

**INSTITUTE IV:
SURFACE SCIENCE
AND
CORROSION**



Institute IV: Surface Science and Corrosion	121
General	123
Staff	124
Laboratory and Offices	125
Teaching	126
Graduates	128
Research Projects / Co-operation with Industry	129
Publications (Papers, Books, Conference Proceedings)	144
Conferences, Seminars and Invited Lectures	146
Seminar Presentations by External Lecturers	147
Activities in Professional Societies, Editorial Boards, Advisory and Organization Committees	148
Patents	148



Institute IV: Surface Science and Corrosion

General

The Institute of *Surface Science and Corrosion* within the Department of Materials Science and Engineering targets basic and applied aspects of surfaces and interfaces, electrochemistry and corrosion science. The Institute supports the transfer of fundamental knowledge into modern surface technology and promotes advancements leading up to technical applications. Due to this highly transdisciplinary approach, the scientific staff is recruited from various faculties and consists typically of physicists, chemists and materials science engineers.

The primary scientific objective is the modification of surfaces and interfaces of materials in order to improve their technological properties. Emphasis is placed on the reactivity and functionalization of metal- and semiconductor surfaces. On one hand, mechanisms of undesired deterioration of materials, such as metallic corrosion, are being studied to extract key factors for failure prevention. Research in this field deals particularly with aqueous corrosion, high temperature corrosion, stress corrosion cracking and experimental modeling of corrosion processes using PVD or CVD deposited thin metal and oxide films of a highly defined nature.

On the other hand, defined and controlled material structuring processes are developed for patterning and functionalizing surfaces. Particular interest focusses on processes in the micro- and nanoscale. A main aim of the effort is to explore new pathways to achieve selective chemical or electrochemical nanogrowth or -patterning of materials on locally sensitized single crystal semiconductor surfaces. Typically, sensitization is carried out by a direct writing process using e-beam, focused ion beam (FIB) or scanning probe microscopy (AFM/STM). At these locally activated surface locations a subsequent chemical or electrochemical reaction is triggered selectively leading to the nanosize material or functionality.

Teaching activities cover a wide range of subjects in surface science and corrosion engineering such as physical chemistry of surfaces and interfaces, electrochemistry of semiconductors and metals as well as modern aspects of micro- and nanotechnology. Additionally, specific subjects of direct industrial relevance like corrosion phenomena in practice are taught by colleagues from the industry.



Staff

Teaching Faculty:

Prof. Dr. Patrik Schmuki (Head of Institute)

Prof. Dr. Elsbeth Wendler-Kalsch (retired since 05/2001)

Prof. FH Dr. Ralf Feser

PD Dr. Gernot Grötsch, lecturer from industry (Intra Serve Hoechst, Frankfurt)

PD Dr. Bernd Stellwag, lecturer from industry (Siemens AG, Erlangen)

Secretary:

Mrs. Barbara Scholz

Administration, Teaching and Research Scientists:

Dr. Hermann Kaiser (Academic Director)

Dr. Werner Auer (Chief engineer)

Dr. Stefan Maupai

Dr. Irina Kobanenko

Research Associates:

Dipl.-Chem. Lionel Santinacci

Dipl.-Chem. Thierry Djenizian

Dipl.-Ing. Udo Schlierf

Technical Staff:

Anja Friedrich

Ingeborg Tontsch

Helga Hildebrand

Italo Wassermann

Martin Kolacyak

Karl Werner

Hans Rollig

Visiting Graduate Students & Scientists:

Ludovic Achour, University of Lyon, France

Khalid Khairoun, University of Marseille, France

Mourad Kallaoui, University of Marseille, France

Radim Beránek, Institute of Chemical Technology, Prague, Czech Republic

Junji Sasano, Institute of Advanced Energy, Kyoto University, Japan



Laboratory and Offices

Accommodation:

Total space: 1 328 m²

Laboratory space: 717 m²

Main Equipment:

Surface Analysis and Microscopy

- SEM incl. EDX
- AES/XPS
- XPS/UPS/ISS incl. sample transfer into a UHV-preparation chamber
- UHV-preparation chamber (cleaning by sputtering, heating) incl. SIMS, AES; sample transfer into a reaction chamber
- SAM incl. fracture apparatus and transfer vessel to XPS
- XRD
- Optical microscopes

Optical Spectroscopy

- FT-IR spectroscopy
- Raman spectroscopy
- Spectroscopic ellipsometry

Scanning Probe Techniques

- STM/AFM (non-contact) / friction microscopy in air and in electrolytes
- STM/AFM for electrochemical investigations

Electrochemical Characterization

- Potentiodynamic and potentiostatic methods
- Electrochemical impedance spectroscopy
- Rotating ring-disc electrode
- Kelvin-Probe

High Temperature Oxidation

- Furnaces equipped with thermogravimetric and volumetric detection

PVD

High-vacuum-vapour deposition system (electron-beam, thermal, Magnetron-sputtering)

Materials Testing

- Temperature-humidity and salt-spray chambers
- Stress corrosion cracking testing facilities



Teaching (weekly hours)

Winter Semester 2000/2001 (WS 2000/2001):

Basic Studies (Grundstudium, till Vordiplom):

Lectures:

- Materials science III, 2 h (P. Schmuki)
for students of materials science and engineering
- Materials science II, 2 h (E. Wendler-Kalsch)
for chemical engineers

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

- Physico-chemical fundamentals of corrosion and surface technology, 2 h (P. Schmuki)
for students of materials science and engineering
- Electrolytic corrosion, part I, 2 h (P. Schmuki)
with exercises, 2 h (S. Maupai)
- Electrochemical methods, 2 h (H. Kaiser)
- Practical surface technology, 1 h (E. Wendler-Kalsch)

Seminars:

- Current research topics, 2 h (P. Schmuki)

Laboratory Courses:

- Advanced laboratory course: Corrosion and surface technology, part I



Summer Semester 2001 (SS 2001):

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

- Kinetics of electrochemical reactions (P. Schmuki)
for students of materials science and engineering
- Electrolytic corrosion, part II, 2 h (H. Kaiser) with exercises, 1h
- Interfacial chemistry, 2 h (P. Schmuki)

Seminars:

- Current research topics, 2 h (P. Schmuki)

Laboratory Courses:

- Advanced laboratory course: Corrosion and surface technology, part II

List of Optional Lectures offered during WS 2000/2001 and SS 2001

(A total of 7 h weekly is required for majors):

- Surface analysis, 1 h (P. Schmuki)
- Corrosion and corrosion protection in power plants, 2 h (B. Stellwag)
- Corrosion of technical materials in industrial plant buildings, 1 h (R. Feser)
- Tribology, 1 h (H. Kaiser)
- High temperature corrosion, 1 h (W. Auer)
- Corrosion in the chemical industry, 1 h (G. Grötsch)
- Corrosion monitoring and prediction in industrial plants, 1 h (B. Stellwag)
- Stress-corrosion cracking, 1 h (E. Wendler-Kalsch)



Graduates

Diplom Thesis:

- **Achour, Ludovic**
e-beam induced C-deposition based on a negative resist for electrochemical reactions
- **Khairoun, Khalid**
e-beam induced carbon deposition for selective porous formation
- **Kallaoui, Mourad**
Selective electrochemical deposition of CdS onto semiconductors surfaces

Doctorate Theses:

- **Eckstein, Gerald** (July 1997 till February 2001)
In-situ rastertunnelmikroskopische Untersuchungen zur selektiven Korrosion von niedrigindizierten $\text{Au}_3\text{Cu}(hkl)$ -Legierungseinkristallen
- **Plagge, Andreas** (January 1997 till February 2001)
Neuartige Cellulosepolymere
- **Gerold, Bodo** (September 1996 till January 2001)
Gefüge- und Eigenschaftsänderungen von FeCr-Legierungen mittels Excimerlaser-Belichtung
- **Maupai, Stefan** (September 1997 till May 2001)
Elektrochemische Nanostrukturierung von Legierungsoberflächen durch spitzen-induzierte Metallabscheidung: eine *in-situ* STM-Studie



Research Projects / Co-operation with Industry

Overview

The Institute of Surface Science and Corrosion has broad research interests ranging from very fundamental studies of elementary processes of surface modification or corrosion to technological studies:

- Aqueous corrosion
- High temperature corrosion
- Surface modification by ultrathin inorganic layers
- Electrochemical nanotechnology
- Porous semiconductors

Materials under investigation range from semiconductors to structural materials like steel or galvanized steel and modern light-weight alloys. Many research projects are based on an international collaboration.

List of Research Projects

Research project: Sensitization of semiconductor surfaces for totally selective electrochemical reactions

Principal investigator: P. Schmuki

Responsible researcher: L. Santinacci

Funded by: Swiss National Science Foundation

Beginning of project: July, 1999

Duration: 3 years

Research project: AFM induced nanopatterning of Si surfaces

Principal investigator: P. Schmuki

Responsible researcher: L. Santinacci

Funded by: Swiss National Science Foundation

Beginning of project: July, 1999

Duration: 3 years

Research project: Electron-beam induced nanomasking for metal electrodeposition on semiconductor surfaces

Principal investigator: P. Schmuki

Responsible researcher: T. Djenizian

Funded by: Swiss National Science Foundation

Beginning of project: July, 1999

Duration: 3 years



Research project: Nanostructured Materials by Selective Surface Activation using Ion Implantation

Principal investigator: P. Schmuki

Responsible researcher: A. Spiegel

Funded by: COST 523

Beginning of project: July, 1999

Duration: 3 years

Research project: Nanostructuring of alloy-surfaces with in-situ scanning tunneling microscopy

Principal investigator: P. Schmuki, A. Dakkouri

Responsible researcher: S. Maupai

Funded by: DFG-Schwerpunkt: "Grundlagen d. elektrochem. Nanotechnologie"

Beginning of project: July, 1997

Duration: 6 years

Research project: AFM induced nanopatterning of silicon surfaces

Principal investigator: P. Schmuki

Responsible researcher: L. Santinacci

Funded by: DFG-Schwerpunkt: "Grundlagen d. elektrochem. Nanotechnologie"

Beginning of project: March, 2001

Duration: 2 years

Research project: Laser Assisted Nickel Deposition onto Porous Silicon

Principal investigator: P. Schmuki

Responsible researcher: J. Sasano

Funded by: Kyoto University

Beginning of project: May, 2001

Duration: 2 years

Research project: Electrochemical Surface Modification of III-V Materials

Principal investigator: P. Schmuki

Responsible researcher: U. Schlierf

Funded by: BMBF

Beginning of project: March, 2001

Duration: 2 years

Research project: Chemical modification of semiconductor surfaces

Principal investigator: P. Schmuki

Responsible researcher: L. Santinacci

Funded by: Ecole Polytechnique Paris

Beginning of project: March, 2001

Duration: 2 years

Research project: Tribocorrosion

Principal investigator: P. Schmuki

Responsible researcher: T. Korn

Funded by: Industry

Beginning of project: December, 2001

Duration: 3 years



Selected Research Highlights

Electron-beam induced nanomasking for metal electrodeposition on semiconductor surfaces (T. Djenizian, L. Santinacci, P. Schmuki)

Lithography using beams of electrons is one of the most employed approach used for integrated circuit fabrication. In technological applications electron beam (e-beam) systems play two vital roles: they are used to fabricate masks for optical exposure systems (as well as x-rays systems) and create ultrasmall features for very high performance devices. The principle is mainly based on the exposure of resists (e.g. PMMA) to e-beam. In research, however, exploratory of direct processes have been investigated to generate ultrasmall linewidths on semiconductor surfaces as well as to create 3D nanostructures in the nm range using e-beam induced deposition (EBID) reactions [1-3]. In this approach, the e-beam activates gaseous precursor species introduced into the vacuum chamber of the e-beam instrument leading to a solid deposit at the irradiated surface and consequently a cone of resist builds up at the point of impact of the e-beam. Typically the precursor vapor species used for EBID are metallorganic compounds.

The residual hydrocarbons issued from the pump oil can also be used as precursors species. It has been widely reported that deposition of carbon occurs in vacuum systems pumped with untrapped oil diffusion pumps. Indeed this contamination resist is formed when the e-beam “cracks” the thin layer of hydrocarbon molecules condensed at the sample surface. In that case, the hydrocarbon molecules adsorbed on the surface react under e-beam to form an amorphous structure of carbon, more specifically a layer of diamond-like carbon (DLC). Such contamination writing has been successfully applied as a mask using ion milling [4] or to fabricate devices like microbridge SQUIDs [5]. Recently this technique has been used to achieve high definition patterning of semiconductor surfaces for subsequent metal electrodeposition [6-8]. In this work it has been showed how to use C-masks produced by contamination writing in a SEM to suppress completely and selectively metal electrodeposition at treated surface locations.

In order to study in details e-beam induced carbon deposition reactions, a series of ten lines was deposited using different electron doses in a JEOL 6400 SEM. Subsequently, the lines were analysed by various techniques including AFM, AES and Raman spectroscopy (Fig. 1).

Due to the predominant amount of C sp³, it has been demonstrated that such carbonaceous deposits in the order of only few nm in thickness can be sufficient to achieve a negative resist effect [6,7]. Figure 2a shows a SEM image of a sample carrying the C-line pattern

previously described after a potentiostatic experiment consisting of applying a cathodic potential (-1.8 V vs (Ag/AgCl)) for 30 s. From this picture it is apparent that the surface is

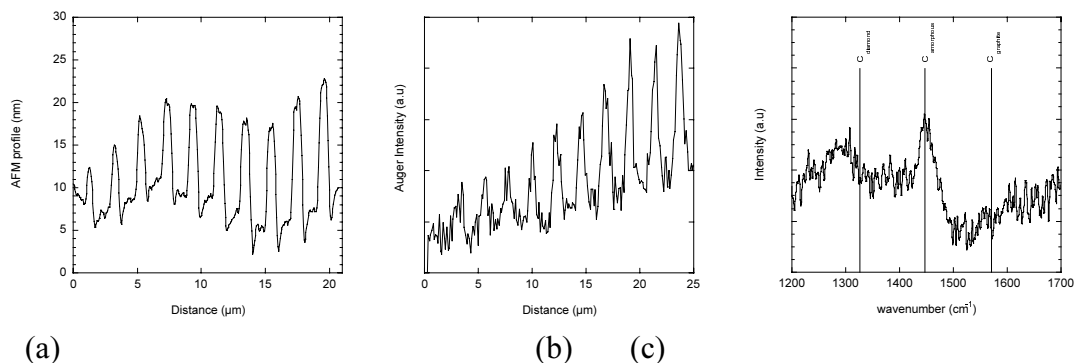


Fig. 1.: AFM profile of 10 C-deposits produced under a 5 kV e-beam for increasing electron dose exposures from the left to the right (a), AES line scan for C across the lines (b) and typical Raman spectrum of the C-deposits (c).

entirely covered by a Au deposit except for lines that correspond to the location of the carbon lines. Therefore it is evident that C-deposit acts as a mask for the electrodeposition of metal and constitutes a negative resist if a sufficient contamination layer is present. In order to explore the lower size limit of the deposition process, a series of experiments was performed by minimizing the distance between parallel C-lines. Figure 2b shows an example of the best resolution attained so far where two arrays of perpendicular C-lines were produced under a 5 kV e-beam. The space between lines is reduced from the left to the right and from the top to the bottom. C-deposits lead to confined Au clusters with the smallest size in the order of 30 nm.

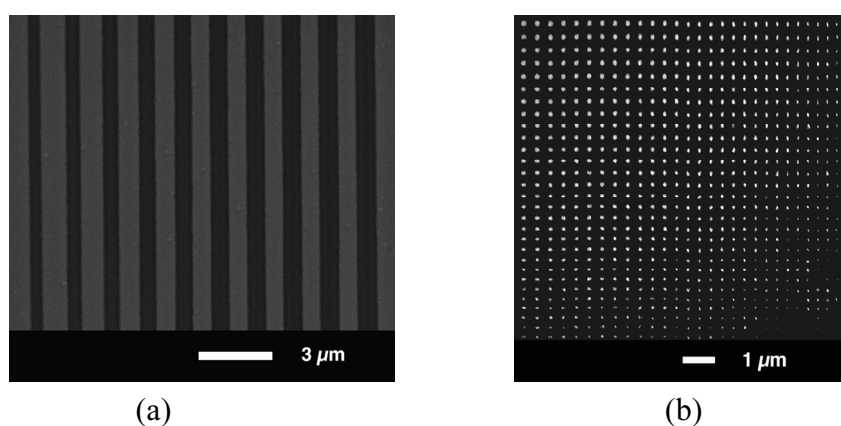


Fig. 2.: SEM image of a sample carrying the C-line pattern previously described in Fig.1 after a potentiostatic experiment consisting of applying a cathodic potential (-1.8 V vs (Ag/AgCl)) for 30 s (a). Fabrication of Au clusters by decreasing the space between two arrays of perpendicular C-lines (b).



Recently, this technique has also been successfully used to produce selective CdS on silicon [8] and to fabricate porous silicon [9,10] opening new perspectives for the patterning of surfaces of a wide large palette of materials in the sub-100 nm range.

References:

- [1] H. W. P. Koops, J. Kretz, M. Rudolph, M. Weber, G. Dahm, and K. L. Lee, *Jpn. J. Appl. Phys.*, **33**, Part 1, 12B, (1994) 7099
- [2] M. Komuro, and Hiroshima, *Microelectronic engineering*, **35** (1997) 273
- [3] N. Miura, H. Ishii, J. Shirakashi, A. Yamada, and M. Konagai, *Applied Surface Science*, **113/114** (1997) 269
- [4] A. N. Broers, W. W. Molzen, J. J. Cuomo, and D. Wittels, *Appl. Phys. Lett.*, **29** (1976) 596
- [5] P. Chaudari, A. N. Broers, C. C. Chi, R. B. Laibowitz, E. Spiller, and J. Viggiano, *Phys. Rev. Lett.*, **45** (1980) 930
- [6] T. Djenizian, L. Santinacci, and P. Schmuki, *Appl. Phys. Lett.*, **78** (2001) 2940
- [7] T. Djenizian, L. Santinacci, and P. Schmuki, *J. Electrochem. Soc.*, **148** (2001) 197
- [8] T. Djenizian, B. Petite, L. Santinacci, and P. Schmuki, *Electrochim. Acta*, **47** (2001) 891
- [9] T. Djenizian, L. Santinacci, and P. Schmuki, *Surf. Sci.*, submitted (2001).
- [10] T. Djenizian, L. Santinacci, and P. Schmuki, *Appl. Phys. Lett.*, submitted (2001).

Investigations on the Passivity of Iron in Borate and Phosphate Buffers, pH 8.4

(I.V. Kobanenko, P.Schmuki)

In the present work surface analytical experiments (XPS and AES) on the passive film on iron have been carried out, in order to refine or verify models previously suggested for reaction mechanisms of passive films on iron [1-5]. Of a special interest is to elucidate the influence of solution chemistry (especially a comparison of borate and phosphate buffer, pH 8.4) on the nature of the passive film on Fe, and the mechanism of the reduction of the passive film.

The nature of the passive film (chemical composition and thickness) depends on the buffer solution used for passivation, even at an identical pH value. In the passive film formed in phosphate buffer, pH 8.4, a significant amount of phosphates is found in the outer part of the film. Boron species, however, are not significantly incorporated in the passive film formed in borate buffer (Fig. 3).

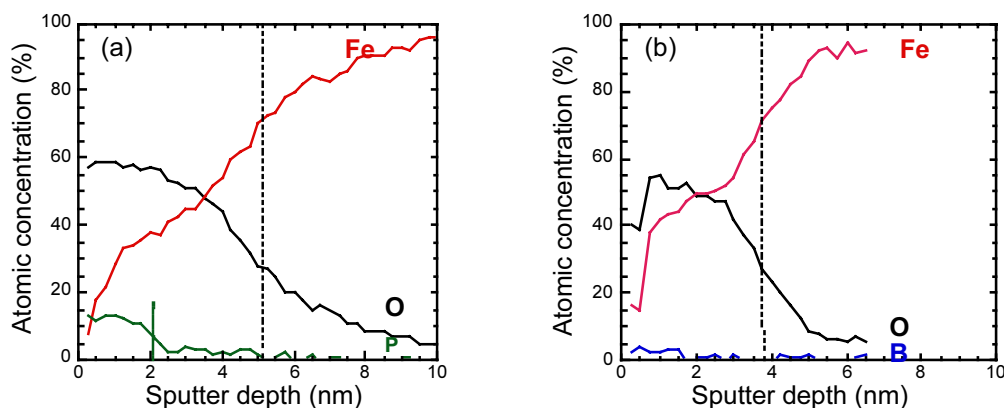


Fig. 3: AES depth profiles for passive film formed on iron at +0.800V (SCE), a) in phosphate buffer; b) in borate buffer.

The mechanism of the reduction of the passive film depends strongly on the electrolyte composition. In both solutions, the current/time curves (Fig. 4) show characteristic peaks during the reduction time. In borate buffer, cathodic polarization leads to reductive dissolution of the passive film whereas in phosphate buffer the passive film is converted into metallic iron without dissolution. This conversion of the passive film into metallic iron proceeds via a formation of an intermediate Fe (II) phosphate layer. The function of the phosphates therefore is to capture the iron (II) species formed in the reduction reaction (very low solubility of Fe (II) phosphates) and therefore to hinder reductive dissolution.

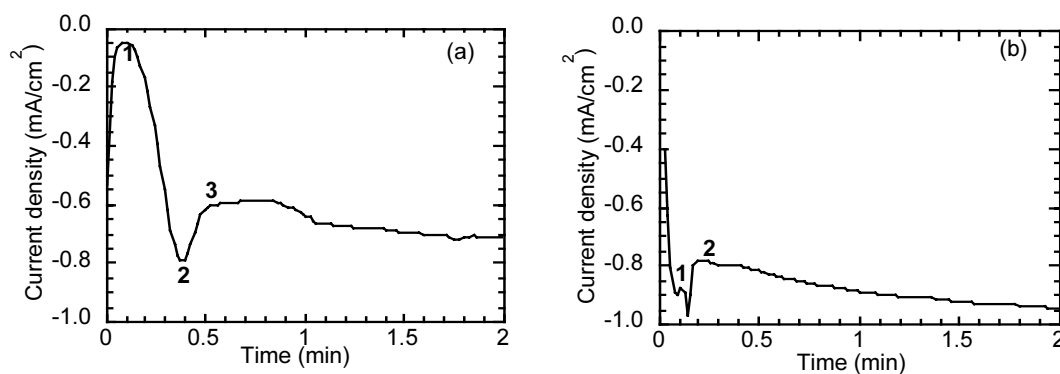


Fig. 4: Current/time-behaviour of Fe during a potentiostatic step from 0.8V (SCE) to -1.2V (SCE): a) in phosphate buffer, b) in borate buffer.

The conversion of the passive film into metallic iron via the intermediate phosphate film seems to proceed laterally inhomogeneously over the sample surface.

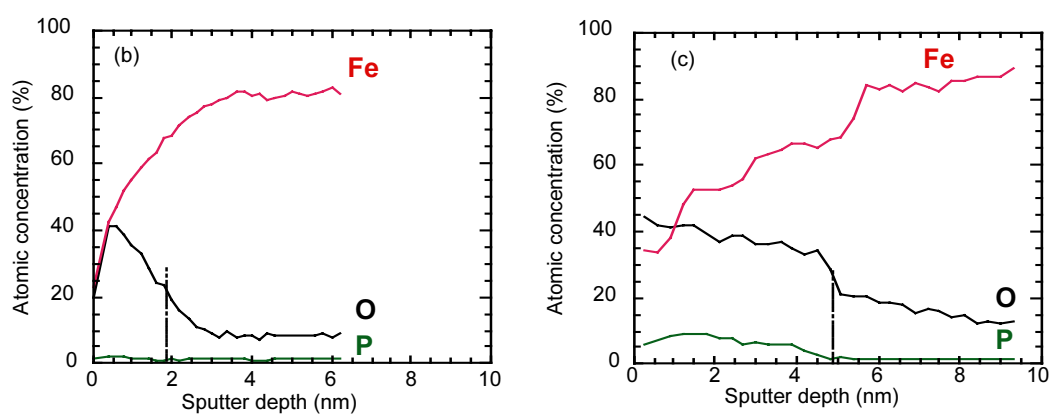
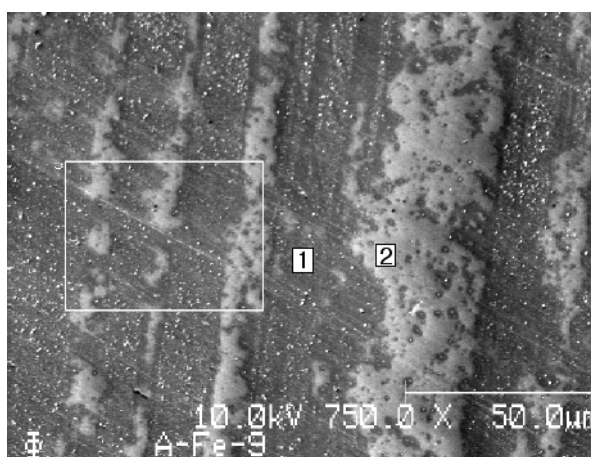


Fig. 5: Fe polarized at -1.2V (SCE) in phosphate buffer (after passivation at +0.800V (SCE)) removed from electrolyte at point 2 in fig.2a: a) SEM image of the surface, b) AES depth profile at location 1; c) AES depth profile at location 2.



This suggests that the reaction starts at certain active sites of the surface, and then the reaction front spreads over the sample surface. In order to clarify the role of phosphate species in the reduction process, the following experiments were carried out: Fe was polarized anodically in phosphate (borate) buffer and after that cathodically reduced in borate (phosphate buffer) buffer. Similar current/time curves for this treatment and SEM images of samples were found. The current shows the same characteristics peaks during reduction, which are the same as in the case if the whole treatment was carried out in phosphate buffer. The SEM image (Fig. 5 a) shows the presence of different regions on the samples, which correspond to a native passive film (2 nm) and to a phosphate layer (5-7 nm). Thus the cathodic reduction mechanism of the passive film on iron is determined by the presence/absence of phosphate species in the system. In the presence of the phosphate species, cathodic reduction of the passive film always proceeds through the intermediate stage of phosphate compound formation. The phosphate compound required for this type of reduction mechanism can be formed either during anodic polarization or during cathodic reduction.

References:

- [1] A. J. Davenport, J. A. Bardwell, and C. M. Vitus, *J. Electrochem. Soc.*, **142**, 721 (1995).
- [2] L. J. Oblonsky, A. J. Davenport, M. P. Ryan, H. S. Isaacs, and R. C. Newman, *J. Electrochem. Soc.*, **144**, 2398 (1997).
- [3] S. Virtanen, P. Schmuki, A. J. Davenport, and C. M. Vitus, *J. Electrochem. Soc.*, **144**, 198 (1997).
- [4] P. Schmuki, M. Büchler, S. Virtanen, H. S. Isaacs, M. P. Ryan, and H. Böhni, *J. Electrochem. Soc.*, **146**, 2097 (1999).
- [5] P. Schmuki, S. Virtanen, H. S. Isaacs, M. P. Ryan, A. J. Davenport, H. Böhni, and T. Stenberg, *J. Electrochem. Soc.*, **145**, 791 (1998).

***AFM induced nanopatterning of Si surfaces*** (L. Santinacci, T. Djenizian, P. Schmuki)

Patterned metal layers are incorporated into integrated circuits for electrical conductivity, junction devices, connection pads, and optical attenuators (in optodevices). These are usually fabricated by depositing the metal (using chemical vapor deposition or electroplating) over the entire surface and then removing the undesired metal by etching the pattern through a mask, by chemical mechanical polishing, by metal evaporation over a patterned resist and lift off or by electroless plating through a mask [1]. For high resolution patterning, most frequently electron-beam, X-ray or ion-beam lithography are used (see, e.g., [2-4]). Other techniques consist of direct patterning such as *in-situ* modification of surfaces by scanning tunneling microscopy [5]. An alternative approach to achieve “patterned” metal deposition has been presented before [6]. It is based on an electrochemical process, where the “maskless” patterning results from the electrochemical sensitivity to intentionally created surface defects using focussed ion beam implantation.

The present work investigates the use of AFM-scratching method on silicon as an approach for selective metal (e.g., Au, Cu and Pd) deposition. The first step of this technique was the introduction of mechanical defects by AFM-scratching onto *p*- and *n*-type silicon, see Fig. 6. Single-crystalline diamond coated tips mounted on cantilevers with high spring constant were used in contact mode on a traditional AFM. Well-defined scratches were obtained and protrusions along the sides of the grooves were observed exhibiting a surface deformation induced by the mechanical treatment and indicate the presence of stress. The grooves show a V-shape and their dimensions vary between 7 nm to 40 nm in depth and between 50 nm to 300 nm in width depending on the applied parameters (normal load, number of cycles or scan velocity). Intrinsic properties of the substrate like doping concentration and crystallographic orientation have also an influence on the groove morphology.

In a second step, metal electrodeposition onto Si surface was carried out by applying a cathodic potential step. Higher reactivity of the scratched area was observed showing that the nano-scratches act as deposition activators. However, total selectivity of the process can only be achieved if scratching is performed through an oxide layer (native oxide or thermal oxide film) present on the surface. After scratching, two zones were established on the silicon surface, one passive (oxide layer) and one active (within AFM-scratches). By this approach nanoscale metallic lines could successfully and selectively be plated onto the *p*-type and *n*-type silicon substrates.

Parameters like scratch morphology as well as duration and voltage of the potential step used for electrodeposition were studied in this work. The metallic lines were characterized by different microscopies (AFM and SEM) and AES spectroscopy, see Fig. 7. The work therefore demonstrates a new and direct technique for semiconductor patterning and functionalization by electrodeposition.

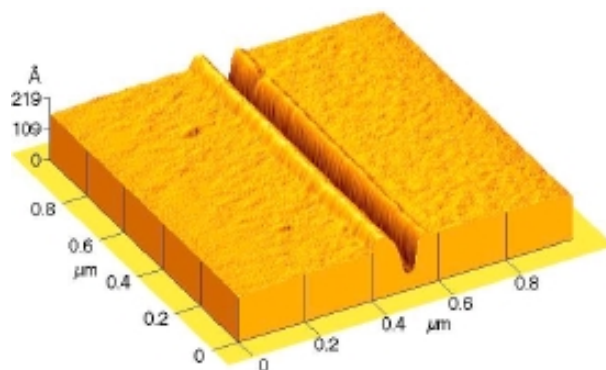


Fig. 6: AFM 3D-view of an AFM-scratch in *p*-type Si (100) performed with a normal load of 14 μN .

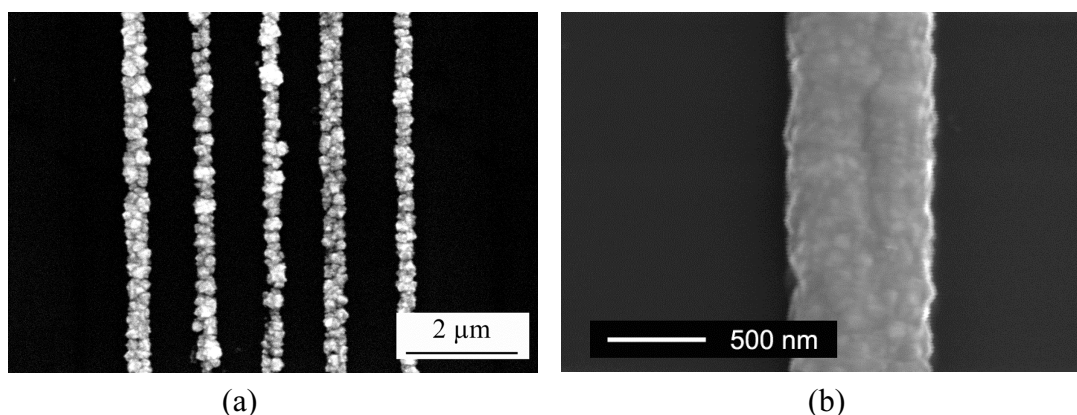


Fig. 7: (a) SEM picture of sample carrying 4 AFM-scratches (200 nm wide). Pd was deposited by potential step at -400 mV for 60 s in acidic solution. (b) SEM picture of sample carrying AFM-scratches (100 nm wide). Cu was deposited by potential step at -500 mV for 10 s in acidic solution.

References:

- [1] S. Furukawa and M. Mehregany, *Sens. Actuators A*, 56 (1996) 261.
- [2] A. N. Broers, *IBM J. Res. Develop.*, 32 (1988) 502.
- [3] J. R. Sheats and B. W. Smith, *Microlithography: Science and Technology*, Marcel Dekker Inc., New York (1998).
- [4] P. Rai-Choudhury, *Hanbook of Microlithography, Micromachining, and Microfabrication*, SPIE Press, Bellingham (1997).
- [5] D. M. Kolb, R. Ullmann, and T. Will, *Science*, 275 (1997) 1097.
- [6] P. Schmuki and L. E. Erickson, *Phys. Rev. Lett.*, 85 (2000) 2985.

Nanostructured Materials by Selective Surface Activation using Ion Implantation

(A. Spiegel, P. Schmuki)

It has been shown before that focused ion beam (FIB) induced damage on *p*-Si can be used to trigger selective electrochemical reactions [1]. Our research has shown that at semiconductor defect sites the local Schottky barrier breakdown potential is significantly altered when compared to the intact surface. This difference can be used to trigger selective electrochemical reactions at the defect sites only. Hence, maskless metal deposition in the sub-micrometer range becomes possible and may offer new methods for nanostructuring semiconductors [2].

For ion implantation we used the FIB system installed at PSI. We have been working with a Ga ion sources built inhouse. Ions were implanted with an energy of 30 keV and implant fluences were varied over 4 orders of magnitude (10^{12} - 10^{16} ions/cm²); the influence of fluence on electrochemical behaviour was investigated. All electrochemical experiments were carried out using a standard three-electrode set-up (sample as working electrode, Pt-counter electrode, standard calomel reference electrode -SCE) under potentiostatic or -dynamic conditions. Different electrolytes were used (0.01 M CuSO₄ + 0.05 M H₂SO₄ (+ 0.1mM BTA) for Cu deposition under varying electrochemical conditions (time, potential, and scanning speed were varied).

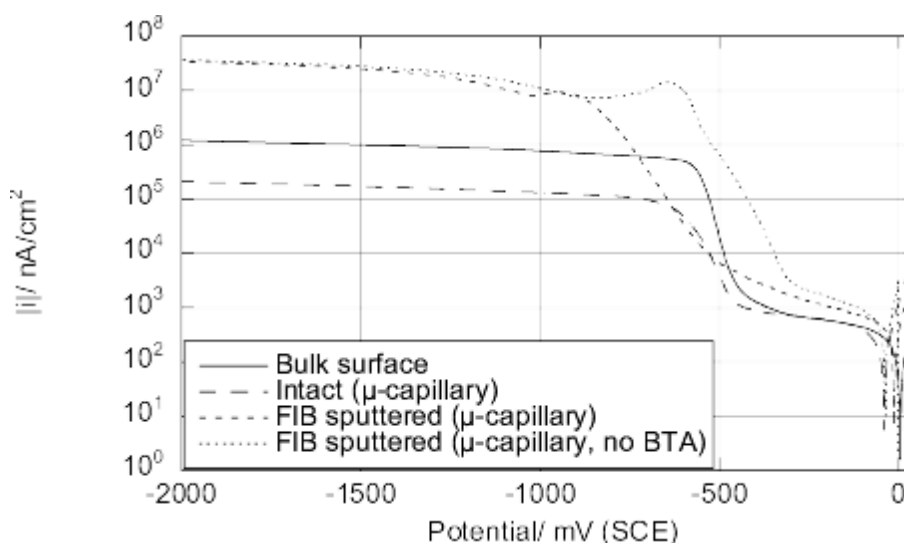


Fig. 8: Current-voltage behaviour FIB sensitized *p*-Si (BTA containing electrolyte)

Using microapillary measurements [3] we were able to show the influence of electrochemical parameters (electrolyte, potential) and the ion implant dose on deposition behaviour. The addition of benzotriazole (BTA) to the electrolyte lead to significantly decreased Cu-crystallite size; it is generally assumed that BTA inhibits crystallite growth by adsorbing to the sample surface where it limits surface diffusion of adsorbed ionic species (in this case Cu⁺⁺ ions).

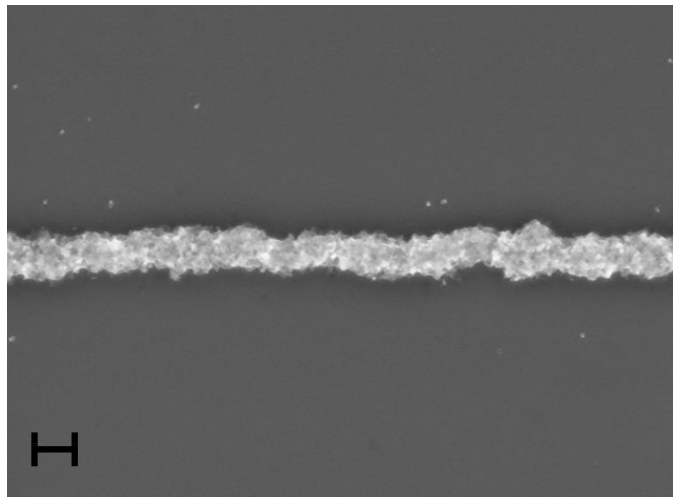


Fig. 9: Cu line on p-Si sensitized by FIB (marker is 200nm).

Fig. 9 shows a Cu line deposited on *p*-Si implanted with $\sim 1 \cdot 10^{15}$ ions/cm² (20s at – 1500mV, electrolyte as before). The electrochemical process visibly reaches the resolution given by the FIB and structures in the sub-micrometer range are easily obtainable. No distinguishable grains or crystallites can be seen in Fig. 9 indicating that even smaller structures are possible. Selectivity is excellent and coverage of the implant site is complete. In the near future we will focus our attention on further optimizing the deposition procedure and we are confident to reach the sub 100 nm-resolution soon. Also, more fundamental aspects of the electrochemical behaviour will be investigated.

References

- [1] H. Böhni, T. Suter, and F. Assi, "Micro-electrochemical techniques for studies of localized processes on metal surfaces in the nanometer range", *Surface and Coatings Technology*, **130** (2000) 80.
- [2] P. Schmuki, L. E. Erickson, and D. J. Lockwood, "Light emitting micropatterns of porous Si created at surface defects", *Phys. Rev. Lett.*, **80** (1998) 4060.
- [3] A. Spiegel, L. E. Erickson, and P. Schmuki, "Selective growth of porous silicon on focused ion beam patterns", *J. Electrochem. Soc.*, **147** (2000) 2993.

Nanostructuring of electrode surfaces with an electrochemical STM

(S. Maupai, P. Schmuki)

With an electrochemical Scanning Tunneling Microscope (EC-STM) it is possible to observe and modify electrode surfaces under potential control on a nanoscale [1]. One approach to understand nucleation and growth in homo- or heteroepitaxy is to follow the initial steps of electrochemical metal deposition on the surface [2].

In some electrochemical systems the first step of metal deposition is the so called underpotential deposition, that is the formation of one atomic layer of metal to be deposited on a foreign substrate. In the case of Cd-deposition on Au(111) the deposition of such a monolayer starts at about 350 mV positive of the reversible Nernst-potential for Cd-bulk deposition [3].

When a flame annealed Au(111)-surface is used as a substrate, the Au-surface is reconstructed and shows the typical “herringbone”-structure of parallel corrugation rows due to a contraction of the upmost atomic layer for about 4 %. By observing the initial nucleation of Cd on this surface we found, that the angles of the reconstruction rows are the sites of preferred nucleation (Figs. 10a, b). The well defined distance between the reconstruction rows can therefore be used to cover the hole surface in a self-assembling way with Cd clusters that consist just of a few atoms (Fig. 10c).

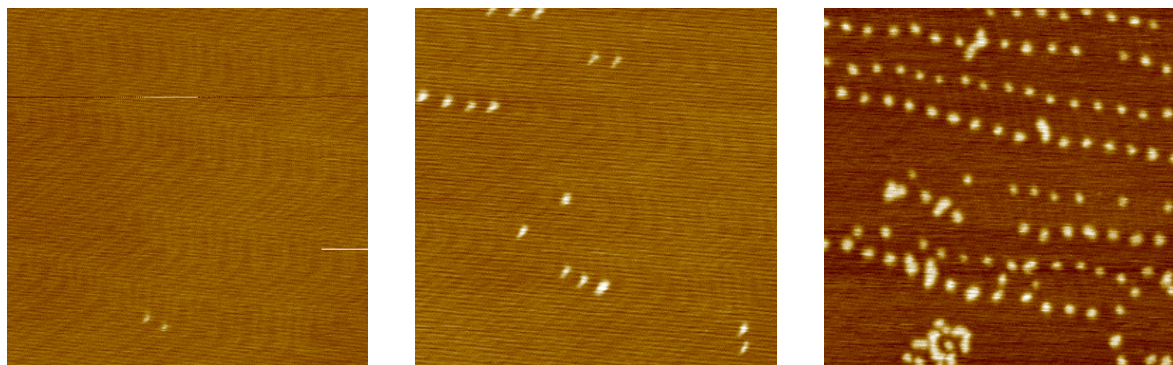


Fig. 10: (100 nm x 100 nm) Au(111) in 0.05 M H₂SO₄ / 0.5 mM CdSO₄, a) E = 330 mV vs. Cd/Cd²⁺, b) E = 260 mV vs Cd/Cd²⁺, c) E = 220 mV vs. Cd/Cd²⁺.

The next step of this work will be to emerge the cluster covered surface from the electrolyte under potential control and transform the Cd clusters chemically into CdS clusters. The CdS clusters of such size should exhibit real quantum confinement effects that will be measured as photoluminescence for example.

References:

- [1] S. Maupai, M. Stratmann, A.S. Dakkouri, Ex Situ Characterization of Electrochemically Generated Cu Nanostructures, *Electrochem. Sol. State Lett.*, **5** (2002) C35.

- [2] R.J. Randler, D.M. Kolb, B.M. Ocko, I.K. Robinson, Electrochemical copper deposition on Au(100): a combined in situ STM and in situ surface X-ray diffraction study, *Surf. Sci.*, **446** (2000) 187.
- [3] R. Vidu, S. Hara, In Situ EC-AFM Observation of Cd Electrodeposition on Au(100), *Scripta Mat.*, **41** (1999) 617.

Anodic Oxidation of Titanium (R. Beranek, P. Schmuki)

The objective of this project is to study characteristics and growth mechanism of the anodic oxide films formed on commercially pure titanium under various conditions.

The anodic oxidation experiments are carried out in various electrolytes by using various types of current/potential control of formation conditions.

For the characterization of titanium oxide films electrochemical methods (e. g. Mott-Schottky analysis) are used as well as spectroscopic methods such as scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and X-ray diffractometry (XRD).

Selective porosification and dissolution of n-InP surfaces after focused ion beam implantation of Si⁺⁺ (U. Schlierf, P. Schmuki)

In previous investigations it has been shown, that porous Si can be produced electrochemically at defined surface locations of a Si substrate by sensitizing the surface with implanted Si⁺⁺ ions [1]. The same was shown for GaAs [2]. Also for InP it is known, that it can be electrochemically porosified [3]. In cooperation with the National Research Council of Canada it has been shown now, that InP surfaces can also be sensitized and selective porosified by a writing process using focused ion beam technology combined with electrochemistry.

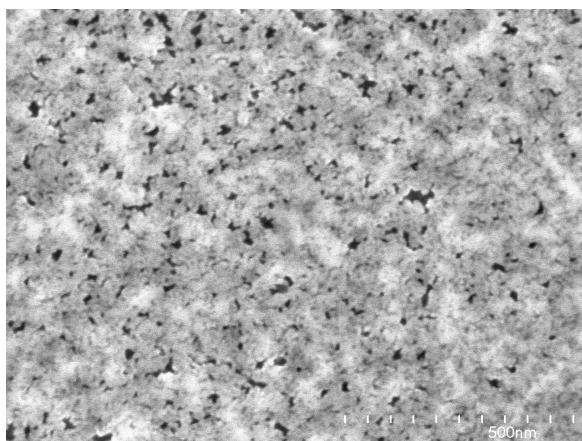


Fig. 11: SEM image of a selective porosified InP sample implanted with 1.75×10^{14} ions/cm² Si⁺⁺ (160keV) after polarizing in 1M HF from -0.5V to 0.3V.

electrochemistry.

Selective porosification takes place at defect surface areas, such as scratches, by an electrochemical polarization lower than a threshold potential (the pore formation potential (PFP)). Highly defined defect patterns can be created using FIB ion bombardment. At these defect patterns a subsequent electrochemical dissolution reaction can be triggered selectively. The work shows that not only a selective porosification (Fig. 11, 12) can take place but also, by varying the parameters, a total removal of

the pattern could be achieved (Fig. 13). Finally only a small range of potential, time and implantation dosage combinations was found to lead to a local porous surface, in most other cases the patterns were completely dissolved. To obtain detailed information of the pore formation process, further investigations on InP samples had been carried out [4].

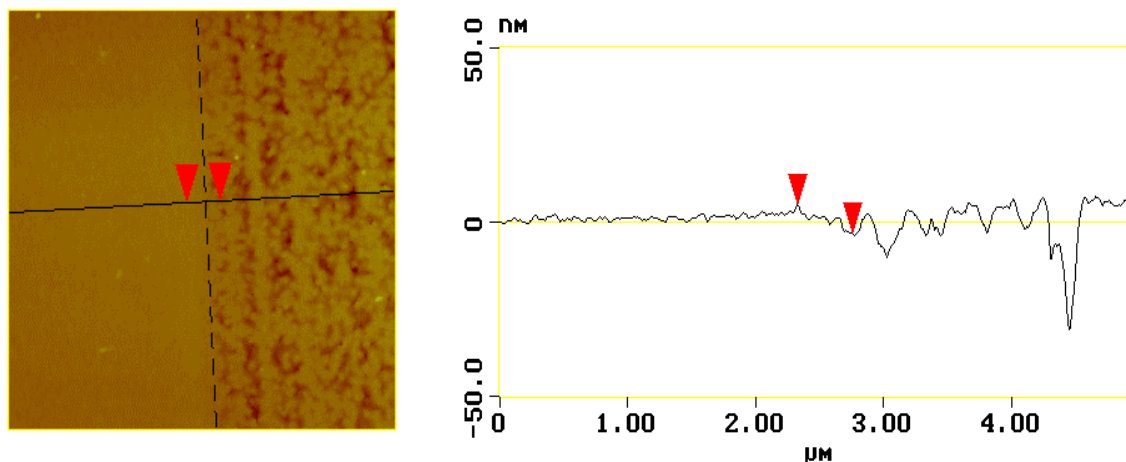


Fig. 12: AFM image of a selective porousified InP sample implanted with 1.75×10^{14} ions/cm² Si⁺⁺ (160keV) after polarizing in 1M HF from -0.5V to 0.3V.

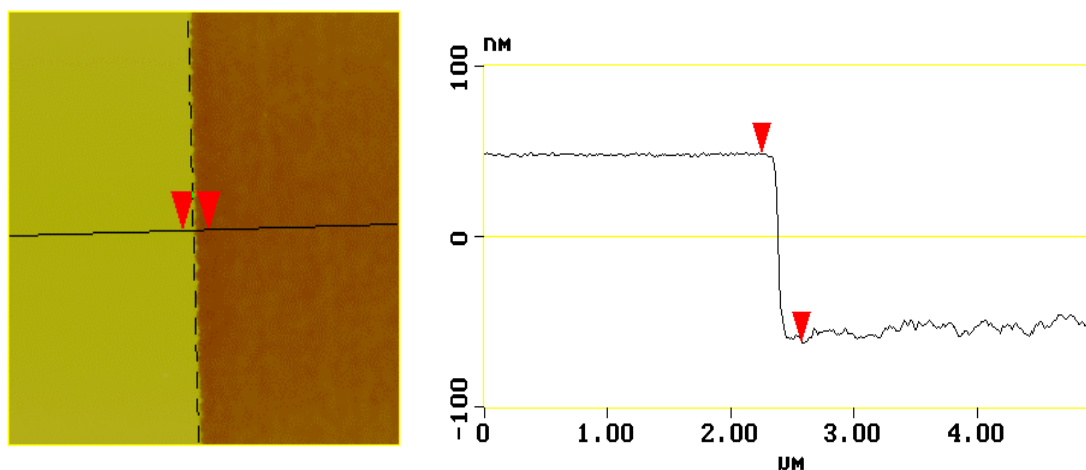


Fig. 13: AFM image of a selective porousified InP sample implanted with 1.75×10^{14} ions/cm² Si⁺⁺ (160keV) after polarizing in 1M HF from -0.5V to 0.5V.

References:

- [1] A. Spiegel, L.E. Erickson, and P. Schmuki, Selective Growth of Porous Silicon on Focused Ion Beam Patterns; *Journal of The Electrochemical Society*, **147** (2000) 2993.
- [2] P. Schmuki, L.E. Erickson, D.J. Lockwood, B.F. Mason, J.W. Fraser, G. Champion, and H.J. Labbé, Predefined Initiation of Porous GaAs Using Focused Ion Beam Surface Sensitization; *Journal of The Electrochemical Society*, **146** (1999) 735.
- [3] P. Schmuki, L. Santinacci, T. Djenizian, and D.J. Lockwood, Pore Formation on n-InP; *phys. Stat. Sol. (a)*, **182** (2000) 51.
- [4] P. Schmuki, U. Schlierf, T. Herrmann, G. Champion, Pore Initiation and Growth on n-InP(100); *Electrochim. Acta*, submitted (2001).



Publications (Papers, Conference Proceedings, Books)

Papers

- 1/01 **T. Djenizian, L. Santinacci and P. Schmuki**
Electron beam induced carbon masking for selective porous silicon formation;
in 6th International symposium on the physics and chemistry of luminescent materials, M. Cahay (ed.), PV 2001, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- 2/01 **T. Djenizian, L. Santinacci and P. Schmuki**
Electron-beam induced nanomasking for metal electrodeposition on semiconductor surfaces; J. Electrochem. Soc., **148** (2001) C197.
- 3/01 **T. Djenizian, L. Santinacci and P. Schmuki**
Electron beam-induced carbon masking for electrodeposition on semiconductor surfaces; Appl. Phys. Lett., **78** (2001) 2940.
- 4/01 **L. Santinacci, T. Djenizian and P. Schmuki**
AFM induced nano-patterning of Si surfaces;
J. Electrochem. Soc., **148** (2001) C640.
- 5/01 **L. Santinacci, T. Djenizian and P. Schmuki**
Nanoscale patterning of Si(100) surfaces by scratching through the native oxide layer using atomic force microscope;
Appl. Phys Lett., **79** (2001) 1882.
- 6/01 **T. Djenizian, B. Petite, L. Santinacci and P. Schmuki**
Electron-beam induced carbon deposition used as mask for cadmium sulfide deposition; Electrochim. Acta, **47** (2001) 891.
- 7/01 **T. Djenizian, L. Santinacci and P. Schmuki**
Report from the scientific on-line journal "Inside R&D Alert" about sub-100-nm technology for device fabrication "Sub-100 nm mask is repairable", Frost & Sullivan, New York, June 8 (2001).
- 8/01 **M. Vergé and P. Schmuki**
Formation of porous composites by a voltage pulse technique;
Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ(2001) p. 262.
- 9/01 **L. Santinacci, T. Djenizian and P. Schmuki**
AFM induced nanopatterning of Si surfaces;
Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ(2001) p. 189.



- 10/01 **T. Djenizian, L. Santinacci and P. Schmuki**
Electron-beam induced nanomasking for metal electrodeposition on semiconductor surfaces; Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ(2001) p. 200.
- 11/01 **P. Schmuki, L. Santinacci, T. Djenizian and D. Lockwood**
Formation and properties of porous InP;
Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ (2001) p. 554.
- 12/01 **D. Lockwood, L. Santinacci, T. Djenizian and P. Schmuki**
Optical properties of porous InP;
Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ (2001) p. 567
- 13/01 **G. Lammel, S. Schweizer, P. Schmuki and Ph. Renaud**
Microspectrometer of Porous Silicon;
Proc. 198th Meeting of the Electrochemical Society, Proc. Vol. 2000-25, The Electrochemical Society, Pennington, NJ (2001) p. 543.
- 14/01 **P. Schmuki, L.E. Erickson and G. Champion**
Selective electrodeposition of micropatterns on predefined surface defects on p-Si (100), J. Electrochem. Soc. **148** (2001) C177.



Conferences, Seminars, Invited Lectures

Invited Lectures

- **P. Schmuki**, “Elektrochemische Nanostrukturierung”, Kronacher Impedanztage 2001, Mitwitz-Bächlein, May 2001
- **P. Schmuki**, “Direktes hochauflösendes Strukturieren von Halbleiteroberflächen”, Kolloquium des Sonderforschungsbereichs "Mehrkomponentige Schichtsysteme", Universität Erlangen-Nürnberg, January, 2001
- **P. Schmuki**, “Electrochemical high resolution techniques for structuring solid surfaces”, Institute for Advanced Energy, Kyoto University, March 2001
- **P. Schmuki**, “Vom Zahn der Zeit zur Nanostruktur - korrosiver Zerfall und selektive Funktionalisierung reaktiver Werkstoffoberflächen”, Universität Erlangen-Nürnberg, Juli 2001
- **P. Schmuki**, “Mikro- und Nanostrukturierung von Werkstoffoberflächen”, Erlanger Werkstofftag, Universität Erlangen-Nürnberg, Juli 2001
- **P. Schmuki**, “Moderne Ansätze und Techniken zur Untersuchung lokaler Korrosionserscheinungen”, DECHEMA Weiterbildungskurs Moderne Messmethoden in der Elektrochemie und Korrosionsforschung, November 2001
- **P. Schmuki**, “Ion implantation patterning and pore formation on GaAs and InP”, Internatl. Workshop on III-V Porous Materials, Kiel, Germany October, 2001
- **T. Djenizian**, “Electron-beam induced carbon nano-masking for selective electrodeposition of metals on Si(100)”, in Electrochemical Deposition and Dissolution, Joint International Meeting: 200th ECS meeting and the 52nd ISE meeting, San Francisco, September 2001
- **L. Santinacci**, “AFM induced nanoscale electrochemical deposition of metals on Si (100) surfaces” in Electrochemical Deposition and Dissolution, Joint International Meeting: 200th ECS meeting and the 52nd ISE meeting, San Francisco, September 2001
- **S. Maupai**, “Tip-induced nanostructuring of AuCu-alloys with an electrochemical scanning tunneling microscope”, in Surface Science and Thin-Film Growth in Electrolytes, MRS 2001 Fall Meeting, Boston, November 2001
- **Spiegel**, “Controlled and selective aggregation of submicrometer Cu-crystallites on FIB sensitized p-Si”, in Nanopatterning - From Ultralarge-Scale Integration to Biotechnology, MRS 2001 Fall Meeting, Boston, November 2001
- **H. Kaiser**, “Das Rosten des Eisens”, Lehrerfortbildung, Dillingen, September 2001
- **E. Wendler-Kalsch**, “Erscheinungsformen der Korrosion an metallischen Werkstoffen“, Lehrerfortbildung, Dillingen, September 2001



Seminar Presentations by External Lecturers

Lectures at the Institute

- 18.10.2001 **Prof. Dr. M. Graham**, Institute for Microstructural Science, National Research Council Canada, Ottawa, Canada: “Oxide formation on III-V materials and heterostructures”

Lectures in the Departmental Materials Science Colloquium

- 06.02.2001 **Dr. Quadackers**, Institut für Werkstoffe und Verfahren der Energietechnik, Forschungszentrum Jülich, Jülich, Germany: “TiAl-based intermetallics; Corrosion/creep interaction; Coating development”
- 19.06.2001 **Prof. Dr. Hofmann**, ETH-Lausanne, Switzerland: “Manufacturing of nanostructured materials by self assembling of particles”
- 30.10.2001 **Dr. Mietz**, Bundesanstalt für Materialprüfung, Berlin, Germany: “Elektrochemischer Korrosionsschutz für Stahlbetonbauwerke - Stand der Technik und Entwicklungstendenzen”
- 18.12.2001 **Dr. R. Boukherroub**, Ecole Polytechnique, Paris, France: “Organic monolayers on hydrogen-terminated silicon surfaces: Fundamental aspects and applications”



Activities in Professional Societies, Editorial Boards, Advisory and Organization Committees

P. Schmuki:

- Member of the Executive Committee of the International Corrosion Council, ICC
- Member of the Electrochemical Society (ECS) and Member of the Executive Committee of the Corrosion Division of ECS
- Editor of “Pits and Pores Formation, Properties and Significance for Advanced Materials”, The Electrochemical Society, PV 2000-25, (2001)

Patents

- P. Schmuki, L.E. Erickson, D.J. Lockwood: “A selective electrochemical process to create porous semiconductor nano- and micro-patterns”; US patent No: 6,284,671(2001); Canadian patent, filed 1998, No. 09/196 641