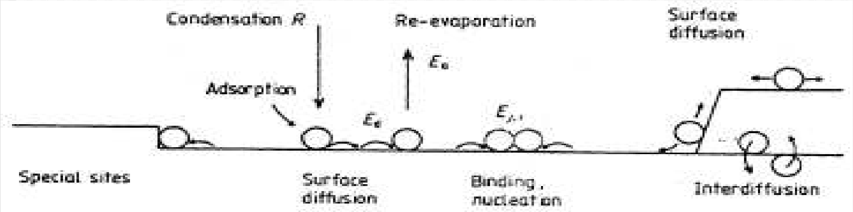
Thin Film
Nucleation and Structure

THIN FILM NUCLEATION

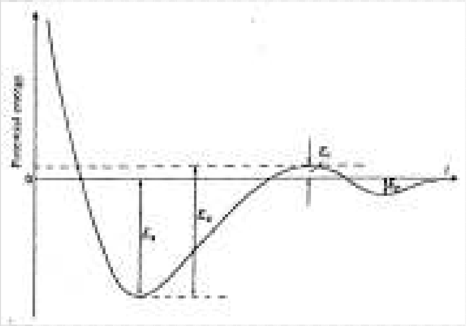
- Flux *J* supplied from the vapor using techniques described above
- Key questions:
  - What fraction of arriving flux deposits on substrate?
  - Structure and morphology of initial deposit?
  - Differences depending on deposition method?
- Importance of nucleation
  - Initial growth stage helps determine final structure
  - Nucleation-controlled growth methods
    - Atomic-layer epitaxy
    - Selective nucleation on one material but not on another

Surface Kinetic Processes



- Adsorption
- Desorption
- Surface diffusion
- Cluster formation (nucleation)
- Cluster dissociation
- Step edge adsorption/desorption
- Film/substrate interdiffusion

Adsorption

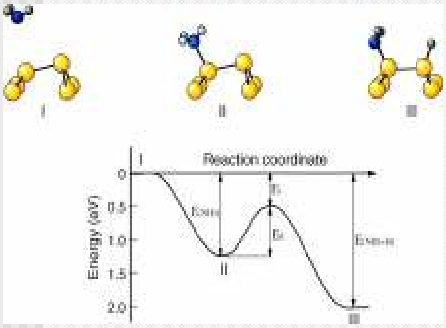


- Two types of adsorbed species
  - Physisorption
  - Chemisorption

Surfaces are Complex

- Example: Adsorption of Si on Si(001)
- Scanning tunneling microscope (STM) image
  - 30 nm x 30 nm area
  - Rows of dimers indicate "reconstruction"
    - Dimer pair model (bottom image)
  - Surface steps (vicinal)
  - Individual adsorbed Si atoms and dimers shown
- Many possible adsorption sites

Dissociative Adsorption



- Example: NH_3 on Si(001)2x1
- Schematic models and potential energy diagram
  - Theoretical calculation and IR absorption spectroscopy
- NH_3 interacts with "down" dimer atom
  - Adsorption energy 0.9-1.3eV
- Dissociation of adsorbed NH_3 into Si–NH_2 and Si–H
  - Activation barrier 0.5–1.0 eV

Surface Diffusion

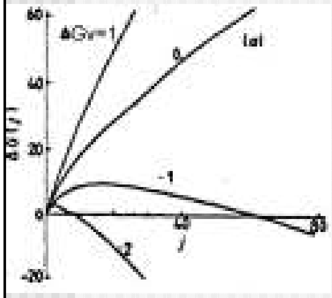
- Lateral motion of adsorbed atoms
  - Atoms move between energy minima
  - Lowest intervening potential barrier E_d
  - Average time τ_d between diffusion events

    $\tau_d = (1/\nu_1)\exp(E_d/kT_s)$
    - ν_1 = lateral vibrational adatom frequency ($\approx 10^{13}$/s)
- Potential energy vs. surface position altered at surface defects
  - *E.g*. typically stronger bonding at up side of step edges

Nucleation: Supersaturation

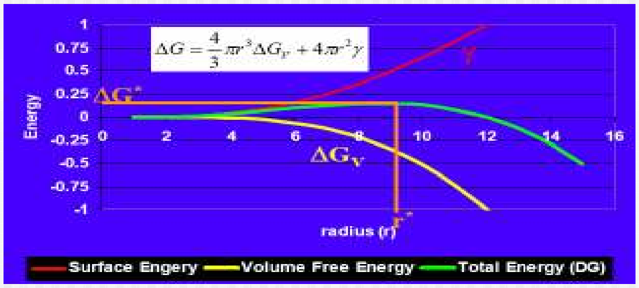
- Consider formation of solid nucleus from the vapor:
  - Volume free energy ΔG_v decrease due to condensation
  - Surface energy increase due to new interfaces
- Example: CVD reaction
- $A(g) \rightarrow C(s) + B(g) \quad \Delta G^o$
  - $\Delta G_v = \Delta G^o + RT\ln(p_B/p_A)$
  - But $\Delta G^o = RT\ln(p_A^e/p_B^e)$
  - Thus, $\Delta G_v = RT\ln(p_A^e p_B/p_A p_B^e)$ (negative for growth)
- Deviation from equilibrium pressures can provide ΔG_v driving force (supersaturation)

Nucleation Barrier / Surface Energy Criterion



- Consider monolayer thick cluster on substrate
- $\Delta G = j\Delta G_v + j(\gamma_{fv} + \gamma_{fs} - \gamma_{sv})\Omega^{2/3} + j^{1/2}\gamma_e$
  - j = number of atoms in cluster
  - γ = surface energy (*e.g.* 'fs' refers to film/subs interface)
  - Ω = atomic volume of a film atom
  - γ_e = energy per unit length of step edge
- Nucleation barrier!
- Sign of $\gamma_{fv} + \gamma_{fs} - \gamma_{sv}$ determines mechanism
  - $\gamma_{fv} + \gamma_{fs} - \gamma_{sv} \leq 0$
    - Film and film/substrate surface energies, that replace the substrate surface energy, have lower or equal total energy
    - 2D cluster is stable - Layer-by-layer nucleation
  - $\gamma_{fv} + \gamma_{fs} - \gamma_{sv} > 0$
    - 2D cluster not stable
    - 3D islands form to minimize film-substrate contact

Hemispherical Nucleus



$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

- Assume hemispherical cluster of radius *r*
- Plot: free energy components
  - Volume free energy decreases (assuming $\Delta G_v < 0$)
  - Surface free energy increases
  - Overall: free energy barrier

Nucleation Mechanisms

Usually classified into three categories:

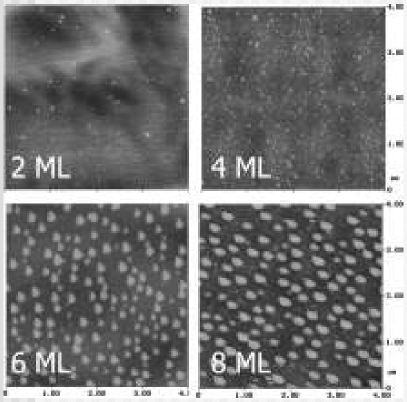
- Layer-by-layer (Frank-van der Merwe)
  - $\gamma_{fv} + \gamma_{fs} - \gamma_{sv} \leq 0$
- Three-dimensional island (Volmer-Weber)
  - $\gamma_{fv} + \gamma_{fs} - \gamma_{sv} > 0$
    - Covering surface with film increases interfacial energy
    - 3D clusters favored to minimize film surface area and film/substrate contact area
- Stranski-Krastanov
  - Initially layer-by-layer, followed by 3D islands

Example: GaAs on GaAs/SiO_2

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

- GaAs patterned with SiO_2 (MBE)
  - Smooth deposit on GaAs area
    - Layer-by-layer growth
  - 3D GaAs islands on SiO_2
    - Volmer-Weber growth
- Also illustrates nearly selective growth
  - Only a few GaAs islands on SiO_2 at highest *T*
  - Increasing *T* decreases supersaturation
    - $\Delta G_v \sim RT ln(p_{Ga}^e/p_{Ga})$
    - Recall that p_{Ga}^e increases rapidly with increasing *T*
    - Nucleation barrier increases!

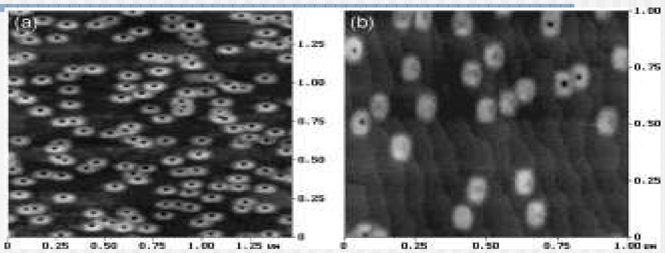
Stranski-Krastanov Nucleation



- Example: Ge/Si(001)
  - Atomic force microscope images
  - Initial layer-by-layer growth
  - Onset of 3D islands at ~ 2ML
  - Island size growth with time

  J. Konle, Mat Sci Engin B 89 (2002) 160-165
- Application: Self-assembly of quantum dots

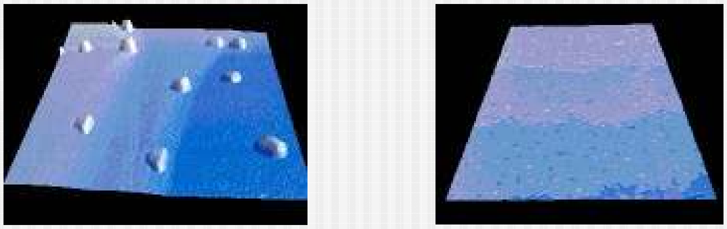
Example:
InGaAs on GaAs (001)



- Transition from layer-by-layer to SK:
  - Occurs for lattice constant mismatch strain $\varepsilon > 1 - 2\%$
    - Mismatch strain $\varepsilon = (a_f - a_s)/a_s$
- AFM images show islands superimposed on 2D growth surface
  - Vicinal growth steps visible

  A. Lorke et al., Mat Sci Engin B 88 (2002) 225-229
- Problem: quantum devices require uniform nano-dot size and spacings

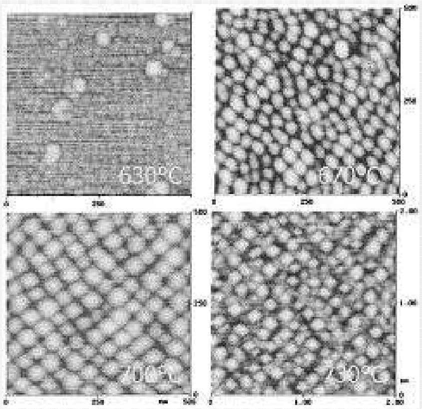
Surfactant-Aided Nucleation 1



- Well-chosen surface impurities promote FM nucleation
  - Impurity should strongly adsorb on surface (lowers γ_{fv})
  - Impurity may also limit diffusion kinetics
  - Surface segregation - impurity stays on surface without incorporating
- Left: Ge on Si(111) without surfactant. (area: 3µmx3µm) coverage 30ML, T=450^{o}C
- Right: Ge growth on Si(111) with Sb as surfactant (coverage 30ML, T=450^{o}C) (area: 1.5x1.0µm)

STM images from: J. Vac. Sci. Technol. A 12 (1994) 1932

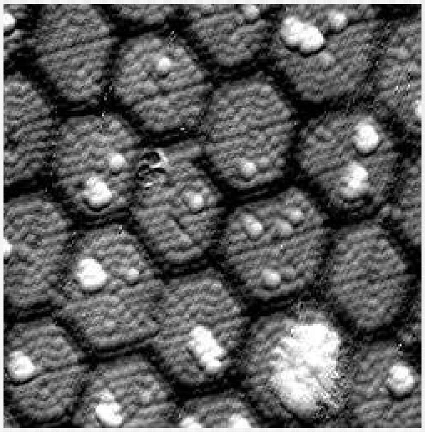
Surfactant-Aided Nucleation 2



- Ge/Si(001) with Sb surfactant
  - 8 ML nominal Ge coverage
  - 630C, 670C, 700C, 730C
    - Islanding suppressed at low T
- Sb effects
  - High island density
  - Increased ordering
  - Uniform size density

J. Konle, Mat Sci Engin B 89 (2002) 160-165

Surfactant-Aided Nucleation 3



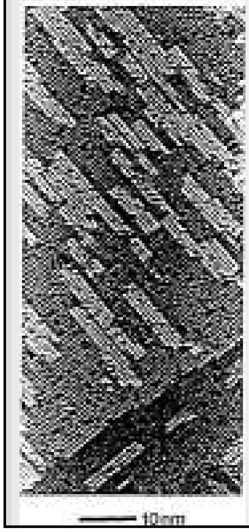
- Sb-Ge/Si(111) SK layer
  - (200x300Å)
  - Hexagons consist of six triangles, divided by smaller trenches
  - Single Sb atoms are lighter protrusions
  - Driving force for hexagonal structure:
    - Relief of stress induced by large Sb atoms

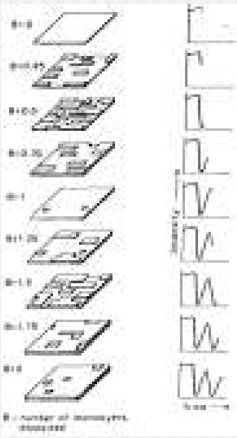
STM image from: Surface Sci. Lett. 351 (1996) L233

Frank-van der Merwe Growth

- Two limiting cases:
  - Step propagation
  - 2D island nucleation

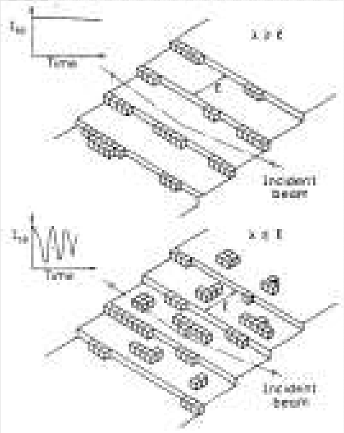
Layer-By-Layer Growth By 2D Island Nucleation





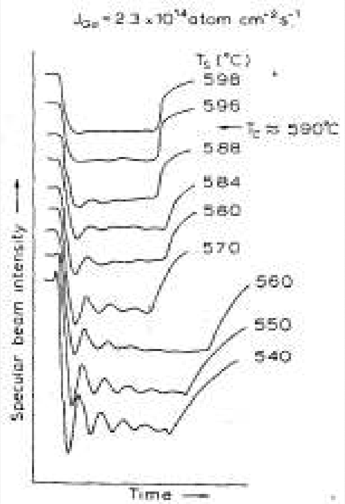
- Low *T*, low step density
  - Diffusion length < step spacing
- STM image after 0.2 ML Si on Si(001) at 690K
- Schematic shows ML roughening/smoothening cycle
  - Readily observed by reflection high-energy electron diffraction during growth
- Transition to step-flow at low supersaturation, high step density
  - Diffusion length > step spacing

2D to Step Flow Transition



- Transition between step flow and 2D island modes
  - Schematic shows two extremes
  - Observed by RHEED oscillations
    - Step propagation: little roughness variation, no oscillations
    - 2D island: roughness variation, oscillations
  - Depends d_s, J, and T_s
- Experiment: GaAs growth on GaAs(100) miscut by 2.25^{o} towards (110)
  - Step spacing $\approx$ 7.2 nm

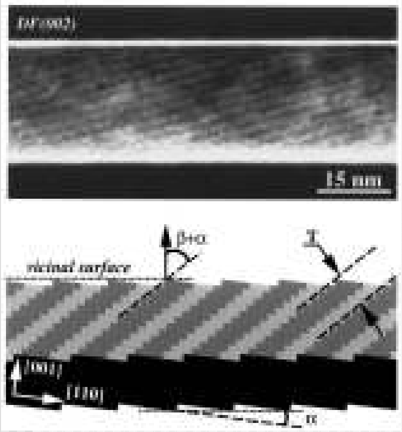
Interpretation of RHEED Oscillation Extinction



- Assume that transition temperature is given by $x_d \sim d_s$
- Neglect desorption for high supersaturation ($R = J$)
- Use standard expression:
  - $x_d^2 = Dt_{ML} (\sim d_s^2)$
- t_{ML} = time to deposit a monolayer = N_o/R

  $D = Rd_s^2/N_o$
  - D vs. T_s obtained
    - Yields E_d = 1.3 eV

Application To Nano-Films: Tilted Superlattices



- Normal superlattice growth: ≥1ML of each material deposited sequentially to form alternating layers
- Tilted superlattices: deposit <1ML per layer
  - Use conditions giving step propagation
- BOTTOM: schematic of growth scheme
- TOP: XTEM image for CdTe/MnTe structures
  - Minimal step bunching

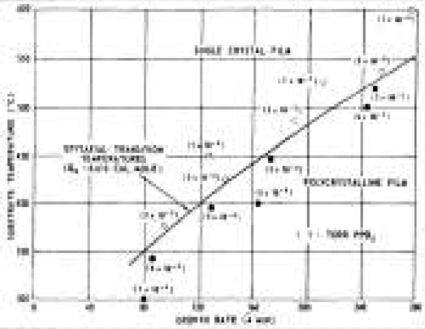
Hartmann et al. Appl Phys Lett 70 (1997) 1113

Thin Film Microstructure

Epitaxial growth

Polycrystalline and amorphous films

Conditions For Epitaxy

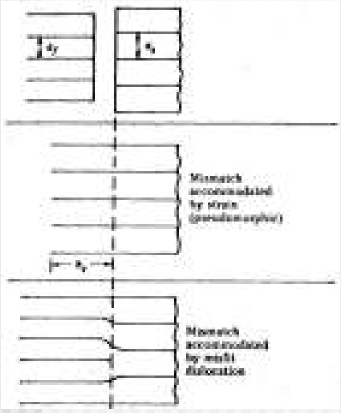


- Film/substrate structure match:
  - Same crystal structures
  - Different crystal structures, but good match between atomic positions at surface planes
  - Lattice mismatch typically < ~20%
- Clean and well-ordered substrate surface
  - Contaminants interfere with nearest-neighbor atomic bonding
  - Cleaning procedures must leave the surface in a well-ordered state
- Sufficient adatom mobility
  - High substrate temperature & low growth rate
  - Example: sapphire growth

Defects in Epitaxial Films 1

- Defects can be divided into four classes:
  - Defects from the substrate
    - E.g. threading dislocations
  - Defects due to non-ideal crystal growth conditions and/or entropic effects:
    - Point defects from adatoms not reaching their correct lattice positions → dislocation loops
    - Equilibrium statistical point defect density
    - Stacking faults on crystal planes with low faulting energy

Defects in Epitaxial Films 2



- Defects due to film-substrate mismatch
  - Anti-phase domains when the film has lower symmetry than the substrate (e.g. III-V on Si)
  - <u>Plastic deformation due to lattice mismatch coherency strains (pictured at left)</u>
  - Plastic deformation during temperature changes (thermal expansion coefficient mismatch)
- Defects due to 3D island nucleation
  - Dislocations, stacking faults, or low-angle grain boundaries that accommodate translational or rotational misalignment between islands
  - Stacking faults occurring on facet planes of 3D islands

Misfit Dislocation Array

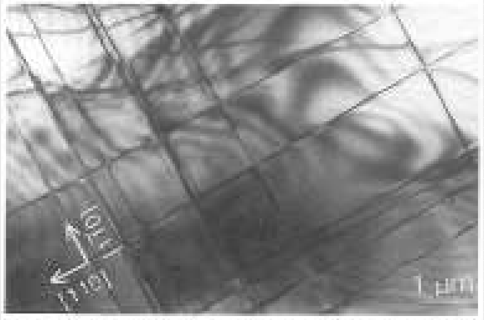


Figure 5.6: Bright-field plan-view transmission electron micrograph of the interface between a 200-nm $Si_{0.9}Ge_{0.1}$ layer grown on a Si (001) substrate. The misfit dislocations are arranged in a crossed grid running along the ⟨110⟩ directions within the (001) interface.

- Plan-view TEM image
  - Film-substrate interface
- $Si_{0.9}Ge_{0.1}$ layer
  - 200 nm thick
  - On Si(001)
- Crossed dislocation grid along <110> directions
  - Within the (001) interface
- Some dislocations continue into film
  - Deleterious effect on materials properties and device performance

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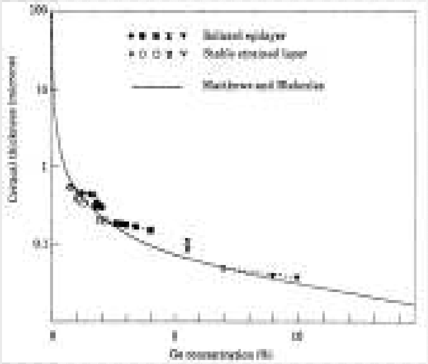
Energy Balance Calculation 1

- Equilibrium criterion for forming misfits:
  - Energy of dislocation lines less than coherency strain energy
  - Substrate assumed to be unstrained
- Estimate critical thickness h_c for forming misfits
- Strain energy per unit volume in film: $(Y/2)\mathcal{E}^2$
  - Y = Young's modulus
  - $\mathcal{E} = (a_f - a_s)/a_s$ = lattice mismatch
- Strain energy per unit area: $U_s = (Y/2)h\mathcal{E}^2$
- Energy per unit length of edge dislocation $\Gamma_e \approx \alpha\mu b^2 \approx \alpha Y b^2$
  - b = Burgers vector
  - α = geometrical constant (~ 1)
  - μ = shear modulus (assumed ~Y)
- The dislocation energy U_d per unit area:

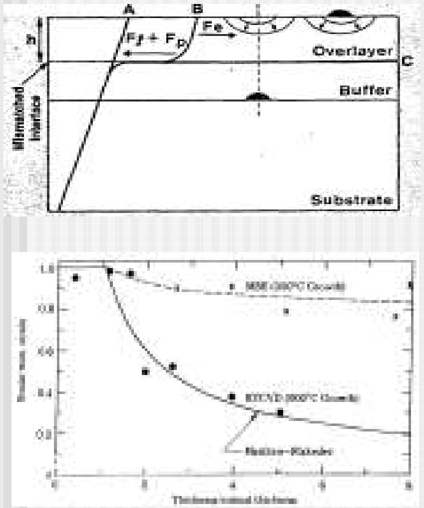
  $U_d = (2D/D^2)\Gamma_e = 2\alpha Y b^2/D$
  - D^2 = area of a two-dimensional dislocation grid
  - $2D$ = dislocation length per grid square

Energy Balance Calculation 2



- If the mismatch is taken up entirely by dislocations, then the dislocation spacing is: $D = a_f/f$, and
- $U_d = 2\alpha Y b^2 \varepsilon / a_f \approx 2\alpha Y b \varepsilon$
  - The latter since $b \approx a_f$
- Equating U_d and U_s yields critical thickness: $h_c \sim 4\alpha b/\varepsilon$
  - Above h_c, energetically favorable to form misfit dislocations
  - Figure: data for $Si_{1-x}Ge_x$ on Si(001)
    - $\varepsilon = 0.04x$
    - Good agreement with Matthews-Blakeslee model (more accurate version of above calculation)

Misfit Dislocation Formation Mechanisms

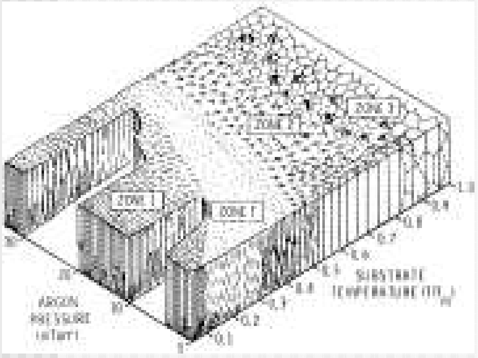


- Dislocations threading from the substrate
- Dislocation half-loop nucleation
  - Homogeneous nucleation at film surface
  - Heterogeneous nucleation on substrate or film surface defects
    - Reduced nucleation barrier
- Kinetic limitations: Misfit density may be less than predicted
  - Internal resistance to dislocation motion (plastic deformation)
  - Example of Ge relaxation on Si
    - High T growth - near equilibrium
    - Low T growth - limited relaxation

Polycrystalline and Amorphous Thin Films

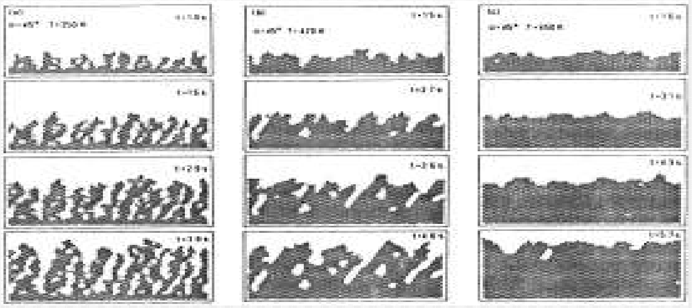
- Issues:
  - Morphology development
  - Structure
  - Defects
- Films are usually deposited far from equilibrium
  - Non-equilibrium film state
  - Structure determined by processing parameters
- 'Structure-zone' models
  - Correlate deposition conditions and microstructure
  - Divide into zones
    - Specific structure types
    - Specific physical processes dominate

Sputter Deposited Films - Structure-Zone Diagrams



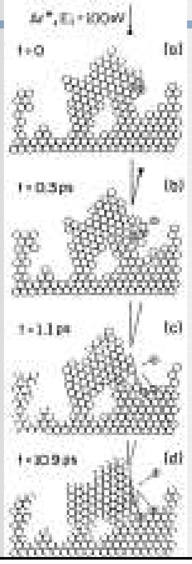
- Zone model based on magnetron sputter deposited metals
  - Ti, Cr, Fe, Cu, Mo, and Al
- Structure vs. T_s and sputtering gas pressure P
- High P: agrees reasonably well with structure-zone diagram for evaporation
  - Zone 1: columns with voided boundaries
  - Zone 2: dense columns
  - Zone 3: equiaxed structure
- Low P: fourth zone (zone T)
  - Between zone 1 and 2
  - Zone T grows with decreasing P, down to $T_s/T_m < 0.1$

Zone 1 to Zone 2 Transition



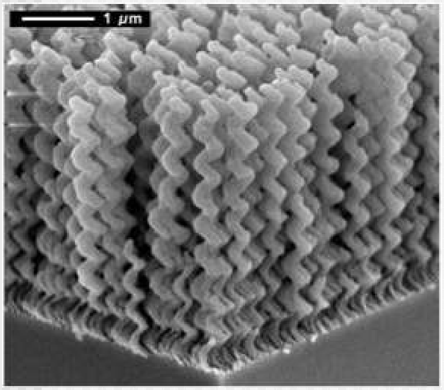
- Computer simulation of Ni growth by evaporation
  - Low T shows growth of isolated columns (zone 1)
  - Higher T shows effect of increasing surface diffusion
    - Ni fills in columnar void yielding a more dense microstructure

Zone 1 To Zone T Transition: Ion Impact Effects



- Single 100 eV Ar ion impact on Ni
  - Film has a typical zone 1 structure
  - Snapshots during collision process
  - Straight lines lines indicate atom displacement (not actual trajectories)
- Effects of ion impact
  - Removal of overhanging atoms
    - Incipient void remains open for subsequent filling
  - Enhanced atomic motion over a few atomic spacings
  - Local heating and crystallization
  - Collapse of micro-void
- Motivates many “ion-assisted” deposition methods

Glancing-Angle Deposition: Porous Nano-Structures



- Evaporate from glancing angle
  - Typically ~80^{o} from substrate normal
  - Tangent rule: tan α = 2 tan β
    - α = vapor impingement angle (relative to normal)
    - β = column angle (relative to normal)
  - Substrate azimuthal rotation yields specific structures such as spirals, zigzags, etc.
  - Nano-columns with controlled shapes, unique properties
    - E.g. optical properties, 3D photonic bandgap materials

Deposition on Patterned Substrates

- Deposit thin films onto nano-scale integrated circuits
- Metallization/insulator layers
  - Selective deposition
  - Conformal coverage
  - Step coverage
  - Surface planarization
- CVD provides conformal coverage and selective deposition
  - In the surface reaction rate limited mode
    - No gas pressure gradients, deposition rate uniform
  - Allows continuous metal lines over deep holes
  - No planarization
- Sputtering better for step coverage and planarization

Hole Filling By Sputtering

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

- Deposit in via hole with tilted flux
  - Experiment: Ti (a)
  - Shows closing of hole at top
  - Minimal side-wall and bottom deposition
- Simulation Results (b),(c)
  - Different views of simulated deposit
  - Agrees well with experiment
  - Simulation codes widely used in semiconductor industry

Tungsten Vias: CVD

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

- Left: experimental result for hole filling with W
  - Hole ~ 200 nm diameter
  - Good filling, but minor void in center
    - Gas diffusion limitation into narrow void
- Right: calculation results
  - Modeled using a single constant sticking coefficient
  - Surface reaction limited conditions give good side-wall coverage
  - Reproduces experimental data well