

Electrochimica Acta 44 (1999) 1847-1864

ELECTROCHIMICA

Review

Microstructuring of conducting polymers

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Received 27 July 1998

Abstract

Intrinsically conducting polymers (ICPs) represent a special class of materials with variable properties. Microstructuring of ICPs is possible by either pre- or poststructuring or direct microstructuring. The localization of both nucleation as well as the growth is important, especially for systems with a high negative aspect ratio. There are numerous microanalytical techniques for the characterization of electrochemical functionality, topography, stoichiometry and opto-electronic properties. Advantages and disadvantages are discussed for various laboratory techniques such as laser induced polymerization. Sharpness of ICP microstructures can be improved by combination of two or more localization techniques. The application of ICPs in the through-hole plating of printed circuit boards is discussed as an example of the technical production of a multiple microsystem with a high negative aspect ratio. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Intrinsically conducting polymers (ICPs) are new materials with promising properties. The almost metallic conductivity of an organic material has offered some applications for antistatic films [1], as metallic electrode of condensors [1] or as substrate for metallizations [2, 3]. As a matrix for enzymes, they can be applied for biosensors [4, 5]. New and wider applications of these materials were discussed due to the variable properties from conducting to semiconducting state combined with changes of colour. This difference to traditional inorganic materials such as metals and insulators offers the possibility for application in batteries, displays and mirrors. Recently, electronic devices could be realized, e.g. transistors [6] and LEDs [7].

In addition to the electronic switching properties, mechanical or chemical properties change with the redox process. Due to the intercalation of anions, ICPs become hydrophilic [8]. The flexibility of ICPs is an advantage for manufacturing and some applications. On the other hand, the lack of stiffness hinders their application in micromechanics. A principal advantage of ICPs is the swelling and shrinking during the redox process, which can be measured by ellipsometry [9]. The permeability [10] of ICPs allows the application as membranes which may also change with the redox state. Finally, an organic polymer is free of heavy metals and can therefore easily be recycled. Advantages and disadvantages of ICPs are summarized with some special data for poly(bi)thiophen (PBT) in Table 1.

Some properties of ICPs make this class of materials favourable for microtechnologies. While metals, insulators and silicon are widely applied in microtechniques, the knowledge of microstructuring of ICPs is scarce. This may be caused by the special requirements of electrochemical technologies which from outsiders may be considered as barriers. Therefore, it is the aim of this review to present the fundamental concepts of electrochemical microstructuring, and to explain them with some examples. Subsequently, the characterization of ICP microstructures will be demonstrated. Then special processes will be discussed with reference to their requirements. In this paper, electrochemical

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Advantages and disadvantages of intrinsically conducting polymers. Data and properties of PBT for comparison with other materials

Properties		PBT ox.	PBT red.			
Advantage	Conductivity	$1 \ \Omega^{-1} \ \mathrm{cm}^{-1}$	$10^{-7} \ \Omega^{-1} \ \mathrm{cm}^{-1}$			
variable properties	Reflectivity/colour	Blue	Red			
	Photosensiblity	No	Yes			
	Hydrophilicity	Hydrophobic	Hydrophilic			
Advantage	Mechanical flexibility					
-	Permeability					
	Organic material, no heavy metal					
	Easy recycling					
	Good adhesion					
Disadvantage	Corrosion by overoxidation					
-	Swelling during oxidation					
	Mechanical weakness and instability					

preparation of ICPs is emphasized. The literature on other techniques for microstructuring of insulating polymers is not considered here, e.g. micromolding [11] or photoetching [12]. tems can be distinguished from other systems with a more or less Gaussian profile which e.g. appear in the focused laser beam.

Classification of ICP-microstructures

2. Concepts for microstructuring of ICPs

Table 1

2.1. Characterization of microstructures

In the rapidly evolving field of microsystem technologies, various structures and different processes are known [16]. In extension of a first concept [17], we will classify ICP systems by their order, symmetry, aspect ratio, profile and conductivity as shown in Fig. 1. Such a classification will allow a more appropriate theoretical treatment and description of processes. Systems typical for research are shown on the right side, while technical relevance increases are on the left side.

While random systems are often formed by statistic nucleation in surface technologies, microsystem technologies prefer systems with a defined geometry. For the technical preparation process multiple and even periodic systems are prepared, while research mostly refers to single systems. The desired symmetry depends on the application. In research systems, the two-dimensional symmetry of the disc electrode is preferred for mathematical reasons. On the other hand, lower symmetry dominates in technology, e.g. one-dimensional lines or trenches [18]. With respect to the aspect ratio A = depth/width = x/y, systems with negative or positive aspect ratio can be distinguished. Flat systems with an aspect ratio near 0 are preferred in hydrodynamic systems, e.g. the RDE or in microelectronics. For micromechanics, however, high A values (A < 0 in production, A > 0 for the product) are typical. According to the topography, defined rectangular sys-



Fig. 1. Classification of microstructures by their order, symmetry, aspect ratio, composition and profile.

With reference to the number of components, binary or multiple systems must be distinguished. The conductivity of the components is important for the processing and the properties as well. By analogy to thin film systems, we use abbreviations M = metal, Ins = insulator, SC = semiconductor and ICP = intrinsically conducting polymer. The description of microsystems, however, is more complex than that of thin film systems: lateral and vertical structures have to be distinguished.

2.2. Processes

There are various processes used for the polymerization reaction. The anodic polymerization is widely applied in electrochemistry due to the possibilities of process regulation. For microstructuring, it can be applied in combination with geometric blocking, chemical modification or in a droplet (see Section 2.3).

For some systems, chemical polymerization by an oxidizing species in the solution can be applied in holes or tubes [19]. It can be used for microstructuring by the electrochemical microscope, if the oxidizing species is produced at the counter electrode [20, 21]. The deposition of a solid oxidizer at the substrate surface is a similar approach [2] (Section 5.5).

On semiconductors, e.g. n-TiO₂ [22] or n-Si [23], photoinduced polymerization is preferential. Photons generate electron/hole pairs in the semiconductor. At anodic polarization the holes oxidize the monomer at the semiconductor-electrolyte interface, and the polymerization takes place. Naturally, this principle of course is limited by the supply of photons to the semiconductor. If the polymer itself absorbs the light, the polymerization stops after reaching a limiting thickness.

Writing of microcircuits by laser processing of polymers is described in only a few publications. The preparation starts from a thin film of an intrinsically conducting polymer macroscopically spin coated or electrochemically deposited on a substrate. In a further step these thin films are modified under laser irradiation [24] or dry plasma etching to produce micropatterns, e.g. by photoetching [25], photoablation [26] or photopolymerization [27].

2.3. Localization of the reaction

For microstructuring, the localization of the reaction is necessary. The basic principles are summarized in Fig. 2. The application of geometric blocking by photoresist, a movable mask or the embedding of the microsubstrate in an inert material is well known. The limitation of the electrolyte using the localized wetting of the surface [28] is a similar principle. The consequent extension of this method consists of investigations in a small droplet [29]. The application of a chemical modification of the surface is possible either by localized poisoning of the surface by an inhibitor [30] or by localized oxidation of the substrate



Fig. 2. Principles of the localization of polymerization reactions by geometric blocking, chemical modification, localized signals and other methods.

reaction boundaries

Table 2						
Overview	of different	methods a	and processes	for mi	icrostructuring of	of ICPs

	Method	Model/System	Aspect ratio	Edge sharpness/ width/misfit	Analysis	Reference
1	Laser	Si/PBT, Si/PT	< 1	ES 4μm, W 10 μm	Profilometry, microscopy, SEM, CV, XPS, ellipsometry	[23], [32]
2	Laser + mask or geometric blocking Fig. 10, Fig. 12 after mask removal Fig. 4	Si/InsPBT	-1 +1	ES 1 μm W 10 μm M 1μm	Profilometry, microscopy, CV	[32], [50]
3	Laser, anisotropic etch structure Fig. 8	Si/Si ₃ N ₄ /PBT	≈ 1	ES 4 μm (Fig. 8) W 10 μm	Profilometry, EDX	[35], [50]
4	Laser + implantation (negative prestructuring) Fig. 11	Si/Si ₃ N ₄ /PBT	< 1	ES 8 μm W 30 μm M 7 μm	Profilometry, SEM	[35]
5	Anodic deposition + implantation positive prestructuring	PS/PS(met.)/PANI	< 1	ES 5 μm W 25 μm	Profilometry, SAM, linescan	[28]
6	Anodic deposition + implantation Poststructuring Fig. 9	Au/PBT/PBT(mod)	<< 1	ES 1 μm W 15 μm M 5 μm	Scanning i _{ph} Imaging ESCA	[36]
7	Anodic deposition in a LIGAstructure	M/Ins/PPy	A > 1 (neg.)	ES 1 μm W 50 μm	SEM, CV, ESR,	[57]
8	Laser, direct writing by microlithographie after dilution	Ins/P3HT	<< 1 <<1	W 4 μm	SEM	[61]
9	SECM	Au/PANI [20], [21] Au/PPy [60]	< 1 > 1 [60]	ES 5 μm W 40 μm [60]	SEM	[20], [60], [21]
10	Localized oxidant Fig. 13	Printed circuit boards/PEDT	≥ 5		Profilometry, ESCA, SEM, EDX, CV	[2], [59]
11	Deposition into porous Al ₂ O ₃	PPy,/PANI nanotubes	>> 1	W 70 nm	SEM, conductivity	[19]
12	Deposition into porous silicon		> 1	W 10 nm	Galvanotatic transients, SEM, XPS	[62]
13	STM	Au/PPy	≈ 1	SE 1 nm W 5 nm	STM	[59]

Model of intended microstructure: ICP (black), semiconductor (grey), metal (white), insulator (dark grey). Aspect ratio A: rough values taken from original publications. Edge sharpness ES: taken from visual inspection of images. Width W: given by mask or process parameters. Misfit M: overlap (>0) or insufficient filling (<0). Characterization by methods described in Section 4

to prepare insulating areas [31]. Another approach can be realized by the implantation of ions [32] which inhibit or catalyse the polymerization. A localization of the polymerizing signal can be realized by a focused laser beam (local heating or photoreaction) or in diluted electrolytes by an electric field.

The limitation of the mass transport in the solution, for example with the electrochemical microscope or by localization of a solid oxidizing species, has also been applied [20, 21]. Most of these localizations are used for the preparation of positive microstructures, but with masks, photoresist or molds with a negative aspect ratio, negative or flat microstructures can also be prepared. For technical aspects it is necessary to differentiate between the preparation process and the final structure. For example, the preparation in masks causes the problems associated with negative microstructures, but after removal of the mask a positive structure remains (Section 6, Table 2).

Often the application of one localization principle may be sufficient. For special techniques and high quality, however, the integration of various principles, for example laser techniques in combination with masks or ion implantation, may be useful [33].

2.4. Nucleation in negative structures

So far, i.e. for microstructures with a positive aspect ratio, the nucleation always takes place in the area limited or addressed by the signal. It can be accelerated by so-called activation processes which yield surface areas with a small nucleation work function resulting in a high nucleation rate. The activation of insulating polymers by Pd salts before electrochemical metal deposition is a typical example.

For micro and nanostructures with a negative aspect ratio, it is necessary to start the reaction at the bottom of the pore [17, 34]. This is schematically shown in Fig. 3(b) for increasing periods of time t_1 to t_{∞} . Otherwise the reaction starts at the surface and the filling of the microstructure will not be successful (Fig. 3(c)). A simultaneous occurring homogeneous reaction all over the pore wall can be achieved only in case of a self-inhibiting reaction. The high field oxide formation is a good example [35]. The case of Fig. 3(b) can be achieved, if the bottom of the negative microstructure is conducting, while the wall is insulating. With *p*-type porous Si, this case is approximated, since the pore bottom consists of crystalline Si (band gap 1.2 eV) while the pore walls have a higher band gap (almost 2 eV) [17].

2.5. Pre- and post-structuring

In Section 2.3 the localization of the polymerization reaction itself was described, e.g. by applying a focused



Fig. 3. Mechanistic scheme of polymerization in pores. (a) Ideal case, (b) nucleation at the bottoms of the pores, (c) nucleation at the walls of the pores, (d) inhibited layer growth, (e) reaction rates v_i versus time t, (f) current density i versus charge q.

laser beam. The application of a boundary prepared by ion implantation is a special case of pre-structuring of the semiconductor surface [36]. In such a case the microstructuring can be achieved by ion implantation through a mask. This pre-structuring yields an insulating part of the surface, next to a remaining semiconducting part of the surface. Such a microstructured substrate can then be used for a traditional microscopic polymerization process taking place only at the semiconducting surface. Examples are described in Fig. 4(b). Using this terminology, the application of structured photoresists is classified as a prestructuring technique as well (Fig. 4(a)). In both cases positive structures are formed.

In contrast to such a prestructuring process, a poststructuring is also possible (Fig. 4(c) and (d)). In this case an infinite thin film of the polymer is prepared by macroscopic polymerization. The following microstructuring can be carried out by a chemical reaction, such as surface oxidation by chromate/sulfuric acid (Fig. 4(c)). Other examples are given by photoreactions (laser ablation [26]) or mechanical removal of the polymer film (Fig. 4(d)). An example of such a poststructuring process is the structuring of the polymer film by ion implantation described in Fig. 4(c) and Fig. 9 [37]. By poststructuring, flat or positive microstructures are obtained.



Fig. 4. Models for pre- and poststructuring of ICPs. Left side: prestructuring by ion implantation of the substrate and following localized polymerization. Right side: homogeneous polymerization with a following poststructuring. Localized modifications by ion implantation or laser ablation.

2.6. Sharpness of the microstructure

The quality of the microstructure depends critically on the sharpness of its edges. For example, the steepness dz/dx of the edge approach is infinity for an ideal rectangular structure, but in practice one often obtains more or less Gaussian profiles as shown in Fig. 1. The sharpness should determine by the following primary effects:

- -sharpness of the primary structure or limitation
- (e.g. implantation mask, or laser beam),
- -localization of the nucleation,
- —localization of the reaction.
- In practice, secondary effects cause a broadening [38]:

- —formation of insulating species in the laser spot, e.g. SiO_2 on Si [31],
- -heating,
- -diffusion of reactants in solution,
- —lateral diffusion of minority carriers, e.g. holes, in semiconducting substrates,
- —ohmic drop in the electrolyte in the case of electrochemical processes.

A typical example is given by laser induced processes on semiconductors: while the primary signal may be localized to 1 μ m, secondary effects yield a broadening to 10 μ m or more. In the case of pre-structured substrates, the broadening of microstructures with an positive aspect ratio may be caused by an unlimited growth of a conducting phase beyond the insulating border in the substrate. Thus, broadening may be caused by different steps of the overall process.

For negative aspect ratios, most problems arise from incomplete filling of the structures (see Fig. 1 ('Shell') and Fig. 3).

Summarizing, the quality of the microstructure can be characterized by:

-minimum width of the structure,

-edge sharpness (roughness of the wall),

-edge steepness,

-distance to the border (overlap or insufficient filling).

Examples will be discussed in the following sections and in Table 2.

2.7. Micro- and nanostructuring

The principles of micro- and nanostructuring are very similar. A polymerization reaction has to be initiated and localized [17, 19]. Especially the nucleation of the polymer should start at a special site, for example at the bottom or pores [17]. The preparation of polymer films in porous silicon is a typical example. In addition to the problems of microstructuring, however, the wetting of the pores becomes a problem with decreasing radius r. According to the Thomson equation, the term $\sigma V/r$ has to be considered. In addition to that, the characterization of the nanostructures is more difficult [19].

3. Experimental aspects

3.1. Equipment

The equipment for microstructuring of single systems in research or periodic systems in a technological process shows fundamental differences. At first, there are different measuring techniques: while single microstructures require electronic equipment in the nA range, periodic systems in the technical production can be managed by traditional equipment in the range of mA.

Secondly, research cells can be miniaturized for single systems and the reactions can be observed in situ under the microscope. Technical processes, on the other hand, e.g. in the production of printed circuit boards, are carried out in large galvanising machines. This can be explained by the LIGA process [39] as an example. A silicon wafer covered with a conducting metal, e.g. titanium, is used as substrate for the galvanizing process. Masks consist of an insulating polymer, e.g. polymethylmethacrylate (PMMA). Due to the large numbers of microstructures (some 1000) the free surface of the macroscopic substrate is large. Therefore, the production of a periodic or at least multiple microsystem on a macroscopic wafer can be carried out in galvanizing machines with similar currents as in traditional process.

On the other hand, the preparation of a single microsystem has to be carried out under the microscope which requires all techniques of microelectrochemistry. A schematic diagram of such a multifunctional microelectrochemical equipment is



Fig. 5. Schematic diagram of a multifunctional equipment for microstructuring of polymers and their characterization.

shown in Fig. 5 [40]. This includes most of the elements which are standard for macroscopic cells:

—The electrochemical cell can be miniaturized using masks or small droplets [41, 42]. It is mounted on an x, y, z stage and can be controlled with μ m accuracy.

—The geometric position of electrodes (reference or counter electrode) can be arranged by mechanical micropositioners or Piezo positioners with an accuracy in the nm range.

—The microscopic observation is possible with longdistance microscopes.

—A registration of the images is possible via a CCD camera on a monitor.

—Optical and spectroscopic equipment can be adjusted. For example light from an Xe lamp or a laser beam can be coupled in glass fibres and focused on small spots with a diameter of 1 μ m. In the optical path, a reflection spectrometer can be addressed. Wavelength dependent mirrors, objectives and filters are used for measurements with UV or visible light [43].

—The electrochemical control must be available for small currents in the region of pA. DC measurements are possible now down to electrodes with 2 μ m diameter, but AC measurements can be carried out on larger electrodes only [44].

—Microelectrodes can be prepared with noble metals. Ion-sensitive electrodes are available for some special systems in the μ m range [45].

3.2. Multiple process steps

While the polymerization process itself can be carried out under common conditions, the whole procedure of microstructuring can include the following steps:

- -cleaning of the substrate,
- -introduction of masks or prestructuring,
- -removal of oxides and other inhibiting substances,

-hydrophilization of pores,

-activation of the surface, e.g. roughening or metallization,

-introduction of the monomer solution,

- -polymerization,
- -electrolyte change,
- -removal of masks or poststructuring,
- -post treatment, annealing etc.

During these steps the experimental conditions such as solvent, electrolyte concentration, temperature, potential, surface state etc. will change stepwise or continuously. A detailed description includes all parameters during the sequence of the single steps. Examples were given for the polymerization in porous Si or cathodic deposition of metals in porous Al oxide [17,46]. A part of such an analysis will be described in Section 5.5. 3.3. Techniques of characterization and modification

For characterization of the polymer films, the following techniques are available:

—Pulse techniques for fast potentiostatic measurements [47],

--scanning electrochemical microscope (SECM) [33],

-scanning auger (SAM) and scanning electron microscopy (SEM),

-XPS and other surface analysis techniques [37, 48], -laser profilometry,

-photocurrent measurements [37],

—for modification we used ion implantation [48] with an ion gun (3 keV) for Fig. 9. This was performed in a UHV vessel with an IQP 10/63 Penning ion gun (Leybold) arranged perpendicular to the surface.

4. Analysis of microstructures

The final microstructure of an ICP has to be checked with reference to the following points:

--functionality such as contacts and charge efficiency of redox processes,

-optical and electronic properties,

- -surface topography,
- -sharpness of the microstructure,
- -stoichiometry of the deposit.

Therefore, various electrochemical, analytical and optical investigations have to be applied.

4.1. Functionality check of the ICP deposit

At first, the contacts have to be proved. Fig. 6(a) shows a simple arrangement for measurement of the *n*-Si/PBT contact. In the dark, it behaves as a diode blocking in the anodic direction. By illumination of the contact, the expected anodic current is observed.

In a subsequent step, the conductivity has to be checked. It can be obtained by microelectronic techniques, for example the four-point method measuring the resistance between two needles in contact to the microstructure [48]. The contacting by two Hg droplets is simpler. It was applied for PBT lines in this study. The change of resistivity from 100 k Ω in the oxidized state to $10 M\Omega$ in the reduced state could be proved [49]. The scanning electrochemical microscope is useful for in situ measurements in various oxidation states using different redox systems [32]. Fig. 6(b) shows an example for a microstructure of polybithiophene which is measured at 0.36 V and 0.95 V respectively. The small positive feedback in the reduced state and the large cathodic feedback in the oxidized state prove the change of conductivity during the redox process. Simultaneously, the geometry is proved. The resolution of the analytical technique is not as high as the



Fig. 6. Check of functionality of ICP microstructures. (a) U/I curve of a Au/Si/PBT/Au structure in the dark and under illumination. (b) SECM analysis of 3 PBT lines on Si.

structure, and the three peaks in x-direction give only an idea of the insulation between the three lines.

For the application of ICPs in fast switching systems, the electrochemical functionality has to be checked by pulse experiments. Due to the small ohmic drop at microelectrodes, experiments with ICP microelectrodes have the advantage that the ohmic drop decreases with the radius of the electrode. Therefore, discharge or charge experiments with conducting polymers on microelectrodes allow an interpretation of the measured data within the μ s range [50]. Fig. 7 shows an cathodic and anodic transient for a microelectrode covered with polyaniline in a double logarithmic plot as an example. The charge transient $q(\log t)$ shows that the cathodic process takes place within 100 μ s, while the anodic process needs 1 ms. This delay is due to the electronic properties of the reduced state, and not connected with the functionality of the deposit.

4.2. Topography

In the next step the topography has to be checked. For most systems, sharp edges and sharp walls are desired. For others, e.g. biosensors, a rough permeable surface may be useful. Pictures from optical and scanning electron microscopy give good information on the lateral position. Real topographical information, however, can only be obtained from three-dimensional techniques. Profiles could be measured with a steel nee-

dle applied with a constant force in the μ m range or with the tip of an atomic force microscope, even in the nm range. ICPs, however, are not hard enough for such measurements and are usually destroyed or shifted by the application of small forces. Therefore, atomic force microscopy can only be applied in the non-contact mode. Another possibility is laser profilometry which can be applied for reflecting surfaces with the typical resolution of an optical measurement of about 1 μ m. Fig. 8 shows an example of the topography of a polymer microstructure deposited into an anisotropic etch structure and detected with a laser profilometer. The structure is part of a microelectrode array produced by means of semiconductor processing technology, partially passivated with Si₃N₄. Due to the stability of Si₃N₄ against KOH etching [51], the aspect ratio of the non-passivated Si areas can be increased by anisotropic etching. Fig. 8 shows an empty channel with a depth of 17 μ m next to the almost rectangular structure filled with polymer. The square electrode was addressed with the focused laser beam, applying a potential of U(ACE) = 600 mV and a laser power of P = 0.2 mW. The addressed area was completely filled with polymer. The linescans, also recorded with the laser profilometer, exhibit a positive height of the polymer of about 10 μ m with a roughness of approx. 1 μ m for the recorded scan. The linescan measured along the empty channel and the filled microelectrode shows a total height of the polymer of 25 μ m. The edge has a



Fig. 7. Check of functionality of an ICP microstructure. Current and charge transients for the oxidation (at 0.6 V) and reduction (at 0 V) of a microelectrode covered with 1.5 μ m PANI. 1 M HCl, 25°.

steepness dz/dx = 0.3 caused by lateral growth of the polymer overlapping the passive layer (Si₃N₄).

4.3. Chemical analysis

For the functionality, the optical, electronic and chemical properties, the chemical composition of the microstructure is important. A check of these properties is necessary, since the mechanism of polymerization and growth may change with the introduction of reaction boundaries, especially in systems with high aspect ratio [19]. Moreover, special processes such as laser-induced polymerization may cause a slight change of composition.

Various surface analytical techniques are available which can be characterized by the type of chemical information, the depth of information and the local resolution. The most common methods are XPS, Auger and EDX. For example, EDX is a useful technique for elemental analysis with an information depth of 1 μ m. ESCA analysis is sensitive only for the upper 10 nm of the film. With imaging XPS, the lateral resolution has now been enhanced down to some μ m, but the analysis needs a long time. Fig. 9(b) shows a high resolution



Fig. 8. Laser profile of PBT deposited in an anisotropic etch structure at U(ACE) = 600 mV and $P_{\text{laser}} = 0.2 \text{ mW}$. The linescans on the left side show the horizontal profile of the empty anisotropic etched channel and the area completely filled with polymer. At the right side a perpendicular linescan along the whole system is shown.



Fig. 9. Characterization of N-implanted PBT films $(1 \times 10^{17} \text{ cm}^{-2}, 1.5 \text{ keV N}^+ > \text{PBT})$. (a) Schematic view of the honeycomb mask applied for structured ion implantation. (b–d) Laterally resolved investigations of the structured PBT surface. (b) Imaging XPS: N1 s map; white: 6% N. (c) Microscopic picture. (d) Photocurrent map obtained by laser excitation; black: 10 nA, white: 1 nA.

XPS image as an example: the mask bridge of $8 \mu m$ width is indicated, but not as clearly resolved as in the optical picture. An advantage is the possibility to analyse both chemical state and stoichiometry (10%). For example, it could be shown that the ESCA spectra of microstructured PBT are the same as those of macroscopic films. Auger spectra have a higher lateral resolution down to 100 nm, but the chemical state cannot be detected.

All these methods yield three different types of information which will be explained by PBT on partially implanted Si in Fig. 11:

-point analysis (check for foreign compounds),

-the qualitative image (see also Fig. 9(b) as an example),

—a line scan: from that the sharpness of the structure can be obtained, if the resolution of the analytical technique is sufficient.

4.4. Comparison of various methods

The examples given in the previous sections show that a lot of methods are available to check the properties of the microstructure, but each of them gives very different information. For technical information it is always necessary to combine several techniques, e.g. optical pictures with XPS and photoelectrochemical images by a laser beam. In the latter case the microstructure is scanned by a focused laser beam and the resulting photocurrent is measured. The resolution of that technique is in the range of a few μ m.

Fig. 9 shows such pictures with three different characterization techniques in the same scale. PBT poststructured by ion implantation is used as an example. All techniques more or less show accuracy of the honeycomb structure achieved by ion implantation. The sharpness of the picture is best in the optical microscope. The optical picture, however, only shows the different colours of the surface sites. The XPS image proves the different chemical compositions, while the laser scan reveals different photoelectrochemical properties of the implanted and not implanted parts of the surface. For details see Section 5.3 and [37].

5. Discussion and examples of microstructuring techniques

In this section we discuss the advantages and disadvantages of various techniques with respect to the type of intended microstructures, the principle of localization and the mechanism of growth. At first, direct structuring and pre- and poststructuring will be discussed. As an example of a technical process for multiple microsystems, the through-hole plating of printed circuit boards (PCB) is analysed. Finally, nanostructuring is briefly mentioned.

5.1. Laser induced polymerization

Light-induced polymerization can be applied on *n*type semiconductors at low anodic potentials. In the dark, anodic reactions are blocked, but light with an energy exceeding the band gap energy of the semiconductor generates photoholes which are necessary for the anodic reaction. Miniaturization can best be achieved by the focusing of a laser beam with simultaneous optical control. Therefore, it is a typical laboratory technique for single systems. By a programmed shifting of the substrate arbitrary figures without any symmetry can be produced. The spot size can be decreased down to $1 \,\mu m$, but secondary effects cause a broadening which increases with electrode potential and laser power. The profile is Gaussian. For sharper profiles and a smaller surface roughness, a combination with geometric blocking is useful. Negative or positive structures can be prepared, but the method depends on the production of electron/hole pairs in the semiconductor. Therefore, the thickness of light-absorbing polymer deposits is limited.

Extending first experiments by Yoneyama [23] we have demonstrated the deposition of polybithiophene in various microstructures with negative aspect ratios or the deposition without barriers with an almost

Gaussian profile of the deposit. In this paper we want to show the combination of various methods. For the application as conductors with the switching behaviour to insulators, a ternary system SC/Ins/ICP would be ideal. We decided to produce the system Si/SiO₂/PBT. Lines of SiO₂ were prepared on *n*-Si at anodic potentials under illumination in aqueous solution. Between two lines of SiO₂, a small line $(5-10 \,\mu\text{m})$ with only thin or negligible silicon oxide was left. Along this line, PBT was deposited in a second reaction. The result is a sharper PBT line embedded in an insulator. As can be shown by video microscopy, the lines could be switched from conducting to almost insulating behaviour which only needs a very small reduction charge of about 500 μ C for a PBT line which is 1 mm in length, 30 μ m broad and 1.5 μ m high.

Fig. 10 shows an example of SiO₂ lines directly written by laser-induced oxidation on silicon at U = 40 V and $P_{\text{laser}} = 150$ W. Due to the interference colour they exhibit, the layer thickness is estimated to be 27-53 nm [52]. Similar to the silicon nitride layers prepared by ion implantation (Fig. 11), no deposition should occur on these insulating regions, because holes are not available at the surface. The lateral extension of the SiO₂ structures was varied from 10 to 200 μ m dependent on applied potential and laser power. With increasing potential as well as increasing laser power the extension of the SiO₂ lines is getting larger. This can be explained by the lateral hole diffusion caused by a stronger band bending. The layer thickness was estimated by the observed interference colours and varies between 30 nm (brown) and 120 nm (blue). After the preparation process we combined these microstructures with conducting polymer patterns. It was observed that in both cases, lateral and normal scanning of the laser, the polymerization exclusively occurs on the remaining free silicon surface (Fig. 10) and not on the oxidized areas. The SAM picture as well as the laser profilometry in reflection mode clearly confirm the deposition on the surface not modified by laser induced oxidation (yellow parts). The blue regions represent the prepared silicon oxide patterns.

5.2. Pre-structuring of PBT by polymerization on an implanted silicon surface

If the localization of the polymerization reaction is difficult, a prestructured substrate may be used. This can be prepared by any other microprocess, e.g. localized oxidation, ion implantation or wetting or partially hydrophobic surfaces. The advantage is that the polymerization can be carried out without any masking technique for multiple systems on macroscopic substrates. Positive (catalysing) and negative (inhibiting) prestructuring must be distinguished. For example, anodic polymerization is impossible on insulators, e.g. polystyrene (PS). Microstructured deposition of PANI on PS was demonstrated by Jung as an example of positive prestructuring [28]. Using low-energy ion implantation, the surface was locally metallized. In a second process, aniline was polymerized on the contacted implanted part of the insulator. A combination with a limited wetting of the surface yielded an additional localisation of the process.

Polymerization of PBT on a prestructured *n*-Si is an example of negative prestructuring. Here the implantation was used to insulate the silicon surface. Fig. 11 shows pictures of scanning Auger analysis (SAM) of a flat PBT-microstructure on *n*-Si. The substrate was prestructured by low-energy ion implantation of N_2^+ (3



Fig. 10. Microstructuring using locally oxidized silicon as barriers. The lateral extension of the SiO₂ patterns can be varied between 10 and 200 μ m dependent on the applied potential and laser power. The presented lines were prepared at U = 40 V, $P_{\text{laser}} = 150$ W at dx/dt = 1 m/s in 1 M KMO₃. The polymerization only occurs on the non-passivated areas as can be shown in a scanning Auger image (right side).



Fig. 11. Result of polymer microstructuring using prestructuring of silicon surfaces. Top: SEM linescan and image of the implantation mask. Middle part: after the implantation the N_{KLL} image and the Auger point spectra (1) and (2) show a sharp distribution of Si/Si₃N₄. Bottom: after polymer deposition PBT can be detected in C_{KLL} and S_{LMM} images (bottom) and the composition of the deposited polymer can be determined (Auger point spectra (4), C:S = 3.8:1). The line scans on the left side show the sharpness of the final microstructure.

keV, dose = 2×10^{17} cm⁻²) into a freshly etched *n*type Si surface. N_2^+ was chosen due to the insulating properties of the formed Si₃N₄ even with layer thicknesses below 10 nm. XPS sputter profiles after an implantation time of 10 min demonstrated the thickness of 10 nm. To obtain laterally resolved structures a global implantation through a TEM mask was carried out. The result of implantation through a honeycomb structure is shown in Fig. 11. The line scan on the left side depicts a quantitative N_{KLL} analysis of the lateral structure, while the mean part gives the Auger image of the prestructured substrate. Finally, PBT was formed by light-induced polymerization, which takes place on the non-implanted edges only. The sharpness of the SEM picture of the mask (15 μ m, steep edge), the Auger spectra of the Si/Si₃N₄ and the final PBT microstructure decrease in this order. While the ion implantation causes a small broadening, the final PBT lines have a width of about 30 μ m. Auger spectra of special points show:

-1: Si and a usual surface contamination by C and O,

-2: Si and N signals only,

-3: Si, small N and the usual contamination after the polymerization process,

-4: S and C signals from the polymer only.

Pictures on the left side show a model of the surface state.

During the N_2^+ implantation process, insulating silicon nitride was formed as described in Section 3.3. Due to the insulating properties, no electron/hole pairs can be generated under illumination and therefore no polymerization should occur. On the other hand, the remaining silicon surfaces showed semiconducting properties, and microstructured PBT can be deposited by photocatalysis. The lateral extension of the polymer structure is given by geometry of the TEM mask used during the implantation process. By applying Auger measurements it is seen that the only compounds the modified wafer surface consists of are silicon nitride in the implanted area and pure silicon in the nonimplanted region. Fig. 11 shows an NKLL Auger mapping after implanting the silicon surface and the spots where the Auger spectra are recorded. After characterizing the modified silicon surface, it was locally covered by PBT. In the case of the honeycomb structure, we illuminated for 5 s with a 1 kW xenon arc lamp at a potential of U(ACE) = 550 mV. We also prepared some structures where only a few regions were modified by a focused laser beam. Some examples are

shown in [36]. The characterization by laser profilometry showed a height of $2 \mu m$ and a lateral extension similar to the implanted areas of $20 \,\mu\text{m}$. The atomic composition (C:S) was checked by SAM and XPS measurements. Fig. 11 shows the CKLL (left) and SLMM (right) Auger mapping as well as two-point spectra recorded in the modified and the non-modified region. It can clearly be shown by an atomic ratio of C:S = 3.8:1 that the deposited structures consists exclusively of PBT. These results were confirmed by locally resolved XPS measurements, where the composition within a micro-electrode, which is part of a special array [49] produced by means of semiconductor processing technology, was determined to be C:S:Cl = 4:1:0 [49]. Both the XPS and the SAM spectra are in very good agreement with results obtained for macroscopically deposited polymer on a gold electrode [54].

5.3. Post-structuring of polymer films

As an alternative to prestructuring, poststructuring may be useful. Due to the separation of the polymerization process and the microstructuring, pre- and poststructuring provide similar advantages. An homogeneous polymer film can be microstructured by laserablation, chemical attack, anodic oxidation, mechanical removal or ion implantation; the choice of the method depends on the final aim. If the surface only is to be modified, anodic oxidation or ion implantation is acceptable. If the ICP is to be completely removed, the other techniques are advantageous.

Fig. 9 can be used as an example of poststructuring. PBT was implanted by N_2^+ to change the electronic properties of the PBT surface. Fig. 9(b) and (c) show the chemical effect of the implantation and the optical picture respectively. The efficiency of the modification can be estimated from Fig. 9(c) the photocurrent is reduced by a factor of 10.

5.4. Deposition of polymers in microstructures with negative aspect ratio

Another example of prestructuring but without modifying the silicon surface is shown in Fig. 4(a). Therefore we apply different kinds of masks either for the deposition of single or periodic systems. Two different methods are known. One possibility for the preparation of periodic ICP systems is mentioned in [55]. The polymers were electrochemically deposited in a LiGA structure. After removing the mask a periodic system of ICP towers remains, which can be schematically described as shells (Fig. 1). The application of these structures as sensoric devices as well as for transport systems is proposed. Another approach by a laser-supported technique is shown in Fig. 12. Two



Fig. 12. Deposition of positive PBT microstructures applying different masks. On the left side, a photostructurable glass was applied and addressed with the focused laser beam for the deposition of a single two-dimensional microsystem. The right side shows the deposition of a positive periodic two-dimensional system.

kinds of masks were applied (Fig. 12(a, b)). For periodic systems we applied a LiGA structure of Ni (Fig. 12(a)) due to their high aspect ratio. Addressing the honeycomb with the laser beam, the reaction occurs within the determined reaction site. Every single cell can be filled with different kinds of ICP or metals [49]. As expected after removal of the mask no deposition is observed between the silicon substrate and the barrier (Fig. 12(c)). For the production of single polymer pillars a photostructurable glass [56] was combined with silicon. During the polymerization reaction the deposition of the ICP starts at the siliconelectrolyte interface and further growth occurs preferentially at the glass-electrolyte interface. We obtain towers with heights of 70 μ m, the roughness of the wall being determined by the glass. Due to the closed and rough structure inside they can be filled in a subsequent step with ion-sensitive materials for sensor applications.

5.5. Application of ICPs in the production of printed circuit boards (PCBs)

Until now, high-tech processes have been discussed, but modern mass production requires fast and cheap technologies. High-tech printed circuit boards (PCBs) consist of multilayer systems (up to 20 single layers) which have to be connected by conducting copper lines through holes to perform electronic contacts of the

Cu

MANOX

single layers (direct metallization process). The holes will be drilled mechanically. Then, the through-hole metallization of the PCBs has to be performed. The technology is necessary for holes of about 0.2 mm diameter and a height up to 1 mm, i.e. the aspect ratio A is about 5. Chemical copper deposition was not effective. A direct electrochemical metallization of these holes by copper deposition is impossible because of the insulating nature of the PCB base material, i.e. epoxy resin or polyimide. This insulator has to be activated by means of a conducting material. Several classical processes use carbon or platinum as a nucleation initiator, but the disadvantages of heavy metals, low conductivity or non-selective coatings (coating of the whole board) are obvious. Other disadvantages are the use of environmentally critical substances like formaldehyde. Finally, the process could be made faster, cheaper and non-polluting using ICPs, i.e. polypyrrole or polythiophene derivatives.

A direct metallization process (DMS-E) developed by Hupe et al. [2] consists of a localized chemical surface modification of the insulator by KMnO₄. The deposited non-stoichiometric MnO_x (exactly $MnO_{1.7}$) is used to polymerize a thiophene derivative which has electrical contact to the neighbouring Cu. On top of the polyethylendioxythiophene (PEDT) Cu can be cathodically deposited.

Fig. 13 shows the most important parts of an engineering diagram and a model of the hole on top. For

CUPROSTAR



DMS-E

PEDT

Fig. 13. Model and engineering diagram of relevant processes Manox, DMS-E and Cuprostar for through-hole plating of printed circuit boards.

full details see [57, 58]. In the 'Manox process step' the epoxy resin surfaces are oxidized and covered with the reduction product, a compact manganese oxide layer of about 1 μ m thickness. The copper surfaces, however, are passivated by KMnO₄, and a small amount of MnOx is deposited. Then the manganese oxide is dip-coated with the thiophene monomer, and the polymerization reaction is started in acidic solution (H_yA). The polymer is formed in the conducting (oxidized) state and the anions A^{y-} are incorporated in analogy to electrochemically polymerized films. A great advantage is the reduction of the process time and the high surface conductivity (about 0.1 mS of the polymer in the conducting state vs 0.001 mS for palladium particle deposition).

In terms of Fig. 1 the relevant process step consists of the ICP deposition in a multiple, non-periodic system with a negative aspect ratio of 1:5. The rotational symmetry of the hole is not important for the process. The intermediate system can be classified as lateral M/ICP/M, but the final system as vertical I/ICP/M. According to Fig. 2, the localization of the polymerization is achieved by MnO_x which is locally deposited with a limited redox charge. Thus, the microstructuring is in fact determined by the prestructured substrate obtained by the Manox process.

The polymerization reaction itself is an interesting electrochemical solid–solid–liquid reaction which is explained in Fig. 14. The anodic oxidation of EDT takes place at the MnOx electrode at high potentials

 $n-\text{EDT} + m(z/y) \text{ H}_y \text{A} \rightarrow$ (EDT)_n^{mz+} + m(z/y) $A^{y-} + 2n \text{ H}^+ + (mz+2n) \text{ e}^-.$

This is achieved by cathodic reduction of MnO₂:



Fig. 14. Schematic diagram of the transfer and transport reactions during the formation of PEDT on $MnO_{1.7}$.

 $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O.$

Therefore, ions have to be transported through the solid phases: H^+ to the MnOx and Mn^{2+} to the electrolyte. In fact, transport reactions are sufficiently fast: the MnOx is totally reduced and Mn is completely eliminated from the surface (see Fig. 12). It seems that the thickness of the PEDT film does not limit the reaction very much since the thickness increases homogeneously up to 200 nm.

5.6. Nanostructures with ICPs

ICPs are of great interest for special nanostructures, e.g. in porous aluminium oxide or silicon. Nanotubes of Al₂O₃ were used for a template synthesis of polyaniline fibers with increased conductivity [19]. In p-Si, deep nanopores can be formed with an aspect ratio A = 100 and more. Filling of pores was of great interest for luminescent devices. Problems arise from the nucleation site as was discussed in Fig. 3. Since the band gap energy of porous Si exceeds that of bulk Si, the larger concentration of holes at the bottom allows a localized start. On the other hand, the anodic polymerization is blocked by thin films of SiO₂ which form in aqueous solution with about 0.5 nm/V. Special conditions which allowed the polymerization are given in [28]. The final structure obtained is a ternary system Si/SiO₂ /PBT.

6. Conclusions

The examples show that microstructuring of ICPs is possible by various simple or sophisticated processes. The choice of the process and the final properties depend very much on the characteristics of the substrate, especially its conductivity (Fig. 1). The other important factor is the required quality and the allowed price of the product. There is a large difference between laboratory techniques for single systems and technological processes for multiple systems. The sharpness of the structure depends very much on primary and secondary effects of the localization technique (Fig. 2).

Table 2 summarizes some examples presented here and discussed in the literature. Non-electrochemical techniques with insulating polymers are not considered here. The models (second column) give the intended structure of the polymer (black) on a semiconducting (grey) or metallic (white) substrate. Data on the aspect ratio A, edge sharpness ES, width W and accuracy or misfit M depend very much on the mask characteristics. They refer to the figures of this paper or the special data given in the reference. They do not give principal limitations of the method. In various cases,

e.g. examples 4 and 5, W can be decreased down to $1 \,\mu\text{m}$. Moreover, accuracy is improved by adjusting the polarization time, e.g. in example 4. The edge sharpness could be defined by the steepness dz/dx. This can be obtained from profilograms such as shown in Fig. 8. Such data, however, are usually not available. Therefore, we estimated values of ES from the optical or other images. We define the misfit M by the distance of the edge from the mask border. For example, Fig. 11 proves that PBT structures are much broader than the walls of the mask. The positive misfit $M = + 7 \mu m$ is due to the growth of a thicker film. In case of thinner films, this misfit can be diminished or even be negative. The sign of the aspect ratios A can change from the preparation to the final product, e.g. in examples 2 and 7 the ICP is prepared in negative structures (A < -1) but after mask removal A becomes positive.

Table 2 shows some principal effects of different processes. Maskless formation of positive structures always produce surfaces similar to spheres or Gaussian profiles. The typical roughness is that of polymer surfaces, $\pm 5-10 \mu$ m. The roughness can be avoided by the application of smooth boundaries. As it is shown in Fig. 12 the ICP reproduces the wall surface very well. However, the inner part of the microstructure is not filled. This effect of a shell or tube formation can be used for special aims [57]. The misfit of the mask border can be diminished by process parameters such as illumination time and intensity and electrode potential. They determine the rate of nucleation, growth and the overlap of borderlines.

The transition from micro- to nanosystems seems to be continuous with exception of all photon-dependent processes. Due to light diffraction $1 \mu m$ presents the lower limit of all direct-writing optical techniques. The chemical and electronic properties of the ICP microstructures are in general similar to macroscopic samples, but exceptions in the nm range are due to directed growth [19].

Acknowledgements

The support of this work by the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie is gratefully acknowledged.

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