INSTITUTE IV:

SURFACE SCIENCE

AND

CORROSION

4.4 Institute IV: Surface Science and Corrosion

4.4.1 General

The Institute of *Surface Science and Corrosion* within the Department of Materials Science and Engineering, is an interdisciplinary institute between science and technology. The Institute targets basic phenomena of surface science, electrochemistry and interfacial chemistry leading up to technical applications and supports the transfer of fundamental knowledge into modern surface technology. Due to this transdisciplinary approach, the scientific staff is recruited from various faculties and consists of physicists, chemists and materials science engineers.

The general scientific scope is the modification of interfaces and surfaces 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 temperatur 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 removal 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 –structuring of materials on locally sensitized single crystal semiconductor surfaces. 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 nanosize material or functionality.

The scientific interests are also reflected in teaching. Courses 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 industrial relevance like corrosion phenomena in practice are taught by colleagues from the industry.

4.4.2 Staff

Teaching Faculty:

Prof. Dr. Patrik Schmuki (Head of Institute)
Prof. Dr. Elsbeth Wendler-Kalsch
Prof. Dr. Martin Stratmann (now at MPI for Iron Research, Düsseldorf)
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:

Magali Constant
M. Scholz

Administration, Teaching and Research Scientists:

Dr. Hermann Kaiser (Academic Director)
Dr. Werner Auer (Chief engineer)
Dipl.-Chem. Stefan Maupai

Research Associates:

Dipl.-Chem. Lionel Santinacci
Dipl.-Chem. Thierry Djenizian
Dipl.-Ing. Udo Schlierf
Dipl.-Chem. Gerald Eckstein *
Dipl.-Ing. Bodo Gerold *
Dipl.-Chem. Andreas Plagge *
Dipl.-Phys. Matthias Rebhan *
Dipl.-Ing. Margrit Dannenfeldt *
Dipl.-Min. Roger Meier *

* now in industry

Technical Staff:

Anja Friedrich
Helga Hildebrand
Martin Kolacyak
Hans Rollig
Ingeborg Tontsch
Italo Wassermann
Karl Werner

4.4.3 Laboratory and Offices

Accommodation:

Total space: 1 328 m^2

Laboratory space: 717 m^2

Main Equipment:

Surface Analysis and Microscopy

- SEM incl. EDX
- AES/XPS (attached preparation chamber for gas-adsorption & electrochemical cell)
- 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
- UHV-high-temperature STM ($T \leq 1500$ K for semi-conductors, $T \leq 750$ K for metals)

Electrochemical Characterization

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

High Temperature Oxidation

- Furnaces equiped 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

4.4.4 **Teaching** (weekly hours)

Winter Semester 1999/2000 (WS 1999/2000):

Basic Studies (Grundstudium, till Vordiplom):

Lectures:

- Materials science III, 2 h (M. Stratmann)
  for students of materials science
  with experiments (I. Wassermann)

Laboratory Courses:

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

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

- Physico-chemical fundamentals of corrosion and surface technology,
  2 h (M. Stratmann)
  for students of materials science and engineering
- Electrolytic corrosion, part I, 2 h (M. Stratmann)
  with excercises (S. Maupai, G. Eckstein)
- Electrochemical methods, 2 h (M. Stratmann)
- Practical surface technology, 1 h (E. Wendler-Kalsch)

Seminars:

- Current research topics, 2 h

Summer Semester 2000 (SS 2000):

Basic Studies (Grundstudium, till Vordiplom):

Lectures:

- Materials science II, 2 h (E. Wendler-Kalsch)
  for chemical engineers

Laboratory Courses:

- Basic laboratory course in materials science

Advanced Studies (Hauptstudium, after Vordiplom):

Lectures:

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

Seminars:

- Corrosion and surface technology, 2 h (E. Wendler-Kalsch)
- Current research topics, 2 h

Laboratory Courses:

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

List of Optional Lectures offered during WS 1999/2000 and SS 2000
(A total of 7 h weekly is required for majors):

- Surface analysis, 1 h (W. Auer)
- 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)

4.4.5 Graduates

Diplom Thesis:

- **Schlierf, Udo**
  Korrosionsverhalten laserstrahlgeschweißter/-gelöteter Aluminium / Stahl-Verbindungen für Mischbaukonstruktionen im Automobilbau

Doctorate Theses:

- **Rebhan, Matthias** (November 1994 till November 2000)
  Untersuchungen des Wachstums, der elektrischen und der elektrochemischen Eigenschaften von auf Eisen gebildeten Silizid-Verbundschichten
- **Meier, Roger** (January 1998 till December 2000)
  In-situ UHV-Raster-Tunnelmikroskopie der Anfangszustände der Hochtemperaturoxidation von Eisen
- **Dannenfeld, Margrit** (September 1994 till June 2000)
  Korrosionsverhalten und materialspezifischer Korrosionsschutz von Eisen-Aluminium-Legierungen und aluminiumhaltigen Leichtbaustählen
- **Hecht, Uta** (March 1995 till February 2000)
  Untersuchungen ultradünner Polycyanuratfilme auf Aluminium zu grundlegenden Aspekten der Haftung von Polymeren auf Metallen

4.4.6 Research Projects / Co-operation with Industry

Overview

The Institute of Corrosion Science and Surface Technology 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.
In the following part a summary of the funding sources and a survey of all research activities are given.

Funding Sources	**Total Expenses in 2000, DM**	**Funding granted in 2000, DM**
Deutsche Forschungsgemeinschaft	187 748.00	0.00
Schweizer National Fond	135 400.00	279 905.00
European Community	187 500.00	93 300.00
Tasks for Industry	50 642.00	0.00
Total	**561 290.00**	**373 205.00**

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**: 6 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**: 6 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**: 6 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**: 6 years

Research project: Nanostructuring of alloy-surfaces with in-situ scanning tunneling microscopy
Principal investigator: A. Dakkouri **Responsible researcher**: S. Maupai
Funded by: DFG-Schwerpunkt: "Grundlagen d. elektrochem. Nanotechnologie"
Beginning of project: July, 1997 **Duration**: 6 years

Research project: Investigation of de-alloying mechanisms on atomic scale by EC-STM
Principal investigators: A. Dakkouri, H. Kaiser **Responsible researcher**: G. Eckstein
Funded by: DFG
Beginning of project: September, 1997 **Duration**: 3 years

Research project: Changes in grain structure and typical properties of FeCr-alloys after quick heating and cooling down with an excimerlaser
Principal investigator: E. Wendler-Kalsch **Responsible researcher**: B. Gerold
Research partners: Universität Bayreuth, Universität Göttingen, ATZ EVUS
Funded by: DFG-Schwerpunkt "Kurzzeitmetallurgie"
Beginning of project: August, 1996 **Duration**: 4.5 years

Research project: Cellulose - Adhesion promoter and corrosion protection
Principal investigator: M. Stratmann **Responsible researcher**: A. Plagge
Research partner: MPI f. Polymerforschung, Mainz
Funded by: DFG-Schwerpunkt "Cellulose"
Beginning of project: July, 1996 **Duration**: 4 years

Specific Projects

Research group of P. Schmuki:

- **Sensitization of semiconductor surfaces for totally selective electrochemical reactions**

In a collaboration with the National Research Council of Canada it has been shown that red light emitting porous Si can be produced at defined surface locations of a Si substrate by a direct writing process using focused ion beam technology combined with electrochemistry [1], see Fig. 4.4.6.1.

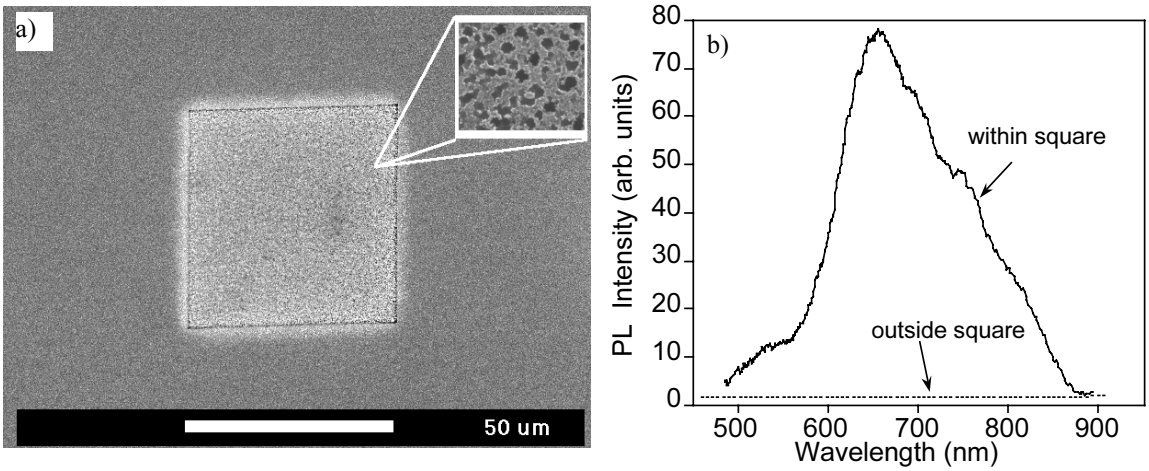

Fig. 4.4.6.1: Selective formation of red-light emitting porous Si on a FIB implanted area. a) SEM image of a 50 x 50 µm square implanted with 3 x 10^{14} cm^{-2} Si^{++} (200 keV) after polarization in 20% HF from -0.5 V to 3.5 V. Inset shows higher magnification of the porous Si structure within the square. b) Room temperature photoluminescence spectra acquired in the center of the square and on adjacent area.

The principle is that the growth of porous Si growth can electrochemically be initiated preferentially at surface defects created in a single crystal Si substrate by ion bombardment. Using a focused ion beam (FIB) as a source of ions, arbitrary defect patterns in the 50 nm to 200 nm range can be written into a substrate, compare Fig. 4.4.6.2. The selectivity of the subsequent electrochemical dissolution reaction seems to be due to a facilitated Schottky barrier breakdown at the implanted surface defects which leads to the desired "localized current flow".

In more general terms this preliminary work shows the feasibility of a new principle for locally activating or sensitizing a semiconductor surface for a subsequent chemical or electrochemical reaction. This principle is not only applicable to trigger the growth of porous Si structures on pre-defined and confined surface locations but can also be exploited for highly localized direct electrochemical deposition reactions [2]. This provides the basis

for much wider applications in surface physics, chemistry and materials science, as deposition of all materials that currently can be electrodeposited on a larger scale (metals, other semiconductors or ceramics) should be possible in a submicron scale.

Further work will investigate this local porous semiconductor formation mechanism in detail (including recently discovered light emitting porous GaAs [3,4]). On the other hand, key factors and perspectives of local electrodeposition processes will be studied.

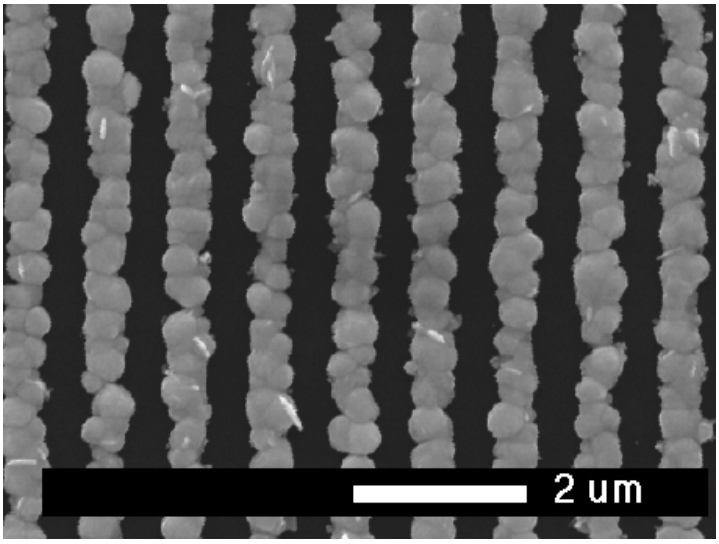

Fig. 4.4.6.2: Selective Au deposition on Si sensitized with FIB lines.

References:

[1] P. Schmuki, L.E. Erickson, D.J. Lockwood, Light emitting micropatterns of porous Si created at surface defects; Phys. Rev. Lett. **80** (1998) 4060

[2] P. Schmuki, L.E. Erickson, Selective deposition of metal nano-patterns on silicon; Phys. Rev Lett. **85** (2000) 2985

[3] P.Schmuki, D.J. Lockwood, H.J. Labbe, J.W. Fraser, Visible photoluminescence from porous GaAs; Appl. Phys. Lett. **69** (1996) 1620

[4] P. Schmuki, L.E. Erickson, D.J. Lockwood, J.W. Fraser, G. Champion, H.J.Labbe, Formation of visible light emitting porous GaAs micropatterns; Appl. Phys. Lett. **72** (1998) 1039

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

During past decades, there has been a great deal of interest in micro- and nanometer scale generation on semiconductors. The field is particularly driven by semiconductor technology and its continuous demand for shrinking dimensions in the development of established and novel devices enhancing techniques to achieve sub-µm resolution [1]. Except for UV lithography, e-beam lithography is currently one of the most employed approaches to obtain high resolution patterning on one hand to fabricate photolithographic masks on the other hand to create ultra small line-widths on both silicon and silicon dioxide [2,4], see Fig. 4.4.6.3.

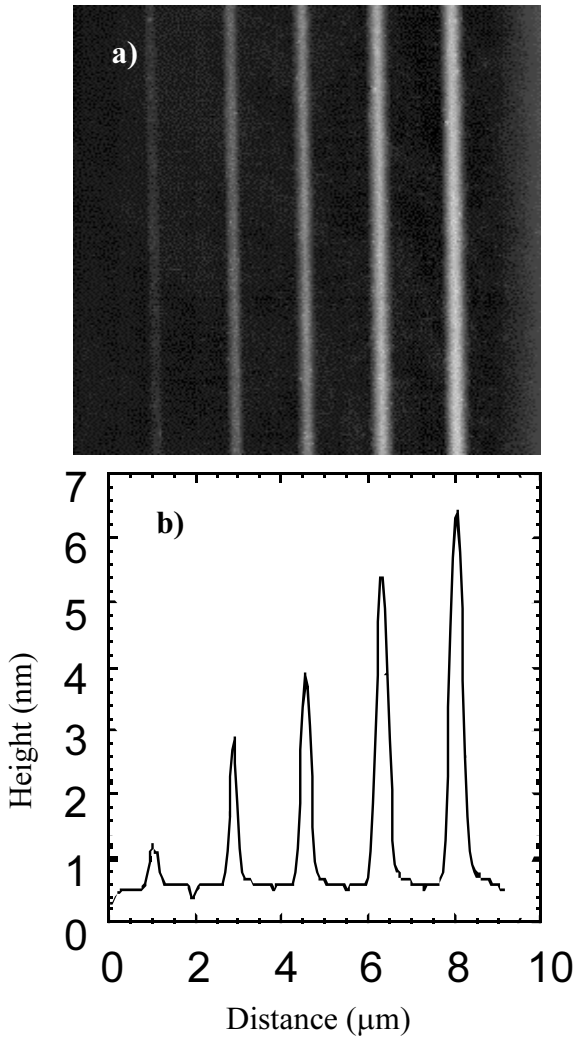

Fig. 4.4.6.3: AFM top view of an array of 5 contamination lines, e-beam deposited on silicon with 10, 30, 60, 120 and 180 s exposure time (a). AFM cross section of the contamination lines (b).

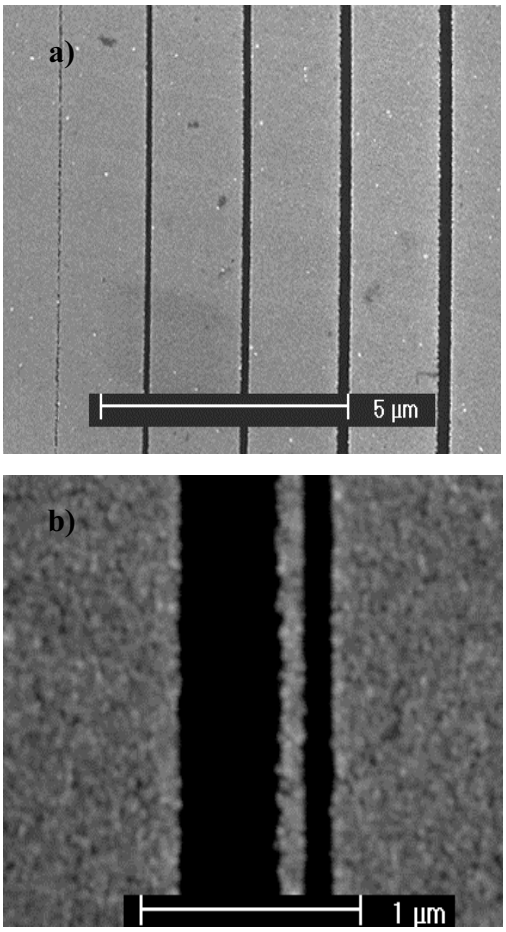

Fig. 4.4.6.4: SEM image of Au deposit on Si surface carrying the C-line pattern of Fig.4.4.6.3. Au deposition was carried out in 10 mM $KAu(CN)_2$ + 1 M KCN potential step to -1.6 V (Ag/AgCl) for 5 s (a). SEM image of a 90 nm wide gold line between two masking C-lines (b).

Additionally, a number of studies deals with e-beam induced deposition reactions: the precursor molecules present or introduced into the instrument are decomposed under the direct electron bombardment to form a deposit on the substrate surface [5,6] (3D nanostructures in the 1 nm - 100 nm). A specific case of e-beam induced patterning is the formation of carbon rich contamination layers in SEMs. The e-beam activates reactions of the residual hydrocarbons (molecules from the pump oil) to form a deposit with mechanical and electrical properties close to the diamond [7,8] (*i.e.* the deposits are electrically insulating).

The present work explores possibilities to use C-masks produced by contamination writing in a SEM to suppress selectively metal electrodeposition at treated surface locations and thus provide the basis for a novel patterning method in the sub-μm range. Carbon contamination lines were written at different electron doses on n-type Si(100) surfaces. Subsequently Au was electrochemically deposited from a 1 M KCN + 0.01 M $KAu(CN)_2$ solution on the e-beam treated surfaces. The carbon masks as well as the Au deposits were characterized by scanning electron microscopy, atomic force microscopy and scanning Auger electron spectroscopy, Fig. 4.4.6.4. We demonstrate that carbon deposits in the order of 1 nm thickness can be sufficient to achieve a negative resist effect, i.e., can block the electrodeposition of Au completely selectively. The lateral resolution of the process is in the sub 100 nm range. The nucleation and growth of Au deposits and their morphology as well as the selectivity and resolution of the process depend on several factors such as the electron dose during masking, and the applied potential and polarization time during Au deposition. The process opens new perspectives for selective electrodeposition, *i.e.*, for high definition patterning of surfaces with a wide range of materials.

References:

[1] S. M. Sze, Semiconductor Devices, Physics and Technology; John Wiley & Sons. Inc., New York, 1985

[2] D. R. Allee and A. N. Broers, Appl. Phys. Lett. **57** (1990) 2271

[3] X. Pan, D. R. Allee, A. N. Broers, Y. S. Tang and W. Wilkinson, Appl. Phys. Lett. **59** (1991) 3157

[4] T. O. Sedgwick, A. N. Broers and B. J. Agule, J. Electrochem. Soc. **119** (1972) 1769

[5] H. W. P. Koops, J. Kretz, M. Rudolph, M. Weber, G. Dahm and K. L. Lee, Jpn. J. Appl. Phys. **33**, Part 1, (1994) 7099

[6] M. Komuro and Hiroshima, Microelectron. Eng. **35** (1997) 273

[7] N. Miura, T. Numaguchi, A. Yamada, M. Konagai and J. Shirakashi, Jpn. J. Appl. Phys. **36** (1997) L1619

[8] N. Miura, A. Yamada and M. Konagai, Jpn. J. Appl. Phys. **36** (1997) L1275

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

In the recent years, copper electrodeposition has become of great interest to microelectronics and microsensor industries. Copper layers are used as electrical interconnects with a thickness ranging from several micrometers down to a few nanometers [1]. More recently, copper has been introduced as a valid replacement of aluminium in ultralarge-scale integration (ULSI) metallization with improved and reliability of interconnection. The direct deposition onto silicon is also of interest to build Schottky diodes on semiconductor surfaces [2].

Scanning probe microscopy (SPM) such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) have been widely used as tools for surface imaging with atomic resolution [3,4]. But AFM can also be used to investigate the mechanical properties of surfaces or to nanomachine the surfaces in the micro- and nanoscale, e.g. in scratching and wear [5]. It has been demonstrated that it is possible to obtain nano-scratches on silicon surface using an AFM equipped with a monocrystalline diamond tip [6].

This work explores the possibilities to use AFM-scratching as pre-sensibilization for selective copper deposition onto silicon. The principle of the selectivity has been demonstrated before [7,8]. It is based on the intentional modification of the semiconductor/electrolyte interface behavior and controlled defect creation.

The first step of this work was the introduction of mechanical defects by AFM-scratching onto *p*-type silicon, see Fig. 4.4.6.5. Diamond coated tips mounted on cantilevers with heavy force constants were used in contact mode on a traditional AFM. In a second step, copper electrochemical deposition onto silicon surface was carried out by applying a cathodic potential step in a $CuSO_4$ (0.01M) and H_2SO_4 (0.05M) electrolyte, compare Fig. 4.4.6.6. These experiments that during the electrochemical deposition, the nano-scratches act as deposition activators. However, total selectivity of the process can only be achieved if scratching is performed through the native oxide layer (NOL) present on the surface. After scratching, two zones were established on the silicon surface, one passive (NOL) and one active (within AFM-scratches). By this approach nanoscale copper 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 copper lines were characterized by different microscopies (AFM and SEM) and AES spectroscopy, compare Fig. 4.4.6.7. The work therefore demonstrates a new and direct technique for semiconductor patterning and functionalization by electrodeposition.

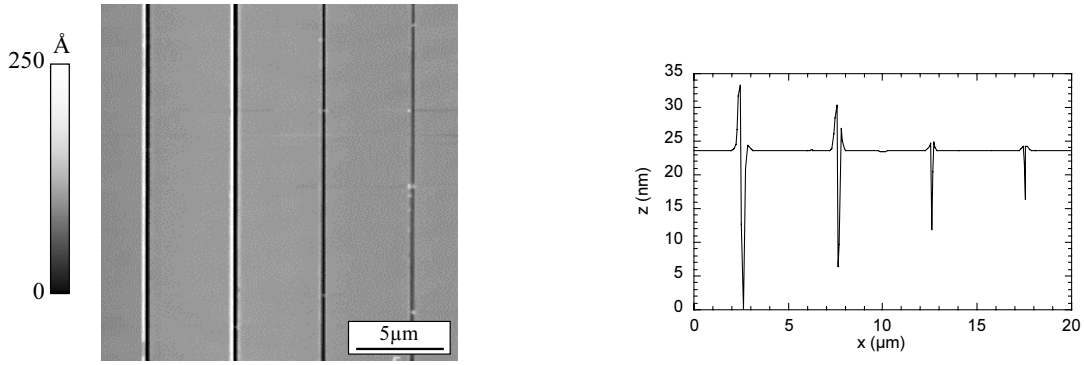

Fig. 4.4.6.5: a) AFM top view of a scratched *p*-Si(100) surface. The 4 AFM-scratches are 40 µm long and have a spacing of 5 µm. The normal applied force varies from left to right: 23, 20, 17, 14 µN. b) Height cross section of a).

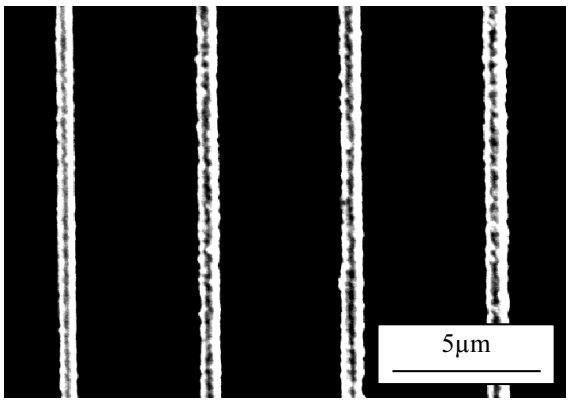

Fig. 4.4.6.6: SEM image of Cu deposit realized on AFM scratches of a NOL covered *p*-type Si (100) surface. The scratches were produced with a force of 15 µN. Deposition was carried out from $CuSO_4$ (0.01 M) + H_2SO_4 (0.05 M) electrolyte applying a potential step to – 400 mV (vs. Ag/AgCl) during 15 s.

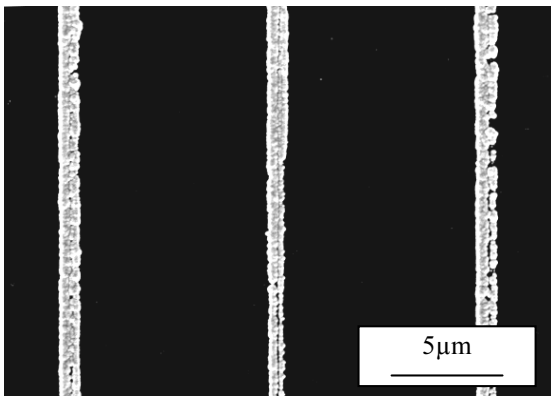

Fig. 4.4.6.7: SEM image of copper deposit on *n*-type silicon (scratched through the NOL) present. Deposition was carried out by a cathodic potential step to – 600 mV (vs. Ag/AgCl) during 30 s in $CuSO_4$ (0.01M) + H_2SO_4 (0.05M).

References:

[1] X. Ye, M. D. Bonte, J. P. Celis and J. R. Roos, J. Electrochem. Soc. **139** (1992) 1592

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[3] C. F. Quate, Surf. Sci. **299/300** (1994) 980

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[6] B. Bhushan and V. N. Koinkar, J. Appl. Phys. **75** (1994) 5741

[7] P. Schmuki, L. E. Erickson and D. J. Lockwood, Phys. Rev. Lett. **80** (1998) 4060

[8] P. Schmuki and L. E. Erickson Phys. Rev. Lett. **85** (2000) 2985

- **Tip induced nanostructuring of Au_xCu_y-alloys with an electrochemical scanning tunneling microscope** (S. Maupai, A.S. Dakkouri)

By tip-induced metal deposition using an EC-STM it is possible to generate small metal clusters on a metal surface in an electrochemical environment. The principle of this method is schematically shown in Fig. 4.4.6.8. In a first step metal is electrodeposited on the apex of the tip of an electrochemical STM (a). This metal loaded tip is approached to the substrate surface (b). At a certain distance between tip and substrate, metal atoms of the tip jump to the surface and build a connective neck (c). When retracting the tip, a small amount of metal from the tip remains on the surface and forms a cluster (d). The apex of the tip is regenerated by a redeposition of metal and is immediately ready for further cluster deposition (e).

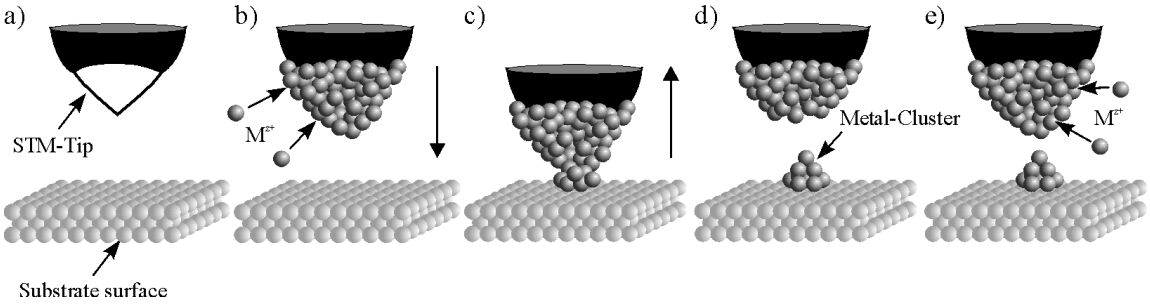

Fig. 4.4.6.8: Principle of the tip-induced metal deposition.

This method was introduced by D.M. Kolb, University of Ulm, in 1992 and applied to generate metal clusters (Cu, Pb, Ag, Pd) on different substrates (Au, Ag) [1]. Clusters consist typically of 100-500 atoms and show an unexpected electrochemical stability positive of the reversible Nernst potential for metal dissolution in the specific system [2]. As the existing theories explain this stability not satisfactorily yet, our aim was to gain additional information by generating Cu-clusters on binary alloy surfaces instead of pure metal surfaces. Using Au_xCu_y single-crystals of different composition opened the possibility to vary the tip-substrate interaction and the influence of adsorbates like monolayers of Cu that may be present on the surface due to underpotential deposition. The electrochemical STM was modified to access and control the STM-scanner directly.

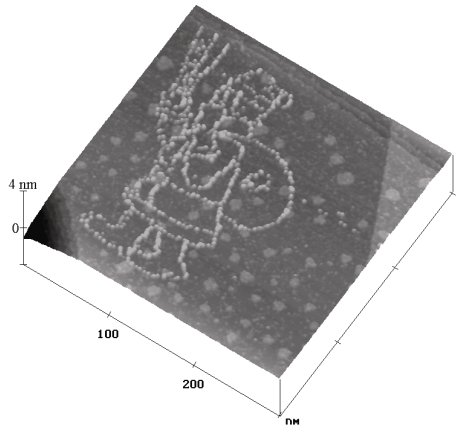

Fig. 4.4.6.9: Nanoclaus of copper on Au(111) drawn with 1109 Cu-Clusters; each Cluster is 2-3 atomic layers high and consists of 100-500 Cu-atoms.

With this modified setup it is possible to move the metal loaded STM-tip in a controlled way by applying a defined voltage pulse onto the driving voltage of the scanner. This allows us to generate almost any arrangement of Cu-Clusters on a substrate during the scanning process. As an example for such an arbitrary pattern a “Nanoclaus” is shown in Fig. 4.4.6.9, consisting of more than 1000 Cu-Clusters, each 2-3 monolayers high and consisting of 100 - 500 atoms.

To properly investigate Au_xCu_y-surfaces a vigorous UHV-preparation and characterization of the alloy-single crystals is necessary [3]. Additional characterization was carried out with electrochemical current-densitiy/potential-measurements and investigations using the EC-STM. The results give evidence that the stability of the metal clusters is not intrinsic but more an effect of interfacial alloying and inhibition of surface diffusion in the system due to the adosrption of a monolayer of metal on the substrate (under potential deposition). On copper rich alloy surfaces this UPD is only partially present and thus smaller and less stable Cu-clusters are observed.

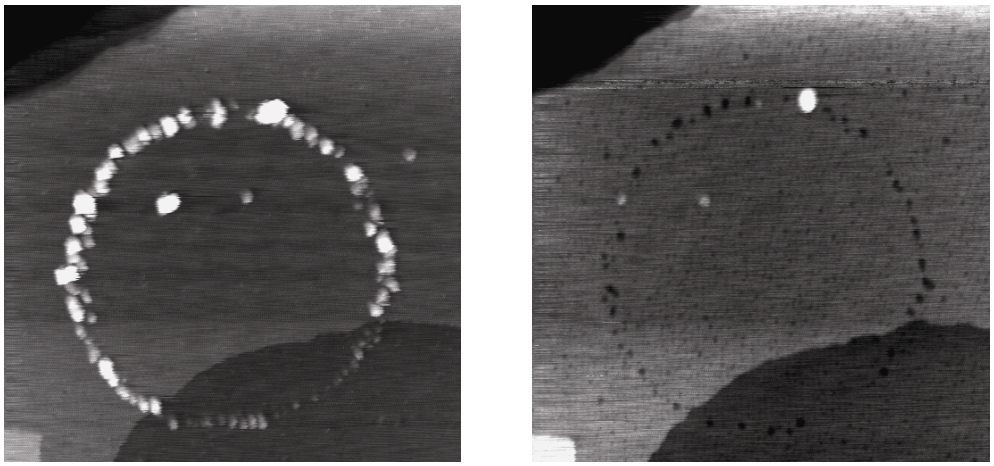

Fig. 4.4.6.10: (300 nm x 300 nm) Cu-Clusters on $Au_3Cu(111)$ at 0 mV vs. Cu/Cu^{2+} (a) and 300 mV vs. Cu/Cu^{2+} (b).

Signs for interfacial alloying on this nanoscopic scale is the beginning of a localized corrosion process at anodic potentials exactly at positions where the clusters were located prior to the anodic treatment (see Fig. 4.4.6.10). This is especially obvious on the alloy surfaces where a corrosion process starts parallel to cluster dissolution and preferentially at copper rich positions of the surface.

References:

[1] D.M. Kolb, R. Ullmann and T. Will, Science **275** (1997) 1097

[2] D.M. Kolb, G.E. Engelmann and J.C. Ziegler, Angew. Chem. Int. Ed. **39** (2000) 1123

[3] G.A. Eckstein, S. Maupai, A.S. Dakkouri, M. Stratmann, M. Nielsen, M.M. Nielsen, R. Feidenhans, J.H. Zeysing, O. Bunk and R.L. Johnson, Phys. Rev B **60** (1999) 8321

4.4.7 Publications (Papers, Conference Proceedings, Books)

Papers

1/00 **A. Spiegel, L.E. Erickson and P. Schmuki**
Selective porous silicon growth on focused ion beam patterns; J. Electrochem. Soc. **147** (2000) 2993

2/00 **P. Schmuki, L. Santinacci, T.Djenizian and D.J. Lockwood**
Pore formation on InP(100) and GaAs(100), Phys. Stat. Solidi A **182** (2000) 51

3/00 **P. Schmuki and L.E. Erickson**
Selective deposition of metal nano-patterns on silicon, Phys. Rev. Lett. **85** (2000) 2985

4/00 **L.E. Erickson, P. Schmuki and G. Champion**
Maskless deposition of gold patterns on silicon; J. Vac. Sci. Tech. B **18** (2000) 3918

5/00 **B. Gerold and E. Wendler-Kalsch**
Jahresbericht 1999/2000 der Max - Buchner – Forschungsstiftung, „Erhöhung der Korrosionsbeständigkeit von FeCr - Legierungen durch Oberflächenmodifikation mit Excimer – Laser – Strahlung“

6/00 **E. Wendler-Kalsch, H. Mueller and S. Bonner**
Progress in biomedical research **3,** 2000, p. 179

7/00 **P. Schmuki, L.E. Erickson and D. J. Lockwood**
Porous micropatterns formed on focussed ion beam implants; Journal of Porous Materials **7** (2000) 233

4.4.8 Conferences, Seminars, Invited Lectures

Conferences and Seminars organized by Members of the Institute

- **Fachveranstaltung E-H030-12-021-0 im Haus der Technik**
  "Vermeidung von Rißschäden bei statischer und dynamischer Belastung"
- **Fachveranstaltung E-H030-12-015-0 im Haus der Technik**
  "Vermeidung von Korrosionsschäden durch Wasserstoff"
- **198th ECS-Meeting, Phoenix, AZ, USA**
  "Pits and äpores: Formation properties and significance for advanced materials"

Invited Lectures

- **E. Wendler-Kalsch**
  "Gefügeausbildung und Eigenschaften der nichtrostenden Stähle", Seminar: Werkstoffe/Schweißen; Nichtrostende Stähle; Haus der Technik, Essen, Germany
- **E. Wendler-Kalsch**
  "Spannungsriß- und Schwingungsrißkorrosionsverhalten nichtrostender Stähle"; Seminar: Werkstoffe/Schweißen; Nichtrostende Stähle; Haus der Technik, Essen, Germany
- **E. Wendler-Kalsch**
  "Eigenschaften und Anwendungen von Kupfer und Kupferlegierungen", Seminar: Unterschiede im Korrosionsverhalten metallischer Werkstoffe und ihre Auswirkungen auf den praktischen Einsatz; Haus der Technik, Essen, Germany
- **G.A. Eckstein**
  "In-situ STM studies on dealloying of low index $Au_3Cu(hkl)$ and $Cu_3Au(hkl)$ single crystal alloys", 18th General Conference of the Condensed Matter Divison of the European Physical Society (CMD18-2000), Montreux, Switzerland
- **G.A. Eckstein**
  "In-situ STM studies on dealloying of low index $Au_3Cu(hkl)$ and $Cu_3Au(hkl)$ single crystal alloys", Materials Research Society (MRS) Spring Meeting, San Francisco, USA
- **S. Maupai**
  "Nanostructuring of single crystal Au_xCu_y-alloys with an electrochemical STM", Seminar at Laboratory for Micro- and Nanotechnology, Paul-Scherrer Institut, Villigen, Switzerland

- **E: Wendler-Kalsch**
  "Schäden durch Wasserstoff"; DECHEMA – Weiterbildungskurs: Korrosion und Korrosionsschutz, Teil A: Grundlagen und Untersuchungsmethoden, Frankfurt a. Main, Germany
- **E. Wendler - Kalsch**
  "Die Bedeutung der mechanischen Belastungsarten bei der Rißbildung an Metallen"; Seminar: Vermeidung von Rißschäden bei statischer und dynamischer Belastung, Haus der Technik, Essen, Germany
- **E. Wendler – Kalsch**
  "Spannungsrißkorrosion von Cu – Basislegierungen"; Seminar: Vermeidung von Rißschäden bei statischer und dynamischer Belastung, Haus der Technik, Essen Germany
- **G.A. Eckstein**
  "In-situ STM studies on dealloying of low index $Au_3Cu(hkl)$ and $Cu_3Au(hkl)$ single crystal alloys", Hamburger Synchrotronstrahlungslabor (HASYLAB), Hamburg, Germany
- **E. Wendler – Kalsch**
  "Spannungsrißkorrosion der Al – Basislegierungen"; Seminar: Vermeidung von Rißschäden bei statischer und dynamischer Belastung, Haus der Technik, Essen, Germany
- **E. Wendler – Kalsch**
  "Wechselwirkung von absorbiertem Wasserstoff mit Metallen"; Seminar: Vermeidung von Korrosionsschäden durch Wasserstoff Haus der Technik, Essen, Germany
- **E. Wendler – Kalsch**
  "Wasserstoff – induzierte Rißbildung in wässrigen Lösungen"; Seminar: Vermeidung von Korrosionsschäden durch Wasserstoff, Haus der Technik, Essen, Germany
- **G.A. Eckstein**
  "Legierungskorrosion von niedrigindizierten $Au_3Cu(hkl)$- und $Cu_3Au(hkl)$-Einkristallflächen: UHV- und elektrochemische Methoden zur Charakterisierung von lokalen Korrosionsprozessen", Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany.
- **S. Maupai**
  "Nanostrukturierung von $Au_3Cu(hkl)$- und $Cu_3Au(hkl)$-Einkristalloberflächen – eine in-situ ECSTM Studie", Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany
- **S. Maupai**
  "Stabilität von Nanostrukturen auf $Au_xCu_y(hkl)$-Oberflächen", DFG-Workshop: Stabilität und Reaktivität von Nanostrukturen, Rathen, Germany

- **G.A. Eckstein**
  "In-situ STM studies on dealloying of low index $Au_3Cu(hkl)$ and $Cu_3Au(hkl)$ single crystal alloys", Gordon Conference on Aqueous Corrosion, New London, NH, USA
- **S. Maupai**
  "Nanostructuring of $Au_3Cu(hkl)$ and $Cu_3Au(hkl)$ single crystal alloys – an in-situ EC-STM study", Gordon Conference on Nanostructure Fabrication, New London, NH, USA
- **G.A. Eckstein**
  "Legierungskorrosion von niedrigindizierten, ungeordneten $Au_3Cu(hkl)$- und geordneten $Cu_3Au(hkl)$-Einkristalloberflächen", Korrosion und Grenzflächen - Werkstoffsymposium des Max-Planck-Instituts für Eisenforschung, Düsseldorf, Germany.
- **S. Maupai**
  "Stabilität von Nanostrukturen auf $Au_xCu_y(hkl)$-Oberflächen", Seminar, Abteilung Elektrochemie, Universität Ulm, Ulm, Germany
- **P. Schmuki**
  "In situ XANES investigations of artificial passive films", keynote lecture at Symposium on Oxide Films, 197th Meeting of the Electrochem. Soc., Toronto, Canada
- **P. Schmuki**
  "Science and innovation at Swiss universities", invited lecture at Symposium on Science and Technology in the 21st Century, Alcoi, Spain
- **P. Schmuki**
  "Elektrochemische Herstellung von Nanostrukturen auf gezielt sensitisierten Halbleiteroberflächen", DFG-Workshop: Stabilität und Reaktivität von Nanostrukturen, Rathen, Germany
- **P. Schmuki**
  "Pore formation on InP(100) and GaAs(100)", Porous Semiconductors-Science and Technology (PSST-2000), Madrid, Spain
- **P. Schmuki**
  "Formation and properties of porous InP", Symposium on Pits and Pores: Formation, Properties and Significance for Advanced Materials, 198th Meeting of the Electrochem. Soc., Phoenix, AZ, USA
- **P. Schmuki**
  "Writing functional nanopatterns into semiconductors", SNF meeting, Bern, Switzerland
- **P. Schmuki**
  "Nanostructured materials by selective surface activation using focussed ion beam implantation", COST 523 meeting, Brussels, Belgium

- **L. Santinacci**
  "AFM induced nanopatterning of Si surfaces", Symposium on Pits and Pores: Formation, Properties and Significance for Advanced Materials, 198th Meeting of the Electrochem. Soc., Phoenix, AZ, USA
- **T. Djenizian**
  "Electron-beam induced nanomasking for metal electrodeposition on semi-conductor surfaces", Symposium on Pits and Pores: Formation, Properties and Significance for Advanced Materials, 198th Meeting of the Electrochem. Soc., Phoenix, AZ, USA

4.4.9 Seminar Presentations by External Lecturers

Lectures at the Institute

02.11.2000 **Dr. C. Olsson**, EPFL Lausanne, Switzerland, "Analyse von Passivschichten nichtrostender Stähle mit elektrochemischer Quarzmikrowaage"

Lectures in the Departmental Materials Science Colloquium

06.06.2000 **Dr. G. Grötsch**, Höchst KG, Frankfurt, "Betriebliche Korrosionsüberwachung in der chemischen Industrie"

11.07.2000 **Dr. B. Reinhold**, Audi AG, Ingolstadt, "Schichtsysteme für einen beanspruchunsgerechten Einsatz von Leichtmetallen im Automobilbau"

05.12.2000 **Dr. M. Spiegel**, MPI für Eisenforschung, Düsseldorf, "Hot corrosion in power plants"

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

P. Schmuki:

- Advisory board, International Conference "Porous Semiconductors Science and Technology", Madrid, Spain, March 2000
- 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
- Organizer of the symposium "Electrochemical Formation of Advanced Materials" of the 198th Meeting of The Electrochemical Society, Phoenix, AZ, USA, October 2000

4.4.11 Patents

- P. Schmuki, L.E. Erickson, D.J. Lockwood: "A selective electrochemical process to create porous semiconductor nano- and micro-patterns"; US and Canadian patent, filed, No. 09/196 641