation is often used to generate high quality thin oxidation layers since the oxidation velocity is very low (< 1.7 nm/min) while wet oxidation is often used to produce oxide layers for insulation and passivation techniques because of a high oxidation velocity (> 29 nm/min).

The densities of SiO_2 and Si are similar, but SiO_2 has a larger molecular weight. During the oxidation process firstly oxygen has to move through the silicon-oxide layer prior to the reaction

and then to react with the original silicon surface. Approximately, 54 % and 46 % of the final oxide film are above and below the original surface of the silicon wafer, respectively (see Figure 6.2 (left)).

6.1.2 Silicon thermal oxidation model

The basic model for oxidation was developed in 1965 by Deal and Grove [63]. As given in Figure 6.1 the silicon substrate is covered by an oxide layer of thickness x_0 , which is in contact with the gas phase. The reacting species must go through the following stages: (1) It is transported from the bulk of the oxidizing gas to the outer surface where it reacts or is absorbed (F₁). (2) It is transported across the oxide film towards the silicon (F₂). (3) It reacts at the silicon surface to form a new layer of SiO₂ (F₃).



Figure 6.1 Basic model for oxidation of silicon. F and C represent the flux and concentration at the surface, respectively.

At first, the flux⁹ of the oxidant from the gas to the vicinity of the outer surface is given by

$$F_1 = h \left(C^* - C_o \right) \tag{6.2}$$

where h is a gas-phase transport coefficient, C_o is the concentration at the surface and C* is the equilibrium concentration of oxygen in the surrounding gas.

In the second step, the flux of the oxidant across the oxide layer is described after Fick's law as

⁹ The flux of oxidant is the number of oxidant molecules crossing a unit surface area in a unit time.

$$F_{2} = -D_{eff} \frac{dC}{dx} = D_{eff} \frac{(C_{o} - C_{i})}{x_{o}}$$
(6.3)

where D_{eff} is the effective diffusion coefficient, dC/dx is the concentration gradient of the oxidizing species in the oxide, C_i is the concentration of the oxidant near the Si-SiO₂ interface and x_o is the oxide thickness.

Finally, the flux corresponding to the oxidation reaction is proportional to C_i

$$F_3 = k C_i \tag{6.4}$$

where k is the reaction ratio of the oxidation process. Under steady state condition,

$$F = F_1 = F_2 = F_3 = \frac{k C^*}{1 + k / h + kx_0 / D_{eff}}$$
(6.5)

If N_1 is the number of oxidation molecules in-corporated into a unit of the oxide layer, the rate of growth of the oxide layer is described by the differential equation

$$\frac{dx_o}{dt} = \frac{F}{N_1} = \frac{k C^* / N_1}{1 + k / h + kx_0 / D_{eff}}$$
(6.6)

The analytic solution of this differential equation Eq. (6.6), with the initial condition $x_0=x_i$, at t=0 is a quadratic equation of the form

$$x_{o}^{2} + Ax_{0} = B(t+\tau) \tag{6.7}$$

where

$$A \equiv 2D_{eff} (1/k + 1/h),$$

$$B \equiv 2D_{eff} C^* / N_1,$$

$$\tau \equiv (x_i^2 + Ax_i) / B$$

The quantity τ corresponds to a shift in the time coordinate which corrects the presence of the initial oxide layer x_i. Eq. (6.7) is a mixed two limiting form, i. e., a linear-parabolic relationship.

The solution of Eq. (6.7) yields the form

$$x_0 = \frac{A}{2} \left(\sqrt{1 + \frac{t+\tau}{A^2/4B}} - 1 \right)$$
(6.8)

which gives the oxide thickness as a function of time.

On the one hand, for long oxidation time, i. e., $t > \tau$ and $t > A^2/4B$,

$$x_0 = \frac{A}{2} \sqrt{\frac{t}{A^2/4B}} \quad or \quad x_0 \cong \sqrt{Bt}$$
(6.9)

can be established. Eq. (6.9) shows the well known parabolic oxidation law for relatively long time. B is referred to as the parabolic rate constant.

On the other hand, for relatively small oxidation times, i. e., $t << A^2/4B$,

$$x_0 \cong \frac{B}{A}(t+\tau) \tag{6.10}$$

As shown Eq. (6.8) the general equation reduces to a linear law. The coefficient is given by

$$\frac{B}{A} = \frac{kh}{k+h} \left(\frac{C^*}{N_1}\right) \tag{6.11}$$

B/A is referred to as the linear rate constant. It is only possible to know the parameters A and B from a fit of experimental values. The parabolic rate constant B is proportional to the pressure and is exponentially depending on temperature for both dry- and wet-oxygen cases while the linear rate constant A is independent of the pressure.

Also the oxidation rate depends on various parameters: orientation of silicon surface, i. e., (110) > (111) > (100), surface concentration, ambient gas $(O_2 + HCI > O_2 > O_2 + Ar)$ [62, chapter 4].

6.1.3 Fundamental properties of Si-SiO₂

6.1.3.1 General types of oxide charges

The Si-SiO₂ interface consists of a transition region which is related to the various charges and traps which are associated with the thermally oxidized silicon. Four types of charges are associated with the interface of Si-SiO₂. As shown in Figure 6.2 the charge Q is described by N = Q/q, the net effective charge per unit area (C/cm²) at the Si-SiO₂ interface, where N is the net number of charges per unit area (numbers/cm²), and q is the electric unit charge (C). These charges are measured mostly by capacitance-voltage (C-V) or the surface photovoltage (SPV) technique.

Q_f (fixed oxide charge)

The fixed oxide charge Q_f is located in the oxide within approximately 2 nm of the Si-SiO₂ interface which results in a field effect passivation [12]. As shown in Figure 6.2, Q_f is usually positive, immobile and insensitive to the position of the Fermi level. Therefore, its density is constant and it ranges from 10¹⁰ to 10¹¹ cm⁻². This positive charge is mainly related to the three

oxide dangling bonds of $O_3 \equiv Si \cdot (P_{ox})$ which are significantly related with the surface recombination velocity, S_{eff} (see section 6.1.3.2) at the same time. Q_f has a very strong influence on S_{eff} , e.g., a reduction of Q_f from 2×10^{12} to 1×10^{12} cm⁻² results in an increase of S_{eff} of about a factor of 8 [64]. Q_f depends on the silicon orientation ((100) < (111)), silicon doping concentration (high > low), oxidization temperature (high > low), ambient (wet $O_2 > dry O_2$) and cooling rate (slow > rapid) [62].



Figure 6.2 (left) General types of oxide charges in thermal oxidized silicon. (right) Idealized band structures of the interfaces between Si- and Si-SiO₂ [11] [64].

• Q_{it} (interface trapped charge)

The interface trapped charge Q_{it} is located at the Si-SiO₂ interface and is positively or negatively charged or discharged by changing the silicon surface potential. Q_{it} is about 10¹³ cm⁻² on the unpassivated wafer and about 10⁹ cm⁻² on the passivated wafer with thermal oxidation, respectively. D_{it} ([cm⁻² eV⁻¹]) with $N_{it} \equiv D_{it} E_g$ is the interface state density within the forbidden gap E_g of silicon. The surface recombination velocity at the silicon depends strongly on D_{it} . D_{it} can be reduced by hydrogen passivation, e. g., annealing in forming gas. D_{it} depends on process temperature (high < low) whereas D_{it} is independent on the process ambient (wet $O_2 = dry O_2$), as discussed in detail in section 6.1.3.2.

• Q_{ot} (oxide trapped charge)

The oxide trapped charge, Q_{ot} is positively or negatively charged or discharged by holes or electrons trapped in the bulk of the oxide. Its density is in the range of 10^9-10^{13} cm⁻². This charge is associated with defects in SiO₂, caused by ionizing radiation, avalanche injection, or high currents in the oxide, and can be eliminated by low-temperature annealing.

• Q_m (mobile oxide charge)

The mobile oxide charge Q_m is attributed to positively charged alkali ions such as sodium (Na⁺), potassium (K⁺), lithium (Li⁺) in the oxide as well as to negative ions and heavy metals as shown in Figure 6.2. The alkali ions are mobile even at room temperature when electric fields are present. Na is important because of its rapid transport in SiO₂ and its abundance in the environment and human body, whereas Li and K are not important because its low concentration in the environment and low mobility (mobility: Li>Na>K, concentration: K=Na>>Li). The density of Q_m is in the range of 10^{10} – 10^{12} cm⁻². In order to minimize this charge density the oxidation is performed in the chlorine ambient for chemical gettering.

6.1.3.2 Defect model for the Si-SiO₂ interface

The structure of the Si-SiO₂ interface and also the density of state distribution of interface traps $D_{it}(E)$ strongly depend on the oxidation and post-treatment conditions. The experimentally determined $D_{it}(E)$ has been interpreted as originating from a superposition of contribution from various kinds of defect states which arise from different types of Si-dangling bonds with different backbond configurations. A scheme of such a model for the $D_{it}(E)$ which dominates the electric properties of the Si-SiO₂ interface is shown in Figure 6.3. D_{it} (E) is composed of a few individual groups of states at the interface; band tails (U_T), symmetrical midgap states (U_M), two peaked distributions at a low and high position in the gap (P_L , P_H) [65] [66]. Each defect is explained in the following section.



Figure 6.3 Defect model of the Si-SiO₂ interface [65] [66].

A. Intrinsic Defects (U_T , U_M)

Defects from stretched silicon-silicon bonds and silicon dangling bonds can be described as intrinsic defects, since they are proper defects of the silicon lattice (i. e., no oxygen atoms are involved).

Stretched silicon-silicon bonds $Si_3 \equiv Si - Si \equiv Si_3$ (U_T) represent small distortions of the silicon lattice. The related states distribute from the band edges into the gap and show the nearly symmetrical distribution around midgap as the band tails states as shown in Figure 6.3. U_T is apparently insensitive to post-oxidation treatments and stress. If the distortion becomes larger a rupture of on bond may be favored energetically creating a dangling bond center. This defect caused by Si-Si dangling bonding $Si_3 \equiv Si \cdot (U_M \text{ or } P_b)$ distributes a broad double peak around the midgap [65].

 U_M lies totally inside the Si band gap almost symmetrically to midgap with a small gap left to the band edges as shown in Figure 6.3. The total width is about $\frac{3}{4} E_g$, filling just about the space left in the gap by U_T with a small overlap. The chemical character of the states in the humps and the states at midgap is completely equivalent, only the geometrical structure of the defects differ in hybridization [67].

The symmetrical distribution of intrinsic defects is caused by their amphoteric character. Therefore, each defect gives rise to corresponding levels, i. e., one bonding state in the low half (donor-like) and one antibonding state in the upper half (acceptor-like) of the gap. All intrinsic defects have the same symmetry point E_o which is located about 40 meV below midgap (E_i) and the same binding behavior. E_o acts as charge neutral level and determines the Fermi-level pinning for high intrinsic-dominated state densities (N_{it} >10¹² cm⁻²).

B. Extrinsic defects (P_L, P_H, P_{ox})

Extrinsic defects are related to silicon dangling bonds with one to three oxygen back bonds. The defects with one (P_L) and two (P_H) oxygen back bond are located inside the silicon bandgap as donor-like states. The distribution is a broad peak in the lower (P_L) and upper (P_H) half, respectively. The corresponding acceptor-like states are assumed to be inside the silicon conduction band. The dangling bond defect with three oxygen back bonds, $O_3 \equiv Si \cdot (P_{OX})$ is located inside the silicon conduction band as the donor-like. This state could be related to the positive fixed oxide charge (Q_f) since the state is occupied and positively charged in equilibrium. Table 6.1 shows the corresponding characteristic data of five defect groups.

Defect group	Si dangling bond	$E_t - E_V [eV]$	$\sigma_t [eV]$	Si-H bond
$U_{\rm M}~{\rm or}~P_{\rm b}$	$Si_3 \equiv Si \bullet$	0.2*	0.4*	strongest
U _T	Si₃ ≡ Si - Si≡Si₃	0.02	0.04	no
PL	$Si_2O \equiv Si \bullet$	0.4	0.12	less strong
P _H	$SiO_2 \equiv Si \bullet$	0.7	0.08	weakest
P _{ox}	$O_3 \equiv Si \bullet$	>E _C	$\infty 0$	nearly no

Table 6.1 Characteristics of defect groups in the Si-SiO₂ interface [67]. E_t and σ_t represent the center value of width of distribution. * values are given for the donor part of the distribution.

6.1.3.3 Influence of thermal annealing

For solar cell operation the interface trap density should be as low as possible. By annealing, the high concentration of interface trap density can be reduced. Füssel et al. [65] demonstrated the importance of thermal anneal processing steps. Typical defect state distributions after different treatments are shown in Figure 6.4. The important results from Figure 6.4 are presented in the following points.

- The interface trap density, D_{it} at the Si-SiO₂ interface forms a V-shaped distribution. V-forms of D_{it} are measured independently on the different kind of high temperature and surface orientation (curve 1). V-forms are due to the domination of U_M and P_L states.
- The dangling bonds of U_M, P_L and P_H can be reduced drastically by hydrogen annealing which is supplied by the annealing ambient (curve 3), post-metal anneal, i. e., alneal (curve 4 and 5) and a hydrogen-containing layer (i. e., SiN), whereas by annealing in N₂ D_{it} does not reduce (curve 2). It can be concluded that better passivation after annealing is related to hydrogen.
- This Si-H reaction for the P_L and P_H groups is more important than for the U_M group. Therefore U_M leads to more U-shaped distributions as increasing the supply of hydrogen. Unfortunately, the Si-H bond is unstable. For example, the Si-H bonds might be broken by subsequent anneal in N₂ or vacuum, by extended anneal in a finite supply of H [68] and by annealing at high temperatures (>450 °C).



Figure 6.4 Influence of low temperature annealing treatments at 450 °C for 30 min on the D_{it} distribution of the Si-SiO₂ interface (n-Si, 10 Ω cm, thermally oxidized at 1180 °C in wet O₂). Curve1: oxidized sample; 2: annealed in dry N₂ before Al evaporation; 3: annealed in forming gas before Al evaporation; 4: post metallization (dots) annealed in forming gas; 5: post metallization (total) annealed in forming gas [65].

6.1.3.4 Influence of irradiation

Degradation of lifetime caused by radiation-induced interface traps is a significant problem in solar cells as well as in MOS technology. Helms et al. [69] summarized radiation damage under a physically oriented viewpoint. Initially the oxide particle collision or ionization event is caused by radiation such as γ -ray, x-ray and neutrons. Secondary injected entities migrates to the Si-SiO₂ surface. Hydrogen, exactly H⁺, is known as a dominant player in regard to D_{it} increased by irradiation. H⁺ has been transported rapidly to the interface, yielding an increase in Q_{ox} there. However, H⁺ is eventually neutralized by capture of an electron attracted to the interface under the action of positive bias. Soon thereafter the neutral H reacts with passivated U_M groups to produce interface traps:

$$\equiv Si - H + H \quad \rightarrow \quad \equiv Si \bullet + H_2 \uparrow \tag{6.12}$$

It must be noted that the reaction in Eq. (6.12) is not the same reaction as the lifetime degradation by annealing at high temperatures (see section 6.1.3.3).

Recently, Strahlbush [70] investigated the mobile H^+ into buried oxides. After irradiation, the concentration of mobile H^+ in the oxide remains nearly the same. However, H^+ transmission in the oxide is significantly slower than in the interface. Therefore, the irradiation produces more defects near the bottom interface than near the top caused by the speed of H^+ transport. He

suggested that more traps are produced near the interface where H⁺ is at that interface during the irradiation.

6.1.3.5 Capture cross section

Surface recombination depends on the interface trapped density D_{it} and the capture cross section of holes and electrons. Yablonovitch et al. [71] found that the maximum recombination at the Si-SiO₂ interface occurs when the hole density at the surface p_s is about 100 times greater than the electron density at the surface n_s since the electron capture cross section σ_n is about 100 times greater than hole cross section σ_p :

$$\frac{\sigma_n}{\sigma_p} = \frac{p_s}{n_s} = 100 \tag{6.13}$$

Aberle et al. [72] measured the energy dependent capture cross section at the Si-SiO₂ interface for a thermally grown SiO₂ at 1050 °C. The determined σ_n/σ_p ratio are about 1000 at midgap. The trap energy level E_t lies on E_V +0.35 eV for σ_n and E_t = E_c - 0.45 eV for σ_p .

Recently, two different capture cross sections σ_{n1} (E) and σ_{n2} (E) for thermally oxidized n-type silicon wafers were found by Albohn et al. [66]. They observed both σ_{n1} (E) and σ_{n2} (E) in material prepared under different conditions. σ_{n1} (E) was found 2 orders of magnitude higher than σ_{n2} (E). Both σ_{n1} (E) and σ_{n2} (E) decrease monotonously with decreasing separation from the conduction band. However, the interface trap density D_{it} related to σ_{n1} (E) is broadly distributed in the upper half of the gap and tends to decrease towards midgap, whereas D_{it} related to σ_{n2} (E) is small in the upper half of the gap and increases considerably towards midgap. Therefore they assigned that σ_{n1} (E) and σ_{n2} (E) are attributed by an acceptor state of Si₃=Si- ($U_M^{0/-}$) and a donor state of Si₀=Si ($P_L^{+/0}$).

6.1.4 Oxidation process

6.1.4.1 Classical Thermal Oxide (CTO)

Using a classical thermal oxide (CTO) by means of a classical furnace a very high passivation quality SiO_2 layer can be achieved even though the wafer is processed at very high temperatures (about 1050 °C) and for long process times. In this work high quality FZ silicon material was used.

A typical CTO process is described in the following. Prior to the high temperature step the wafers receive a RCA cleaning. CTO is performed in an oxygen ambient with an addition of DCE (Dichloroethene ($C_2H_2Cl_2$)- an environmentally friendly alternative of TCA) at 1050 °C for 38 min resulting in a thickness of 105 nm. The 105 nm oxide is used simultaneously as the antireflection layer and passivation on the front and rear side, while a 200 nm oxide is used as a diffusion or etch mask. After the oxidation the gas atmosphere is changed to argon and the wafer is treated by post-oxidation anneal for 1 h. Subsequently, the furnace is cooled down to 850 °C in argon

and the wafers were extracted from the furnace. Finally, the wafers are annealed in forming gas at 450 °C for 25 min.

Figure 6.5 shows the thickness distribution of a typical CTO by means of ellipsometry on the left and its effective lifetime using the carrier density imagine (CDI) method on the right (see appendix B.2). The distribution of the oxide thickness is relatively homogeneous. The difference of the thickness between maximum and minimum is only 8 nm from 99 nm to 108 nm (9 %). The average of the effective lifetime is about 300 µs. The trapped charge density, D_{it} is 2×10^{10} cm⁻²eV⁻¹ and the fixed charge density Q_f is 1.3×10^{11} cm⁻² in this Si-SiO₂ interface [72].



Figure 6.5 Oxide thickness (left) and lifetime distribution (right) of the typical classical thermal oxide (CTO) by a classical furnace. CTO is processed at 1050 °C for 38 min Oxide thickness and lifetime are measured by ellipsometry and carrier density imagine (CDI).

6.1.4.2 Rapid Thermal Oxidation (RTO)

In comparison to the classical oxidation, rapid thermal oxidation (RTO) reduces the oxidation time from 330 min to 5 min including ramping up and down times. Also the passivation qualities of RTO and CTO for the same thickness are comparable. For exemple, Doshi et al. [73] investigated that for the same oxide thickness 10 nm, the density of interface state D_{it} at midgap and the oxide charge density Q_{ox} by RTP are 1.1×10^{11} cm⁻²eV⁻¹ and 6.0×10^{11} cm⁻², respectively, while for CTO sample both D_{it} and Q_{ox} are 1.6×10^{11} cm⁻²/eV and 1.4×10^{11} cm⁻², respectively. Also the surface recombination velocity S at the front of the solar cells can be effectively decreased by means of RTO 10 nm from 7.5×10^5 cm/s (unpassivated) to 2×10^4 cm/s.

Another general property of RTO, the interface state density distribution D_{it} is nearly independent of the oxidation temperature in comparison to the same oxide thickness, and it has a U-shaped distribution. The leakage current is decreased to increase the oxide thickness and the process temperature [74]. Also It is reported that there is no difference of the chemical structure of RTO and CTO oxides [75].

For RTO characterization FZ-Si wafers with resistivity 1 Ω cm were chosen. The RCA cleaned wafers were put in the quartz chamber. After purging the quartz chamber with N₂ at room

temperature in order to clean the chamber, O_2 flows into the chamber at room temperature and fill the chamber as O_2 ambient. Then, the wafer was heated by irradiation up to 400 °C using tungsten halogen lamps. The total gas flow during heating should not exceed 3 slm (standard liter per minute) in order to control the temperature well. The temperature is ramped up from 400 °C to the given plateau temperature. The ramping up and down rate can be varied 1-100 °C/s. Subsequently, the process temperature was ramped down until 600 °C with a defined ramp. Simultaneously, N₂ flows again and the flow rate is decreased more and more until the end of the process. Finally, the irradiation is switched off and the quartz chamber is purged again.



Figure 6.6 Typical RTO process schematic by rapid thermal processing.

Figure 6.6 shows the typical RTO process schematic by rapid thermal processing. In the upper part in Figure 6.6 the black line presents the measured process temperature by pyrometer and red solid line represents the given lamp power in the process. The blue dot line represents the set temperature. In the bottom part in Figure 6.6 the solid and dot line show the flow rates of N_2 and O_2 in the oxidation process, respectively.

In this study both the ramping up and down rate were chosen to be 50 °C/s. The plateau temperature and the plateau time are varied in the range of 900-1050 °C and 60-180 s, respectively. Figure 6.7 shows the thickness of the silicon oxide by rapid thermal processing vs. plateau time and the measured effective lifetime as a function of process time and temperatures.

The oxide grows linearly and the process temperature effects the growth rate. The effective lifetime depends on the oxide thickness. The effective lifetime is increasing with an increase of the oxide thickness.



Figure 6.7 (Left) Oxide thickness and (right) effective lifetime dependent on plateau time with four different temperatures. FZ 1Ω cm silicon materials were used in this work.



Figure 6.8 Maximum surface recombination velocity (SRV) as a function of the oxide thickness. $S_{eff, max}$ is decreasing strongly with increasing oxide thickness up to around 8 nm. Above 8 nm the relatively low $S_{eff, may}$ remains constantly.

Figure 6.8 shows the maximum surface recombination velocity $S_{eff, max}$ determined by the measured effective lifetime assuming a very high bulk lifetime ($\tau_b \approx 2000 \ \mu$ s). $S_{eff, max}$ is decreased with increasing oxide thickness. The determined S values show that with RTO a low surface recombination velocity can be obtained.

Figure 6.9 shows the influence of a ramping down rate on the thickness distribution. The ramping down rate was varied between very high (100 °C/s) and extreme slow (0.2 °C/s). Both RTO were performed at a temperature of 1050 °C for 120 s. The distributions of RTO have a

typically radial form independent of the ramping down rate. It shows clearly that the oxide thickness decreases more and more from middle to edge. This means that the temperature on the middle of the wafer is higher than that on the edge. Chatterjee [76] showed that radiation from the lamps alone can not be the cause of this temperature non-uniformity. An additional reason is a radiative loss which is related to transfer of heat to the gas by conduction and/or convection.

The oxide thickness for the sample with 100°C/s ramping rate is about 10 nm, while the oxide thickness for the one with 0.2 °C/s is about 20 nm. This difference of thickness between middle and edge is 3 nm from 9 nm to 11 nm (22. 2%) using a ramping down rate of 100 °C/s and 5 nm from 17 nm to 22 nm (29.4 %) using a ramping down rate of 0.2 °C/s. The inhomogeneity of the RTO-samples is relatively larger than that of the CTO-samples (9 %).



Figure 6.9 Oxide thickness distribution of RTO at the temperature of 1050°C for 2 min with ramping down of (a) 100 °C/s and (b) 0.2 °C/s. The radially shaped distribution are due to inhomogeneous temperature profile.

6.2 Silicon nitride by PECVD

In the previous section 6.1 it has been shown that a thermal oxidation provides excellent surface passivation on silicon wafers. In spite of its advantages, the high process temperature of both RTO and CTO can degrade the lifetime. Especially, Czochralski (Cz) and multicrystalline (mc) silicon are known to suffer from a reduction of carrier bulk lifetime during high temperature treatments.

In order to solve this problem associated with the high temperature during the thermal oxidation the formation of SiN_x layer by means of plasma enhanced chemical vapor deposition (PECVD) has been used for passivation in solar cells [77] [78] [79] [80]. The low temperature deposition, the higher passivation quality and the adjustable refractive index are the reasons why silicon nitride layers are increasingly interesting. Therefore, silicon nitride layers by PECVD find more and more applications in solar cell processing as antireflection or passivation layer for front and rear side. In the following section SiN_x layers by PECVD will be discussed.

6.2.1 Growth mechanism

For the plasma deposition of silicon nitride, silane (SiH₄) for Si, ammonia (NH₃) or nitrogen (N₂) for N, and hydrogen (H) are usually used. The gases form a plasma in the reactor due to the microwave energy. Decomposed electrons influence ionization, excitation, elastic scattering and dissociation and create ions such as H⁺, SiH_3^- , SiH_2^+ and free neutral particles such as H, SiH₃, SiH₂. The general chemical reaction of the four gases with electrons in plasma can be described as

$$e^{-} + SiH_{4} \rightarrow SiH_{a}^{b} + xH_{c}^{d} + ye^{-}$$
 with a=1...3, b={-,+,0,*}, c=1...2,
d={-,+,0,*}, x=0...2, y=0...2 (6.14)

$$e^{-} + NH_{3} \rightarrow N_{a}^{b} + xH_{c}^{d} + ye^{-}$$
 with a=1...3, b={-,+,0,*}, c=1...2,
d={-,+,0,*}, x=0...2, y=0...2 (6.15)

$$e^- + N_2 \rightarrow N_a^b + ye^-$$
 with a=1...2, b={-,+,o,*}, y=0...1 (6.16)

$$e^- + H_2 \rightarrow H_a^b + ye^-$$
 with a=1...2, b={-,+,o,*}, y=0...1 (6.17)

where -, +, o, and * correspond to negative, positive, neutral and excited elements. The chemical reaction of the gas mixtures $SiH_4/N_2/H_2$ or $SiH_4/NH_3/H_2$ are more complete interactions between Eq. (6.14) and Eq. (6.17) and other chemical reactions (ion-molecule reaction, excitation transfer...) must be considered.

On the other hand, there are two interesting regimes for deposition which is called 'molecule' and 'atomic' [81]. The gas mixtures SiH_4/NH_3 are contained in the molecular regime, whereas SiH_4/N_2 are in the atomic deposition regime. The deposition mixtures behave very differently among each other with regard to the formation of deposition precursor molecules within the plasma and effect the properties of the film.

For example, SiH_4 and NH_3 react with each other in the plasma to form the precursor molecule, tetra-aminosilane- $Si(NH_2)_4$ - and hydrogen. The precursor molecules, after losing one aminogroup (NH_2) each, deposit on the wafer surface. The wafer heat helps neighboring surface molecules condense to form ammonia and new silicon-nitrogen bonds [82]. The reaction is given by

$$SiH_4 + 4NH_3 \rightarrow Si(NH_2)_4 + 4H_2$$

$$3Si(NH_2)_4 \rightarrow Si_3N_4 + 8NH_3$$
(6.18)

 SiH_4/N_2 mixtures form no Si-N precursors, so depositing species are SiH_x and NH [83]. A silicon nitride layer using NH₃ shows high a hydrogen content in the films and, therefore, a high intrinsic stress. Instead of NH₃, N₂ can be used since N₂ is not toxic and can be obtained in high purity and also leads to a low hydrogen content in the layers.

Silane is dissociated more easily than ammonia in the plasma. Therefore, a very high abundance of ammonia or nitrogen is needed for stoichiometrical Si_3N_4 . Not only the process parameters but also the flow ratio of each process gas affects the properties of the layer, e. g., refractive index, layer thickness, and passivation qualities [49] [64] [84] [85]. More detailed information can be found in [82] [86] [87].

6.2.2 Fundamental properties of silicon nitride

6.2.2.1 Properties of parameters

Like for the thermally grown Si-SiO₂ interface, state density D_{it} , the fixed insulator charge density Q_f and the electron and hole capture cross section σ_n and σ_p at Si-SiN_x interface are important for the passivation properties. Figure 6.10 shows a diagram of charge location and the energy band structure for the silicon-nitride interface.



Figure 6.10 (Left) Diagram of located charges and (right) energy band structure of in the Si-SiN interface by PECVD [64].

• Q_f (positive insulator charge)

A very high positive insulator charge density Q_f in the range of 1×10^{11} – 5×10^{12} cm⁻² for the Si-SiN_x interface is observed. This value of Q_f is quite high compared to the thermal oxide.

Whereas Q_f in the Si-SiO_x interface is fixed, the value of Q_f at the Si-SiN_x interface is variable since Q_f consists of both fixed positive charge (Q_{f1}) and varied positive charge (Q_{f2}) as shown in Figure 6.10.

 Q_{f1} is related to positively charged oxygen-correlated dangling bond defects, i.e., $O_2N\equiv Si\bullet$, $ON_2\equiv Si\bullet$ and $O_3\equiv Si\bullet$. These defects associate with a SiO_x layer (≤ 2 nm) which is grown on the silicon surface in the time period between the loading of the silicon wafer into the deposition chamber and the start of the SiN_x layer deposition. The energetic position of these defects is located above the silicon conduction band edge and the positive insulator charge is fixed as in the case of thermally grown Si-SiO₂ interface. Q_{f1} is located in approximately 2 nm of the Si-SiN interface and its density is about 10^{11} cm⁻².

The variable charge Q_{f2} consists of nitride-correlated dangling bond defects, i.e., $N_3 \equiv Si \bullet$, $Si_3 \equiv Si \bullet$, $Si_2N \equiv Si \bullet$ and $SiN_3 \equiv Si \bullet$. Elmiger and Kunst [88] reported that the insulator charge density in the SiN_y layer increases with the layer thickness and reaches a constant level at about 20 nm. This implies that the Q_{f2} charge centers are located within 20 nm from the Si-SiN_x interface. Also, they investigated that the surface recombination velocity is drastically decreased with the first 20 nm and then is constantly low [89]. This means that Q_{f2} has a strong effect on the lifetime caused by the field effect passivation.

• D_{it} (interface trapped density)

The interface trapped density D_{it} is in the range of $1 \times 10^{11} - 5 \times 10^{12}$ cm⁻²eV⁻¹. The value of D_{it} for SiN_x by PECVD can be quite high compared to thermal oxide. The values of D_{it} in n-type materials are a factor of 2 to 3 higher than in p-type materials whereas the values of Q_f are independent of the type of the material [11].

A ratio of the gas flux, nitrogen to silicon ratio (x), has an influence on properties of $Si-SiN_x$ interface [90]. The tendency of the fixed charge Q_f and the spin density, which is contributed to the Si dangling bond, is similar as shown in Figure 6.11 (left). The Si dangling bonds will be easily formed by breaking Si-Si bonds in the range of x=0.91-1.38. At around x=1.4, the spin density and Q_f results in their maximum value while the presence of hydrogen at the layer is a minimum. Thus, the number of unpassivated Si-dangling bonds has reached its maximum concentration.



Figure 6.11 (left) Fixed trapped charge at the insulator () and spin density (\blacksquare), as a function of x. (right) Minimum value of D_{it} (\blacksquare), concentration of P_{bN0} centers (\lor) and concentration of N-H bonds (*), as a function of layer composition, x [90].

Furthermore, for composition ratios lower than x=1.38, the minimal value of D_{it} , of the concentration of U_M center which is related to silicon dangling bonds \bullet Si=Si₃ at the Si-SiO₂ surface and of the N-H bonds remains roughly constant as shown in Figure 6.11 (right), while

for values of x higher than 1.4, the three parameters increase sharply. From the results it is deduced that N-H bonds have the main influence on the electrical characters of SiN_x layers and the influence is different depending on the location of these bonds. When N-H bonds are located in the bulk of the layer, they encourage an improvement of Si dangling bonds and a decrease of the fixed charge density. On the other hand, N-H bonds located at the interface, act as a precursor site to defect generation of the type of Si dangling bonds. Therefore, the interface is more defective as the concentration of the N-H bonds increases.

6.2.2.2 Influence of thermal annealing

After annealing at temperatures in the range of 250–550 °C, not only the D_{it} values, but also Q_f reduce [91]. However, the lifetime after an annealing depends on deposition technologies. For example, experiments showed that after annealing at temperatures of 500 °C, the lifetime of remote SiN_x layer is degraded with different thickness whereas the lifetime of the low frequency direct SiN_x layer is increased by a factor of 4 [92]. Furthermore, after an annealing at 850 °C for 20 s a decrease of Q_f and of the surface recombination velocity was observed by the Corona charging measurement [93].

Hydrogen in the nitride layers is generally bonded to silicon (Si-H) or nitrogen (N-H). When PECVD deposited SiN_x is annealed at temperatures slightly above the deposition temperature, the N-H bonds break first, and the density of Si-H bonds increases. At temperatures higher than about 500 °C, also the Si-H bonds break. Released H₂ due to the bond break can also passivate silicon dangling bonds at the interface between silicon and the silicon nitride [64].

6.2.2.3 Influence of UV illumination

 D_{it} of SiN_x deposited wafers is increasing over the whole bandgap with the UV irradiation time at high UV doses since more interface states are created in the upper half of the bandgap [91]. A lifetime degradation after UV illumination was observed for all SiN_x layer types either by remote high or low frequency direct SiN_x layers [92]

On the other hand, the reduced lifetime by illumination is completely recovered by thermal annealing at 500 K for 1 h. This physical phenomenon could be explained with the K center model [94]. The diamagnetic center K^+ can be discharged by UV irradiation into the neutral K° . This reduces the field effect passivation and thus the effective lifetime reduces. However, K° is metastable and returns to its initial space charge state K^+ by the annealing which results in an electric field across the interface and an increase in lifetime.

The K⁺ center is found very close ($\leq 0.1 \text{ eV}$) below the silicon conduction band edge and is responsible for the large positive Q_f values (~10¹² cm⁻²) at Si-SiN_x interfaces obtained from standard dark C-V measurements. In the dark K center is positively charged and is responsible for Q_f. As illumination lifts the electron quasi-Fermi level Φ_n above the energy level of the K center, the positively charged K⁺ center is neutralized by the capture of electron from the silicon conduction band and Q_f is given by the fixed positive charges within the oxynitride film between the Si and the SiN [95]. K⁺ center is related to a silicon dangling bond back bonded to three nitrogen atoms (N₃ =Si \bullet) [96].

6.2.2.4 Capture cross section

Elmiger et al. [97] investigated the capture cross section of acceptor states (charged: σ_{ca} , neutral: σ_{na}) at the Si-SiN_x interface which dominate the surface recombination using of the Shockley-Read-Hall formalism and the C-V measurements. The acceptor capture cross sections of $\sigma_{ca} = 5 \times 10^{-15} \text{ cm}^2$, $\sigma_{na} = 5 \times 10^{-21} \text{ cm}^2$ for n-Si and $\sigma_{ca} = 1 \times 10^{-14} \text{ cm}^2$, $\sigma_{na} = 5 \times 10^{-20} \text{ cm}^2$ for p-Si were determined. On the other hand, the donor capture cross sections have no influence on the surface recombination, since high positive charges at the Si-SiN_x surface invert the energy band and repels holes from the surface whereas electrons are accumulated at the surface. That means that the many donor states are occupied by electrons and are neutral. Therefore, donor states do not contribute to the interface charge density Q_{it} because their neutral capture cross section is several orders of magnitude smaller than the charged capture cross section.

Schmidt et al. [98] investigated three different types of defects which are located in the lower half of the silicon bandgap at the Si-SiN_x layer by DLTS measurement. They found that the ratios of the electron and hole capture cross sections at midgap are extremely different for the three defects ($\sigma_n/\sigma_p > 10^4$ for defect A, > 10 for defect B, and < 1 for defect C) and therefore, they have a different influence on the surface recombination although appearing at the same energies (0.4 eV–0.5 eV) and with comparable state density (3-6×10¹¹ cm⁻²eV⁻¹). The defect C dominates the recombination velocity caused by the large hole capture cross section whereas the defect A and B is negligible.

6.2.3 Plasma enhanced chemical vapor deposition (PECVD)

Plasma enhanced chemical vapor deposition (PECVD) is working by means of a direct-plasma or remote-plasma technology [99]. The direct methods are widely used in laboratory as well as industrial applications while remote PECVD is only used for laboratory purposes. In direct PECVD reactors all processing gases are excited by an electromagnetic field and the samples are located within the plasma, whereas in the remote-plasma technology the excitation of the plasma is spatially separated from the sample and the plasma excitation actually occurs outside the vacuum chamber and the excited gases are directed onto the sample.



Figure 6.12 (left) Schematic of the direct PECVD reactor for deposition and (right) remote PECVD reactor for etching.

Figure 6.12 shows the schematic of the direct PECVD reactor at ISE used for the experiments of this work. In this direct PECVD reactor three 4 inch samples and nine 5×5 cm² samples can be processed per run. All processing gases are excited by an electromagnetic field using a frequency of 13,56 MHz. The plasma excitation frequency has a strong impact on the electronic properties of the Si-SiN interfaces. Using frequencies below the so-called plasma frequency (~4 MHz) ions are able to follow the plasma excitation frequency and produce a strong surface bombardment during the SiN_x deposition. Thus, the surface of the silicon wafers deposited by low frequency direct PECVD is damaged and the passivation quality is lower than that by high frequency [92]. This problem can be avoided as for excitation frequencies above 4 MHz the acceleration periods are too short for the ions to absorb a significant amount of energy. Therefore, SiN_x layers by direct PECVD at high frequency provide a better surface passivation and a much better UV stability than SiN_x layer deposited at low frequency [99].

The gas flow ratio is very important since the process gases determine the nature and properties of the layer that is deposited. Although a large variety of different layers can be deposited, here we will concentrate on the silicon nitride layer.

The samples used in this work are high-quality 1 Ω cm FZ p-type silicon wafer with a thickness of 250 µm. After a standard RCA-cleaning different SiN_x layers are deposited on the wafers. In this work we used three different silicon nitride layers, i. e., *passin*, *em223h*, and *pas_mac*. For all SiN_x layers the substrate temperature is kept at 350 °C and the pressure at 800 mTorr for 9 min

The flow rate from three different gases, i. e., silane (SiH₄), nitrogen (N₂) and hydrogen (H₂) and the microwave power were varied as summarized in Table 6.2. Therefore, the physical characteristic from those layers are not the same. After SiN_x layer deposition, all wafers were

annealed at temperatures of 425 °C for 25 min. Subsequently, the oxide thickness and the refractive index were measured at a wavelength of 632.8 nm by ellipsometry.

Parameter	Ranges	
Process temperatures [°C]	350	
SiH ₄ [sccm]	430	
N ₂ [sccm]	1002000	
H ₂ [sccm]	300500	
Pressure [mTorr]	800	
Power [W]	3060	
Time [min]	9	

Table 6.2 Range of process parameters of three different silicon nitride layers, i e., *passin*, *em223h* and *pas_mac*.

Figure 6.13 shows the SiN_x thickness and refractive index for the three different SiN_x layers. The first SiN_x layer *passin* is a Si-rich layer. The SiN_x thickness and refractive index result in the range of 70-74 nm and 2.8-2.85, respectively. This process is very homogeneous on the 9 inch quartz plate. The lateral distribution varies only by 2.7 % in thickness and 0.2 % in refractive index, even though the wafer lies on the edge during the SiN_x deposition. The effective lifetime is about 900 µs. This corresponds to a very low surface recombination velocity (SRV) S_{eff} ≤ 10 cm/s.

The second SiN_x layer em223h has a lower Si content and is optimized for the use as an antireflection layer. The 'em223h' has a radial distribution of the SiN_x thickness. The lateral variation of he SiN_x thickness and refractive index is about 19 % from 54 nm to 64 nm and from 2.16 to 2.18, respectively.

The third SiN_x layer *Pas_mac* has again a radial inhomogeneity of the SiN_x thickness. The variation of the thickness is 24 % from 45 nm to 56 nm. The refractive index results in a mean value of 3.7^{10} . This means that *Pas_mac* is almost amorphous silicon caused by less contents of N₂ from total gases (only 20 %), also, has a very high lifetime (over 1000 µs), since the lifetime increases with decreasing N₂ flow rate in the processing [100] caused by low D_{it}. This a-SiN_x layer can be used as passivation for lifetime measurements, however, is not optimal for the use in solar cells, because after an annealing the lifetime decreases drastically.

¹⁰ The refractive index of silicon is about 3.865 in the wavelength of 632. 8 nm.



Figure 6.13 (Left) Oxide thickness distribution and (right) index distribution for three different layers measured by means of ellipsometry. Note that all thickness and refractive indices were measured after annealing at 425 °C for 25 min.

6.3 SiO₂/SiN_x stacks

Double layers, especially SiO₂/SiN_x stacks are relatively new for the application in solar cells. Firstly, SiO₂/SiN_x stacks were applied to industrial type solar cells as a front antireflection layer by Rohatgi et al. [101]. Lauinger et al. [102] investigated SiO₂/SiN_x structures with varied oxide thickness. These oxides were grown by means of CTO and SiN_x layers using either low or high frequency plasma deposition were investigated. They showed that low-frequency SiN_x results in high lifetimes without oxide while for high-frequency SiN_x lifetimes are higher when using an oxid intermediate layer. Both SiO₂/SiN_x stacks were stable during a temperature step at 500 °C for over 60 min. Moschner et al. [103] studied various stack structures as front and rear surface passivation for solar cells. They concluded that the RTO/SiN_x stacks passivate better than a single layer, i. e., RTO or SiN_x. Furthermore, the high-quality passivation withstands the heat treatment associated with the firing of screen-printed contacts.

RTO/SiN_x stacks are an interesting layer for solar cells since both RTO and SiN_x are not only fast and low-cost methods, but also effective surface passivation methods. In this work, two different SiN_x layers were deposited on a *RTO*-oxide. The oxide has a thickness about 12 nm and is grown at temperatures of 1050 °C for 120 s. Figure 6.14 shows the effective lifetime distribution of a *RTO*/passin and a *RTO*/em223h passivated 4 inch wafer measured by carrier image density (CDI) [104]. The lifetime map for the *RTO*/passin stack shows homogeneous and excellent values higher than 1000 µs.

The wafer passivated with *RTO/em223h* stack shows a radial distribution caused by nonhomogeneous deposition of layers. τ_{eff} is relatively low in the middle of wafer. However, the average value is 680 µs and the passivation quality is relatively good. Even though the same *RTO* oxide by RTO is used in experiments, the passivation quality of stacks is different due to the type of the SiN_x layer.



Figure 6.14 Effective lifetime distribution on a 4 inch wafer measured by carrier density imaging (CDI) (see Appendix B.2). The wafer on the left is passivated with a *RTO/passin* stacks and the average lifetime is 1073 µs. The wafer on the right is passivated with a *RTO/em223h* stack and the average lifetime is 686 µs. For both causes the thickness of the RTO oxide is about 12 nm.



Figure 6.15 Effective lifetime of 1 Ω cm p-type FZ samples passivated with *RTO/em223h* (\blacksquare) and *RTO/passin* (\bullet) stacks versus oxide thickness. τ_{eff} is measured after an anneal at 425 °C for 25 min.

In order to investigate the influence of the oxide thickness on τ_{eff} , the oxide thickness was varied up to 12 nm. The different oxide thickness is prepared with different temperature and time by RTO. In Figure 6.15 τ_{eff} of *RTO/passin* and *RTO/em223h* stacks are shown as a function of the oxide thickness after an annealing at 425 °C for 25 min. As shown in Figure 6.15 depending on the oxide thickness, very different behavior of the passivation properties is observed between two SiN_x layers.

On the one hand, all *RTO/passin* stacks reached higher τ_{eff} than a single *passin* SiN_x layer. τ_{eff} of a *RTO/passin* SiN_x layer improves with increasing an oxide thickness The maximum lifetime value of about 800 µs is reached at an oxide thickness of 12 nm.

On the other hand, a stack with *em223h* SiN_x layer shows improved τ_{eff} with increasing oxide thickness up to a maximum at around 4.5 - 5.4 nm. For oxide thickness over 5.5 nm, τ_{eff} decreases drastically and for oxide thicker than about 8 nm, τ_{eff} is lower than for a single SiN_x layer.

Ebong et al. [105] performed measurements of the total hydrogen content in oxide/SiN stacks after different anneals by FTIR (Fourier transmit infrared spectrometer). They summarized that the N-H and Si-H bonds concentration is the same before and after annealing at 400 °C, while after an anneal at high temperatures (over 700 °C) the N-H peak is completely eliminated and the Si-H peaks remains below 10 % of the total hydrogen content. They suggested that hydrogen releases from SiN_x during the anneal and passivates the Si-SiO₂ interface in stacks. However, this model can not explain our improved τ_{eff} of the stack passivated samples, because all wafers in this work were annealed at 425 °C (not at high temperatures).

We assume that the improved τ_{eff} of SiO₂/SiN_x stacks can be attributed to a combined effect of advantages of both oxide and nitride layers. The interface trap density D_{it} at Si-SiO₂ interface is lower than at Si-SiN_x interface, whereas the fixed charge density Q_f causing a field effect is higher in SiN_x layer is higher than that in SiO₂ layer.

6.4 Passivation of solar cells

6.4.1 Passivation of the rear surface

In the previous section, the fundamental properties of SiO₂, SiN_x and SiO₂/SiN_x stacks were shown. In this section, different layers were investigated to passivate on the 1 Ω cm p-type silicon surfaces without emitter. The effective lifetime is shown in Figure 6.16 and the other characteristics of the investigated layers are summarized in Table 6.3. The lifetime of all wafers after forming gas annealing (FGA) at temperatures of 425 °C for 25 min was measured except for *Pas_mac*. τ_{eff} of *Pas_mac* is decreased from 1000 µs to 287 µs, while τ_{eff} of the others layers is improved after FGA.



Figure 6.16 Effective lifetime of different passivation schemes on 1 Ω cm p-type FZ silicon surface without emitter.

For all three SiN_x layers a better passivation is achieved than for the oxide layer. SiN_x layers *Passin* and *Pas_mac* show an excellent lifetime of about 900 μ s and 1000 μ s, respectively. Improved results are obtained by SiO₂/SiN_x stacks. *RTO/passin* shows excellent lifetime values of 935 μ s and lifetime of *CTO/passin* is 1361 μ s. *RTO/em223h* shows the effective lifetime of 154 μ s and *CTO/em223h* has the lifetime172 μ s.

The SiN_x layer is optimal for the passivation of p-type material, since the high positive charge density in the layer inverts the energy band and repels holes from the surface and thus Shockley-Read-Hall recombination at the silicon surface is strongly reduced.

	Thickness	Indox n	R_{w}	$ au_{eff}$	$S_{eff,max}$	Homogeneity
	[nm]	muex, n	[%]	[µs]	[cm/s]	in chamber
RTO	12	1.46	39	48	273	relative
СТО	105	1.46	17	155	82	good
Passin	~74	~2.8	24	898	14	good
Em223h	~60	~2.2	12	315	40	Only middle
Pas_Mac	~53	3.7		1000*	12	Only middle
RTO/passin			28	935	13	
CTO/Passin			54	1361	9	
RTO/em223h			13	154	82	
CTO/em223h			49	172	74	

Table 6.3 Summery of characteristics of various passivation layers on the 1 Ω cm p-type FZ silicon. Eq. (3.37) is used for calculating of S_{eff,max}. The bulk lifetime is assumed to be 2000 µs.

* value shows without annealing at 425 °C for 25 min.

6.4.2 Passivation and reflection of the front surface

The samples for the emitter passivation experiment were diffused on both sides in a classical furnace using POCl₃. Emitter with a sheet resistivity of 100 Ω/\Box and 40 Ω/\Box were investigated optimized for evaporated contacts and for screen-printed contacts, respectively. Figure 6.17 shows the effective lifetime resulting from the various passivation schemes on 100 Ω/\Box and 40 Ω/\Box .

On 100 Ω/\Box emitters, passivation of *RTO* and *CTO* is improved by a factor of 4 and 2 compared with passivation on the surface without emitter, whereas both nitride layers, *passin* and *em223h* passivate worse compared to case without emitter. Stacks with *passin* passivate not bad on emitter surfaces, however, in comparison to τ_{eff} on the surface without emitter, τ_{eff} of *RTO/-* and *CTO/passin* reduces drastically from 935 µs to 299 µs and from 1361 µs to 414 µs, respectively. On the other hand, τ_{eff} of *RTO/passin* and *CTO/em223h* is increased by a factor of 2.

On 40 Ω/\Box emitters, the effective lifetime is lower than that on 100 Ω/\Box emitters for all passivation layers. This results are due to dominate Auger recombination by the high surface doping concentration. The best passivation is achieved with *CTO/passin* stack (124 µs). However, the difference of the lifetime between the best and worst passivation is not too high.

An oxide layer can passivate more effectively on the emitter surface than on the pure p-Si. The maximal recombination at oxide passivated surfaces occurs when the ratio of p_s/n_s is 100 on the

surface as shown in Eq. (6.13) and the ratio p_s/n_s is always below 100 in emitter layers the recombination is strongly reduced. On the other hand, the field effect pasivation of SiN_x layers is not so effective anymore in highly doped silicon.



Figure 6.17 Effective lifetime for different passivation schemes on wafer with emitter, 100 Ω/\Box and 40 Ω/\Box .

For the front surface of solar cells the reflection is also important. The weighted reflection is given by

$$R_{w} = \frac{\int d\lambda \ S(\lambda) \ IQE(\lambda) \ R(\lambda) \ \frac{e\lambda}{hc}}{\int d\lambda \ S(\lambda) \ IQE(\lambda) \ \frac{e\lambda}{hc}}$$
(6.19)

where $S(\lambda)$ is the solar spectrum at AM1.5 as function of wavelengths [W/m²]. $R(\lambda)$ is the measured reflection as shown in Figure 6.18. The internal spectral efficiency (IQE) is taken from reference solar cells.

For the group of single layer systems, *RTO* and *em223h* show the lowest R_w 17 % and 12 %, respectively. For the stack systems *RTO/em223h* has the lowest reflection of 13 %. On the other hand, R_w values of *CTO/passin* and *CTO/em223h* layer which result in excellent passivation quality are about 50 %. The R_w is higher than that for bare reflection (over 30 %).

In order to calculate the optimal layer thickness for the front surface of solar cells, PC1D simulations were used. The oxide thickness was fixed as 10 nm and the thickness of *em223h* was varied in the ranged of 50-70 nm. Assuming a realistic IQE a maximal J_{sc} of 34.77 mA/cm² can be obtained with 58 nm *em223h* and 10 nm oxide.



Figure 6.18 Reflection (left) for single layer passivation schemes and (right) for SiO_2/SIN stacks.

Also the MgF thickness was varied in the range of 0-150 nm as shown in Figure 6.19 (right). This result shows that with an optimized three layer systems, i. e., SiO_2 10 nm, *em223h* 58 nm and MgF 110 nm a very low weighted reflection of about 5 % and a high J_{sc} of 36.6 mA/cm² can be reached without texture on the front surface.

These results show that *RTO/em223h* is an optimal layer for the front surface of solar cells because of its good passivation quality for the emitter and because of low reflection. On the other hand, *RTO/passin* is suitable for the rear surface because of its excellent passivation on pure p-Si.



Figure 6.19 Optimizing the thickness for high short-circuit current density using PC1D simulation. The optimized three layer systems, i. e., SiO_2 10 nm, em223h 58 nm and MgF 110 nm allows to reach a high J_{sc} of 36.6 mA/cm² without texture.

6.5 Solar cells

6.5.1 Cell Design and fabrication

In the previous section we have investigated a lot of different layers in order to find the optimal passivation for the front and rear surface of solar cells. It was concluded that *RTO/em223h* is the optimal layer for the front and *RTO/passin* is optimal for rear surface of solar cells. The purpose of this section is to demonstrate that these RTO/SiN stacks are appropriate to passivate the front and rear surfaces of solar cells and obtain high open circuit voltages.

For this goal we have chosen the passivated emitter and rear cell (PERC) structure as shown in Figure 6.20. The simplified PERC cells can reach an efficiency above 20 % and high-open circuit voltages V_{oc} above 660 mV even on Cz silicon materials [2]. We have chosen the PERC structure since it is suitable to demonstrate high efficiencies and high V_{oc} using SiO₂/SiN stacks.

0.5 Ω cm p-type FZ silicon materials with a thickness of 250 μ m were used for solar cells. The cell size was 2×2 cm², seven cells were processed on one 4 inch wafer. Both planar and textured solar cells with inverted pyramids were passivated with RTO/SiN_x stacks.

After standard RCA cleaning, a masking oxide was grown on the wafer with a thickness of 200 nm (Figure 6.21). Using photolithography technology, the front surface of some cells was textured with inverted pyramids. The emitter was formed in a classical furnace resulting in the sheet resistivity of about 120 Ω/\Box . The front and rear surface of cells were passivated by RTO simultaneously at temperatures of 1050 °C for 120 s resulting in a thickness of 10-12 nm. Two different SiN_x layers were deposited *RTO/passin* on the front and *RTO/em223h* on the rear surface. After etching of the rear and front contact grids by means of PECVD the rear and front were metallized with Al 2 µm and Ti/Pd/Ag, respectively. Finally, solar cells were annealed at temperatures 310 °C for 25 min for the metal contacts. MgF was deposited to a thickness of about 110 nm.



Figure 6.20 The standard planar PERC (passivated emitter and rear cell) structure.



Figure 6.21 Processing sequence for simplified PERC cells passivated with thin RTO/SiN_x stacks layers.

6.5.2 Results

The best results for each type of solar cells are summarized in Table 6.4. The samples, NRP2 2_4 and No51_5 passivated with an oxide of thickness 105 nm were used as a reference for the RTO/stacks passivated solar cells.

The planar RTO/SiN_x cell has a high V_{oc} of 675.6 mV and a J_{sc} of 35.1 mA/cm². In comparison to the CTO cell (NRP2 2_4) V_{oc} is only 2.9 mV (0.4 %) lower and J_{sc} is 2.8 mA/cm² (8.6 %) higher.

On the other hand, V_{oc} and J_{sc} of the inverted pyramids RTO/SiN_x cells are both reduced by 13.3 mV (2 %) and 1.1 mA/cm² (3 %) in comparison to the inverted pyramids CTO cells. The planar and textured RTO/SiN_x cells have lower FF than reference cells.

Cell	No2_3	No8_2	NRP2 2_4	No51_5
Base resistivity $[\Omega \text{ cm}]$	0.5	0.5	0.5	0.5
Front structure	planar	Invert pyramids	planar	Invert pyramids
Front passivation	RTO/em223h/MgF	RTO/em223h/MgF	СТО	СТО
Rear passivation	RTO/passin	RTO/passin	СТО	СТО
Contact grids	Plasma etch	Plasma etch	Chemistry etch	Chemistry etch
V _{oc} [mV]	675.6	662.4	678.5	675.7
J _{sc} [mA/cm ²]	35.1	36.8	32.3	37.9
Fill Factor [%]	78.1	77.2	80.7	80.6
η [%]	18.5	18.8	17.7	20.1

Table 6.4 Solar cell results with respect to different front structure and different layers. The oxide thickness of *RTO* and *CTO* is 12 nm and 105 nm, respectively. *Em223h* and *passin* denote different SiN_x layers.

6.5.3 Analyses and discussions

6.5.3.1 J_{sc} losses

From the measured results we have known that J_{sc} and the fill factor of RTO/SiN_x stacks passivated textured solar cells are lower than those of CTO passivated solar cells. The reasons of short-circuit current losses could be considered as follows:

- A. Higher reflection losses
- B. More recombination in the bulk and at surfaces
- C. Broader metal grids
- D. Light absorption in the layer

A. High reflection losses

Firstly, an optical reflection measured on four different types of solar cells was carried out. As shown in Figure 6.22 the weighted reflection R_w of both RTO/SiN_x/MgF cells are lower than reference cells. Especially, the R_w of 5.4 % can be obtained by textured cells passivated with RTO/SiN_x/MgF. Note that the reflection was measured including the metallization, i. e., fingers. Therefore, the loss in J_{sc} of RTO/SiN_x textured cells can not be attributed by an optical reflection.



Figure 6.22 Reflection of four different solar cells. Planar cell No2_3 and textured cell No8_2 are passivated with SiO_2/SiN_x stacks on the front and rear, while planar cell NRP2 2_4 and textured cell No51_5 are passivated with SiO_2 105 nm.

B. Recombination in the bulk and at surfaces

In order to further investigate the loss J_{sc} of RTO/SiN_x stack passivated cells, spectral response measurements were performed. The external quantum efficiency (EQE) is described as the ratio of the number of charge carriers, which contribute to the light current, to the number of photons in a wavelength range which fall on the cell. EQE is given by

$$EQE(\lambda) = \frac{hc}{\lambda e} \frac{I(\lambda)}{E(\lambda)} = \frac{hc}{\lambda e} SR(\lambda)$$
(6.20)

where I (λ) is the short-current density and E (λ) is the unit incident power of monochromatic light as a function of wavelength. SR (λ) is defined as the spectral response. λ is the free space wavelength. The internal quantum efficiency is calculated to eliminate external optical effects, which can be determined by a measurement of the total reflectance R(λ). Therefore, the internal quantum efficiency (IQE) is defined as

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda)}$$
(6.21)

The measured EQE and calculated IQE of four different types of solar cells are shown in Figure 6.23. In comparison to both RTO/SiN_x-stack-passivated cells, the textured cell No8_2 shows an improved EQE comparable to planar cell No2_3, for short wavelengths < 500 nm and for the long wavelengths > 1000 nm caused by a low reflection and internal light-trapping. Both cells have identical EQE for intermediate wavelengths which indicates that the bulk lifetime and rear surface recombination velocity are practically identical.

Both RTO/SiN_x stack cells and both CTO cells have a similar IQE over 1000 nm. A hump of both planar cells (No2_3 and NRP2 2_4) in long wavelengths over 1000 nm can be caused by drastically increased reflection in Figure 6.22. In comparison to CTO cells, both RTO/SiN_x stacks cells have a reduced IQE in short wavelengths (>500 nm) and in long wavelengths (<800 nm), whereas both have a identical IQE in the intermediate wavelengths. It is concluded that RTO/SiN_x stacks stacks cells have a weak passivation at the front and rear surface.



Figure 6.23 (Left) External spectral response (EQE) and (right) internal spectral response (IQE) of four different solar cells. Planar cell No2_3 and textured cell No8_2 are passivated SiO_2/SiN stacks on the front and rear. Planar NRP2 2_4 and textured cell No51_5 are passivated with SiO_2 105 nm.

In order to investigate the reason for these losses, the effective diffusion length L_{eff} was determined from the measured IQE using the method from [60].

Table 6.5 and Figure 6.24 show the calculated L_{eff} and S_{eff} from IQE for four different types of solar cells. Both RTO/SiN_x cells (No2_3 and No8_2) have lower L_{eff} values (300-400 µs) whereas the CTO reference cells have high L_{eff} values over 1000 µs. The S_{rear} of RTO/SiN_x cells is 3-4.5 times lower than of the CTO reference cells.

parameters	No2_3	No8_2	NRP2 2_4	No51_5
L _{eff} [µm]	370	270	1120	1250
J _{sc} [mA/cm ²]	34.9	37.1	31.8	37.8
J _{sc, max} [mA/cm ²]	39.7	39.0	42.8	42.5
S _{rear} ,[cm/s]	750	1000	250	222
S _{rear, max} [cm/s]	2300	13400	277	320
$ au_{eff,\ PC1D} \left[\mu s ight]$	350	350	700	700
S _{front, PC1D} [cm/s]	3000	4000	400	400
S _{rear, PC1D} [cm/s]	1500	3000	150	200

Table 6.5 Calculated parameters from measurement IQE (upper) and simulated values using PC1D (bottom).



Figure 6.24 Bulk diffusion length vs. rear surface recombination velocity for four different layers passivated solar cells.

The V_{oc} of RTO/SiN_x cells is high. Therefore, the bulk lifetime and the SRV at an injection level corresponding to 1-sun illumination (over 10^{15} cm⁻³) have to be good [78]. It is possible that the bulk lifetime and the surface passivation quality at the low level injections (about 10^{13} cm⁻³) corresponding to short-circuit conditions are lower.

This results are unexpected since the τ_{eff} of RTO/SiN_x stacks passivated wafer in the previous work results in around 1000 µs and the τ_{eff} of CTO is only 155 µs (see Figure 6.16). More precisely speaking, τ_{eff} shown in Figure 6.16 is not the absolute lifetime, but the differential effective lifetime. Normally, the differential effective lifetime is higher than absolute one [6].



Figure 6.25 Effective lifetimes for 1 Ω cm p-type FZ silicon passivated with *RTO/passin*, *RTO/em223h*, *CTO* and *RTO* on both surface by means of QSSPC (quasi-steady-state photoconductance). *RTO/em223h* passivates the 90 Ω/\Box emitter on both surfaces.

In order to investigate the dependence of lifetime on the injection level, the quasi-steady photoconductance method (QSSPC) was used on the lifetime test samples (see Figure 6.16 and Figure 6.17 in section 6.4). As shown in Figure 6.25 the τ_{eff} of the RTO/SiN_x cell, is higher than CTO reference cells not only at the high injection, but also at the low injection. Thus, the reason of a low J_{sc} and high SRV of RTO/SiN_x cells cannot be explained by this assumption.

Another reason could be that passivation qualities of RTO/SiN_x stack layers would be different on surfaces without metal contacts (test wafer) and with metal contacts (solar cells). The band structure under the SiN_x layer is bended caused by a high Q_f and this results in an inversion layers at the silicon surface. Electrons are accumulated at the surface and form a shallow n⁺ inversion layer which acts as a floating junction passivation layer [13]. However, a parasitic shunt between the floating and the real metal contacts caused a decrease of V_{oc}, J_{sc} and fill factor [106].

On the other hand, the parasitic shunt is not critical in SiO_2 passivated cells, since SiO_2 layers contain the low Q_f resulting in no or only weak inversion layers. Dauwe et al. [107] have investigated the influence of the SiN_x and SiO_2 layers on solar cells as a rear surface passivation. SiN_x passivated cells had a lower J_{sc} and FF than SiO_2 passivated cells while SiN_x/SiO_2 cells which are passivated with SiO_2 lines of about 200 µm width around the metal contacts and with SiN_x layer on remaining areas had the same J_{sc} and FF as SiO_2 passivated cells.

C. Broad metal grids

The broader metal grids are a reason of J_{sc} losses blocking the incoming light in solar cells. In this experiments the front and rear metal grids of RTO/SiN_x stacks passivated solar cells were etched by remote plasma shown on the right in Figure 6.12.

The rear surface passivated with *RTO/passin* was etched about 5 min, whereas the front layer *RTO/em223h* needed more time to etch. The refractive index was measured by ellipsometry after each etching. After etching for 7 min the refractive index was still 2.2 which is the initial value of *em223h* as shown in Figure 6.26. The refractive index resulted in 1.36 after etching for 12 min and this value is similar to the one of oxide (n=1.46). We can deduce from this measurements that the SiN_x layer *em223h* is completely etched a way after etching for 12 min. Schaefer [108, chapter 5] has shown that the etch rate in SiN_x is lower than in silicon. Therefore, the etch rate is increased with increasing refractive index since higher refractive index means in general that the SiN_x layer has higher silicon content.

The width of finger and bus were measured after the metallization. The width of the fingers is in the range of $36-38 \mu m$ and about 214 μm for the bus. The area covered with finger and bus on the front surface is about 5.6 %, while that is about only 4 % using chemical etching (which is only possible for pure SiO₂ layer). The J_{sc} loss increases 0.75 mA/cm² from 1.8 mA/cm² to 2.55 mA/cm² due to the increased metal covered areas.



Figure 6.26 Measured refractive index of each etching times by ellipsometry.
D. Light absorption in the layer

The refractive index of the passivation layer on the front surface, em223h, is 2.2 and that of SiO₂ is 1.46. SiO₂ is very transparent but in em223h layer light can be absorbed resulting in current losses.

In the previous section 6.4.2, PC1D was used to calculate the optimal thickness of the AR-layers resulting in an optimal J_{sc} of 36.16 mA/cm² as shown in Figure 6.19. However, in the PC1D-simulation an absorption of light in the layer is not considered, because only the measured refractive index of *em223h* at 630 nm was used.

To account for J_{sc} losses due to the absorption in the layer, the wavelength dependent refractive index is needed for the analysis. The wavelength dependent refractive index N of a medium can be represented by a real part and an imaginary part (N=n-ik). The absorption coefficient α is in direct relation to the imaginary part, i.e., the extinction coefficient k (α =4 π k/ λ). Figure 6.27 shows the wavelength dependence of the extinction coefficient for an *em223h* SiN_x layer. As can be seen from Figure 6.27, the *em223h* SiN_x layer shows a pronounced absorption in the ultraviolet range of the spectrum (<400 nm), even though the k values are low. It can be deduced from this measurement that there is J_{sc} loss caused by an absorption of light in the layer.



Figure 6.27 Measured extinction coefficient k and refractive index n of a em223h SiN_x layer as a function of wavelength.

The spatially dependent generation rate of electron-hole pairs can be calculated with respect to a wavelength dependent absorption coefficient α (λ) and multiple reflections of vertical incident light on the front surface. Therefore, the losses due to the reflection at the front and rear surfaces can be calculated analytically in the case of planar cell surfaces. Figure 6.28 shows a planar silicon wafer illuminated with light under normal incidence. R_{fe}, R_b and R_{fi} indicate the primary external reflection, the reflection of the rear cell surface and the internal reflectivity.



Figure 6.28 Multiple light reflection in a planar wafer [60].

The normalized generation rate including internal reflections in the cell is given by

$$g(\lambda, z) = (1 - R_{fe}(\lambda)) \alpha(\lambda) \frac{e^{-\alpha(\lambda)z} + R_b e^{\alpha(\lambda)(z-2W)}}{1 - R_{fi}(\lambda)R_b e^{-2\alpha(\lambda)W}}$$
(6.22)

The absorption of incident light of wavelength λ in silicon is described as

$$f_{abs}(\lambda, z) = \int_{0}^{z} d\xi g(\lambda, \xi) = (1 - R_{fe}) \frac{1 - e^{-\alpha z} + R_{b} e^{-2\alpha W} (e^{\alpha z} - 1)}{1 - R_{fi} R_{b} e^{-2\alpha W}}$$
(6.23)

That is the maximum achievable external quantum efficiency. $f_{abs}(\lambda, z)$ equal unity, if the primary external reflection R_{fe} is zero and the internal reflections are unit ($R_b = R_{fi} = 1$). That means that all incident light is absorbed in the medium. From the normalized generation rate function the maximum achievable short circuit current density can be calculated:

$$J_{sc,\max} = q \int d\lambda \int_{0}^{z} d\xi \, j_{\lambda}(0) \, g(\lambda,\xi)$$
(6.24)

 J_{λ} (0) is ascribed as the incident photon flux. More detailed explanation can be found in a diploma thesis by Schumacher [60].

This improved model of optical performance is used in order to calculate the absorption in the SiO_2/SiN_x stacks layers. Figure 6.29 shows the different current losses due to absorption in the front and rear layer and the reflection of the different layers. Those different J losses are explained in the following:



Figure 6.29 (Left) Improved simulation of optical performance using the enhanced model with wavelength dependent n and k of Figure 6.27. (Right) Total current density and calculated current losses. Note that this simulation is valid only for the planar solar cells.

- $J_{max} = 45.56 \text{ mA/cm}^2$: Maximum current if all incident light generates photon current.
- Loss $J_{FR1} = 2.14 \text{ mA/cm}^2$: Loss due to the reflection of the front surface. It is calculated by setting the rear reflection infinite ($R_b = \infty$) and the medium is absorption zero, i. e., R = 1-T.
- Loss $J_{AR1} = -0.57 \text{ mA/cm}^2$: Loss due to the absorption in the front layer. It is calculated by setting the rear reflection infinite ($R_b = \infty$), i. e., R = 1-(T+A).
- Loss $J_{FR2} = 2.14 \text{ mA/cm}^2$: Loss due to the external reflection in the front surface of the reflected light on the rear surface. It is calculated by setting the rear reflection finite ($R_b \neq \infty$) and the medium absorption zero, i. e., R = 1-T.
- Loss $J_{AR2} + J_{BF2}$ =-0.6 mA/cm²: Loss due to the front and rear absorption of the reflected light on the rear surface. It is calculated by setting the rear reflection finite ($R_b \neq \infty$) and the medium absorption zero, i. e., R = 1-(T+A).

If we consider all current losses including the light reflection on the finger and bus, the total current density of the SiO_2/SiN_x stacks for planar solar cells is given 35.7 mA/cm² as shown in Figure 6.29 (right), while the measured J_{sc} is 35.1 mA/cm².

6.5.3.2 Fill factor losses

The losses of Fill factor are associated with the saturation current in the base (J_{01}) and on the depletion region (J_{02}) , a series resistance (R_s) and shunt (parallel) resistance (R_p) . The two-diode model explained in section 2.2.3 was used to calculate dark current-voltage (I-V) characteristic parameters.

Figure 6.30 shows the measured dark parameters of four different types of cells. Unfortunately, No2_3 could not be fitted with the two-diode model because of a 'hump' in the dark I-V curve caused by high n_2 (about 5) whereas other cells are ideal ($n_1=1$, $n_2=near$ of 2).

In comparison to CTO reference cells, the J_{02} and R_s of RTO/SiN_x cells are higher. We assume that during the plasma etching which was used due to open the front and rear metal grids, not only SiN_x, but also the emitter is etched because the plasma-etch process is not optimized. Therefore, the surface concentration of the plasma-etched emitter is lower than that etched with chemistry. Furthermore, the non-optimal plasma etching can damage the cell surface. It induces electrically active defects which causes a high J_{02} and R_s .

Another reason of low fill factors is the injection-level-dependent surface recombination velocity at the rear surface [109]. It was found that the long-wavelength response of the cell improves strongly with an increase bias light intensity whereas the bias light has no effect on the blue response of the cell. This behavior is attributed that S_{eff} at the rear surface of solar cell depends on the injection level. On the other hand, the S_{eff} at front surface doped high level (over 10^{18} cm⁻³) is not effected by the bias light ensuring that the front surface operates at low injection conditions under 1-sun illumination.



Figure 6.30 Measured dark I-V curve of three different silicon solar cells.

6.6 Conclusion

The various surface passivation layers were schemed in this study: SiO_2 layers by conventional thermal oxidation (*CTO*) and by rapid thermal oxidation (*RTO*), SiN_x layers *passin* and *em223h* deposited by plasma enhanced chemical vapor deposition (PECVD) and combined SiO_2/SiN_x stack layers *CTO/passin*, *RTO/passin*, *CTO/em223h*, and *RTO/em223h*. The physical properties and the passivation quality have been investigated on the without emitter and on the with 100 Ω/\Box and 40 Ω/\Box emitter.

On the without emitter, both SiN_x layers and SiO₂/SiN_x stack layers passivate better than SiO₂ layers. τ_{eff} for *passin* results in around 900 µs, while τ_{eff} for *RTO* and *CTO* were given only 45 µs and 155 µs. In addition, the wafers passivated with *RTO/em223h* and *CTO/passin* stack layers have the excellent effective lifetime of 935 µs and 1360 µs on the 1 Ω FZ materials, respectively.

On the emitter, CTO (105 nm) and SiO₂/SiN_x stack layers passivate relatively good. a passivation quality of the CTO was improved a factor of 2 from 155 µs to 306 µs, whereas lifetime of *RTO/passin* stack layer was decreased a factor of 3 from 900 µs to 276 µs. However, even through τ_{eff} of SiO₂/SiN_x stacks was decreased a factor of 3 on the emitter, τ_{eff} lies on relatively good in the range of 300-400 µs.

The efficiency potential of RTO/SiN_x stack layers passivated cells with planar surface and textured surface with inverted pyramids has been investigated. The excellent V_{oc} of 675.6 mV and high J_{sc} of 35.1 mA/cm² is obtained for the planar cell with RTO/SiN_x stack. However, all RTO/SiN_x cells have lower J_{sc} and FF than the CTO reference cells. Three main reasons of the losses of J_{sc} and FF could be considered: (1) Contribution by the parasitic shunt current between the strong inverted layer at the rear surface due to high Q_f and metal rear contacts. In the dark-condition related to J_{sc} the parasitic shunt current has a significant impact on S_{eff} and reduces J_{sc} and FF. (2) The loss J_{sc} of 0.57 mA/cm² due to an absorption in the SiN_x layer *em223h* was calculated. (3) High J₀₂ and R_s caused by etched and damaged emitter due to the non-optimal etch process by PECVD.

In order to improve the efficiency of the SiN_x -passivated solar cells, more transparent silicon nitride layer are required as a optimal antireflection layer. The detrimental parasitic shunt can substantially decrease or eliminate the advantage of SiN_x layers which introduce a weak inversion layer. The damages due to etch by plasma could be pretended by using laser fire contact (LFC) or screen printing contacts for which no etching step is needed.

7 Rapid thermal diffusion with spin-on dopants

Diffusion of impurity atoms in silicon is a necessary step for the fabrication of semiconductor devices. Controlling of doping concentration, junction depth, uniformity, reproducibility and reducing the manufacturing costs are the main goals in this field. Rapid thermal processing is one method for diffusion which is widely being used for the fabrication of solar cells. In this chapter, firstly, general diffusion theories from Fick's diffusion equation is described for the intrinsic and extrinsic case. Secondly, the method of spin-on dopants used in this work is introduced where dopant atoms are applied directly on the silicon surface. The diffusion of phosphorus and boron into silicon from spin-on dopants using rapid thermal processing is studied. Furthermore, the resulting diffusion samples were characterized by measuring sheet resistivity, and concentration profiles. Lastly, phosphorus as a emitter and boron as a back surface field are applied to produce RTP-solar cells and their parameters are analyzed.

7.1 Basic diffusion theory

7.1.1 Models of diffusion

Diffusion in a semiconductor can be visualized as atomic movement in the crystal lattice. There are two different atomic diffusion models, i. e., Interstitial diffusion models such as interstitial, interstitialcy, and crowdion mechanisms and substitutional diffusion models such as vacancy, exchange, and ring mechanisms. Figure 7.1 shows common atomic diffusion mechanisms for interstitial (a-c) and substitutional diffusion (d-f).

In the case of interstitial mechanism atoms migrate by jumping from their original site to a neighboring equivalent one (Figure 7.1 a). An atom smaller than the host atom often moves interstitially. If the interstitial atom displaces a lattice atom, which in turn becomes an new interstitial atom, the mechanism is called interstitialcy (or kick-out) mechanism (Figure 7.1 b). The crowdion mechanism (Figure 7.1 c) is related to interstitialcy mechanism, in which an interstitial atom located half-way between two lattice sites migrates into one of the lattice sites and displaces the lattice atom which becomes an interstitial atom to the neighboring site of the vacancy. When two neighboring substitutional atoms exchange these substitutional site directly, this mechanism is called exchange mechanism (Figure 7.1 e). Substitutional atoms exchange indirect with a lattice atom. This occurs through a simultaneous jump of two or more atoms. This mechanism is called ring mechanism (Figure 7.1 f). For example, the diffusion of group III and V elements in silicon are generally considered to diffuse predominately substitutionally by vacancy and self-interstitials mechanism .



Figure 7.1 Models of atomic diffusion mechanisms for a interstitial (a-c) and substitutional (d-f): (a) interstitial mechanism (b) interstitialcy (or kick-out) mechanism (c) crowdion mechanism (d) vacancy mechanism (e) exchange mechanism (f) ring mechanism.

7.1.2 Diffusion equations

Diffusion is the movement of particles from high concentration to low concentration. The mathematical basis for the diffusion process was published by Fick [110]. He hypothesized that the rate of transfer of a diffusing particle through unit area is proportional to the magnitude of the gradient concentration to that area. In the x-direction this Fick's law is given by

$$J = -D\frac{\partial C(x,t)}{\partial x}$$
(7.1)

where J is a diffusion flux and C is the concentration of particles, which is assumed to be a function of position x and time t only. D is the diffusion coefficient. The negative sign indicates the opposite direction of the flux compared to the concentration gradient.

In a steady state the concentration and the flux are related according to

$$\frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}$$
(7.2)

the transport equation in one dimension. Combing the transport and diffusion equations, i. e., (2.3) or (2.4) and (7.2) yields

$$\frac{\partial C(x,t)}{\partial t} = -D \frac{\partial^2 C(x,t)}{\partial x^2}$$
(7.3)

The concentration from the solution of Eq. (7.3) should be considered for intrinsic diffusion and extrinsic diffusion, since the properties of the diffusion coefficient for the intrinsic and extrinsic cause are different. If the impurity concentration is lower than the intrinsic carrier concentration n_i (T), the silicon is considered as intrinsic silicon and the diffusion is defined by Fick's diffusion law with a constant diffusion coefficient. When the impurity concentration is higher than n_i (T), the silicon is considered as extrinsic silicon and the diffusion coefficient is not constant. Therefore, in the following section properties of diffusion are described for intrinsic and extrinsic cases.

7.1.3 Intrinsic Diffusion

7.1.3.1 Diffusivities

In the intrinsic diffusion (n (T) < n_i (T)) the diffusion process occurs due to the random movement of the impurity atoms and is a thermally activated process independent of the concentration. Therefore, the diffusion coefficients determine experimentally over a range of diffusion temperatures can often be expressed as

$$D = D_o \, \exp\!\left(\frac{-E_a}{kT}\right) \tag{7.4}$$

where D_o is the frequency factor (in unit of cm²/s) and E_a is the activation energy (in eV), T is temperature (in K), and k is the Boltzmann constant (in eV/K). Figure 7.2 (left) shows the diffusion coefficient of many impurities in silicon. As shown in Figure 7.2 (left) D is a straight line in an arrhenius-plot 1/T. D_o is related to the atomic jumping frequency or the lattice vibration frequency (typically 10¹³ Hz) [62].

The activation energy E_a depends on the energies of motion and the energies of formation of defect-impurity complexes. For example, the activation energy for substitutional impurities in silicon, which includes the group III and the group V element of the periodic table, is in the range of 3 to 4 eV, while the activation energy for self diffusion in silicon is approximately 5 eV. On the other hand, the activation energy for interstitial impurities, which consists of hydrogen, helium, and the alkali metals results in the range of 0.5 to 1.6 eV [111]. Therefore, substitutional diffusion has to be thermally activated by a larger energy than interstitial diffusion, since substitutional diffusion needs not only the jumping energy comparable to the one for interstitial diffusion, but also the energy which gives rise to the vacancies.

Often in solar cells fabrication diffusion of Al, P and B are used. The diffusion coefficient of Al in Si is 8×10^{-13} cm²/s at 980 °C. P and B are reaching the same diffusion coefficient around 1080 °C. Therefore, for the diffusion Al needs a low temperature, whereas P and B need a high temperature.



Figure 7.2 (left) diffusion coefficient (right) solubility in silicon [111].

Table 7.1 Properties of the intrinsic diffusion of boron and phosphorus [62].

Properties	Boron	Phosphorus
Dominating element for diffusion	$(D^+_i)_{\scriptscriptstyle m B}$	$(D^x_i)_{P}$
D _o [cm ² /s]	0.76	3.85
E _a [eV]	3.46	3.66

Table 7.1 shows the properties of the intrinsic diffusion coefficient of boron and phosphorus in terms of dominated diffusion element, a frequency factor D_o and an activation energy E_a . The boron intrinsic diffusivity is dominated by the interaction of boron with an donor-type vacancy V^+ ($D^+_{i,B}$) and for phosphorus the intrinsic diffusivity is dominated by interaction of impurity atom with the neutral vacancy V^x ($D^x_{i,P}$) [62].

7.1.3.2 Diffusion Profile

A. Constant-surface concentration diffusion profile

This situation occurs when an undoped wafer is exposed to a source of constant concentration during diffusion. For example, this method can be applied when impurity atoms are transported from a vapor source onto the semiconductor surface and diffused into the semiconductor bulk.



Figure 7.3 (a) Constant-surface-concentration diffusion profile. The normalized error function (erfc) is plotted vs. distance from the surface x, for different time: $t_1 < t_2 < t_3$. (b) Constant-total-dopant diffusion profile. The normalized Gaussian function is plotted.

The vapor source maintains a constant level of surface concentration during the entire diffusion period. The impurity concentration C(x,t) is given by

$$C(x,t) = C_s \operatorname{erfc} \frac{x}{2\sqrt{Dt}}$$
(7.5)

where C_s is a concentration at surface (x=0), D is an intrinsic diffusion coefficient, x is the distance from surface and t is the diffusion time. A schematic plot of concentration profiles in linear and semilogarithmic scales is given in Figure 7.3.

B. Constant-total-dopant diffusion profile

In constant-total-dopant diffusion a fixed amount of dopant is deposited onto the semiconductor surface and is subsequently diffused into the wafer.

The impurity concentration C (x,t) is given by

$$C(x,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left[-\left(\frac{x}{2\sqrt{Dt}}\right)^2\right]$$
(7.6)

where Q is amount of source material in the surface, D is intrinsic diffusion constant, x is the distance from source and t is the diffusion time. A schematic plot of the Gaussian type of concentration profiles in linear and semilogarithmic scales are shown in Figure 7.3 (b).

7.1.4 Extrinsic Diffusion

7.1.4.1 Diffusivities

In the previous section 7.1.3 properties of the intrinsic diffusion have been described. In extrinsic diffusion the diffusion coefficient is altered due to an electric field effect (h) and mass action effect (n (T)/n_i (T)).

The vacancy and interstitial atoms can become ionized when they accept or loose electrons. The generalized diffusion coefficient considers the various charge states of vacancies and interstitial can be described by [62]

$$D = h \left\{ D^{x} + \sum_{r=1}^{m} \left(D^{-r} \int \left[\frac{n}{n_{i}} \right]^{r} + \sum_{r=1}^{m} \left(D^{+r} \int \left[\frac{n}{n_{i}} \right]^{r} \right\} \right\}$$
(7.7)

where

$$h = 1 + \left[\frac{n}{xn_i}\right] \left\{ \left[\frac{n}{2n_i}\right]^2 + 1 \right\}^{-1/2} \qquad x = 1.....2$$
(7.8)

 D^x , D^{-r} , and D^{+r} are diffusion coefficients of the diffusing species combined with charged neutral, acceptor or donor defects of the native lattice. h is the electric-field enhancement factor which approaches a maximum of 2 at high active doping levels. x is varied between 1 and 2 and depends on impurities. For example, x is 2 for boron impurities and 1 for phosphorus impurities.

The diffusion of boron in silicon is associated with the interaction with neutral point defect and single donor-type vacancy V⁺. The diffusion coefficient varies approximately linearly with dopant concentration. From Eq. (7.7) the diffusion coefficient D for boron can be expressed by [112, chapter 7]

$$D_B = h \left\{ D_B^x + D_B^+ \left[\frac{p}{n_i} \right] \right\}$$
(7.9)

where

$$D_B^x = 0.04 e^{-(3.46)/kT}$$
, $D_B^+ = 0.72 e^{-(3.46)/kT}$ (7.10)

As shown in Eq. (7.10) single donor-type vacancies V^+ have a dominated effect on the diffusivity for boron.

On the other hand, the diffusion of phosphorus in silicon is more complicated than that of boron due to a dissociation effect. Figure 7.4 shows the phosphorus diffusion profiles for various surface concentration. When the surface concentration is low, the diffusion profile corresponds to an erfc profile (curve a). As the concentration increases, the profile begins to deviate from the simple expression (curve b and c).



Figure 7.4 Phosphorus diffusion profiles for various surface concentrations after diffusion into silicon for 1 hour at 1000 °C [113]. n_e is indicated to the electron concentration in the kink region.

Curve d in Figure 7.4 shows a very interesting profile. This characteristic profile of phosphorus can be described as consisting of three regions: the high concentration region, the 'kink' region (or the transition region) and the tail region. In the very high concentration region in curve d the diffusivity is associated with the double-charged acceptor vacancy V^{2-} (P⁺ + $V^{2-} \rightarrow P^+V^{2-}$) and is proportional to n². The diffusion coefficient at high concentrations can be described as

$$D_{P} = h \left\{ D_{P}^{x} + D_{P}^{2-} \left[\frac{n}{n_{i}} \right]^{2} \right\}$$
(7.11)

where

$$D_P^x = 3.85 e^{-(3.66/kT)}, \qquad D_P^{2-} = 44.2 e^{-(4.37/kT)}$$
(7.12)

When P^+V^{2-} pairs leave the flat region and diffuse down the steep doping gradient, it is proposed that they do not dissociate until the concentration drops to n_e which corresponds to a Fermi level 0.11 eV below the conduction band. The binding energy of the P^+V^- pairs is about 0.3 eV lower than that of P^+V^{2-} pairs. Therefore, when $E_F = E_C - 0.11 \text{ eV}$, P^+V^{2-} pairs dissociate to P^+ , V^- and $e^- (P^+V^{2-} \rightarrow P^+V^- + e^-)$ and an abrupt change occurs in the profile diffusivity by going from an n^2 dependence to an n^{-2} dependence. Then, the concentration has dropped to the 'kink' region. In the tail region the dissociation generates a large number of single-charged atoms and the diffusion coefficient is proportional to the increasing $V^- (P^+V^- \rightarrow P^++V^-)$. Therefore, the diffusivity can be described as

$$D_{P,tail} = D_P^x + D_P^- \left[\frac{n_i}{n}\right]^2 \left(1 + e^{0.3 \ eV/kT}\right)$$
(7.13)

with

$$n_e = 4.65 \times 10^{21} \, e^{0.39 \, eV/kT} \tag{7.14}$$

 n_e is the electron concentration. The diffusivity in the tail region is over 10^{-12} cm/s, which is about two orders of magnitude larger than the intrinsic diffusivity at 1000 °C [62].

7.1.4.2 Diffusion Profile

In extrinsic diffusion $(n(T)>n_i(T))$ the diffusion coefficient becomes concentration-dependent as a result of the internal electric field effect and changes the ionized vacancy doping level as shown in Eq. (7.7). Therefore, impurity distribution in the extrinsic diffusion can be calculated numerically by solving the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \tag{7.15}$$

The doping concentration in the extrinsic diffusion has been less investigated than the diffusion coefficient. The calculation of the surface concentration is complicated, since the diffusion profiles include anomalous effects such as a concentration-dependent diffusion coefficients, orientation-dependent diffusions under oxidizing conditions, and retarded or accelerated diffusion in the presence of n- or p-type impurities.

Fair [114] described the surface concentration for boron and phosphorus based on experimental data. The total surface concentration for phosphorus can be described as function of an electron concentration (n):

$$C_{P} = n + 2.04 \times 10^{-41} n^{3} \tag{7.16}$$

The surface concentration for boron can be describe as [112]

$$C_{B} = F_{\rm I} \left(\frac{Q_{T}^{2} n_{i}}{D_{B}^{+} t}\right)^{1/3}$$
(7.17)

where F_1 is an empirical constant of value 0.53. Q_T is the total boron concentration which is associated with the junction depth and C_B . Q_T is assumed constant during the diffusion. More detailed information can be found in the literature by Wang [112].

7.2 Back surface field

To obtain high efficiency solar cells, both bulk and surface recombination must be low. The various surface passivation methods have been investigated in chapter 6 in this work. Another effective surface passivation method is the built-in electric field at the back surface as a low-high junction which enhances not only the short-circuit current, but also the open-circuit voltage of a solar cell. Widely used back surface field dopants are aluminum and boron.

In Table 7.2 the properties between Al and B are compared. The Al-dopant layer is normally evaporated or screen printed. The formation of Al-Si alloyed layer at low temperatures is a well-known advantage of Al-BSF. Therefore, the co-diffusion of phosphorus for the emitter and Al for the BSF is possible resulting in an enhancement of the phosphorus diffusion by the so-called push effect [115] and the improvement of the diffusion length in the material by gettering which is able to increase the bulk lifetime during the process [116]. Moreover, a reflector effect is present due to the Al alloying and the thickness of the junction depth can be varied easily. In case of RTP-solar cells efficiencies up to 19.1 % [73] have been achieved by applying of 10 μ m evaporated Al-BSF on the FZ-Si. An efficiency of 17.5 % [59] has been obtained using a standard solar cell structure with 2 μ m evaporated Al-BSF on Cz-Si. However, the rear recombination at the Al-Si rear contacts is relatively high, since the Al concentration of the Al/Si alloy is not more than 3×10¹⁸ cm⁻³ [117].

Properties	Boron	Aluminum
Diffusion technology	necessary of high temperature and long duration	low temperature and short duration
Junction depth	shallow	deep
Junction form	uniform	not uniform (rough)
Solubility	high	low
Surface concentration	high (> 10 ²⁰ cm ⁻³)	low (< 10 ¹⁹ cm ⁻³)
Recombination	low	high
Metal contact resistance	low	high

Table 7.2 Comparison of properties for B- and Al-BSF.

On the other hand, boron is the other attractive candidate for a BSF layer. Boron diffusion has advantages in that boron is more soluble in silicon than aluminum (see Figure 7.2 (right)). In addition, boron diffusion yields more uniform junctions than alloying. Therefore, boron diffused surfaces are more suitable for the contact than aluminum alloyed surfaces. However, for an effective boron diffusion high temperatures (over 1000 °C) and long process time are necessary in order to achieve high concentration and large junction depth. The diffusion at high temperatures can cause diffusion of undesirable impurities present on the surface of the silicon resulting in minority carrier lifetime degradation.

To study the effect of BSF on RTP cell surface doping concentration (C_B) and junction depth (x_j) were varied in the simulation with PC1D. Bulk lifetimes of 2 µs and 300 µs are chosen. All other parameters for the simulation were fixed with an emitter sheet resistivity of 90 Ω/\Box , the base resistivity of 1.0 Ω cm, front surface recombination velocity of 50000 cm/s (which is achievable by a RTO passivation of an emitter with spin-on dopants by RTD) and a rear surface recombination velocity S_{rear} of 1×10⁷ cm/s (which is typical for a metal-covered Si surface).

Figure 7.5 shows the influence of C_B and junction depth on the open-circuit voltage (V_{oc}) with a bulk lifetime of 2 µs and 300 µs, respectively. If the bulk lifetime is 2 µs as shown in Figure 7.5 (left), the open-circuit voltage V_{oc} increases with increasing x_j and C_B . However, the x_j and C_B has not a strong impact on the V_{oc} , because the difference between the maximal and minimal V_{oc} is only about 0.22 mV.

On the other hand, if the bulk lifetime is 300 μ s as shown in Figure 7.5 (right), x_j and C_B are important parameters to obtain a high V_{oc} . V_{oc} increases strongly with increasing x_j and C_B . For example, in the case of a typical Al-BSF using an evaporation method (C_B is 3×10^{18} cm⁻³ and x_j is 2 μ m) a V_{oc} of about 623 mV can be obtained. RTP-cells with B-BSF using a spin-on method (C_B is 1×10^{20} cm⁻³ and x_j is 0.5 μ m) can yield high V_{oc} of about 627 mV.



Figure 7.5 Open-circuit voltage as function of BSF doping concentration (left) with $\tau_b = 2 \ \mu s$ and (right) $\tau_b = 300 \ \mu s$ using a PC1D simulation with $N_A = 10^{16} \ \text{cm}^{-3}$, $S_{\text{front}} = 50000 \ \text{cm/s}$ and $S_{\text{rear}} = 1 \times 10^7 \ \text{cm}^{-3}$.

7.3 Spin-on technique for diffusion

Spin-on dopants (SODs) are solution which are deposited on the semiconductor surface. Advantages of using of SOD are : Convenient application of dopant, easy control of doping concentration and junction depth, optimal for a simultaneous diffusion without mask and low costs. SODs are primarily spin-on glasses that have the dopant atoms incorporated in a chemical form such as phosphosilicate glass (SiO₂P₂O₅), borosilicate glass (SiO₂B₂O₃), silicon oxide (SiO₂), other glasses and organic layers. In this work we used phosphoruss dopants as n-type sources and boron, Al/B and Ga/B dopants as p-type sources.



Figure 7.6 Thin film formation by spin-on technique.

Most of SODs need to be stored in a refrigerator and they must be at room temperature at least 2 hours before applying to the deposition on the silicon wafer. The silicon wafer is prepared using the RCA cleaning procedure. The wafer is placed on the spinner and the SOD is dropped on the center of the wafer. Required SOD for a 5×5 cm² wafer is 350 µl and 750 µl for a 4 inch wafer. An optimized rotation speed is needed which depends on the size of the wafer and the solution viscosity, since the film of SOD should be uniform and must not be deposited on the rear side of wafer. In this work, Rotation speeds for 5×5 cm² is firstly 1500 rpm (rotation per min) for 5 s and then 3000 for 15 s, while that for a 4 inches wafer is firstly 3000 rpm for 5 s and then 3000 for 15 s (Figure 7.6 (a)). The coated wafer is baked on the hot plate firstly at 100 °C for 10 min for evaporating of solvents and subsequently at 200 °C for 15 min to drive out the excess solvents (Figure 7.6 (b)). The next step is the heat treatment with high temperatures to diffuse dopants into the wafer (Figure 7.6 (c)). The phosphorus dopant atoms is diffused into silicon at temperatures of over 850 °C. The diffusion temperature and time depend strongly on the species and concentration of the SOD. After performing at different temperatures the residual SOD source on the wafer is removed in HF (50 %)-dip for 2 min for phosphosilicate glass and for 20–30 min for borosilicate glass.

7.4 Characteristics of rapid thermal diffusion

7.4.1 Experiment procedures

In this work p-type wafers for phosphorus diffusion and n-type wafers for boron diffusion were used. The both n- and p-typed wafer are Float Zone (FZ) silicon with a resistivity of 1 Ω cm and a thickness of 250 µm. Both sides of this material were mirror etched. After RCA cleaning, phosphorus (P) and boron (B) spin-on dopants (SODs) provided by Filmtronics were deposited on the wafer using a spin-on method. Three different P-SOD sources and six different pure and mixed B-SOD sources were used as shown in Table 7.3 and Table 7.4. After baking at 200 °C for 15 min, the diffusion of P and B was performed by RTP. The typical RTD process is shown in Figure 7.7. Heating rate and cooling rate were both 100 °C/s. N₂ was used as a ambient gas for diffusion. Phosphorus was diffused at temperatures between 850 and 1025 °C for process times between 10 and 80 s and boron was diffused at temperatures in the range of 1000-1100 °C for 60-180 s. After diffusion the deposited silica-film glass was removed by a HF-dip.

The sheet resistivity of the doped layers was measured by the four-point probe method. Phosphorus profiles in p-type silicon were investigated by the secondary-ion mass spectroscopy (SIMS) while boron profiles on n-type silicon were measured by electrochemical capacitance voltage (ECV) profiles.

	P507	P508	P509
Dopant concentration [%]	P4.0	P8.0	P15.0

Table 7.3 The different spin-on dopants of phosphorus used in this work.

Table 7.4 The different spin-on boron dopants and mixed boron spin-on dopants with other p-type impurities.

	Boron A	B155	B153	B0.008	Al/B120	Al/Ga130
Dopant		B4.0	B2.0	B0.008	Al4.0	Al1.3
concentration [%]					+B4.0	+ Ga1.3



Figure 7.7 Typical rapid thermal diffusion (RTD) schematic by rapid thermal processing. Heating and cooling rates are both 100 °C/s and plateau temperature and time are varied between 850 and 1025 °C for 10-80 s for P-diffusion and between 1000 °C and 1100 °C for 60-180 s for B-diffusion.

7.4.2 Phosphorus diffusion

7.4.2.1 Sheet resistivity

The evolution of sheet resistivity with the temperature and time after rapid thermal diffusion using three different SODs is shown in Figure 7.8. In all cases the sheet resistivity sharply decreases with increasing annealed temperature and time.

As shown in Figure 7.8, RTD with SODs is very efficient for diffusion since sheet resistivity values lower than 100 Ω/\Box can be easily obtained for process times under a few seconds, whereas the process time for phosphorus diffusion by classical thermal diffusion is over a few minutes. In addition, the typical sheet resistivity range, i.e., 40 Ω/\Box and 100 Ω/\Box suited for silicon solar cells can be also reached with low thermal budgets. Especially, *P507* which has a low phosphorus concentration is useful for solar cells with evaporated contacts while the high phosphorus concentration dopants *P508* and *P509* are optimal for industrial solar cells with screen-printed contacts which need a sheet resistivity of about 40 Ω/\Box .



Figure 7.8 Evolution of sheet resistivity in respect to diffusion time and diffusion temperature using three different phosphorous spin-on dopants. The dot lines denote the sheet resistivity of $100 \Omega/\Box$.

7.4.2.2 Phosphorus profiles

Figure 7.9 shows phosphorus concentration profiles of different SODs at various sheet resistivities after rapid thermal diffusion. The profiles are determined by SIMS technique measuring the total doped atomic impurities. It can be seen that the surface concentration and junction depth increase with temperature. This behavior can be attributed by an increase of solubility and diffusion coefficient of phosphorus into silicon when the diffusion temperature increases (see Figure 7.2).

For same sheet resistivity the surface concentration is identical and junction depth is deeper at long duration of the diffusion time, even though the process temperatures are lower (Figure 7.9 (right)). This trend is observed for both dopants *P507* and *P508*. The 'kink' and 'tail' profile's regions as shown in Figure 7.4 are also shown in the profile from RTD using spin-on dopants. Therefore, it is assumed that the phosphorus diffusion mechanism with SODs by RTP has a same behavior as gas diffusion with a classical furnace.

The study by Usami et al. [118] supports this assumption. They investigated that the diffusion coefficient by RTD is higher than by CTD due to the high heating rate resulting in the induced stress, however, the curves of concentration-dependent diffusion coefficient for RTD and for CTD have a similar V-form. The P-diffusion coefficient remains constant up to 3×10^{19} cm⁻³. At 3×10^{19} cm⁻³ the diffusivity starts to decrease with P concentration of about 3×10^{19} cm⁻³ and reaches the minimum around 10^{20} cm⁻³ and then increases again.



Figure 7.9 (Left) Carrier concentration profile varied process temperature and time using *P507* dopant. (Right) Carrier concentration profile at the same sheet resistivity using *P507* and *P508* dopants.

7.4.3 Boron diffusion

7.4.3.1 Sheet resistivity

Figure 7.10 shows the dependence of the boron sheet resistivity on diffusion time and temperatures using six different p-type spin-on dopants as shown in Table 7.4. The temperature was varied between 1000 and 1100 °C and the diffusion time was chosen between 60-180 s.

The sheet resistivity for pure boron SODs (*Boron A*, *B155* and *B153*) show a similar trend, i.e., the sheet resistivity decreases with an increase of the diffusion time and temperature.

However, the sheet resistivity of *B0.008*, *Al/B120*, and *Al/Ga130* is not absolutely reliable. The sheet resistivity of *B0.008* was measured between 35 and 40 Ω/\Box independent of the diffusion temperature and process time. In addition, during the measurements the four-point device indicated not p-type, but n-type material. It is assumed that the boron layer on the n-type material is very shallow caused by the extremely low boron concentration (0.008 %) and then during the measurement current flows also over the n-type base material.

The sheet resistivity for mixed SOD *Al/B120* shows the same tendency like that of pure boron dopants. But measuring of the sheet resistivity is very difficult. The sheet resistivity could be measured only at a few positions on the wafer. On the other hand, the sheet resistivity *Al/Ga130* is measured to be very low between 0.35 and 0.40 Ω/\Box independent of the temperature and time.

To investigate the reason of the problem when measuring the sheet resistivity for mixed dopants, the surface of the wafer was investigated by microscopy. Figure 7.11 (left) and (right) show the surface after diffusion of *B155* and of *Al/B120*, respectively. The surface from pure boron dopant is clear, whereas aluminum (bright color) included the combined dopant formed crystals on the surface of the wafer resulting in a disturbance of the measurement.



Figure 7.10 Evolution of emitter sheet resistivity with respect to diffusion time and diffusion temperature using different p-type spin-on dopants.



Figure 7.11 Surface after diffusion with *B155* (left) and *Al/B120* (right). Bright crystals of the picture on the right is attributed by Al in the dopant.

7.4.3.2 Boron profiles

Figure 7.12 (left) shows the experimental profiles of the spin-on dopants *Boron A*, *B155* and *B153* diffused into n-type Si at a temperature of 1100 °C for 2 min using RTP. ECV profile measurement which determines the electric active atoms was used to measure the boron concentration profile. The surface concentration results in $2-3\times10^{20}$ cm⁻³ in the case of all three dopants and the junction depth is in the range of 0.5–0.65 µm.

Figure 7.12 (right) shows the boron profiles after subsequent three diffusion steps at high temperatures as usual in a fabrication of RTP-solar cells, i. e., RTD for BSF (boron) diffusion, RTD for emitter (phosphorus) diffusion and RTO for passivation. After this three diffusion steps the surface concentration decreases from $2-3\times10^{20}$ cm⁻³ to 1×10^{20} cm⁻³ and the junction depth increases slightly (about 0.05 µm).

Furthermore, the carrier concentration profile of B155 on a p-type wafer is also shown in Figure 7.12. The surface concentrations on the n-and p-type wafer are the same and the junction depth on the p-type is 0.1 μ m deeper than on n-type wafer. On the other hand, all boron profiles near the peak region (>10²⁰ cm⁻³) are flat. This is due to a higher diffusion coefficient at higher concentrations [119]. Some papers [118] [120] [121] have reported an enhanced diffusion coefficient by RTP using spin-on or ion-implanted sources.

It is noted that the difference in the background concentration of the doping profiles is due to side wall effects in the ECV measurement [117] or to slight differences in the base doping concentrations of the wafers.



Figure 7.12 Three different boron concentration profiles by ECV-profile. (Left) Boron profiles on the n-type material after RTD process at 1100 °C for 2min. (Right) Boron profiles after subsequent three different RTP-processes which are need for fabrics of solar cells : RTD (1100 °C, 2min) +RTD (950 °C, 50 s) + RTO (1050 °C, 2min).

7.5 Solar cells

7.5.1 Cell design and fabrication

Simple planar solar cells n^+pp^+ cells with planar boron BSF were fabricated. The corresponding process scheme is shown in Figure 7.13. 0.5 Ω cm p-type FZ silicon materials with a thickness of 250 µm were used for the fabrication of solar cells.

The wafers were cleaned by a modified RCA sequence. For the different emitters two different steps were needed. In the first version, three different boron spin-on sources were deposited on the back side (on front side SiO₂ 200 μ m was deposited to prevent the diffusion of boron on the front side) and diffused at temperatures of 1100 °C for 2 min. Afterwards the borosilicate glass on the rear side and 200 μ m SiO₂ in the front side were removed simultaneously. After phosphorus spin-on deposition on the front side the wafer was diffused at a temperature of 950 °C for 50 s by RTP. In the second version, the emitter was formed with POCl₃-diffusion by CTP resulting in about 120 Ω/\Box and then three different boron spin-on dopants were deposited on the back side. The emitter was passivated by RTO at a temperature of 1050 °C for 120 s. The front contacts are formed by photolithography and metallized with Ti/Pd/Ag. Then, the rear side was evaporated with 2 μ m Al as a back contact. Finally, solar cells were annealed at 425 °C for 25 min in forming gas.



Figure 7.13 (Left) Structure of planar RTP-solar cells with boron back surface field (B-BSF). (Right) Solar cell process sequence by RTP with two different cases. During the first case the B-BSF and P-emitter are diffused by RTP while during the second case P-emitter by CTD and B-BSF by RTD.

7.5.2 Results

Table 7.5 shows a comparison of results of solar cells fabricated with different methods for emitter and BSF. The upper three cells (*No8_6*, *No10_6*, and *No12_6*) are complete RTP-cells where both emitter and BSF are produced with spin-on dopants by RTP, whereas the lower three cells (*No14_1*, *No15_1*, and *No17_6*) are fabricated with CTD-emitter and RTD-BSF. Additionally, *Ref*, *No23_3*, and *NRP3_3_5* are used as reference cells. Both cells *Ref* and *No23_3* have a same CTD-emitter, whereas cell *Ref* has a boron-BSF using BBr₃ gas by CTD and *No23_3* is passivated with SiO₂ 105 nm on the rear surface. *NRP3_3_5* is a cell with inverted pyramids as front texture which has neither BSF nor a rear surface passivation layer.

All cells which are fabricated with spin-on dopants by RTP (RTD-BSF) have a comparable value of J_{sc} with the reference cells, however, V_{oc} is lower than for the reference cells. For example, the V_{oc} of solar cell with RTD-BSF only reached 596 mV and the V_{oc} is reduced more than 56 mV (8.6 % relative). In addition, this V_{oc} is even lower than that of metal direct contacted cell (*NRP3_3_5*). It is assumed that the RTD-BSF not only has no effect on the passivation quality of the rear surface, but also degrades the bulk lifetime in the processing. The low fill factor is only observed for some RTD-cells which have an RTD-emitter and are edge-isolated by laser. It can be assumed that the low FF is due to the laser isolation or to high emitter-metal contact caused by a thin emitter. In the next section, we will investigate the reason for the losses in V_{oc} which is strongly associated with the passivation quality on the front and rear side in solar cells.

•			5					
No.	Emitter	BSF	AR layer	Isolation	V _{oc} [mV]	J _{sc} [mA/cm²]	FF [%]	η [%]
No8_6	RTD	Boron A	RTO stack	laser	596.4	30.73	0.79	14.4
No10_6	RTD	B153	RTO stack	laser	594.2	30.58	0.80	14.6
No12_6	RTD	B155	RTO stack	laser	592	29.69	0.74	13
No14_1	CTD	Boron A	RTO stack	Х	588.9	29.61	0.79	13.8
No15_1	CTD	B153	RTO stack	х	587.4	29.31	0.78	14.0
No17_6	CTD	B155	RTO stack	х	587.4	30	0.81	13.8
Ref.	CTD	B-CTD	SiO₂ 105 nm	Х	650.1	33.29	0.82	17.8
No23_3	CTD	Only passivated	SiO₂ 105 nm	Х	679.3	33.13	0.80	18.1
NRP3_3_5*	CTD	х	SiO₂ 105 nm	Х	635.2	35.41	0.82	18.5

Table 7.5 Results of solar cell with respect to different type of emitter and back surface field. RTD-emitter is fabricated by rapid thermal diffusion using spin-on method and CTD-emitter is produced and by classic thermal diffusion using gas method. * cell is an invert pyramids cell. RTO stack as an antireflective layer represents SiO_2 10 nm by RTO + SiN_x 60 nm + MgF 105 nm.

7.5.3 Analyses and discussions

7.5.3.1 Spectral response

Figure 7.14 (left) shows the external quantum efficiency (EQE) of eight different solar cells. The EQE of the all cells with spin-on dopants by RTP (RTD-BSF) is fairly independent on the emitter types and on the boron dopants type. In the wavelength between 420 and 600 nm the EQE of RTD-BSF is about 0.2 absolutely higher than the one of the reference cell. On the other hand, in the long wavelengths the EQE of RTD-BSF decreases drastically.

The higher EQE of cells with RTD-BSF in the short wavelengths are explained by the reflection as shown in Figure 7.14 (right). The difference of reflection between RTP-cells and reference cell is also about 0.2 at the wavelength 500 nm. Therefore, the high EQE of cells with RTD-BSF in short wavelengths is due to the low reflection. However, the drastically reduced EQE of RTD-cells in the long wavelengths (800-1000 nm) can not explained with missing the reflection.

This trend is also shown in IQE curve in Figure 7.14 (right). IQE of cells with RTD-BSF is reduced drastically in the long wavelengths (800-1000 nm) which is associated with both the bulk lifetime and S_{rear} . We can not determine whether the sharp drop in IQE of cells with RTD-BSF is attributed to a degradation in rear surface passivation or in bulk lifetime. This will be investigated in the next section.



Figure 7.14. (Left) External quantum efficiency (EQE) and (right) internal quantum efficiency (IQE) and reflection of solar cells.

7.5.3.2 Lifetime and diffusion length

The drastically decreased IQE of cells with RTD-BSF in the long wavelengths range can be caused by τ_b and/or S_{rear}, since IQE for long wavelengths is a function of both τ_b and S_{rear}. Firstly, to determine τ_b the same materials used in solar cells were processed at temperatures of 1100 °C for 2 min by RTP after a deposition of three different boron spin-on dopants. The silicon materials after the RTP process were etched about 20 µm on each side to remove the contamination on the surface and to measure the bulk lifetime. For lifetime measurements the samples are passivated on both sides with excellent passivation SiN_x layer (S<10 cm/s), therefore, measured effective lifetime can be regarded as the bulk lifetime. The lifetimes are measured using microwave-detected photo-conductance decay (MW-PCD).

Figure 7.15 shows the bulk lifetime and diffusion length for samples using three different dopants. The carrier lifetime of all three samples is only 1.5 μ s where the reference sample which is processed same steps except the boron-dopants shows a lifetime of more than over 350 μ s. Thus, it can be concluded that boron-dopants degrade the lifetime of materials.

In order to verify that the τ_b of cells with RTP-BSF is degraded, effective diffusion lengths L_{eff} were calculated from IQE responses. Table 7.6 shows the L_{eff} and τ_b which are calculated from the IQE (see Eq. (5.5)). As shown in Table 7.6 L_{eff} of the cell with RTP-BSF was determined to be in the 50-80 µm range, while L_{eff} for reference cell (*No23_3*) was found be 980 µm. The effective diffusion lengths for cells with RTP-BSF can be substituted with the bulk diffusion length since the L_{eff} is not influenced by the amount of S_{rear} , even though S_{rear} is varied up to very high values of over 10⁷ cm/s which is the value for a metal covered Si surface as shown in Figure 7.16 (left).



Figure 7.15. Bulk lifetime and diffusion length for samples three different boron dopants. Samples are boron-doped FZ-Si materials with a resistivity of 1 Ω cm.

The bulk lifetime of cells with RTP-BSF is obtained in the range of 1.0 - 2.2 μ s. The very low L_b which is less than half the cell thickness of 250 μ m, explains why hardly any effect of boron-BSF is observed in the cell performance. This trend can be seen in Figure 7.5 (left) that for a bulk lifetime of only 2 μ s. The BSF has no effect on the cell parameters and the V_{oc} remains 584.9 mV independently on the doping concentration and junction depth of BSF. This V_{oc} is comparable to the measured V_{oc} for our RTP-BSF cells in the range of 577-583.4 mV. It can be concluded that the bulk lifetime is severely reduced by the boron diffusion using spin-on dopants. It is likely that the contamination from dopants is diffused in the bulk during the high temperature and long diffusion process.

Table 7.0 Litective unrusion lengths and the bulk method determined norm loc
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	No8_6	No10_6	No12_6	No14_1	No15_1	No17_6	No23_3
L _{eff} [µm]	72.54	69.57	79.68	63.89	54.45	68.47	980.3
τ_{b} [µs]	1.84	1.69	2.22	1.43	1.04	1.64	348



Figure 7.16. L-S plot (left) for one of cells with RTP-BSF and (right) for the reference cell which has passivated rear surface SiO_2 105 nm.

Degraded diffusion lengths after boron diffusion with spin-on dopants in conventional diffusions have also been reported by Kreinin et al. [122]. They demonstrated that boron diffusion using spin-on dopant in a conventional furnace reduced diffusion lengths of materials to 70-120 μ m. On the other hand, simultaneous diffusion of evapolated Al and B with SODs enhanced to diffusion length over 600 μ m.

Furthermore, Ohe et al. [123] investigated that after B diffusion with gas-phase (BBr₃) in the conventional furnace τ_{eff} was two times higher than the initial value. However, subsequent thermal processes after boron diffusion degraded τ_{eff} drastically to as low as 3 µs. They suggested that some impurities or defect were gettered by B diffusion and de-gettered into bulk regions by thermal process after the B diffusion.

Boron is less efficient than phosphorus in terms of gettering and has no additional reflector effect like Al. In addition, on the back side an Al-Si eutectic is formed which is molten during the RTP process and thus the diffusion of silicon self-interstitial (Si_i) coming from the front surface will be enhanced in order to fill up the lack of Si_i on the backside induced by the formation of the Al-Si eutectic. This transformation by the kick-out mechanism (substitutional metal into an interstitial) makes the gettering effect more effective [116].

7.5.3.3 Dark characteristic parameters

Another reason of the reduced V_{oc} is due to the high depletion region recombination current, I_{02} , observed in the dark I-V measurement. The I-V characteristics are shown in Figure 7.17 for RTP-BSF cells and reference cell. The measured data as shown in Figure 7.17 were fit by the two-diode model (see section 2.2.3 in chapter 2) and the fitted dark characteristic parameters are shown in Table 7.7.

 I_{01} of cells with RTP-BSF is 10 times higher than that reference cells. I_{02} of three RTP-BSF cells (*No8_6*, *No10_6* and *No12_6*) which are isolated by laser is four orders of magnitude higher

than that of the reference cells, whereas I_{01} of non-isolated RTP-BSF cells is comparable to reference cells. On the other hand, R_s of RTP-BSF cells is similar to the one of reference cells and R_p of isolated RTP-BSF cells is lower than the one of non-isolated RTP-BSF cells. These two factors high I_{02} and low R_p can explain why V_{oc} and FF of isolated RTP-BSF cells are reduced.

We assume that the depletion region at the edge of the cell is damaged during cutting the cells by laser or boron spin-on dopants deposit not only on the rear side, but also on the front side, even through a 200 nm SiO_2 layer which is grown to protect against the diffusion of boron on the front side.



Figure 7.17. Measured dark I-V characteristics of the eight different RTP-cells.

No.	I _{o1} [10 ⁻¹³ A/cm ²]	Ι _{ο2} [10 ⁻⁹ Α/cm ²]	R_s [Ω cm ²]	R_p [Ω cm ²]	N ₁	n ₂
No8_6	15.5	9441.7	0.19	8.7×10 ⁴	1	3.3
No10_6	14.5	8781.19	0.12	>1×10 ⁶	1	3.2
No12_6	11.5	8155.16	0.15	1.2×10 ⁵	1	3.3
No14_1	13.5	29.32	0.19	>1×10 ⁶	1	2.1
No15_1	25.4	0.045	0.26	6×10 ⁹	1	2
No17_6	13.6	0.1	0.25	>1×10 ⁶	1	2
Ref.	2.52	0.405	0.19	1×10 ¹³	1	2
No23_3	1.55	2.83	0.89	7×10 ⁶	1	1.9

Table 7.7 Dark characteristic parameters for eight different RTP-solar cells.

7.6 Conclusion

We have investigated the diffusion of phosphorus and boron using the simple and cost-effective two techniques, i. e., spin-on dopants and rapid thermal processing. Diffusion of three different phosphorus spin-on dopants was performed in the temperature range of 850-1025 °C for 5-80 s. Diffusion for p-type dopants was performed with three pure boron SODs and three AI/B or AI/Ga mixed SODs at temperatures between 1000 and 1100 °C for 60-180 s.

Even though the surface concentration and junction depth are strongly dependent on concentrations of spin-on dopants, process times and temperatures, the surface concentrations and junction depths of phosphorus with spin-on dopants result in a range of $1-6 \times 10^{20}$ cm⁻³ and $0.2 - 0.4 \mu$ m, respectively. In the case of boron dopants the surface concentrations result in $1-3 \times 10^{20}$ cm⁻³ and the junction depths are in the range of $0.5 - 0.7 \mu$ m. In a simulation using PC-1D, V_{oc} of cells with boron BSF with spin-on dopants should reach more than 628 mV.

Phosphorus as a emitter and boron as a back surface field was applied to fabricate n⁺pp⁺ solar cells. Unfortunately, RTP-BSF cells with spin-on dopants have a low V_{oc} of less than 600 mV, while a reference cell passivated with 105 nm SiO₂ on rear surface had a V_{oc} of 679 mV. The main reason for the a low V_{oc} is due to a degradation of the diffusion length after boron diffusion. Diffusion lengths (τ_b) of cells with RTP-BSF from IQE have been measured to be about 54-70 µm (1-2 µs), whereas those of the reference cell have been measured to be 980 µm (348 µs). It is assumed that impurities or contamination from boron-dopants diffuse into the bulk of silicon materials in high thermal processes.

In the next step, one should fabricate n⁺pp⁺ solar cells with BSF by simultaneous deposited Al and B using spin-on dopants diffusion. Al-layer evaporated on the Si wafer surface could prevent diffusion of impurities and provide a gettering effect, since the solubility of many metals in Al is by 4-10 orders of magnitude higher than in crystalline silicon.

8 Summary

In this thesis, the application of rapid thermal processing (RTP) for silicon solar cells has been investigated. This work focussed on the development of an optimized process for Czochralski (Cz) silicon materials and on the characterization of surface passivation. Diffusion with cost-effective techniques using spin-on dopants for silicon solar cells was also investigated.

Influence of rapid thermal processing on the bulk lifetime of Cz-silicon

Boron-doped Cz silicon material is used for about 40 % of the world production of photovoltaic cells. A major issue of this material is a metastable defect which degrades the minority-carrier lifetime after illumination or carrier injection and completely recovers by annealing at low temperature around 200 °C. The properties and proposed model of the Cz-specific metastable defect have been introduced.

Before the main study of the influence of RTP on Cz-metastable defects, SiN_x (60 nm) deposited by PECVD and thermally grown SiO_2 (105 nm and 180 nm) were investigated as barrier layers on the FZ material in order to protect the bulk sample against external contamination. SiN_x has been found to be an excellent barrier layer even with smaller thickness than SiO_2 . The effective lifetime for the SiN_x -covered FZ silicon wafer showed a very high level of 700 µs.

It has been demonstrated that the defect concentration and the stabilized lifetime of Cz-Si materials after degradation by illumination can be enhanced by high-temperature process using RTP. For an accurate process optimization the 'design of experiments' method was used. The most important process parameters were varied in the study: plateau temperature ($T_{plateau}$), plateau time ($t_{plateau}$), heating rate (R_{up}), cooling rate (R_{down}), and cooling point temperature ($T_{cooling Pt}$). It was found that the plateau temperature has the highest influence on the stabilized lifetime after degradation by illumination. The resulting optimized process temperature was approximately 900 °C with a process time of 120 s and yielded an enhancement of stabilized lifetime by a factor of 2. To our knowledge this is the first time that an improvement of the stabilized lifetime started to decrease drastically and this trend has also been observed with FZ materials. It was demonstrated that this degradation at high temperatures can be attributed to warpage and to slip dislocations due to an inhomogeneous temperature distribution across the wafer.

The influence of two sequent high temperature steps on the stabilized lifetime has been investigated either with optimized or non-optimized process parameters. It was shown that the last high temperature step has a major influence on the stabilized lifetime. For example, the stabilized lifetime increased from 14 μ s to 22 μ s after annealing with the optimized process but then was reduced to 11 μ s by a non-optimized last high-temperature step. On the other hand, the stabilized lifetime was reduced from 14 μ s to 9 μ s in the first step using the non-optimized process and then increased up to 20 μ s (a factor of 2.2) using an optimized last high temperature step. Finally, the optimized and non-optimized processes were used to fabricate

RTP-solar cells. The analysis of these cells showed that the cells using the optimized process demonstrated a significant higher open-circuit voltage and short-circuit current density than the ones fabricated using the non-optimized process.

Optimal passivation for solar cells

Low surface recombination is essential for high efficiency solar cells. The surface recombination properties of various single and double layers on pure p-type and phosphorus doped emitters have been systematically and comprehensively studied. The three different single surface passivation technologies investigated in this thesis were CTO (classical thermal oxidation), RTO (rapid thermal oxidation), SiN_x layers deposited by PECVD, and double stack layers SiO₂/SiN_x combining these technologies.

SiO₂ layers formed by either CTO or RTO passivate the emitter surface 2-3 times better than the pure p-type silicon surface. This behavior is attributed to the high capture cross section ratio σ_n/σ_p of 100. On 100 Ω/\Box emitters passivated by CTO the effective lifetime was 308 µs and 196 µs by RTO passivation. That makes possible the fabrication of solar cells with very high-efficiency.

In contrast, SiN_x layers deposited by PECVD passivate the pure p-type silicon 2-3 times better than the emitter surface. A high effective lifetime of about 900 µs was measured on the pure ptype wafers, whereas a lifetime of about 300 µs was measured on the 100 Ω/\Box emitters. The improved lifetime obtained from SiN_x layers on pure p-type is due to the field effect passivation. A high positive charge density at the surface repels holes from the surface and results in a inversion layer. Therefore, the recombination at the p-type surface is strongly reduced.

SiO₂/SiN_x stacks showed excellent surface passivation not only on p-type silicon, but also on emitters. An excellent effective lifetime of about 1400 µs can be obtained with a CTO/SiN_x stack and of about 1000 µs with a RTO/SiN_x stack on the p-type silicon base resistivity of 1 Ω cm. Also, CTO/ SiN_x and RTO/SiN_x stacks provide good passivation resulting in a high lifetime over 400 µs and 300 µs on 100 Ω/\Box emitters, respectively. The RTO/SiN_x stack has a particularly low weighted reflection (R_w) of 13 % on the planar surface. In addition, the optimized triple layer RTO(10 nm)/SiN_x(58 nm)/MgF(110 nm) yielded a very low R_w of only 5 % and a high J_{sc} of 36.6 mA/cm² by the PC1D-simulation without any texturization of the surface.

Cost-effective surface passivation by RTO/SiN_x stacks has been investigated on planar and textured passivated emitter and rear cells (PERC) with 120 Ω/\Box emitters and a base resistivity of 0.5 Ω cm. For comparison CTO-passivated cells have also been extensively investigated. RTO/SiN_x stacks produce very high open-circuit voltages (V_{oc}) of 675.6 mV which are comparable to the highest values ever reported for SiN_x-passivated cells (675 mV). A high J_{sc} of 35.1 mA/cm² and an efficiency of 18.5 % were obtained on planar surfaces. However, the cell with an RTO/SiN_x stack and a cell with textured surface had a lower J_{sc} and fill factor than the CTO reference cell. It has been demonstrated that the main reason for the lower J_{sc} and fill factor is related to the parasitic shunt current between the strong inverted layer at the rear surface due to the high fixed charge density and metal rear contacts.

Rapid thermal diffusion with spin-on dopants

A low-cost diffusion technique using spin-on dopants (SODs) by RTP has been investigated. In this work three different phosphorus SODs, four different pure boron SODs, and mixed B/AI and AI/Ga SODs were used. The resulting doping profiles were determined with electrochemical capacitance-voltage (ECV) measurements and secondary ion mass spectrometry (SIMS) measurements.

Rapid thermal diffusion (RTD) of phosphorus was performed in the temperature range of 850-1025 °C for 5-80 s. The heating rate was kept at 100 °C/s. Sheet resistivities of 40-100 Ω/\Box could easily be obtained within a few minutes compared to approximately 1 hour in conventional processes. The surface concentrations varied between 1-6×10²⁰ cm⁻³ and junction depths of the phosphorus diffusion profiles were 0.2-0.4 µm.

A back surface field (BSF) is the common method to reduce back surface recombination. The influence of the surface concentration and junction depth on the open-circuit voltage which is related to the surface recombination of the BSF has been calculated with the simulation program PC-1D.

In order to form the BSF using boron and mixed p-type SODs RTP-diffusions were carried out at process temperatures of 1000-1100 °C for 60-180 s. Measurements of boron doping profiles showed that a junction deeper than 0.5 μ m with a maximal active doping concentration of 10²⁰ cm³ can be formed by short process times about 2 min at a process temperature of 1100 °C. The resulting boron-BSF has the potential for a high V_{oc} of 630 mV. Finally, phosphorus SODs for emitter and boron SODs for BSF were used to fabricate solar cells. The spectral response, the I-V characteristics, and the other cell parameters of fabricated RTP solar cells are also presented.

It was demonstrated in this work that for all three aspects (i) improvement of the bulk properties, (ii) surface passivation and (iii) diffusion rapid thermal processing can supply cost-effective and efficient alternatives to conventional processing. RTP is becoming more and more important in high volume solar cell production due to the short process times. The processes developed in this work and the investigation of the underlying physics will assist the successful implementation of this technique.
Appendix A Physical constants and properties

Symbol	value	Name or description	
С	2.9979×10 ⁸ m/s	Velocity of light in vacuum	
h	6.624×10 ⁻³⁴ J·s	Plank's constant	
K	1.381×10 ⁻²³ J/K	Poltzmann's constant	
ĸ	= 8.62×10 ⁻⁵ eV/K	BOILZINAIIII S CONSTANT	
Q	1.602×10 ⁻¹⁹ C	Electronic charge	
$ u_{\text{th}}$	1×10 ⁻⁷ cm/s	Thermal velocity at 300 K	
hc/e	1238.84 V nm		
$\sigma_{\scriptscriptstyle B}$	5.77×10 ⁻⁸ W/m ² · K ⁴	Stefan-Boltzmann's constant	
Eg	1.124 eV	Energy gap	
N _C	3×10 ¹⁹ cm ⁻³	Effective density of states in conduction band	
N _V	1×10 ¹⁹ cm ⁻³	Effective density of states in valence band	
n _i	1.0×10 ¹⁰ cm ⁻³	Intrinsic carrier concentration	
KT/q	0.02586 V	Thermal voltage	
μ_{n}	$\leq 0.135 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$	Electron mobility	
$\mu_{ m p}$	$\leq 0.048 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$	Hole mobility	
D _n	0.02586 µ _n	Diffusion coefficients of electron	
D _p	0.02586 μ _p	Diffusion coefficients of hole	
В	3.95×10 ⁻¹⁵ cm ³ /s	Radiative recombination coefficient	
C _n	2,8×10 ⁻³¹ cm ⁶ /s	Auger recombination rate constant for eeh-process	
C _P	9,9×10 ⁻³² cm ⁶ /s	Auger recombination rate constant for ehh-process	
$\varepsilon_{\rm s}/\varepsilon_{\rm 0}$	11.9	Dielectric cosntant	

A.1 Physical constants

Symbol	Unit	Name or description
Al		Aluminum
AM		Air mass
В		Boron
BSF		Back surface field
CDI		Carrier density imaging
C _N	cm ⁶ s ^{−1}	Auger recombination coefficient for eeh-process
C _P	cm ⁶ s ^{−1}	Auger recombination coefficient for ehh-prozess
СТО		Classical thermal oxidation
СТР		Classical thermal processing
CVD		Chemical vapor deposition
Cz-Si		Czochralski-silicon
D	Cm ² s ⁻¹	Minority carrier diffusion coefficient
D _n , D _p	Cm ² s ⁻¹	Diffusion constant of electrons, holes
E	eV	Energy
E	V cm ⁻¹	Electric field strength
ECV-profile		Electrochemical capacitance voltage profile
Eg	eV	Energy gap
EQE		External quantum efficiency
erfc		Error function
ESR		Electron spin resonance
FF		Fill factor
FTIR		Fourier transform infrared spectrometer
FZ-Si		Floatzone-silicon
G	Cm ⁻³ s ⁻¹	Minority carrier generation rate
Ga		Gallium
${f g}_{ehh}$		Coulomb-enhanced coefficient for ehh-process
HF		Hydrofluoric acid
Ι	А	Current
I _o	A cm ⁻²	Diode saturation current density
I ₀₁	A cm ⁻²	Saturation current density of first diode (base and emitter)
I ₀₂	A cm ⁻²	Saturation current density of second Diode (depletion region)
I _{0b}	A cm ⁻²	Base saturation current density
I _{0e}	A cm ⁻²	Emitter saturation current density
I _{mpp}	A cm ⁻²	Current at maximum power point

A.2 List of symbols

Symbol	Unit	Name or description
IQE		Internal quantum efficiency
IR		Infrared
I _{SC}	A cm ⁻²	Short-circuit current density
IDLS		Injection dependent lifetime spectroscopy
L	μm	Lifetime length
L_{eff}	μm	Effective lifetime length
mpp		Maximum power point
MW-PCD		Microwave –detected photo conductance decay
n		Refractive index
n	cm ⁻³	Electron concentration
n _o	cm ⁻³	Electron concentration in thermal equilibrium
n ₁ , n ₂		Diode ideality factor
N_2		Nitrogen
N _A	cm ⁻³	Acceptor concentration in p-type material
N _D	cm ⁻³	Donor concentration in n-type material
n _i	cm ⁻³	Intrinsic carrier concentration
O ₂		Oxygen
Р		Phosphorus
р	cm ⁻³	Minority carrier concentration of hole
p ₀	cm ⁻³	Hole concentration in thermal equilibrium
PECVD		Plasma enhanced chemical vapor deposition
PERC		Passivated emitter and rear cell
POCl ₃		phosphorus oxychloride
PSG		Phosphosilicateglass
q	С	Electronic elementary charge
Q _f	С	Fixed charge density
Q _{it}	С	Charge in interface states
QSSPC		Quasi-steady-state photoconductance
R	Ω	Resistivity
R	%	Reflection
R _{down}	°C/s	Ramping down rate
R _P	Ω cm ²	Shunt resistivity
R _s	Ω cm ²	Series resistivity
R_{sheet}	Ω cm ⁻²	Sheet resistivity
R _{up}	°C/s	Ramping up rate

Symbol	Unit	Name or description
R _w	%	Weighed reflection
RTF		Rapid thermal firing
RTO		Rapid thermal oxidation
RTP		Rapid thermal processing
S		Sensitivity
S	cm/s	Surface recombination velocity
S_{back}	cm/s	Surface recombination velocity at the back side
S_{eff}	cm/s	Effective surface recombination velocity
S _{front}	cm/s	Surface recombination velocity at the front side
SiH ₄		Silan
SiHCl ₃		Trichlorosilane
SIMS		Secondary ion mass spectroscope
SiN _x		Silicon nitride
SiO ₂		Silicon dioxide
SPV		Surface photovoltage technique
SR		Spectral response
SRH		Shockley-Read-Hall
SRV		Surface recombination velocity
t	S	Time
t _{plateau}	S	Plateau time
Т	°C or K	Temperature
$T_{plateau}$	°C	Plateau temperature
T _{plateau, Pt.}	°C	Cooling point temperature
TC		Themocouple
TDLS		Temperature dependent lifetime spectroscopy
U	cm ⁻² s ⁻¹	Recombination rate
Us	cm ⁻² s ⁻¹	Surface recombination rate
UV		Ultraviolet
V		Voltage
V_{mpp}	V	Voltage at maximum power point
V _{oc}	V	Open-circuit voltage
V _{th}	V	Thermal voltage
VUV		Vacuum ultraviolet
W	μm	Wafer or substrate thickness
X _j	μm	Junction depth

Symbol	Unit	Name or description
α	µm⁻¹	Absorption coefficient
3	A s V ⁻¹ m ⁻¹	Permittivity
η	%	Efficiency
λ	nm	Wavelength
τ	μs	Carrier lifetime
$ au_{b}$	μs	Bulk lifetime
$ au_{eff}$	μs	Effective carrier lifetime
$ au_{diff}$	μs	Differential lifetime
τ_{s}	μs	Surface lifetime
$\Delta \sigma$	$\Omega^{\text{-1}}$ cm $^{\text{-1}}$	Excess conductivity
Δn	cm ⁻³	Excess electron concentration
Δρ	cm ⁻³	Excess hole concentration
σ_{n}, σ_{p}	$\Omega^{\text{-1}}$ cm ⁻¹	Electron, hole conductivity
σ_n , σ_p	cm ²	Electron, hole capture cross section
υ_{th}	cm/s	Thermal velocity
μ _n , μ _h	cm ² s ⁻¹ V ⁻¹	Electron, hole mobility

Appendix B Methods for measurement

B.1 Microwave-detected photo conductance decay (MW-PCD)

B.1.1 Theory

In the microwave-detected photoconductance decay (MW-PCD) method excess carriers are generated within a wafer by short a light pulse, increasing the wafer conductance which is detected by microwave reflection. After termination of the light pulse, the excess carriers recombine and the conductance decays exponentially to its initial value.

The conductivity σ is defined by

$$\sigma = q\left(\mu_n n + \mu_p p\right) \tag{B.1}$$

where μ_n is the mobility of electrons and μ_p is the mobility of holes while n is the electron charge carrier concentration and p is the hole charge carrier concentration. When an excess charge concentration Δn , Δp is created by a light pulse, the conductivity of wafer is increased. The change of conductivity is given by

$$\Delta \sigma = \sigma \left(p_o + \Delta p, n_o + \Delta n \right) - \sigma \left(p_o, n_o \right)$$

= $q \left[\mu_p \left(p_o + \Delta p \right) + \mu_p \left(n_o + \Delta n \right) \right] - q \left(\mu_p p_o + \mu_n n_o \right)$ (B.2)

where n_o and p_o are the concentration of electrons and holes in the equilibrium, respectively. For low-level injection ($n_o \ll p_o$, $\Delta n = \Delta p \ll p_o$),

$$\Delta \sigma = q \left(\mu_p + \mu_n \right) \Delta n \tag{B.3}$$

A low-carrier injection is a necessary condition for a linear correlation between $\Delta\sigma$ and Δn .

A microwave detector records the change of the reflectivity. The reflected microwave power P_r is a function of the conductivity of the wafer;

$$P_r = R(\sigma, \varepsilon, \mu) P \tag{B.4}$$

P is the incident microwave power on the sample. For small $\Delta\sigma$ ($\Delta\sigma <<\sigma_o$) the change of the reflectivity is given by

$$R(\sigma + \Delta \sigma, \varepsilon, \mu) = R(\sigma_o, \varepsilon, \mu) + \frac{\partial R(\sigma, \varepsilon, \mu)}{\partial \sigma} \Big|_{\sigma_o} \Delta \sigma + \dots \dots$$
(B.5)

where

$$\frac{\Delta P_r(\Delta \sigma)}{P_r} = \frac{\partial R(\sigma_o)}{\partial \sigma_o} \Delta \sigma = A \Delta \sigma \tag{B.6}$$

After the laser pulse, the carrier density and thus also the conductivity both decay due to carrier recombination within the bulk and at the surface of the sample. From the resulting transient of the reflected microwave power $\Delta P_r(t)$ as a function of time t we obtain a decay time that is commonly interpreted as the effective minority-carrier lifetime τ_{eff} by fitting the transient with an exponential function. The microwave reflection decay has to be mono exponential if a well defined lifetime τ_{eff} shall be deduced. Only a small conductivity change $\Delta\sigma$, i.e., $\Delta\sigma <<\sigma_o$, should be used in order to satisfy the linear approximation of $R(\sigma_o)$ in Eq. (B.5). Furthermore, this restriction is needed since the carrier lifetime τ_{eff} is a function of injection level. Both the bulk lifetime and the surface recombination rate are carrier-density dependent. Therefore, the imposed conductivity change $\Delta\sigma$ for the sample should be adjusted in the experiment in such way that fulfills low-injection condition. Consequently, the derivative $\partial R(\sigma_o)/\partial \sigma_o$ is not a good measurement sensitivity, since Eq. (B.5) would require keeping $\Delta\sigma$ constant for all sample conductivity in order to evaluate the dependence of the sensitivity on the sample conductivity σ_o . In contrast to this earlier definition of sensitivity, we propose a modified definition for the sensitivity S resulting from

$$\frac{\Delta P_r(\frac{\Delta\sigma}{\sigma_o})}{P_r} = \sigma_o \frac{\partial R(\sigma_o)}{\partial \sigma_o} \frac{\Delta\sigma}{\sigma_o} = S \frac{\Delta\sigma}{\sigma_o}$$
(B.7)

The largest values of sensitivity, S indicate the most sensitive microwave reflection measurement when the relative change in conductivity $\Delta\sigma <<\sigma_{o}$ is kept constant for low junction. The maximal signal is obtained where the absolute sensitivity |S| of Eq. (B.6) rather than the absolute slope |A| of Eq. (B.5) is largest. As an example, a sensitivity |S| = 0.3 indicates that the reflected power P_r changes by 3 % relative to the incident microwave power P with a conductivity changes of 10 %.

We use weakly absorbed laser light with a wavelength of $\lambda = 908$ nm (absorption length about 30 µm in silicon) to obtain mono-exponential transients. The generated relative conductivity change is kept lower than $\Delta\sigma/\sigma \leq 10$ % (low-level injection), corresponding to a relative minority carrier density change of 3 % in p-type silicon with respect to the equilibrium majority carrier density. Sensitivity S and reflectivity R were observed with different microwave frequency in order to find linear microwave reflector behind the sample for large signals and linear microwave reflectivity [124]. The frequency of 2.8 GHz is suitable since the frequency have a high sensitivity without a reflectivity in interested conductivity in the range of 0.5-100 Ω cm. In addition to the laser pulses, our system allows to illuminate the sample with bias light from a halogen lamp.

B.1.2 Structure of measurement equipment

Figure B.1 shows a schematic diagram of the contactless MW-PCD measurement system in ISE. From the top, light pulses from a 908 nm GaAs laser (plus length = 100 ns) generate excess carriers within the wafer, increasing the wafer conductance. After termination of each light pulse, the excess carriers recombine within the bulk and at both surfaces of the wafer and the conductance decays to is initial value. From the bottom, microwaves with frequency 2.8 GHz are divided in two parts: one branch going to a phase shifter directly and the other branch going to microwave antenna through a circulator. On this antenna the sample can be placed, reflecting the signal depending upon conductivity differently. The reflected signal from the sample is redirected via the circulator towards the blender. The two signals are combined and amplified. The signal is detected by a high sensitive detector and is recorded by a digital oscilloscope and then analyzed by means of a computer. The measured reflected microwave power during the monoexponential conductance decay is directly proportional to the change of the micro wave conductance. Hence, the measured transient corresponds to the decay of the excess carrier concentration within the wafer. Each single measurement represents the average of 100 to 500 individual transients.

The effective carrier lifetime of each of these measurements is determined by fitting the asymptotic monoexponential part of the excess carrier decay and the mean value of the effective lifetimes is calculated. Figure B.2 shows a typical transient and the fitted effective lifetime.



Figure B.1 block schematic of the light-biased MW-PCD setup used in ISE.



Figure B.2 Measured MW-PCD transient an p-type silicon wafer after excitation with a GaAs-Laser of wavelength $\lambda = 908$ nm (plus duration : $\Delta t = 100$ ns). Both surfaces of the wafer are unpassivated.

B.2 Carrier density imaging (CDI)

Carrier density imaging (CDI) is introduced as a new, spatially resolved carrier lifetime measurement techniques. CDI provides the actual local lifetimes as compared to standard lifetime mapping techniques, e.g., MW-PCD which yield the differential lifetime only [104]. Furthermore, CDI is an extremely fast measurement technique. For example, the measurement of a 100×100 mm² wafer under low-level injection conditions can be performed on a time scale of seconds, whereas a standard MW-PCD map needs about 2 hours for a measurement with identical resolution.

Figure B.3 shows the experimental setup for CDI-measurement. CDI measurements are based on the free-carrier absorption of IR-Light in silicon. The wafer is planced on a hotplate which continuously provides black body radiation. The hotplate emits IR radiation, which is transmitted through the silicon sample under investigation. A fast CCD-camera that is sensitive in the mid infrared (wavelength of 3.5 to 5 μ m) measures the IR-transmission of the sample in two different states: In the first half of the lock-in period (D_{on}), the wafer is illuminated by a semiconductor laser (λ =917 nm) that generates an excess free-carrier density which is approximately equivalent to the generation at 1 sun (AM1.5 G). In the second half of the lock-in period (D_{off}) the sample is in complete darkness, thus with no excess carrier generation. The difference $\Delta D=D_{on}-D_{off}$ is proportional to the IR absorption of the excess free-carriers and thus to the local excess free-carrier density. The complete read-out of all pixels represents an image of the local carrier density distribution with a contrast proportional to ΔD .



Figure B.3 Experimental setup for CDI-measurement.

By applying the correlation procedure for the assumption of homogenous lifetime over the whole sample width W, every pixels I_A are found by

$$I_{a} = \Delta D = -k \,\Delta n \,W \tag{B.8}$$

Where k and Δn are a correlation factor and the excess minority carrier concentration, respectively. If the measurement is performed in steady state, the Δn values may be converted into effective actual lifetime by the relation

$$\tau_{eff} = \frac{\Delta nW}{G} = \frac{I_A}{-kG} \tag{B.9}$$

where G is local generation rate per wafer area [125].

B.3 Profile Measurements

B.3.1 Electrochemical capacitance voltage (ECV) profile

The electrochemical capacitance voltage (ECV) technique depends on the fact that the width of a reverse-biased depletion region of a semiconductor junction device depends on the doping concentration. The ECV profiling method has been used with Schottky diodes using metal electrodes or liquid electrolyte. The electrochemical method using electrolyte is schematically shown in Figure C.4.



Figure C.4 Schematic diagram of the electrochemical cell [126].

When a dc bias V is applied to the electrolyte, the Schottky diode is formed and the reverse bias produces a depletion region of with W_d . The capacitance is defined by

$$C = -\frac{dQ}{dV} \tag{B.10}$$

where Q is the charge in the semiconductor. The negative sign shows the negative charge in the semiconductor in depletion region. The space-charge increment dQ is given by

$$dQ = q A N_A(W_d) dW_d \tag{B.11}$$

and the bias is increased by

$$dV = q W_d N_A(x_d) dW_d / \varepsilon \varepsilon_o \tag{B.12}$$

where W_d is a width of the depletion region. N_A is doping concentration in the semiconductor material. ϵ_0 and ϵ are the permittivity of vacuum and the relative permittivity of the semiconductor material, respectively. A is the measurement area. The capacitance of a reverse-biased junction is expressed as

$$C = \frac{\varepsilon \varepsilon_0 A}{W_d} \tag{B.13}$$

From differentiating Eq. (B.13) with respect to the voltage, the doping concentration N_{A} can be obtained as

$$N_{A}(W_{d}) = \frac{C^{3}}{q\varepsilon_{o}\varepsilon_{r}A^{2}(dC/dV)} = \frac{2}{q\varepsilon_{o}\varepsilon_{r}A^{2}[d(1/C^{2})/dV]}$$
(B.14)

A depth profile can be obtained by dissolving the semiconductor electrolytically. Dissolution of the semiconductor relies on the presence of holes. The etched depth, W_r , is can be expressed by the total charge transferred by integration the dissolution current I:

$$W_r = \frac{M}{ZF\rho A} \int_0^t I \, dt \tag{B.15}$$

where M and ρ are the molecular weight and density of the semiconductor, respectively. F is the Faraday constant (9.64×10⁴ C) and z is the charge transferred per molecule dissolved. For silicon z=3.8 and GaAs z=6. Therefore, the total measurement depth of the carrier concentration is given by

$$x = W_d + W_r \tag{B.16}$$

B.3.2 Secondary ion mass spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) is used widely to measure the dopant profiling of impurities and diffused layers. A beam of primary ions (most common are O^{2+} , Cs^+ , O^-) impinges onto the solid surface of the sample and the atoms at the surface of the sample are sputtered. The sputtered secondary particles carry negative, positive, and neutral charges, but only the ionized species can be detected for SIMS analysis. As primary ion beams oxygen O^{2+} and cesium (Cs^+) are used for electropositive elements (e.g., B and Al in Si) and for electronegative elements (e.g., P, As and Sb in Si). The mass of the selected secondary ions through the mass spectrometer is counted as a function of time using a mass spectrometer. Secondary ion intensity for the selected element (I_E) can be converted into concentration (C_E) by relative sensitive factors (RSFs):

$$C_E = RSF \frac{I_E}{I_M} \tag{B.17}$$

where I_M is the indensity of the sample matrix. RSF (unit is atom/cc) for B and P in Si is about 10^{22} and 10^{24} . To convert the time into depth the SIMS system uses a profilometer to measure the crater depth. It must be noted that SIMS determine the total impurity concentration, not only the electrically active concentration.



Figure C.5 Schematic diagram of SIMS measurements [15].

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감사의 글

'인생은 예측불허, 그래서 살만한 의미가 있다.'

이 문장은 내가 좋아하는 만화책에 나오는 글이다. 내가 독일에 온 것도, 더구나 태양 에너지 에 대해서 공부하게 된 것도 사실 내 계획엔 전혀 없던 일 들 이였다. 7년의 독일생활, 5년의 연구소 생활은 내 인생에서 잊지 못할 아주 귀중한 선물이다. 이 기간에 나는 여러 가지로 많 은 생각할 수 있는 기회를 가졌고 보다 다양한 인생경험을 한 시기이기도 했으며 끝없이 나 자신과 싸운 시기이기도 했으며. 끝없이 나 자신과 싸운 시기이기도 했다. 독일이란 낯선 땅에 서 생활하는데 있어서, 처음엔 다른 문화를 이해하는데 많이 힘들었고, 모든 것이 생각처럼 되 지 않아 나 자신에게도 많이 실망하고 좌절하기도 했다. 어떤 땐, 하루에 몇 번씩 내 자신에게 물었다 '도대체 여기서 뭐하고 있는 거야 ? 그래도 내가 낯선 사람들로 둘려 싸여진 섬에 흘 로 있다고 느낄 때, 두려움과 좌절감에 주저앉고 싶을 때, 나에게로 둥돌려주고 손내밀어 이 끌어 준 사람들이 있었다. 이들의 도움과 믿음과 지원이 없었다면 나는 아마도 나의 꿈을 다 이루지 못했을 지도 모른다. 5년 동안의 박사과정을 마무리하면서 이들에게 감사의 인사를 드 린다.

내 지도교수이신 Wettling(베틀링) 교수님께 감사드린다. 나를 그의 학생으로 기꺼이 받아 주 셨다. 그의 굳건한 책임감과 태양전지뿐만 아니라 모든 분야에서의 해박한 지식에 놀라지 않을 수 없다. 그의 훌륭한 인품이 불가능한 일을 가능하게 하였다.

나를 지도해 주신 Glunz(글룬츠) 박사님께 감사드린다. 나는 그를 사람들에게 자신있게 훌륭한 사람이라고 말할 수 있다. 학자로써의 그는 자기분야에 대단한 정열을 가졌고, 바쁘면서도 문 제를 해결하고 의견을 나누고 새로운 생각들을 의논하는데 있어서 항상 기꺼이 자기시간을 내 주었다. 일상에서의 그는 항상 즐겁게 지내고 무엇이든 흥미 있어하며 긍정적으로 생각하고 또 한 따듯한 마음을 가진 사람이다.

Knobloch(크노블로흐) 박사님께 감사드린다. 처음 연구소 생활에 많은 도움을 주시고 여러 가 지 태양전지에 관한 개념을 정리하는데 도움을 주셨다. 또한 내 논문 수정에도 각별한 도움을 주셨다.

나를 세계적인 태양에너지 연구소에서 일할 수 있도록 허락해 주신 Willeke(빌레케)박사님께도 감사드린다.

함께 박사과정학생으로 일했던 Stefan Rein(스테판 라인)과 Stefan Peters(스테판 페터스)에게 도 감사한다. 스테판 라인은 lifetime을 측정하는데 도움을 주었고 Cz-defect에 대한 많은 정보 를 주고 의견을 나누었다. 스테판 페터스는 나의 처음 연구소 생활에 도움을 준 첫 번째 사람 이며 나에게 RTP라는 기계를 처음으로 소개해준 사람이다. 또한 문제들을 해결해주고 의견을 나누는데 시간을 아끼지 않았다.

Harald(하랄드)와 Toni(토니)에게도 감사드린다. 두 사람들은 실험실에서 나에게 여러 가지 중 요한 일들을 가르쳐주고 많은 도움을 주었다. 항상 내 일을 먼저 해주려고 애쓴 사람들이다. Christian(크리스티안)에게도 감사한다. 내가 플라즈마 기계 때문에 고생할 때 많은 도움을 주 었다. 그가 가끔 복도에서 지르는 소리도 화가 나서 던지는 신발도 이제 그리워 질 것이다. Kamerewerd(캄머에버트)씨에게도 감사 드린다. 갑자기 나의 기계가 작동하지 않다가도 그가 와서 손만 되면 바로 다시 작동하곤 했다. 한마디로 그는 마술의 손을 가졌다.

Elisabeth(엘리자베트)에게 감사한다. 태양전지를 측정해준 것뿐만 아니라 언니와 함께 가족처 럼 점심이나 저녁식사에 초대해 주었다. Daniela(다니엘라)와 Sewita(스위타)에게도 감사한다. 태양전지 만드는데도 많은 도움을 주었고 함께 많은 점심시간을 보냈다.

같은 방 동료인 Marion(마리온), Daniel(다니엘), Oli(올리)와 Henner(헤너)에게 또한 감사한 다. 특히 마리온은 내게 남자들의 세계에서 이질감과 차별을 느낄 때 많은 용기를 주었다. 중 국 음식인 sping roll 이 연구소 식당에 나올 때마다 마리온과 같이 먹었던 일은 잊지 못할 것 이다. Eric(에릭), Daniel(다니엘)과 Gernot(게른오트)에게도 감사한다. 이들을 나는 '나의 소녀 (?)'들이라고 부르는데 같이 장난도 치고 도움도 많이 받고 무엇보다도 마음이 따뜻한 사내아 이들이다. 내가 연구소에서 재미있게 지낼 수 있었던 것은 그들 때문이기도 했다.

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남영자 선생님께도 감사드린다. 항상 따뜻한 마음으로 대해주시고 넓은 시야를 가질 수 있도록 도와주셨다. 또한 하느님을 믿는 사람이 어떻게 살아야 하는지를 몸소 보여 주셨다.

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Curriculum Vitae

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