ISSN 0369-5034

NOVA ACTA LEOPOLDINA

Abhandlungen der Deutschen Akademie der Naturforscher Leopoldina
Im Auftrage des Präsidiums herausgegeben von
Harald zur Hausen, Vizepräsident der Akademie
Neue Folge, Nummer 340, Band 92

From Nanoscience to Nanotechnology

Leopoldina Symposium

Forschungszentrum Karlsruhe
September 4 to 5, 2003

Organizing Committee:

Herbert GLEITER (Karlsruhe)
Member of the Academy

Roland WIESENDANGER (Hamburg)
Member of the Academy

Deutsche Akademie der Naturforscher Leopoldina, Halle (Saale) 2005
In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

From Nanoscience to Nanotechnology

The Symposium was sponsored by Deutsche Forschungsgemeinschaft and Forschungszentrum Karlsruhe.

NOVA ACTA LEOPOLDINA

Abhandlungen der Deutschen Akademie der Naturforscher Leopoldina

Im Auftrage des Präsidiums herausgegeben von

HARALD ZUR HAUSEN

Vizepräsident der Akademie

NEUE FOLGE NUMMER 340 BAND 92

From Nanoscience to Nanotechnology

Leopoldina Symposium

Forschungszentrum Karlsruhe
September 4 to 5, 2003

Organizing Committee:

Herbert Gleiter (Karlsruhe)
Member of the Academy

Roland Wiesendanger (Hamburg)
Member of the Academy

With 26 Figures and 1 Table

1652

Deutsche Akademie der Naturforscher Leopoldina, Halle (Saale) 2005
In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Redaktion: Dr. Michael Kaasch und Dr. Joachim Kaasch

Die Schriftenreihe Nova Acta Leopoldina erscheint bei der Wissenschaftlichen Verlagsgesellschaft mbH, Stuttgart, Birkenwaldstraße 44, 70191 Stuttgart, Bundesrepublik Deutschland.
Jedes Heft ist einzeln käuflich!

Die Schriftenreihe wird gefördert durch das Bundesministerium für Bildung und Forschung sowie das Kultusministerium des Landes Sachsen-Anhalt.

Bibliografische Information Der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie;
detaillierte bibliografische Daten sind im Internet über http//dnb.ddb.de abrufbar.

06019 Halle (Saale), Postfach 11 05 43, Tel. +49 345 4723934
Hausadresse: 06108 Halle (Saale), Emil-Abderhalden-Straße 37
Herausgeber: Prof. Dr. Dr. h. c. mult. Harald zur Hausen, Vizepräsident der Akademie
Printed in Germany 2005
Gesamtherstellung: Elbe-Druckerei Wittenberg
ISBN 3-8047-2199-0
ISSN 0369-5034

Gedruckt auf chlorfrei gebleichtem Papier.

Contents

BERG, Gunnar: Welcome Greetings 7

HILGER, Almuth, HOFE, Thomas VON, and KREIBIG, Uwe: Recent Investigations of Size and Interface Effects in Nanoparticle Composites 9

LAURITSEN, Jeppe V., and BESENBACHER, Flemming: New Insight into Nanocatalysis from Atom-resolved Scanning Tunneling Microscopy. 21

RIEDER, Karl-Heinz, MEYER, Gerhard, HLA, Saw-Wai, MORESCO, Francesca, BRAUN, Kai F., MORGENSTERN, Karina, REPP, Jascha, FOELSCH, Stefan, and BARTELS, Ludwig: The Scanning Tunneling Microscope as Operative Tool: Doing Physics and Chemistry with Single Atoms and Molecules 29

SCHEER, Elke: Electronic Transport through Atomic-size Contacts 37

WEBER, Heiko B., MAYOR, Marcel, and LÖHNEYSEN, Hilbert VON: Electrical Current through Single Molecules 47

GAREEV, Rashid R., POHLMANN, Lars L., BÜRGLER, Daniel E., and GRÜNBERG, Peter A.: Interlayer Exchange Coupling of Fe Films across Si Tunnel Barriers 55

BODE, Matthias, RAVLIĆ Robert, KLEIBER, Michael, and WIESENDANGER, Roland: Spin-polarized Scanning Tunneling Microscopy of Antiferromagnetic Surfaces 61

GOTSMANN, Bernd, ALBRECHT, Thomas R., BINNIG, Gerd K., DESPONT, Michel, DRECHSLER, Ute, DÜRIG, Urs, JUBIN, Daniel, HÄBERLE, Walter, LANTZ, Mark A., ROTHUIZEN, Hugo, STUTZ, Richard, VETTIGER, Peter, WIESMANN, Dorothea, (*Micro-/Nanomechanics Group*), and BÄCHTOLD, Peter, CHERUBINI, Giovanni, DHOLAKIA, Ajay, ELEFTHERIOU, Evangelos, HAGLEITNER, Christoph, LOELIGER, Teddy, PANTAZI, Aggeliki, POZIDIS, Haris, (*Advanced Storage Technologies Group*): A Nanotechnology Approach to Data Storage 69

ALIVISATOS, Paul: Nanocrystals as a New Class of Macromolecules 75

ROTH, Siegmar: Carbon Nanotubes – from Science to Applications 77

WELLER, Horst: Synthesis, Properties and Self-Assembly of Nanoparticles 79

HECKL, Wolfgang M.: Molecular Self-Assembly – A Key Technology in Nanoscience and Templating. 81

FROMHERZ, Peter: Brainchips – from Nano to Milli 83

KRONMÜLLER, Helmut: Magnetic Structures and Magnetization Processes in Small Particles and Thin Films 85

WELLAND, Mark: Novel Methods for Fabrication of Nanostructures 87

GÖSELE, Ulrich: Nanosilicon 89

HAHN, Horst, and STAHL, Branko: Bioreceptors as Model Systems for Functional Nanostructures 91

GORNIK, Erich: Current and THz Spectroscopy of Quantum States 93

WOLF, Dieter: Dislocation and Grain-Boundary Deformation Processes in Nanocrystalline Materials by Multiscale Computer Simulation 95

Nova Acta Leopoldina NF *92*, Nr. 340, 7–8 (2005)

Welcome Greetings

Gunnar Berg (Halle/Saale)
Secretary of the Academy

Dear Professor Popp, dear Professor Gleiter, dear Professor Wiesendanger

Ladies and Gentlemen,

It is a pleasure for me to welcome you to this Leopoldina Symposium on behalf of the Presidium and especially on behalf of the president of the Deutsche Akademie der Naturforscher Leopoldina, who – unfortunately – cannot be here on this occasion.

The aim of this symposium – the whole field of nanoscience – yields interesting and important problems from a purely scientific point of view, which includes all fields of natural sciences, such as physics, chemistry, and biology, but it has also a strong tendency to technical sciences and engineering. It is very commendable that the symposium was organized in a way to connect the two aspects of basic research and of application: From nanoscience to nanotechnology. I would like to thank Professor Gleiter, the nestor of nanoscience in Germany, that he has developed the concept and has undertaken to prepare, to organize and to carry out this symposium. Also I would like to thank Professor Wiesendanger for his willingness to support the preparation and organization of the symposium.

Let me come back to the special aspect of this symposium, the interaction of basic and applied research or – in other words – of science and of engineering. Recently the Leopoldina has extended its spectrum of activities. Traditionally the working field of the Leopoldina since its foundation in 1652 – more than 350 years ago – includes medicine, mathematics and natural sciences. But a few years ago the Senate of the Academy resolved to open its circle to different disciplines with a background similar to that of natural sciences. That means, sections were founded in the academy, which work with so called exact methods. An example is the section of empirical social science and economics, which means economy in a quantitative sense. Another example is a section of empirical psychology and cognitive science and, last but not least, I will give as a third example the section of technical sciences.

This symposium was suggested by the academy section of physics. But it is the first one where consciously a connection to the technical sciences was looked for. We hope that this symposium will be the starting point of a close cooperation of the two sections.

A special aim of the academy is the formation of so called ad hoc commissions. That means the joining of scientists of different disciplines to work together on a field of special scientific significance or of special public interest, of course, with a scientific background. The Presidium of the academy is convinced that nanoscience is such a field of general importance. Therefore we have the hope that one result of this symposium will be the foundation of such an ad hoc commission with members from physics, chemistry, biology and engineering, the way it is planned by Professor GLEITER.

In conclusion, I would like to thank Professor GLEITER and Professor WIESENDANGER once more, especially also their coworkers here in Karlsruhe and also the coworkers of Professor SCHNITZER-UNGEFUG, secretary general of the academy, in Halle for their commitment in organizing this symposium.

On behalf of the Presidium of the academy, I wish all participants of the symposium a successful conference, interesting lectures and discussions and the initiation of forward-looking cooperation.

Prof. Dr. Dr. Gunnar BERG
Martin-Luther-Universität Halle-Wittenberg
Fachbereich Physik
Fachgruppe Experimentelle Physik I
06099 Halle (Saale)
Germany
Phone: +49 345 5525520
Fax: +49 345 5527159
E-Mail: g.berg@physik.uni-halle.de

Nova Acta Leopoldina NF *92*, Nr. 340, 9–19 (2005)

Recent Investigations of Size and Interface Effects in Nanoparticle Composites

Almuth HILGER, Thomas VON HOFE, and Uwe KREIBIG (Aachen)

With 4 Figures

Abstract

Nanoparticles, small in all three dimensions, exhibit pronounced size and surface effects. There are broad fields of technical applications for nanoparticle-based composite materials taking advantage of these effects. An essential drawback is that such systems require stabilization, causing the free and clean particle surfaces to be transformed into very complex interface regions.

After a general introduction, four experiments are presented which shed some light upon different aspects of these complex interfaces. They were performed by using 2 nm Ag nanoparticles and applying optical Mie plasmon spectroscopy. The unique feature of these experiments is that spectroscopy was performed with the free particles in a cluster beam and after depositing and embedding them, and, hence, quantitative comparisons could be performed.

Zusammenfassung

Ausgeprägte Nanostrukturierungseffekte finden wir in Nanopartikeln, da diese in 3 Dimensionen klein sind. In Vielteilchen-Systemen/Kompositen werden sie vielfach für technische Anwendungen eingesetzt, welche die auftretenden Partikelgrößen- und Oberflächeneffekte ausnützen. Grundlegender Nachteil vieler solcher Systeme ist, daß sie durch ein Wirtsmedium stabilisiert werden müssen. Dadurch werden die freien, sauberen Teilchenoberflächen in komplexe Grenzflächenbereiche überführt.

Nach einer allgemeinen Einführung werden vier Experimente vorgestellt, die unterschiedlichen Aspekten dieser Grenzflächen gewidmet sind. Sie wurden alle mit 2 nm großen Ag-Teilchen durchgeführt, und es wurden Mie-Resonanzen als empfindliche optische Sensoren für elektronische Eigenschaften untersucht. Die Experimente sind dadurch ausgezeichnet, daß sowohl an den freien Teilchen im Strahl als auch nach Deposition und nach Einbettung spektroskopiert wurde, so daß Unterschiede quantitativ ermittelt werden konnten.

1. Introduction

The unique properties of nanostructured materials, and in special, of nanoparticles (KREIBIG and VOLLMER 1995), most commonly are interpreted as size-effects, i.e. N-effects, where N is the number of atoms per structural unit.

These effects are extremely interesting for basic research, since we can observe the “birth” of the solid state by varying N.

There is a second class of nano-effects, which is due to the surface of the structural units. Nanostructurization means, thus, both, breaking of crystal symmetry, and creation of new surfaces and/or interfaces. Surface of a particle can, however, only be clearly defined and distinguished from an inner volume, if $N > 50$. This may be introduced as a limit to distinguish between *molecular* and *solid state* clusters.

The nano-effects due to surface are theoretically much less understood, notwithstanding the intense investigations, e.g. in the field of heterogeneous catalysis, or in the succession of the pioneering work of GLEITER'S group with nanocrystalline, grainboundary-rich materials.

We have to distinguish between *surfaces* of the free, uncontaminated particles and *interfaces* covered by foreign dielectric, semiconducting, metallic or superconducting materials, liquids or solids, adsorbates, substrates, embedding media etc. Interfaces are much more complex, consisting, both, of particle surface and foreign material surrounding parts of, or the whole, particle. To give only one example: in special cases of insulating or semiconducting matrix, Schottky barriers emerge.

Surfaces and interfaces include storage of large amounts of surface/interface energy, and this renders many kinds of nanoparticles, in particular the metallic ones, to be energetically instable, one of the worst drawbacks of nanotechnology.

These energies lead to a dramatic struggle between surface and inner volume. Both try to obtain their respective stable energy minima which require controversial particle structures. While for the surface this structure is something close to a spherical shape, it is for the inner volume the crystal structure of the bulk. During particle growth, first the surface is dominating, while towards large particles, the volume is the winner.

To give an example: Using the bulk value of the specific surface energy of silver, this surface energy for the simple case of one spherical silver particle, 10 nm in diameter, yields about 5 keV. In 1 mm^3 of a many-particle system with a filling factor of 10^{-4} the energy of about 10 mJ is stored in the particle surfaces.

The classical Surface Sciences, dealing preferentially with well-defined crystal planes, cannot, however, be very helpful to treat these surfaces/interfaces in a realistic manner, since they consist, beside some flat facets, mainly of irregular structures, edges and corners with low coordination numbers, all with different electron energy states.

The practical situation is even worse, if, as usual for technically applied many-particle composites, these particles are statistically varying in size, shape, interior structure, next-neighbor interactions, etc.

As a consequence of the additional energies, most inorganic nanostructured systems in nature and technology have to be stabilized, either by passivating them with stabilizing coatings, or by depositing them onto some rigid substrate or by embedding them in some host material.

In general, the model of a free nanoparticle is, therefore, not relevant, even approximatively. Instead, the more complex building units are particles plus the special surroundings, i.e. particles "dressed" by interfaces.

As an example, the famous Gold-55-clusters (SCHMID 1993), in fact are "dressed" metal-organic compound clusters, consisting of a metallic core and the surrounding and stabilizing triphenylphosphine shell plus additional bound chlorine ions as structural units.

Despite intense research, our knowledge about these *realistic* interfaces between particles and chemically variable surrounding materials is rather poor, especially because of their immense variability. In most cases, the electronic interface states or "adsorbate" states are unknown, both experimentally and theoretically.

In fact, their knowledge would be very important, not only for existing technological applications like the heterogeneous catalysis, but also for novel technologies like the expected break-through towards true small-scale nanostructurization in digital electronics or the "functionalization” of nanoparticles by directed adsorption of organic or bio molecules in order to use them as selective antibody tracers for special molecules like e.g. special cell-proteins.

For sure, these interfaces are one of the essential challenges for future research in nanoscience. And nanoparticles appear to be the best suited model-systems for this purpose. In particular, embedding them in absorbing semiconductor and metal matrices, (i.e. semiconductor doping with clusters) may open interesting new applications.

In what follows, we present four experimental investigations which shed some light onto different nanoparticle interface properties.

2. Mie Resonances as a Sensor Tool for Interface Investigations

One of the most pronounced nanoparticle effects is the optical excitation of *Mie resonances* in metallic particles (Kreibig and Vollmer 1995). These surface plasmon polaritons are caused by restoring forces which are due to electric surface charging by an external optical field. Hence, they are nano-surface effects, and any changes at the surface, e.g. the transformation of the surface into an interface by covering the surface with some host material, strongly influence these resonances.

Starting 35 years ago (Kreibig and von Fragstein 1969), we still use the Mie resonances as highly sensitive tools for nanoparticle interface investigations, e.g. physical and chemical reactions at the particle surfaces. By the way, this is not a novel idea: in the beginning of the 20th century, R. Zsigmondy introduced the Mie resonances to chemical analysis. He received the first Nobel Prize in the field of nanoscience, at that time called “colloid science”, in 1925 for his pioneering work with gold nanoparticles.

Conventional optical spectroscopy requires macroscopic samples of many particles, i.e. nanoparticle based nanocomposites. Only recently, single particle extinction spectroscopy was successful (Soennichsen et al. 2000).

For practical reasons we selected silver as particle material, since these particles are world champions in strength and spectral selectivity of Mie resonances.

Any quantitative investigation requires comparison with a proper reference. In our case, this is the *same* Ag nanoparticle but with *free*, uncontaminated surfaces. This appears to be the only confidential reference.

For this purpose, we produce a beam of free Ag nanoparticles in vacuum by a thermal, high efficiency source THECLA (Hövel et al. 1993), the particles of which are then, both, deposited onto solid substrates and, by co-deposition, embedded in matrix. In our long-term investigation project, the surrounding materials are systematically varied. Mean particle sizes can be varied between 250 and 2000 atoms/particle, i.e. 2 and 4 nm diameter. Such particles combine (almost) developed bulk electronic band structure with extremely large surface. The unique feature of the experiments is that spectroscopy is performed with the free particles as well as after depositing and embedding them, thus enabling, for the first time, quantitative analysis of the differences between free surface and different kinds of interfaces.

The Mie extinction spectra of Ag nanoparticles resemble Lorentz bands and they have, at least, three features indicative for surface and interface properties: > the band width, > the spectral band position, > the additional background extinction by the optical 4d-5sp interband transition edge. Figure 1 shows the extinction spectra of Ag nanoparticles in the free beam and after deposition on, and after embedding in, glassy SiO_2.

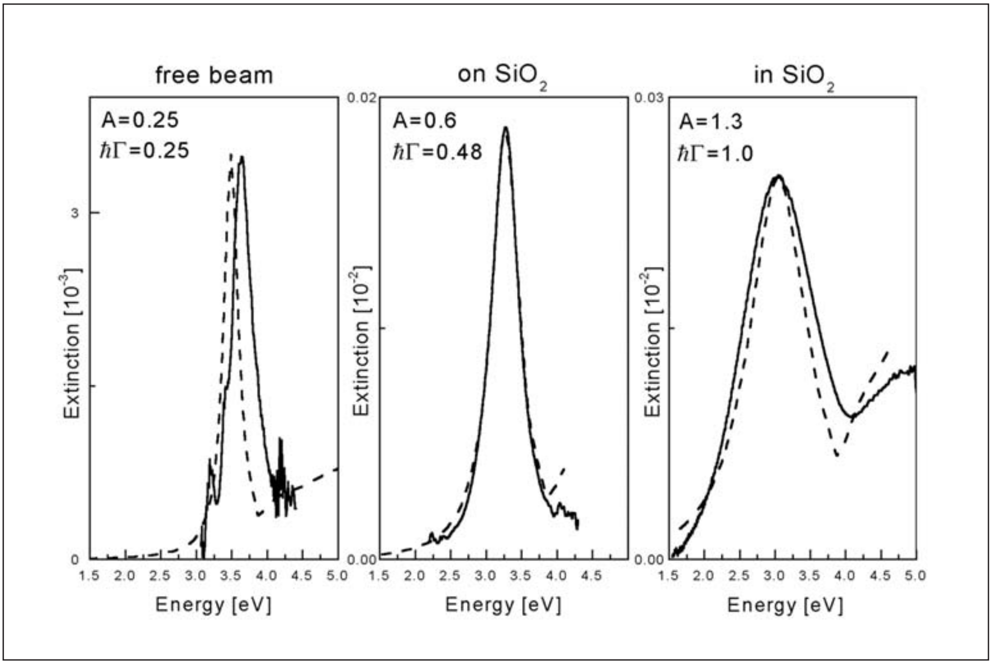


Fig. 1 Measured optical absorption spectra of Ag nanoparticles (2R = 2 nm) and comparison with calculated spectra. *Left*: free particles in the beam. *Center*: Same particles, deposited upon SiO_2-glass substrate. *Right*: Same particles, embedded in SiO_2-glass. Calculations (dashed lines): Mie theory with literature data (JOHNSON and CHRISTY 1972) and *A*-parameter corrections. $\hbar\,\Gamma$ in [eV].

Spectroscopy of composites, yielding averages over many particles, requires well defined, uniform systems to enable quantitative statements about single particles. In our samples, size distributions were determined by TEM and involved in the evaluations. In all investigated samples, the particle distances were sufficiently large to prevent neighbor-interactions. Most problematic are inhomogenities in the substrates and embedding media, causing different interfaces for different particles. If their characteristic lengths are of the order or larger than the particle sizes, their influences will increase with decreasing size due to reduced averaging out. These effects are very general, contributing e.g. to additional broadening of the overall-spectra. They are, of course, absent exclusively in the free particle beam. As an example, in SiO_2 matrix we found an upper limit of 20 % of the bandwidth for this “inhomogeneous” broadening of the Mie resonances.

In the following we present results of four experiments on different substrates and embedding hosts, each to demonstrate one particular interface effect.

2.1 First Experiment: Silver Nanos Embedded in Fullerite: The Static Charge Transfer

Our sensor Ag nanoparticles were embedded in Fullerite, i.e. solid C_{60} material, by co-deposition (GARTZ et al. 1999). Their optical absorption spectrum, obtained by subtracting the spectrum of pure fullerite, proved to be broadened and red-shifted compared to the spectrum of the free particles in Figure 1 (*left*). As a second reference, we calculated the extinction spectra from MIE's theory.

The observed peak shift is explained by two superimposing effects: First, the Maxwell boundary conditions of the particle surface are changed by the dielectric function of the embedding host material, giving rise to strong "dielectric" shift (which is already included in the spectra calculated from MIE'S theory).

Second, non-classical static charging of the Ag particles occurs leading to an additional shift $\Delta\hbar\omega$. Its numerical value is plotted in Figure 2. The underlying model is as follows (HÖVEL et al. 1993, KREIBIG et al. 1998):

(*i*) The whole particle/matrix-system arranges itself such that there is equilibrium of the chemical potential (or Fermi-energy E_F) in the whole sample. This requires charge transfer from the particles into the Fullerite, and the equilibrium is established by thus generated additional Coulomb energy. Since the particles are isolated in the matrix, the conduction-electron density ρ in the particle is thereby changed. Such *static charge effect* is expected to occur generally in nano-composite systems.

(*ii*) The resonance frequency of the conduction-electron plasma in the Ag-particle depends on the electron density ρ. The change of ρ by static charge transfer, thus, causes an additional spectral shift of the Mie resonance.

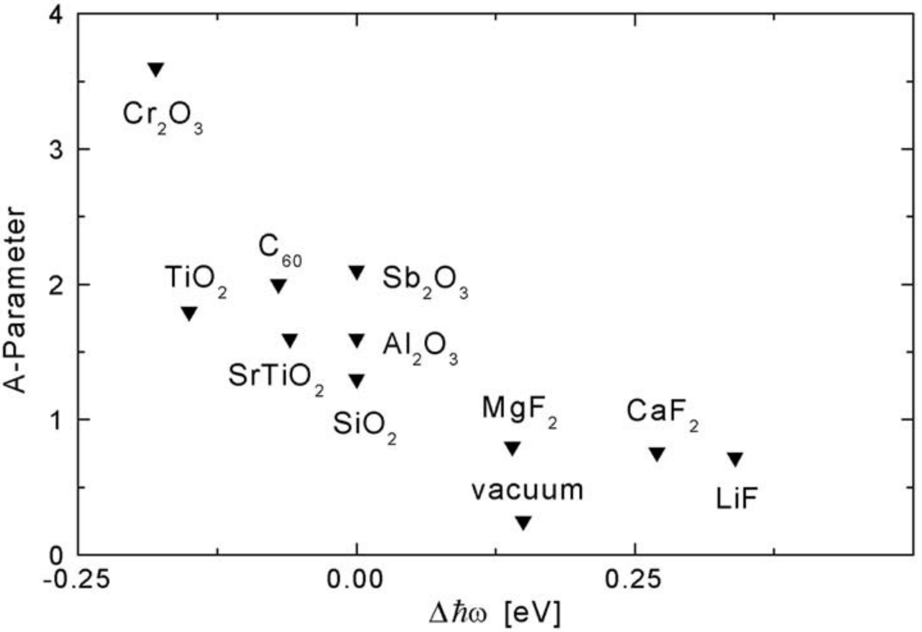


Fig. 2 Summary of experimental results for interface charging effects between Ag nanoparticles and various embedding media: Peak shift $\Delta\hbar\omega$ (static charge transfer) *versus* broadening parameter A (dynamic charge transfer). Due to quantum size effects, A of vacuum amounts to 0.25. Systematic differences of the magnitudes of these effects occur between oxides and fluorides. $\Delta\hbar\omega \neq 0$ for free particles ("vacuum") since the zero was calibrated to Mie calculations using the optical parameters of JOHNSON and CHRISTY (1972).

Numerical evaluation of this model yielded the clear result, that each C_{60} which is in *direct* contact with the Ag nanoparticle surface in the composite, pulls *one* conduction-electron out of the Ag particle which is then located in one of the electronic interface states. In the present case, the particles loose, thus, about 20 % of their (delocalized) conduction electrons with consequences upon Fermi energy, lattice constants, band structure etc. However, charges are not really removed, but an electric double layer is formed in the interface region.

Hence, the particle material might no longer be called "silver"; instead the interface effects have created a novel metal.

2.2 Second Experiment: Interface Damping of Mie Resonances

Again, Ag clusters ($N \approx 250$ atoms) were produced by THECLA and their optical extinction was measured in the three different states of the free cluster beam, the clusters deposited on a solid substrate and the clusters embedded in matrix of the same material. The special feature of this series of experiments was that a wide range of different host materials was investigated.

Drastic differences of the respective Mie resonance spectra were found for most of the different substrate/host materials (HILGER 2001) which are not included in the classical Mie theory. One example with glassy SiO_2 as surrounding medium was shown above in Figure 1.

The resulting peak shifts were already discussed in 2.1. Now we concentrate upon the apparent band broadening. These effects essentially remain, even if we reduce them for the above discussed inhomogeneous broadening effects. For interpretation, the following model of *dynamic interface damping* was introduced (HÖVEL et al. 1993 and KREIBIG et al. 1998):

(*i*) We assume the formation of chemisorption interface states yielding broad energy bands due to interactions with topologically different surface atoms. There are two possible situations: first, these bands are close above E_F of the Ag particles and can be temporarily occupied by tunneling cluster electrons, second, their energies are far above E_F and no such transitions are possible. In the first case, charge fluctuations take place in the interface region.

(*ii*) These fluctuations may be monitored, if a Mie plasmon resonance is excited. Then, part of the impulse of the collective plasma excitation is lost by each electron transition into an interface state and back to the particle. Hence the common phase of the collective motion of the electron plasma is reduced, leading to increased *phase relaxation* of the plasma resonance, and, hence to broadening of the Mie absorption band. In this model, the broadening is characterized by the *interface parameter A* depending on the fluctuation strength and, hence, on the details of the electronic interface states. Formally, A is introduced *via* a reduced relaxation time τ of the free Drude electrons in the cluster due to surface/interface interactions: $\tau_{\text{particle}} = \tau_{\text{bulk}} + A\, v_F / R$ with v_F the Fermi velocity and R the particle radius. A is evolved from the measured extinction spectra by inverting MIE's theory (KREIBIG and VOLLMER 1995).

The different numbers and kinds of interface states for deposited and for embedded clusters explain why the latter exhibit larger broadening, by far (see Fig. 1). For deposited particles, surface tension and possible plastic deformations of the clusters and the underlying substrate determine the relation between the relative amounts of free surface and interface and, hence, the magnitude of interface effects, while embedded clusters exclusively exhibit interfaces (Hilger et al. 2001). In a recent publication, this model has been treated (Pinchuk and Kreibig 2003).

Figure 2 shows a compilation of measured *A*-parameters *versus* charge transfer peak shift $\Delta h\omega$ for different host materials.

A final comment may be added here: as leading order approximations the models of 2.1 and of 2.2 are treated here independently. In fact, part of both effects is interconnected by Kramers-Kronig relations. Efforts to find a common description by introducing some complex interface parameter are in work.

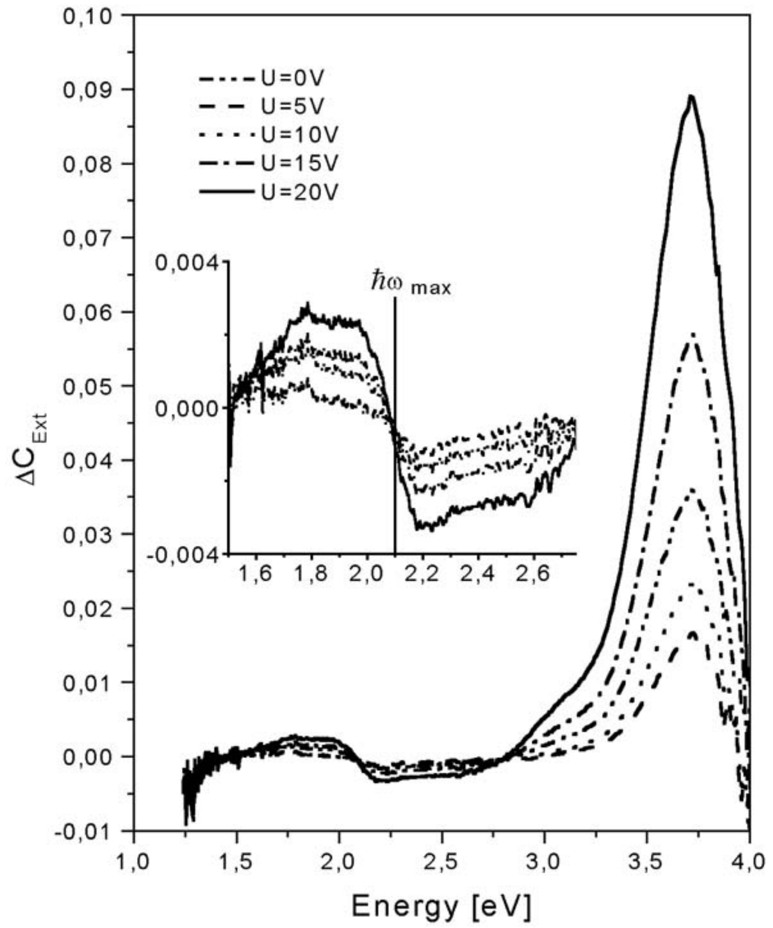


Fig. 3 Ag nanoparticles embedded in ferroelectric PZT: Measured absorption changes ΔC_{ext} due to varying bias voltage. The large contribution at 3.7 eV is due to the PZT interband edge and also present in the particle-free PZT. (Prior to the experiment, –20V had been applied, and thus, first the remaining hysteresis-effect had to be rebuilt, before the positive voltage caused the increase of the absorption). The small contribution at $h\omega_{max}$ =2.1 eV is due to the changes of the Mie resonance of the Ag particles. This effect is magnified in the inset.

2.3 Third Experiment: Ferroelectric Surroundings

An interesting question arises, to which extent the particular charging effects in the interface region may be artificially varied and what are their effects onto the Mie resonances (VON HOFE 2001). We chose ferroelectric PZT (lead-zirconate-titanate) as an embedding matrix[1]. Two films were deposited on a quartz substrate by help of spin coating, and in between a low coverage monolayer of Ag particles was included. The experiments were first only performed at room temperature. DC voltages were applied between a top ITO and a bottom gold electrode and the according Mie resonance spectra were recorded. The same films, but without Ag particles acted (beside the free clusters) as additional reference. First, the ferroelectric behavior of the films was confirmed by measuring their polarization hysteresis loops which proved to be well developed. Next, optical transmission spectra were measured with increasing external bias from –20 to +20 V dc. The resulting electrostatic fields are up to 2.5 10^8 V/m. The field direction was parallel to the Poynting vector; we did not yet search for effects in polarized light. The samples exhibited a static conductivity of $\approx 10^6\ \Omega$ m. A sharp Mie resonance occurred at 2.07 eV with a width of about 0.7 eV and shifted against calculated zerofield spectra by as much as – 0.6 eV. This shift indicates a strong static charge transfer from the Ag particles into the interface region.

By increasing the bias voltage, two effects in different spectral regions occurred. In Figure 3 only the field dependent *differences* between the extinction spectra with and without field are shown.

The stronger effect is a field dependent increase of extinction at the edge of the fundamental absorption of the PZT itself around a fixed energy of 3.7 eV. It exhibits a clear hysteresis behavior and occurs also in the particle free reference sample.

More interesting for our purposes is the bias-effect in the spectral region of the Mie resonance. As also shown in Figure 3, there is a slight extinction change ΔC_{ext} in the particle-containing sample which is clearly enhanced with increasing bias voltage. The shape of the difference spectra indicates a red shift of the Mie peak with increasing electrostatic bias field. Also this effect exhibits clear hysteresis effect.

A careful Kramers-Kronig evaluation yielded the result that about one third of the observed Mie peak shift is due to the changes of the PZT-refractive index induced by the extra field dependent absorption at 3.7 eV (see Fig. 3). Two thirds remain to extra particle and interface effects of unknown origin. Among them might be bias-induced non-linearity of the plasmon excitation, bias induced extra static charge transfer, etc. The interpretation of these results is in work.

2.4 Fourth Experiment: Band Structure Effects

Up to now, all observed and described nano-effects are due to the 5 sp electron (conduction electron) plasma in the Ag particles. We demonstrate now, that additional size/interface effects occur with the 4d electron excitations.

In bulk Ag, the low energy optical interband transition edge at about 3.8 eV is due to 4d→5sp electron-hole transitions. Usually this is described in terms of the complex interband susceptibility

---

[1] We are indebted to R. WASER, R. GERHARDT and U. BÖTTGER (IWE, RWTH) for helping us with the PZT films.

$$\chi^{\text{interband}}(h\omega) = \chi_1^{\text{interband}}(h\omega) + i\,\chi_2^{\text{interband}}(h\omega). \qquad [1]$$

These excitations appear as background in our Mie resonance extinction spectra. They were numerically separated from the Mie extinction in the measured spectra by a careful Kramers-Kronig analysis (HILGER 2001).

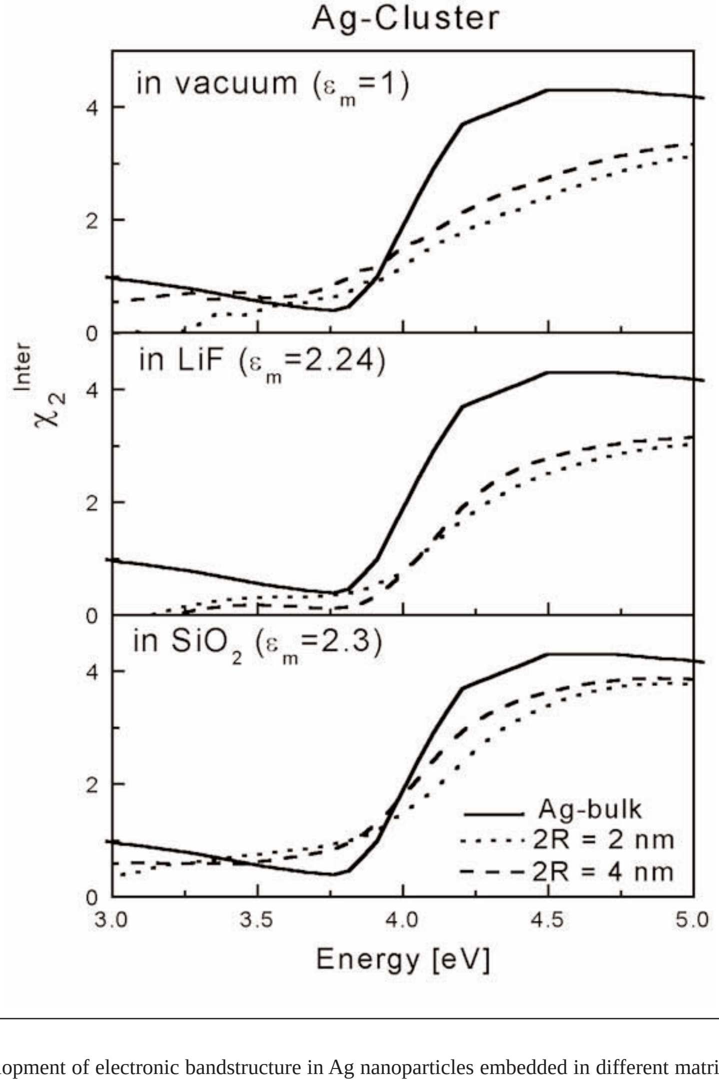


Fig. 4 Development of electronic bandstructure in Ag nanoparticles embedded in different matrix media. The low frequency 4d–5sp interband transition edge is expressed by the imaginary part of the complex electric susceptibility $\chi_2^{\text{interband}}(h\omega) = \text{Im}\{\chi^{\text{interband}}(h\omega)\}$. Shown are the band edges for 2R = 2 nm and 4 nm particles, as evaluated from experiments on Ag nanos in the free beam (vacuum), and embedded in LiF and SiO_2, respectively. For comparison, the edge of bulk Ag is plotted as obtained from proper evaluation of literature data of (HAGEMANN et al. 1974). ε_m is the dielectric function of the respective embedding medium.

By changing the seeding gas of the cluster source from Ar to Xe the mean particle size 2R could be varied from 2 nm (≈ 250 atoms) to 4 nm (≈ 2000 atoms). In Figure 4 the spectra of $\chi_2^{\text{interband}}(h\omega)$ of our particles are compared with calculated bulk values. Results from three different surroundings are shown: vacuum, LiF and SiO_2. There are two important features:

(*i*) In the *free* Ag particles, these transitions prove to differ strongly from the bulk. Clearly, the interband transition edge is smeared out and its onset is red-shifted and this the more, the smaller the particles are. This was already detected earlier in *embedded* Au-clusters (Kreibig 1978). It clearly indicates that the electron interband structure is not yet fully developed in 2 nm and in 4 nm metal particles. The deviations are clearly larger for the smaller particles, yet it appears open whether the leading effect is to be attributed to size or to surface effects. The first would be expected from the fact that the k-vector of Bloch waves is no longer well defined in strongly confined electron systems. The second may be due to the fact that essential part of the particle atoms is forming the surface.

(*ii*) A surprising additional, novel effect was discovered when evaluating analogously the experimental spectra of the same particles *embedded* in different host materials. As also shown in Figure 4, embedding in LiF and SiO_2, respectively, yielded a clearly better approach to the bulk spectra, i.e. a reduction of the interband nano-effect.

As a consequence of these findings, the development of the band structure is obviously supported by the existence of (dielectric) embedding media. These media probably reduce, *via* the formation of the complex interface region, the potential step at the particle surface.

Again, the role of the electronic interface states is an open problem. From Figure 2 we see that the dynamic and static interface effects are large in the case of oxides like SiO_2 but smaller in fluorides like LiF. In correspondence, the interface influence onto the particle band structure is larger in SiO_2 than in LiF. For closer understanding, it appears that band structure calculations including the existence of interfaces are required.

Acknowledgement

We are indebted to the *Deutsche Forschungsgemeinschaft* for financial supports of the investigations.

References

Gartz, M., Keutgen, C., Kuenneke, S., and Kreibig, U.: Novel examples of cluster-matter produced by LUCAS, a new laser cluster source. Euro-Physics Journal D *9*, 1–5 (1999)

Hagemann, H. J., Gudat, W., and Kunz, C.: DESY SR-74/7 and J. Opt. Soc. Amer. *65*, 742 (1975)

Hilger, A.: Grenzflächenanalyse durch Mie-Plasmon-Spektroskopie an Edelmetallclustern. Thesis, RWTH Aachen (2001)

Hilger, A., Tenfelde, M., and Kreibig, U.: Silver nanoparticles deposited on dielectric surfaces. Appl. Physics B *73*, 361–372 (2001)

Hofe, T. von: Neuartige Cluster-Materie auf der Basis von Silberclustern. Diploma Work RWTH Aachen (2001)

Hövel, H., Fritz, S., Hilger, A., Kreibig, U., and Vollmer, M.: Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping. Phys. Rev. B *48*, 18178 (1993)

Johnson, P., and Christy, R.: Optical constants of the noble metals. Phys. Rev. B *6*, 4370 (1972)

Kreibig, U., and Fragstein, C. von: The limitation of electron mean free path in small silver particles. Zschr. f. Physik *224*, 307–323 (1969)

Kreibig, U.: The transition cluster – solid state in small gold particles. Sol. State Commun. *28*, 767–769 (1978)

KREIBIG, U., BOUR, G., HILGER, A., and GARTZ, M.: Optical properties of cluster-matter: Influences of interfaces. Phys. Stat. Sol. A *175*, 351–366 (1999)

KREIBIG, U., GARTZ, M., HILGER, A., and HÖVEL, H.: Optical investigations of surfaces and interfaces of metal clusters. In: DUNCAN, M. (Ed.): Advances in Metal and Semiconductor Clusters. Vol. *IV*, pp. 345–393. London: JAI Press Inc. 1998

KREIBIG, U., and VOLLMER, M.: Optical properties of metal clusters. Springer Series in Material Science *25* (1995)

PINCHUK, A., and KREIBIG, U.: Interface decay channel of particle surface plasmon resonance. New J. Phys. *5*, 1–15 (2003)

SCHMID, G. (Ed.): Clusters and Colloids – From Theory to Application. Weinheim: VCH-Verlag 1994

SOENNICHSEN, C., GEIER, S., HECKER, N., PLESSEN, G. VON, FELDMANN, J., DITLBACHER, J., LAMPRECHT, B., KRENN, J., AUSSENEGG, F., CHAN, V., SPATZ, V., and MÖLLER, M.: Spectroscopy of single metallic nanoparticles using total internal reflection microscopy. Appl. Phys. Lett. *77*, 2949 (2000)

Dr. Almuth HILGER
Dipl.-Phys. Thomas VON HOFE
Prof. Dr. Uwe KREIBIG
I. Physikalisches Institut IA der RWTH
Abteilung Cluster-Materie
Sommerfeldstraße 14
Turm 28
52056 Aachen Postfach
Germany
Phone: +49 241 8027176
Fax: +49 241 8022331
E-Mail: kreibig@physik.RWTH-Aachen.de

Academia 350
Die Leopoldina-Feiern in Schweinfurt und Halle 2002

Vorträge der Festveranstaltungen aus Anlaß des 350jährigen Gründungsjubiläums der Deutschen Akademie der Naturforscher Leopoldina am
17. und 18. Januar 2002 in Schweinfurt und vom 18. bis 20. Juni 2002 in Halle (Saale)

Nova Acta Leopoldina N. F. Bd. *87*, Nr. 325
Herausgegeben von Benno Parthier (Halle/Saale)
(2003, 248 Seiten, 19 Abbildungen, 2 Tabellen, 24,80 Euro, ISBN 3-8047-2000-5)

Die Deutsche Akademie der Naturforscher Leopoldina feierte im Jahre 2002 ihre Gründung vor 350 Jahren mit zwei Festveranstaltungen. Im Januar in der Gründungsstadt Schweinfurt standen die historischen Wurzeln der Akademiegründung im 17. Jahrhundert im Mittelpunkt. Nach der Begrüßung durch Akademiepräsident Benno Parthier untersuchte Lorraine Daston (Berlin) das Thema »Die Akademien und die Neuerfindung der Erfahrung im 17. Jahrhundert«. Richard Toellner (Rottenburg) nannte seine Ausführungen zu den Quellen der Akademiegründung »Im Hain des Akademos auf die Natur wißbegierig sein: Vier Ärzte der Freien Reichsstadt Schweinfurt begründen vor 350 Jahren eine Naturforscherunternehmung«. Der Schweinfurter Festakt brachte nach der Begrüßung durch Frau Oberbürgermeisterin Gudrun Grieser und einer Folge von Grußadressen (u. a. vom bayerischen Ministerpräsidenten Edmund Stoiber) abschließend eine Standortbestimmung der ältesten deutschen Akademie in der Gegenwart von Präsident Parthier (»Die Leopoldina heute«). Außerdem wird die im Rahmen der Feierlichkeiten erfolgte diesjährige Verleihung des Carus-Preises der Stadt Schweinfurt dokumentiert. Die Juniveranstaltung in Halle (Saale) widmete sich nach Grußworten des Bundespräsidenten Johannes Rau und des sachsen-anhaltinischen Ministerpräsidenten Wolfgang Böhmer den internationalen Aspekten des Leopoldina-Wirkens mit einem Symposium »Science und Society«, das gemeinsam von Vertretern der ältesten europäischen Akademien, der Royal Society (Lord Robert May, London), der Académie des Sciences (Jean-Pierre Kahane, Paris), der Accademia Nazionale dei Lincei (Sergio Carrà, Rom) und der Leopoldina (Hans Mohr, Freiburg i. Br.), getragen wurde. Die Beiträge behandeln das gesamte Spannungsfeld von Wissenschaft, Politik, Gesellschaft und Demokratie. Darüber hinaus dokumentiert der Band den von der Jungen Akademie, einer Tochterinstitution von Leopoldina und Berlin-Brandenburgischer Akademie, im Rahmen der Leopoldina-Jubelfeier veranstalteten Workshop »Science und Society: Science Goes Pop?«, der versuchte, der Popularisierung von Wissenschaft und dem Bild des Wissenschaftlers in der Öffentlichkeit nachzugehen.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 21–28 (2005)

New Insight into Nanocatalysis from Atom-resolved Scanning Tunneling Microscopy

Jeppe V. Lauritsen and Flemming Besenbacher (Aarhus)

With 3 Figures

Abstract

When dimensions become sufficiently small the properties of materials often change with size. These dependencies may go beyond the mere scaling with size, resulting in new physical, chemical and electronic properties that are different from those found at larger sizes. The circumstances when small is different in an essential way, often occur when one or more of the physical dimensions of a material approach length scales characteristic of the phenomenon. Scanning tunneling microscopy (STM) has proven to be an outstanding technique for exploring the atomic-scale realm of nanostructures, and it has provided a breakthrough in the understanding of why small is different. Here we will show how STM can give new atomic-scale insight into the structure of nanoclusters relevant to nano-scale reactivity and heterogeneous catalysis in particular. We discuss atomic-scale studies of MoS_2 nano-clusters synthesized on a gold substrate as a model system for the important hydrotreating catalyst, and find from atom-resolved STM images that MoS_2 nanoclusters have electronic and structural properties that are significantly different from what is expected from the bulk properties of MoS_2. This new atomic-scale insight is shown to be important for the understanding of how the catalyst operates.

Zusammenfassung

Bei hinreichend kleinen Materialdimensionen ändern sich die Eigenschaften eines Materials häufig mit der Größe. Es erweist sich, daß diese Größenabhängigkeit über ein bloßes Skalieren hinausgehen kann, und daß neue physikalische, chemische und elektronische Eigenschaften gefunden werden können, die sich von denen bei größeren Materialabmaßen unterscheiden. Die Bedingungen, unter denen kleine Maße grundlegend andere Materialeigenschaften hervorrufen, klein also anders ist, sind oft erfüllt, wenn eine (oder mehrere) der physikalischen Abmaße des Materials die charakteristische Länge des untersuchten Phänomens erreicht. Rastertunnelmikroskopie (STM) ist hervorragend für Nanostruktur-Untersuchungen im Bereich von atomaren Längenskalen geeignet und kann daher zu einem Durchbruch in unserem Verständnis der Gründe beitragen, weshalb klein anders ist. Hier wollen wir zeigen, wie STM ein neues, atomares Verständnis der Strukturen von Nanoclustern mit Hinblick auf die Reaktivität der Nanostrukturen und auf heterogene Katalyse ermöglicht. Wir besprechen Untersuchungen von auf einem Goldsubstrat synthetisierten MoS_2-Nanoclustern, die wir als Modell für einen Katalysator für hydrierende Raffinierung (hydrotreating) benutzen. STM-Bilder mit atomarer Auflösung zeigen, daß die MoS_2-Nanocluster in ihren elektronischen und geometrischen Eigenschaften signifikant vom Bulkmaterial abweichen. Es wird weiter gezeigt, daß diese neuen Einsichten wichtig sind für ein Verständnis der Wirkungsweise des Katalysators.

Nanotechnology and nanoscience have recently become new buzz-terms. Nevertheless, catalysis, which underlies a significant portion of the gross national products in the industrialized countries, has always been a nanotechnology, since the control of structures on the nanometer scale is a central issue in the development of new and more capable catalysts for chemical production. Catalysts daily accelerate and boost thousands of different chemical reactions, thereby forming the basis for the multibillion dollar chemical industry worldwide and indispensable environmental protective technologies. Although most chemical production is performed in large-scale reactors, the chemistry that actually takes place in the catalyst turns out to occur on the surface of highly dispersed metallic or ceramic nanostructures with typical dimensions of ca. 1–100 nm, whose specific properties instantly trigger chemical reactions that would normally take ages. For many years, the only way to develop new or improved catalysts was by empirical testing in so-called trial-and-error experiments. This time-consuming and costly procedure is now beginning to be replaced by more rational methods based on the fundamental knowledge of catalysts, i.e. the design of catalysts from first principles. This has been made possible due to the extensive developments of more sophisticated characterization techniques and theoretical methods, which have increased the fundamental atomic-scale understanding of catalysis. With a nanotechnology bottom-up approach it is now even becoming possible to control matter on the atomic scale and thereby tailor the performance of new heterogeneous catalysts for better and cleaner industrial processes.

An important tool that has revolutionized the way we think about surfaces and their chemistry is the scanning tunneling microscope (STM). Capable of achieving true atomic-scale resolution in real space, the detailed STM investigations have in numerous cases helped solve surface structures with catalytic relevance (ZAMBELLI et al. 1996, VALDEN et al. 1998, OVER et al. 2000). In surface science studies of model catalysts one typically selects the most important part, the chemically active surfaces or clusters, and investigates them under well-controlled conditions (SOMORJAI 1994). The ability of the STM to directly resolve the local atomic-scale structure has revealed essential insight and, in particular, emphasized the catalytic importance of edges, kinks, atom vacancies or other defects, which is often overlooked with other techniques.

In the Aarhus STM Laboratories, we have over the years used a home-built, high-resolution STM to study a number of technologically relevant nano-catalysts, see e.g. (HANSEN et al. 1999, HORCH et al. 1999, PEDERSEN et al. 2000, ÖSTERLUND et al. 2001, VESTERGAARD et al. 2002, SCHAUB et al. 2003, WAHLSTRÖM et al. 2003), and the detailed STM studies have provided a breakthrough in the atomic-scale understanding of their reactivity. In one case it was even demonstrated that a new catalyst, operating at technologically relevant conditions, could be designed on the basis of fundamental surface science insight (BESENBACHER et al. 1998). In a fruitful interplay between theoretical and experimental investigations, it was shown that a traditional Ni catalyst for steam reforming of hydrocarbons (H_2 production) could be replaced by a superior Au/Ni surface alloy catalyst, which is now a patented technology. In this communication we will review recent knowledge obtained in STM studies on a model system for another class of technologically and environmentally very important catalysts, i.e. the hydrodesulfurization catalysts, and we will show that nano-scale insight is essential in order to understand how the catalyst operates.

The hydrodesulfurization (HDS) catalytic reaction is a reductive hydrogen treatment of fuels to clean up sulfur-containing oil compounds and thereby save our environment for many tons of harmful sulfur emissions on a daily basis. At present the process attracts special attention in view of new and more severe legislation in the US and EC calling for significantly improved fuel specifications. In order to achieve the scheduled reduction of the present sulfur impurity level in transport fuels by a factor of ten in 2005, correspondingly more active hydrodesulfurization catalysts need to be developed. Sulfided molybdenum-based catalysts have long been among the most important catalysts for this service (Topsøe et al. 1996, Prins 1997), and the increased interest in HDS catalysts has resulted in numerous investigations. The level of understanding has increased substantially as new and better characterization tools have been developed. By applying *in-situ* techniques like Extended X-ray Absorption Fine Structure (EXAFS), it has been established that the active molybdenum is present as 10–20 Å wide MoS_2-like nanostructures, often promoted with Co or Ni which is imbedded in the so-called CoMoS structures (Clausen et al. 1981, Parham et al. 1984). Combined adsorption and activity measurements have furthermore indicated that the active sites reside at the edges of the MoS_2 clusters, and the creation of sulfur vacancies or so-called coordinatively unsaturated sites (CUS) at the edges has therefore generally been believed to play a key role and is important for the binding of sulfur-containing oil molecules (Topsøe et al. 1996). The traditional characterization techniques that have given this kind of insight, however, do not provide any conclusive information regarding the real space cluster morphology, catalytically relevant edge structures, the exact nature of the active sites or the promotional effect of Co and Ni; consequently a number of fundamental questions regarding the catalyst remain unanswered. We have developed a new preparation method to synthesize few nanometer wide single-layer MoS_2 and CoMoS nanostructures on an inert gold substrate as a model system for the HDS catalyst, and successfully studied the atomic-scale details of the catalytically important nanoclusters with STM for the first time. Since only the cluster edges are believed to be catalytically active, this novel approach produces a model system where it is possible with the STM to directly address the catalytically relevant sites at the atomic scale.

The MoS_2 nanoclusters were grown on a Au (111) single crystal. We have chosen the Au as a substrate for two reasons: (*i*) Gold is a chemically inert substrate and we can therefore investigate the intrinsic properties of the MoS_2 nanocluster. (*ii*) Gold belongs to the class of metals of which the surface reconstructs in its clean state (Barth et al. 1990). Specifically, the Au (111) forms the characteristic “herringbone” reconstruction pattern, which is ideal for providing nucleation sites for some metals deposited by physical vapor deposition and thereby dispersing submonolayer amounts of Mo into nanoclusters. The high degree of Mo dispersion on the surface facilitates easy sulfidation of the Mo into MoS_2, and by initial deposition of the Mo in an 10^{-6} mbar atmosphere of H_2S, followed by annealing to 673 K while maintaining the H_2S background, we find that the majority of the deposited Mo is transformed into ~30 Å wide, crystalline single-layer MoS_2 nanoclusters (Helveg et al. 2000, Lauritsen et al. 2001). This size corresponds to 30 to 50 Mo atoms per cluster, which is a size often encountered in industrial HDS catalysts. Figure 1*A* shows a large-scale STM image of the clusters, and it is found that the majority of the MoS_2 nanoclusters adopt a triangular shape, reflecting that this is the equilibrium shape under the sulfiding conditions. From the crystal structure of MoS_2, the observed triangular shape immediately implies that the single-layer MoS_2 nanocluster is terminated by only one of two low-indexed edge terminations, i.e. the $(10\bar{1}0)$ Mo edges or the $(\bar{1}010)$ S edges, see Figure 1*B*. Finding out which type of edge actually terminates the clusters is complicated by the fact that under the sulfiding conditions of the experiment, the edges may have varying amounts of S adsorbates and exist in several different configurations that differ from a simple bulk-terminated edge (Fig. 1*B*). The two types of edges are structurally and electronically dissimilar and are therefore also expected to possess very different catalytic properties. A direct characterization of the exact edge structure which actually terminates the MoS_2 clusters is there fore of utmost importance in order to understand their catalytic properties.

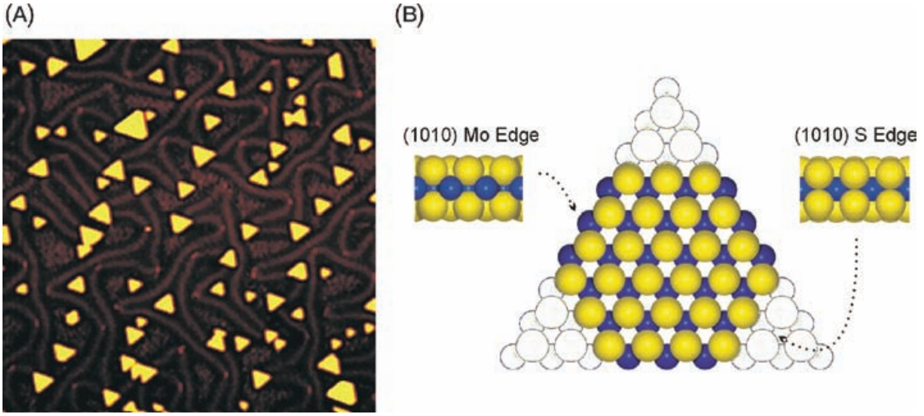


Fig. 1 (*A*) Large-scale STM image (1000 × 1000 Å^2) of single-layer MoS_2 nanoclusters synthesized on a Au(111) substrate. (*B*) Ball model of a hypothetical bulk-truncated single-layer MoS_2 hexagon shown in top view (S: yellow, Mo: blue), flanked by two side-view ball models of the two low-index edge terminations, the Mo edge and the S edge. The experimentally observed triangular shape implies that only one of these types of edge termination is present in the MoS_2 nanoclusters.

Figure 2*A* shows an atomically resolved STM image of a triangular single-layer MoS_2 nanocluster. On the basal plane of the clusters the protrusions are arranged in a hexagonal pattern and an interatomic distance of 3.15 ± 0.10 Å. This is in perfect agreement with the interatomic distances on the (0001) basal plane structure of bulk MoS_2. The height is observed to match that of a single S-Mo-S trilayer, and it is therefore concluded that the clusters are present as MoS_2 single-layer slabs with the (0001) basal plane oriented in parallel with the substrate (Helveg et al. 2000).

A detailed analysis of the triangular MoS_2 nanocluster in the atom-resolved STM image shows that the catalytically important edges are perturbed significantly both geometrically and electronically relative to the bulk-terminated case. This kind of information is important since most of the previous catalyst modeling has been based entirely on the bulk properties of MoS_2. In the atom-resolved STM image in Figure 2*A*, the white dots superimposed to the edges illustrate that protrusions on the edges of the triangular MoS_2 nanoclusters are imaged in a position *out of registry* with the basal plane S atoms. In fact, the protrusions are shifted exactly half a lattice constant along the edge, but retain an interatomic distance of 3.15Å. Furthermore, the STM images show a pronounced bright brim extended all the way around the nano-cluster edge adjacent to the edge protrusions. Rather than pure geometrical effects, we find that these features are associated with electronic effects probed by the STM reflecting subtle changes at the edges, i.e. the existence of so-called *edge states* where electrons are localized strongly in one dimension perpendicular to the edges, but delocalized along the direction of the edges. Indeed, a full density functional theory (DFT) calculation of the structure reveals that the MoS_2 edges have edge states with a distinct metallic character compared to the interior of the cluster which is semiconducting. By means of STM simulations based on the DFT calculations, we have recently identified the exact structure of the edges and determined that the triangular MoS_2 nanoclusters are terminated by Mo edges fully saturated with

S dimers (Bollinger et al. 2001). This configuration is depicted in Figure 2*B*, and the model shows that the sulfur atoms at the edge laterally coincide with the bulk S lattice, but they display a small pairing perpendicular to the MoS_2 (0001) surface, thus forming S_2 dimers or disulfide-like species (Byskov et al. 1999, Raybaud et al. 2000). The electronic band structure for this particular type of edge is furthermore seen in the calculations to have special electronic edge states which render the MoS_2 edges metallic and hence conductive, as seen with STM. The STM simulation in Figure 2*C* is seen to fully reproduce the STM findings, including the shifted position of the edge protrusions and the bright brim associated with a metallic edge state (Bollinger et al. 2001).

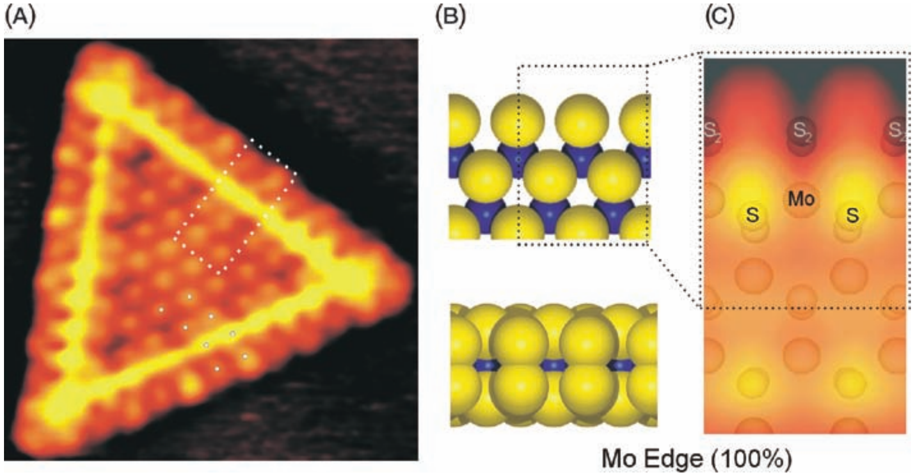


Fig. 2 (*A*) Atomically resolved STM image (41×42 Å^2, I_t = 1.28 nA, V_t= 5.2 mV) of a triangular single-layer MoS_2 nanocluster on Au(111). White dots indicate the registry of protrusion on the edge which is shifted relative to the basal plane. (*B*) Ball model of the fully sulfided Mo edge structure shown in top view (S: yellow, Mo: blue). (*C*) Simulated STM image of the fully sulfided Mo edge constructed with the Tersoff-Hamann theory. The position of the individual atoms is represented with atom balls (Mo: big, S: small). The bright brim is found to be associated with a one-dimensional metallic edge state. Adapted from Bollinger et al. 2001.

From a coordination-chemistry point of view, sulfur-saturated structures like that in Figure 2 are not normally considered among the most reactive, and sulfur vacancies are therefore generally believed to be created at the edge during the catalytic cycle, i.e. undercoordinated Mo atoms must be formed by sulfur removal before hydrodesulfurization can take place. The STM image in Figure 3*A* shows a triangular MoS_2 nanocluster following exposure to atomic hydrogen produced by pre-dissociating hydrogen gas on a glowing W filament. Near the edges the resulting structures show clear evidence of hydrogen having reacted off a few of the S atoms at the edges of the triangular MoS_2 nanoclusters, which means that we are imaging directly the catalytically active sites for the HDS reaction for the first time (Helveg et al. 2000). At high pressure and temperature, sulfur vacancies are expected to be abundant at the MoS_2 edges, and the use of atomic hydrogen in this experiment can be viewed as a simple way of proving hydrogen at the high chemical potential found under real catalytic reaction conditions.

The low-coordinated Mo atoms associated with vacancies are likely to have a high affinity for bond formations with, e.g., sulfur in an oil molecule, thereby facilitating the sulfur extraction. We have recently investigated this affinity with thiophene (C_4H_4S) as the relevant probe molecule, since it is a simple and relatively inert S-containing molecule found in typical oil feeds. So far it has not been possible to follow the S extrusion directly on S vacancies, since it probably occurs on a time-scale much faster than the frame rate of the STM. The studies, however, showed interesting intermediates that are the result of a very interesting reaction of thiophene occurring directly on the metallic edge state associated with the bright brim of the clusters, which seem to give the MoS_2 nanoclusters a rather different chemistry than what has ordinarily been assumed.

Figure 3*B* shows the STM image of a triangular MoS_2 cluster, which was initially exposed to atomic hydrogen and subsequently dosed with thiophene molecules at 500 K. Compared to the clean cluster in Figure 2*A*, several "bean-like" structures are observed to protrude from the basal plane in the row adjacent to the bright brim of the MoS_2 cluster. These features can be associated with individual molecules bonded to the metallic edge state (Lauritsen et al. 2003). The adsorption of every molecule is furthermore seen to always be accompanied by a change in intensity of the edge protrusions located nearest the adsorption site. Unlike the edge with vacancies in Figure 3*A*, these edges do not show any sign of a decreased S coverage, and the molecules therefore do not represent molecules adsorbed to a sulfur vacancy. Furthermore, the molecules adsorbed on the brim are quite mobile (observed in sequential series of STM images), and the fact that we never observed singular vacancies to be mobile confirms that the molecules are not adsorbed on vacancy sites. Instead, by means of STM image simulations based on extensive DFT calculations we find that the molecules reflect *cis*-but-2-ene-thiolates (C_4H_7S) coordinated through the terminal sulfur atom to sites near the metallic brim. These species are formed by a sequential hydrogenation of one of the double bonds in thiophene by hydrogen adsorbed on the edges (from so-called S-H groups) followed by C-S bond cleavage; the DFT calculations show that the reaction barrier associated with the most difficult step, the C-S bond breaking, is actually quite modest ~100 KJ/mol. The configuration observed in the STM image associated with a ring-opened structure is simply an ordinary thiol in which the S is much more reactive. The final extrusion of this S may therefore proceed on the sulfur vacancies. We have thus identified a new route for an initial activation of a relatively inert S-bearing molecule like thiophene, and the reaction intermediates observed in the STM image may therefore be the result of an important first step of hydrodesulfurization. Remarkably, these processes take place on the metallic edge states of the fully saturated Mo edges, which have the ability to accept or donate electrons and thus act as catalytic sites just like ordinary metal surfaces.

In conclusion, we have presented detailed atomic-scale STM images of the morphology and structure of single-layer MoS_2 nanoclusters grown on a gold substrate as a model system for the important hydrotreating catalyst. The capability of the STM to resolve the atomic registry and electronic structure of the MoS_2 nanoclusters enables us for the first time to investigate the location and nature of the catalytically active sites. The present STM results demonstrate that the MoS_2 nanoclusters have physical and chemical properties that are very diffe-

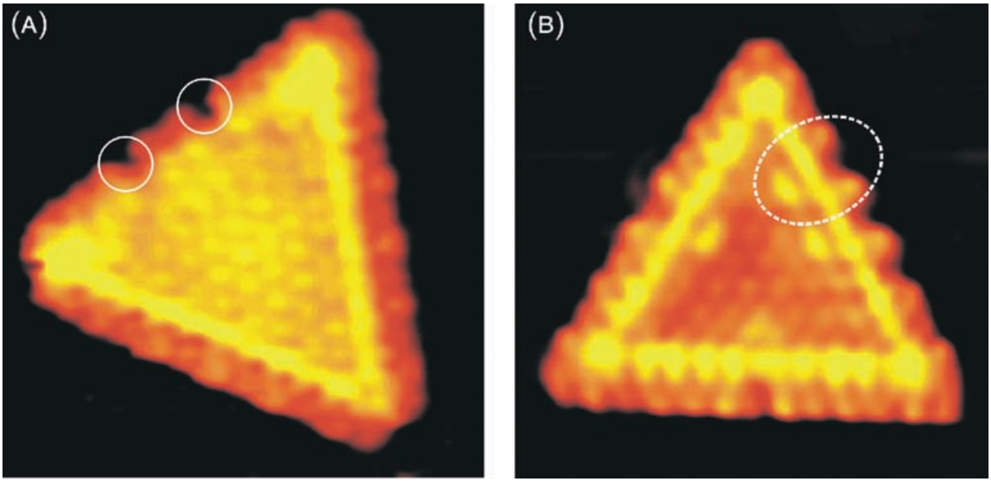


Fig. 3 (*A*) Atomically resolved STM image (46 × 47 Å^2) of a triangular single-layer MoS_2 nanocluster after exposure to atomic hydrogen at 673 K. The white circles indicate two singular S vacancies formed on the edge of the clusters. (*B*) Atom-resolved STM image (50 × 54 Å^2) of an atomic hydrogen pretreated cluster subsequently exposed to thiophene (C_4H_4S). The dashed circle indicates the features associated with individual *cis*-but-2-ene-thiolate (C_4H_7S) molecules adsorbed and reacted on sites at the metallic brim.

rent from what has commonly been assumed from bulk properties of MoS_2. This kind of local information cannot normally be achieved by the traditional *in-situ* techniques for catalyst characterization. Insight on the atomic level is essential in order to achieve a better fundamental understanding of heterogeneous catalysis, and the experimental approach presented here should be applicable to inorganic clusters deposited on conducting substrates in general. Such detailed information will ensure a more rational way of developing, e.g., new catalysts.

References

Barth, J. V., Brune, H., Ertl, G., and Behm, R.: Scanning tunneling microscopy observations on the reconstructed Au(111) surface: Atomic structure, long-range superstructure, rotational domains, and surface defects. Phys. Rev. B *42*(15), 9307–9317 (1990)

Besenbacher, F., Chorkendorff, I., Clausen, B. S., Hammer, B., Molenbroek, A. M., Nørskov, J. K., and Stensgaard, I.: Design of a surface catalyst for steam reforming. Science *279*, 1913–1914 (1998)

Bollinger, M. V., Lauritsen, J. V., Jacobsen, K. W., Nørskov, J. K., Helveg, S., and Besenbacher, F.: One-dimensional metallic edge states in MoS_2. Phys. Rev. Lett. *87(19)*, 196803 (2001)

Byskov, L. S., Nørskov, J. K., Clausen, B. S., and Topsøe, H.: DFT calculations of unpromoted and promoted MoS_2-based hydrodesulfurization catalysts. J. Catal. *187*, 109–122 (1999)

Clausen, B. S., Lengeler, B., Candia, R., Als-Nielsen, J., and Topsøe, H.: EXAFS studies of calcined and sulfided Co-Mo HDS catalysts. Bull. Soc. Chim. Belg. *90*, 1249–1259 (1981)

Hansen, K. H., Worren, T., Stempel, S., Lægsgaard, E., Bäumer, M., Freund, H.-J., Besenbacher, F., and Stensgaard, I.: Palladium nanocrystals on Al_2O_3: Structure and adhesion energy. Phys. Rev. Lett. *83(20)*, 4120–4123 (1999)

Helveg, S., Lauritsen, J. V., Lægsgaard, E., Stensgaard, I., Nørskov, J. K., Clausen, B. S., Topsøe, H., and Besenbacher, F.: Atomic-scale structure of single-layer MoS_2 nanoclusters. Phys. Rev. Lett. *84*, 951–954 (2000)

Horch, S., Lorensen, H. T., Helveg, S., Lægsgaard, E., Stensgaard, I., Nørskov, J. K., Jacobsen, K. W., and Besenbacher, F.: Enhancement of surface self-diffusion of platinum atoms by adsorbed hydrogen. Nature *398*, 134–136 (1999)

Lauritsen, J. V., Helveg, S., Lægsgaard, E., Stensgaard, I., Clausen, B. S., Topsøe, H., and Besenbacher, F.: Atomic-scale structure of Co-Mo-S nanoclusters in hydrotreating catalysis. J. Catal. *197*, 1–5 (2001)

Lauritsen, J. V., Nyberg, M., Vang, R. T., Bollinger, M. V., Clausen, B. S., Topsøe, H., Jacobsen, K. W., Besenbacher, F., Lægsgaard, E., and Besenbacher, F.: The chemistry of one-dimensional metallic edge states in MoS_2 nanoclusters. Nanotechnology *14*(3), 385–389 (2003)

Österlund, L., Rasmussen, P. B., Thostrup, P., Lægsgaard, E., Stensgaard, I., and Besenbacher, F.: Bridging the pressure gap in surface science at the atomic level: H/Cu(110). Phys. Rev. Lett. *86*(3), 460–463 (2001)

Over, H., Kim, Y. D., Seitsonen, A. P., Wendt, S., Lundgren, E., Schmid, M., Varga, P., Morgante, A., and Ertl, G.: Atomic-scale structure and catalytic reactivity of the RuO_2(110) surface. Science *287*, 1474–1476 (2000)

Parham, T. G., and Merrill, R. P.: An EXAFS study of the structure of supported cobalt molybdate catalysts as a function of sulfiding temperature. J. Catal. *85*, 295–310 (1984)

Pedersen, M. Ø., Österlund, L., Mortensen, J. J., Mavrikakis, M., Hansen, L. B., Stensgaard, I., Lægsgaard, E., Nørskov, J. K., and Besenbacher, F.: Diffusion of N adatoms on the Fe(100) Surface. Phys. Rev. Lett. *84*, 4898–4901 (2000)

Prins, R.: Hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and hydrodechlorination. In: Ertl, G., Knözinger, H., and Weitkamp, J. (Eds.): Handbook of Heterogeneous Catalysis. Weinheim**:** 1908. VHC 1997

Raybaud, P., Hafner, J., Kresse, G., Kasztelan, S., and Toulhoat, H.: *Ab initio* study of the H_2-H_2S/MoS_2 gas-solid interface: The nature of the catalytically active sites. J. Catal. *189*, 129–146 (2000)

Schaub, R., Wahlström, E., Rønnau, A., Lægsgaard, E., Stensgaard, I., and Besenbacher, F.: Oxygen-mediated diffusion of oxygen vacancies on the TiO_2(110) Surface. Science *299*, 377–379 (2003)

Somorjai, G. A.: Surface Chemistry and Catalysis. New York: Wiley 1994

Topsøe, H., Clausen, B. S., and Massoth, F. E.: Hydrotreating Catalysis, Science and Technology. Berlin: Springer 1996

Valden, M., Lai, X., and Goodman, D. W.: Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. Science *281*(5383), 1647–1650 (1998)

Vestergaard, E. K., Thostrup, P., An, T., Lægsgaard, E., Stensgaard, I., Hammer, B., and Besenbacher, F.: Comment on “High pressure adsorbate structures studied by scanning tunneling microscopy: CO on Pt(111) in equilibrium with the gas phase”. Phys. Rev. Lett. *88*, 259601 (2002)

Wahlström, E., Lopez, N., Schaub, R., Thostrup, P., Rønnau, A., Africh, C., Lægsgaard, E., Nørskov, J. K., and Besenbacher, F.: Bonding of gold nanoclusters to oxygen vacancies on rutile TiO_2(110). Phys. Rev. Lett. *90*, 026101 (2003)

Zambelli, T., Wintterlin, J., Trost, J., and Ertl, G.: Identification of the “Active sites” of a surface-catalyzed reaction. Science *273*, 1688–1690 (1996)

.

Prof. Dr. Flemming Besenbacher
Interdisciplinary Nanoscience Center (iNANO)
CAMP and Department of Physics and Astronomy
University of Aarhus
Ny Munkegade, Building 520
DK-8000 Aarhus C
Denmark
Phone: +45 89423604
Fax: +45 86120740
E-Mail: fbe@inano.dk

Nova Acta Leopoldina NF *92*, Nr. 340, 29–36 (2005)

The Scanning Tunneling Microscope as Operative Tool: Doing Physics and Chemistry with Single Atoms and Molecules

Karl-Heinz RIEDER[1], Gerhard MEYER[2], Saw-Wai HLA[3], Francesca MORESCO[1], Kai F. BRAUN[1], Karina MORGENSTERN[1], Jascha REPP[2], Stefan FOELSCH[4], and Ludwig BARTELS[5]

With 3 Figures

Abstract

The scanning tunneling microscope, initially invented to image surfaces down to atomic scale, has been further developed in the last few years to an operative tool, with which atoms and molecules can be manipulated at low substrate temperatures at will in different manners to create and investigate artificial structures. These possibilities give rise to startling new opportunities for physical and chemical experiments on the single atom and single molecule level. Here we provide a short overview on recent results obtained with the new techniques.

Zusammenfassung

Das Rastertunnelmikroskop, ursprünglich für die Abbildung von Oberflächen bis hin zur atomaren Skala entwickelt, wurde in den letzten Jahren zu einem aktiven Werkzeug weiterentwickelt, mit dem Atome und Moleküle bei niedrigen Substrat-Temperaturen nach Belieben in verschiedenen Modi manipuliert werden können. Dies erlaubt den Aufbau und die Untersuchung artifizieller Strukturen. Damit eröffnen sich interessante neue Perspektiven für physikalische und chemische Experimente auf der Skala einzelner Atome und Moleküle. Wir geben hier einen kurzen Überblick über jüngere Resultate mit diesen neuen Techniken.

1. Lateral Manipulation and Build-up of Artificial Structures

Figure 1 shows an example for the build-up of an artificial structure on atomic scale.[6] A regular triangle had been formed with 51 Ag atoms on Ag(111) by laterally manipulating them into the proper positions with atomic accuracy (BRAUN and RIEDER 2002). In lateral manipulation an adparticle at the surface is moved with the tip along the substrate surface to the desired place without loosing contact to the substrate. This is achieved by bringing the tip very close to the adparticle, so that besides the ever present van der Waals interactions also chemical forces between tip and particle are coming into play. These forces can be tuned to be large

---

[1] Fachbereich Physik, Freie Universität Berlin, Germany.

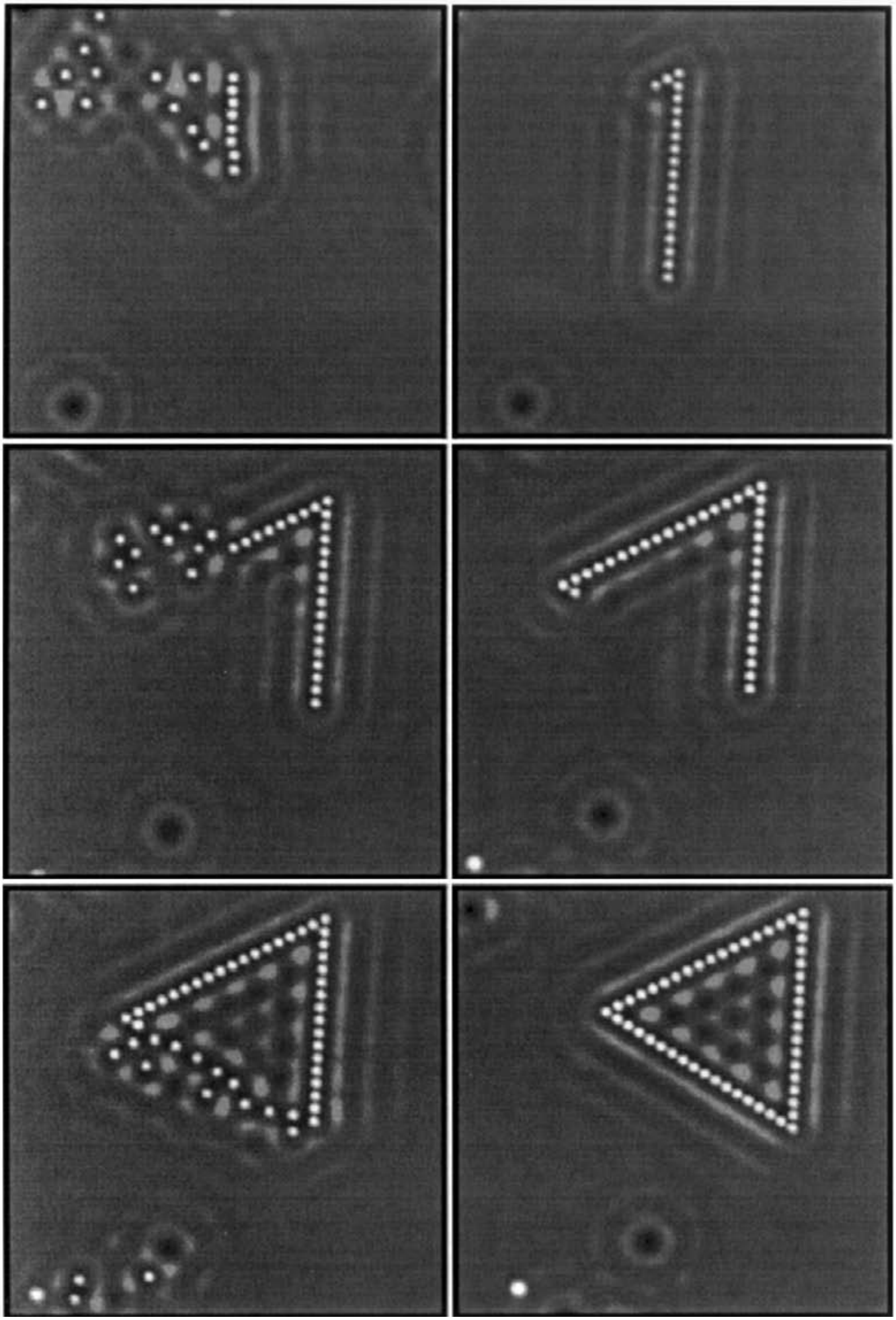
[2] IBM Zurich Research Laboratory, Rueschlikon, Switzerland.

[3] Ohio University, Athens, USA.

[4] Paul-Drude-Institute, Berlin.

[5] UC Riverside, USA.

[6] For films showing the gradual buildup of several artificial surface structures in an atom by atom way by lateral manipulation see the homepage of the authors: http://www.physik.fu-berlin.de/~ag-rieder/index.html.



enough to surmount the surface diffusion barriers, so that the adparticle comes along with the tip, if the tip is moved parallel to the surface to the desired end point. It is fascinating that even at the level of the very atoms, a distinction can be made between different manipulation modes, namely pulling, pushing and sliding (Bartels et al. 1997a). The different modes can be discerned by recording tip-height curves during manipulation in the STM constant current mode. Upon pulling, the atoms follow the tip in regular jumps from one adsorption site to the next due to attractive tip-particle forces. Applying larger forces (measured by smaller tunneling resistivities) a sliding motion is induced, in which the adparticle is trapped under the tip and follows the tip motion continuously, so that the manipulation tip height curve yields a picture of the substrate corrugation. Pulling and sliding are usually applied in manipulating metal atoms. In contrast, CO molecules are usually pushed: The molecules move discontinuously in front of the tip due to repulsive forces. On close packed surfaces like Cu(111), pushing is not very reliable, as the particles tend to move to the side of the tip and get lost. That the buildup of artificial structures in the pushing mode is successful at all is due to the proper choice of the substrate surface: CO adsorbs on Cu(211) at the upper part of the intrinsic step edges, which act as “railway trails” upon pushing. With sufficiently stable and nevertheless sharp tips it is even possible to remove native substrate atoms from highly coordinated defect step sites and even from regular step sites of high index surfaces in a one by one manner (Meyer et al. 1996). This ability was used in analytic chemistry on the atomic scale by investigating the monolayer structure formed on Cu(211) upon Pb-evaporation at room temperature: Atom by atom removement from an island edge revealed that a surface Cu-Pb lead alloy had formed although the two metals do not mix in the bulk (Bartels et al. 1997c). The sole action of tip-particle forces has been proven recently by measuring threshold curves of current for secure manipulation over a wide range of tunneling voltages (Hla et al. 2003).

2. Vertical Manipulation

The deliberate vertical transfer of a particle from the surface to the tip and *vice versa* is called vertical manipulation (Fig. 2*A*). Again the tip is brought close to the particle to be transferred until the force between tip and particle is sufficiently strong, so that the particle can go with the tip upon its withdrawal. Here electron current effects can help to transfer the particle in the wanted direction: The STM pictures in Figure 2*B* refer to an image of Cu(111) with several CO molecules and one oxygen atom in the upper left corner. All species are imaged as depressions with a tip consisting of metal atoms. The CO molecule designated by an arrow is then picked up with the technique of vertical manipulation and the same area is imaged again. Noticeably all CO molecules have changed in appearance to protrusions whereas the oxygen atom remains imaged as a depression (Bartels et al. 1997b). It is obvious that deliberate functionalization of the tip with different molecules may lead to chemical contrast, a feature very much desired in STM and understood only very recently on the basis of theoretical calculations using a Greens function approach, which allows analysis of different electron current paths and their interference (Nieminen et al. 2003).

Fig. 1 Series of images demonstrating the build-up of a regular triangle consisting of 51 Ag atoms on a Ag(111) surface.

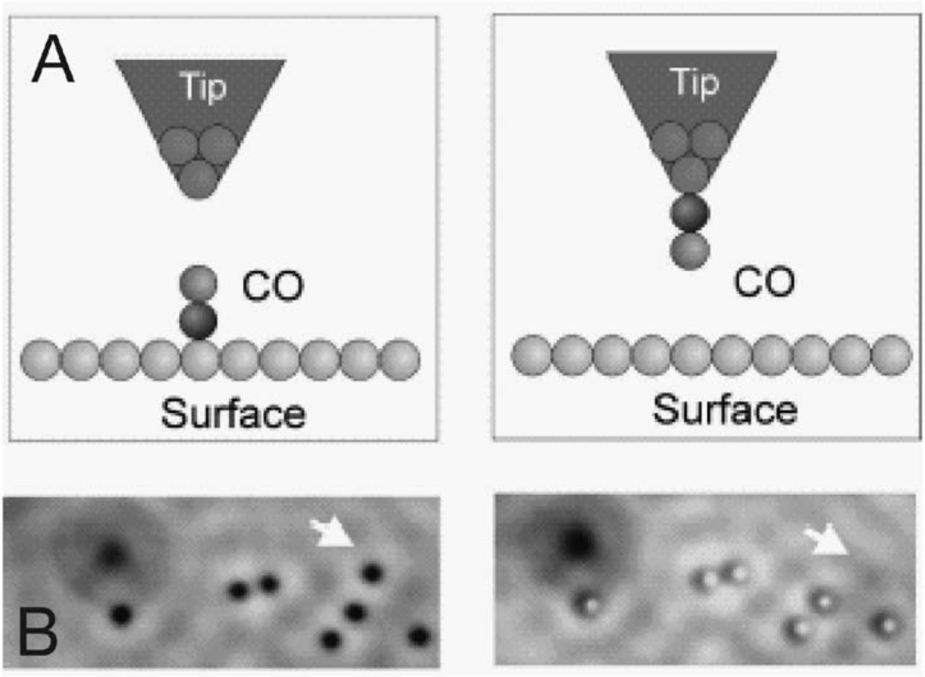


Fig. 2 (*A*) Schematic picture of the flipping of a CO molecule upon vertical manipulation from the surface to the tip apex. (*B*) Demonstration of imaging changes obtained for CO molecules with a CO tip; notice that the image of the oxygen atom is unaffected. The white arrow denotes the CO molecule which was transferred deliberately to the tip.

The vertical transfer of CO is interesting because CO stands upright on metal surfaces with the carbon atom binding to the substrate. Upon transfer to the tip, the molecule consequently has to turn around. A reliable experimental procedure for transferring single CO molecules was found to require ramping of the tunneling voltage and simultaneous decrease of the tip-molecule distance. Investigations of the transfer mechanism yielded the following picture. Voltage ramping supplies the minimum tunneling bias of 2.4 eV required to populate the CO antibonding $2\pi^*$ level. As the CO hopping rate depends linearly on the tunneling current, a one electron process is responsible for the excitation. Although only 0.5 % of the tunneling current pass through the $2\pi^*$ orbital and the lifetime of the electrons in this antibonding level is only of the order of femtoseconds, the continuous supply of tunneling electrons eventually causes release of the CO from the surface. The approach of the tip in the pickup procedure just increases the probability that the molecule is “caught” at or near the tip apex upon desorption (Bartels et al. 1998).

3. Doing Chemistry with the STM-Tip: Inducing All Steps of a Chemical Reaction

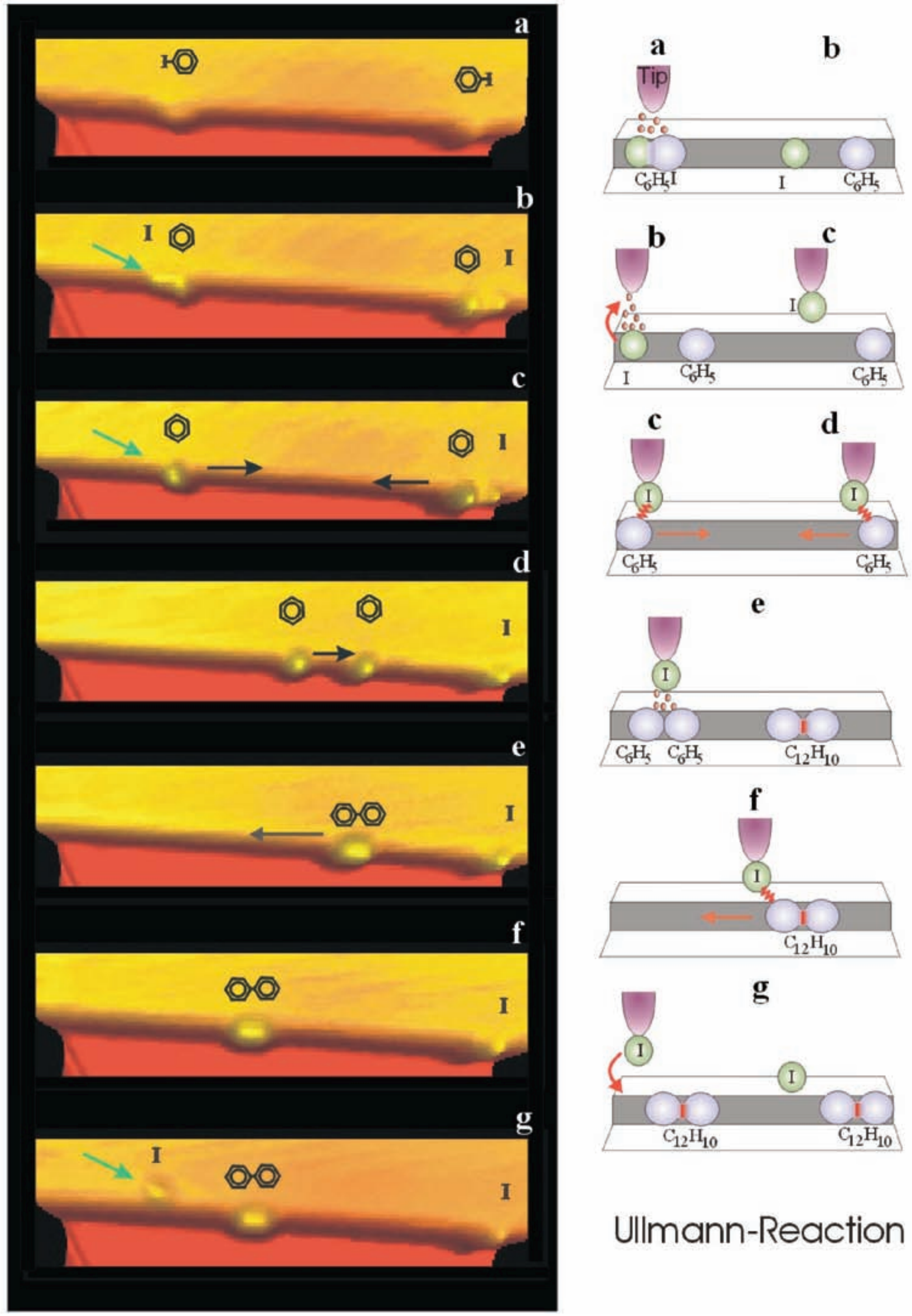
Population of an antibonding state is also important in the preparation of reactants in a full chemical reaction induced by the tip (HLA et al. 2000). In the so called Ullmann reaction, iodine has to be split off from the iodobenzene parent molecules to form the phenyl reactands. Again tunneling electrons populate temporarily the iodine-phenyl antibonding level thus causing the dissociation step (Fig. 3*a*, *b*). Both iodine and phenyl fragments are found on the surface. To induce the diffusion step to bring two phenyls together, lateral manipulation in the pulling mode is employed (Fig. 3*c*, *d*). At the low temperatures of the Cu(111) substrate the proximity of the two phenyls is not sufficient to induce the association to biphenyl: If a pulling procedure is applied to the phenyl couple from one end, the phenyl on the rear does not go along. Only after injection of electrons the synthesis step is performed, which can be proven by pulling the product from one end and realizing that the entire molecule follows the tip (Fig. 3*e*, *f*). Notice that in Figure 3*c*, *d* one of the iodine atoms was transferred deliberately to the tip after dissociation of the iodobezene and all the following steps were performed with the iodine functionalized tip. The iodine was finally put back on the surface (Fig. 3*g*) (HLA and RIEDER 2003). The synthesis of the two phenyls to biphenyl is probably connected with local excitation of vibrational modes in the phenyl groups enabling the two open bonds to find the proper relative orientation for bond formation. Local excitation of the scissoring and the OH-stretching modes was indeed observed to be responsible in tip-induced diffusion of water molecules adsorbed on Cu(111). Furthermore, hydrogen bonds can be formed and broken and thus ice clusters can be crystallized *via* the same mechanism (MORGENSTERN and RIEDER 2002).

4. Switching and Contacting Molecules

Manipulation can also be performed into parts of molecules as demonstrated for the case of a TBPP molecule to whose center porphyrin ring there are four legs attached which are perpendicular to the center ring in the gas phase. On Cu(211), however the legs lie flat (MORESCO et al. 2001b). Using lateral manipulation, a single leg can be transformed into an almost perpendicular conformation and the leg can be pushed back into the flat position with the tip again. As the perpendicular and parallel conformations exhibit orders of magnitude different conductivities these experiments open up the possibility of a molecular switch, in which a mechanical action causes switching from conducting to nonconducting behaviour (MORESCO et al. 2001a). A related molecule with a long polyaromatic conducting board and the same legs, called lander, has been used in a recent study concerning the problem of contacting molecular wires with atomic precision. It could be shown that upon moving the molecule with the legs parallel towards a step edge, the standing wave pattern of the Cu(111) substrate did not change whereas when the molecule was moved with its legs perpendicular to the step the board connected to the step an electron diffraction pattern characteristic for the contact area was observed (MORESCO et al. 2003).

5. Doing Physics with Artificial Structures: Measuring Electron Lifetimes Inside a Quantum Corral

Adparticles arranged in a closed geometry like in Figure 1 act as partial confinement for electrons and can be used to determine the electron lifetime (BRAUN and RIEDER 2002). The elec-


a
b
c
d
e
f
g
I
Tip
C_6H_5I
C_6H_5
$C_{12}H_{10}$
Ullmann-Reaction

trons of the surface state present on the Ag(111) surface are scattered by these Ag adatoms, resulting in a complex interference pattern. Energy resolved data taken in the spectroscopic dI/dV-mode allow measurements of the interference patterns as a function of energy. Calculations of the wave patterns were performed based on a multiple scattering approach taking into account the phase-relaxation lengths of the electrons, which reflect scattering events inside the triangle influencing their phase coherence and can directly be converted into electron lifetimes. Inside of the triangle electron-electron and electron-phonon scattering determine the electron lifetime and the spatial decay of the interference pattern. The evaluations for the electron lifetimes as function of energy clearly show a sharp maximum at the Fermi energy in accordance with Fermi liquid theory for a 2DEG due to a decreased phase-space for electron-electron and electron-phonon scattering. Furthermore two pronounced edge-like features show up in the data at +65 meV and +300 meV which can be attributed to the transition of the surface state into a surface resonance. The former can be interpreted by a change of the scattering probability as the electron energy becomes smaller than the surface state binding energy of 65 meV. Finally, the additional finestructure observed has to be attributed to the geometrical influence of the triangle.

6. Outlook

The results described above relate to many diverse aspects of physics and chemistry on the atomic and nano-scales. Measuring tip-height curves in constant current or current curves in constant height mode during lateral manipulation reveals internal motion of the entities and thus refers to nanomechanics. The fact that small structures can be assembled or taken apart yields important routes to synthetic and analytic chemistry on the atomic scale. The possibility to take atoms out of the substrate from defect or intrinsic surface steps can be used to structure the surface itself with the possibility to include also layers deeper than the topmost one. The use of artificially created adatom-hole pairs as binary units with writing, reading and rewriting possibilities certainly would give rise to the utmost possible storage density. Artificial structures on the surface can be built either with native substrate atoms or adsorbed species and their properties can be investigated with spectroscopic methods. Important progress for nanoelectronics can be expected from the ability to modify with the tip internal molecule conformations. The successful induction of all steps of a complex chemical reaction using force, current and field effects raises the hope that new molecules can be built by taking different parent molecules apart and welding dissociation products together at will to synthesize new molecules, whose properties can be investigated again by tunneling spectroscopy. As controlled atomic manipulation allows the design of arbitrary scattering geometries, on the basis of a deeper understanding of the electron lifetimes it should become possible to even engineer these lifetimes, which are a key quantity in quantum computing and quantum transportation. A further important present goal is to transfer all possibilities outlined here to technologically important substrates like insulators; as for sufficiently thin insulator films on metallic substrates the use of the STM is still possible (REPP et al. 2001, FOELSCH et al 2002).

Fig. 3 Sequence of steps in STM-tip induced single molecule Ullmann reaction on Cu(111). All reaction steps including dissociation of parent iodobenzene molecules, motion of phenyl reactants and iodine byproducts as well as association of phenyl reactants to biphenyl have been induced with an iodine functionalized tip.

References

Bartels, L., Meyer, G., and Rieder, K. H.: Phys. Rev. Lett. *79*, 697 (1997a)

Bartels, L., Meyer, G., and Rieder, K. H.: Appl. Phys. Lett. *71*, 213 (1997b)

Bartels, L., Zoephel, S., Meyer, G., Henze, E., and Rieder; K. H.: Surf. Sci. *372*, L261 (1997c)

Bartels, L., Meyer, G., Rieder, K. H., Velic, D., Knoesel, E., Hotzel, Wolf, M., and Ertl, G.: Phys. Rev. Lett. *80*, 2004 (1998)

Braun, K. F., and Rieder, K. H.: Phys. Rev. Lett. *88*, 096801 (2002)

Foelsch, S., Riemann, A., Repp, J., Meyer, G., and Rieder, K. H.: Phys. Rev. B *66*, 161409 (R) (2002)

Hla, S. W., Bartels, L., Meyer, G., and Rieder, K. H.: Phys. Rev. Lett. *85*, 2777 (2000)

Hla, S. W., Braun, K. F., and Rieder, K. H.: Phys. Rev. B *67*, 201402 (R) (2003)

Hla, S. W., and Rieder, K. H.: Acc. Chem. Res. *54*, 307 (2003)

Meyer, G., Zoephel, S., and Rieder, K. H.: Phys. Rev. Lett. *77*, 2133 (1996)

Moresco, F., Meyer, G., Rieder, K. H., Tang, H., Gourdon, A., and Joachim, C.: Phys. Rev. Lett. *86*, 672 (2001a)

Moresco, F., Meyer, G., Rieder, K. H., Tang, H., Gourdon, A., and Joachim, C.: Phys. Rev. Lett. *87*, 88302 (2001b)

Moresco, F., Gross, L., Alemani, M., Rieder, K. H., Tang, H., Gourdon, A., and Joachim, C.: Phys. Rev. Lett. *91*, 036601–1 (2003)

Morgenstern, K., and Rieder, K. H.: J. Chem. Phys. *116*, 5746 (2002)

Nieminen, J., Niemi, E., and Rieder, K. H.: preprint (2003)

Repp, J., Foelsch, S., Meyer, G., and Rieder, K. H.: Phys. Rev. Lett. *86*, 672 (2001)

Prof. Dr. Karl-Heinz Rieder
Free University of Berlin
Department of Physics
Arnimallee 14
14195 Berlin
Germany
Phone: +49 30 83852805
Fax: +49 30 83851355
E-Mail: rieder@physik.fu-berlin.de

Nova Acta Leopoldina NF *92*, Nr. 340, 37–45 (2005)

Electronic Transport through Atomic-size Contacts

Elke Scheer (Konstanz)

With 3 Figures

Abstract

The progressing miniaturization in microelectronics will soon require the incorporation of single molecules or individual atoms as active elements. A prerequisite of successful design on this scale is the knowledge of the relationship between the macroscopic electrical characteristics of such circuits and the quantum properties of the individual building blocks. Modern nanofabrication techniques including modified scanning tunneling microscopes (STM) and mechanically controllable breakjunctions (MCB) provide adjustable atomic-size contacts between two metallic banks. We investigated the conduction properties of the simplest imaginable circuit – a one-atom contact between two metallic banks. Since the Fermi wavelength in metals is of the order of the inter-atomic distance, macroscopic transport theories break down, but a quantum mechanical description is required, treating the transport as a wave scattering problem. Within this approach the contacts represent electronic waveguides which accommodate only a small number of so-called "conduction channels". The number N and the individual transmission coefficients τ_i of these channels represent the "genetic code" of electronic transport from which many other transport properties such as thermopower, shot noise or the supercurrent in superconducting contacts, can be calculated. We present a method how to determine the set $\{\tau_i\}$ for different elements covering a wide range of the periodic table and explain the findings from the quantum chemistry point of view that the channels are determined by the valence atomic orbitals at the central atom of the contact. First results on the transport behavior of magnetic single-atom contacts will be reported.

Zusammenfassung

Die rasche Zunahme der Integrationsdichte in der Mikroelektronik läßt erwarten, daß schon bald funktionelle Elemente in integrierten Schaltungen nur noch aus wenigen Atomen oder Molekülen bestehen werden. Die Kenntnis des Zusammenhangs zwischen physikalischen und chemischen Eigenschaften der Bauelemente und der elektrischen Leitung durch solche Schaltkreise ist eine Grundvoraussetzung für mögliche zukünftige Anwendungen in der Mikroelektronik.

Mit Hilfe von Methoden der Nanotechnologie, basierend z. B. auf Rastersondenmikroskopen oder mechanisch kontrollierten Bruchkontakten (MCB), lassen sich regelbare Kontakte atomarer Größe zwischen zwei metallenen Zuleitungen herstellen. Wir haben den einfachst-möglichen Schaltkreis untersucht – ein einzelnes Atom zwischen zwei metallenen Zuleitungen. Da die Fermiwellenlänge in Metallen von der Größenordnung der atomaren Abstände ist, ist eine vollständige quantenmechanische Beschreibung des Stromtransports als Wellenstreuexperiment notwendig. In diesem Ansatz werden die Kontakte als elektronische Wellenleiter betrachtet, die nur eine kleine Anzahl sogenannter „Transportkanäle“ zulassen. Die Anzahl N und die Transmissionskoeffizienten τ_i der einzelnen Kanäle bilden den „mesoskopischen Code“ des elektronischen Transports, mit Hilfe dessen viele weitere Transporteigenschaften wie z. B. die Thermokraft, das Schrotrauschen oder der Suprastrom für supraleitende Kontakte berechnet werden können.

Wir stellen eine Methode vor, mit der das Ensemble $\{\tau_i\}$ experimentell bestimmt werden kann. Die experimentellen Ergebnisse werden im Rahmen eines quantenchemischen Modells erklärt, das die Transportkanäle durch die Valenzorbitale und lokale Bandstruktur am Zentralatom des Kontakts aufbaut. Erste Ergebnisse zum Transportverhalten durch magnetische Ein-Atom-Kontakte werden vorgestellt.

1. Atomic-size Contacts

For the realization of atomic-size contacts we use lithographically fabricated mechanically controllable breakjunctions (MCB) (van Ruitenbeek et al. 1996, for a recent overview over the field, see Agraït et al. 2003) (see Fig. 1). These are free standing nanobridges that are fabricated on a flexible metallic substrate, covered by an insulating layer. The initial size of the constriction is of the order 100 nm times 100 nm. The sample is mounted onto a three-point bending mechanism (see Fig. 1) which is thermally anchored to a cryostat (^{3}He or ^{3}He-^{4}He dilution refrigerator). By bending the substrate the bridge is elongated and reduced in lateral size in order to arrange few-atom contacts or tunnel contacts. The axis of the differential screw is driven *via* different reduction gear boxes by a dc-motor at room temperature. Due to the geometry of the sample and the bending mechanism the displacement of the axis is transferred into an elongation of the sample that is reduced by a factor of 5000. A consequence of this reduction is a very precise tuning of the contact size and a high mechanical stability. A typical value for the length drift is 5 pm per day when the sample is kept at low temperature. Since the bridge is broken under cryogenic vacuum conditions the atomic-size contacts remain clean for several days.

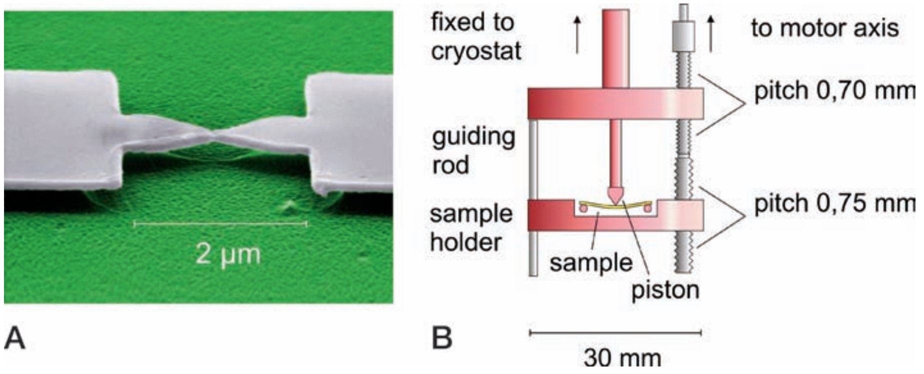


Fig. 1 (*A*) Lithographic MCB made of Co (light blue) on insulating polyimide layer (green). The metal film thickness is 100 nm. (*B*) Principle of the 3-point bending mechanism.

2. Electronic Transport on the Atomic Scale

A usual metal atom between two metallic banks is a possible realization of a quantum point contact (QPC). In general a QPC is a constriction with lateral sizes of the order of the Fermi wave length λ_F between two metallic banks. In the case of a metal like Na, Au or Co, λ_F is of the order of the lattice constant. According to Landauer (1970) the electronic transport through a QPC can be calculated by solving the corresponding quantum mechanical wave scattering problem. The conductance of the sample is then given by the Landauer formula

$$G = G_0 D \text{ where } D = \sum_{i=1}^{N} \tau_i \qquad [1]$$

is the sum of the eigenvalues (transmission coefficients) of the eigenstates (nicknamed "channels") of the scattering problem and $G_0 = 2e^2/h \approx 1/12900\ \Omega^{-1}$ is the conductance quantum. The factor 2 accounts for both spin directions. The τ_i can adopt all values between 0 (back scattering) und 1 (perfect transmission). If there is no back scattering, all $\tau_i = 1$ and thus the conductance is quantized in units of G_0. The phenomenon of conductance quantization has first been demonstrated in QPCs in two-dimensional electron gases with $\lambda_F \approx 30$ nm (VAN WEES et al. 1988, WHARAM et al 1988). In those systems the eigenstates of the leads and the QPC are Bloch waves and can thus be matched perfectly such that all transmission coefficients achieve there saturation value $\tau_i = 1$.

Conductance measurements on a larger number of atomic QPCs have shown a statistical tendency to adopt preferred conductance values (KRANS et al. 1995, COSTA-KRÄMER et al. 1997). For many metals, in particular monovalent metals like Na, Cu and Au these values are close to integer multiples of G_0, and the smallest stable contact (very likely a single-atom contact) has a conductance close to 1 G_0. However, these findings do not necessarily imply transmission saturation, since the measurement of the conductance and thus the total transmission gives no information about the number or the transmission of the individual channels. We report a method for the determination of the whole set $\{\tau_i\}$, based on the analysis of nonlinear current-voltage characteristics (IVs) of superconducting QPCs.

3. Measurement of the Transport Channels

As has been shown previously, the conductance varies stepwise when a metallic nanobridge is elongated. The step height is of the order of G_0, and the step length corresponds to the lattice constant, i.e. the size of an atom in the solid. At a certain point of the elongation the conductance starts to evolve exponentially with the distance – a clear indication of vacuum tunneling and the fact that the bridge has been broken. Since for every experiment the constriction atoms arrange differently the opening traces vary from opening to opening. The typical behavior of a metal is studied by repeated opening and closing of the contact and the construction of a histogram of adopted conductance values. For ferromagnetic metals like Ni, Fe or Co simple models would expect the histogram to have maxima at multiples of $G_0/2$ due to the suppression of one spin direction and the opening traces to show step heights of the same value. Indications of the latter have been reported in the literature (COSTA-KRÄMER et al. 1997), however, none of the reported histograms confirm this statistically. In Figures 2*A* and 2*B* we show our results on Co single-atom contacts with a preferred value of the single-atom contact of around 1.2–1.3 G_0. Furthermore the histograms do not change significantly when applying strong magnetic fields. The histogram of the multivalent metal Al (Fig. 2*C*) shows well pronounced maxima with an average spacing of 1.2–1.3 G_0 and a first maximum around 0.8 G_0.

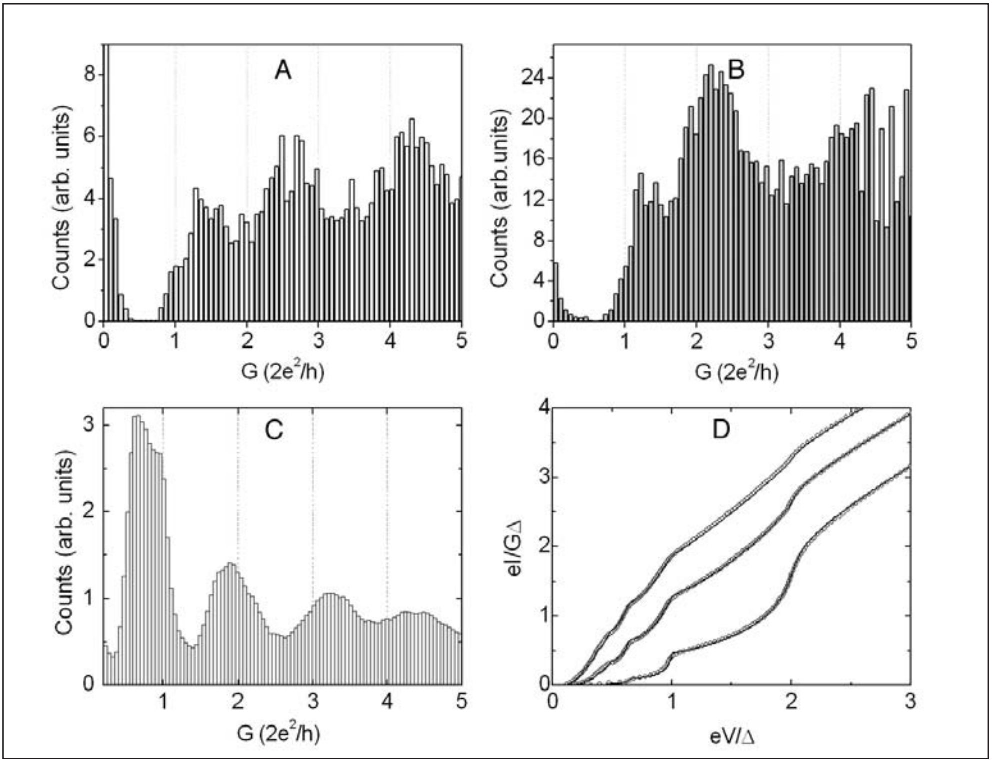


Fig. 2 (*A*) Conductance histogram of a Co sample (No. 1), measured at 1.6 K in zero magnetic field and (*B*) for sample No. 2 in a magnetic field of B = 5T perpendicular to the film plane. (*C*) Conductance histogram of Al, measured at 1.5 K (Yanson et al. 1997). (*D*) IV characteristics of three different configurations with a conductance $G \approx 0.8\ G_0$ of an Al sample measured at $T < 100$ mK and best fits (lines) to the theory of MAR.

Stopping the opening at some point before break and recording IVs in the superconducting state of Al or other superconductors, reveals different characteristics for contacts with the same total conductance and thus the same sum of the τ_i. As an example Figure 2*D* shows three IVs for contacts with $G \approx 0.8\ G_0$ recorded during the same step of an opening curve but in different elongation states. Therefore it is very likely that changes in the IVs are due to rearrangements in the vicinity of the central atom of the contact, because only this part is strongly affected by the deformation of the bridge.

The strong current increases at voltage values $V = 2\Delta/me$ where m is an integer and Δ is the quasiparticle's energy gap of the superconductor are caused by multiple particle transport processes through independent channels. Each current increase marks the onset of a new charge transport process with a different number m of coherently transferred electrons. For example the structure at $eV = 2\Delta$ corresponds to the transport of single electrons. Processes with $m > 1$ are called multiple Andreev reflection (MAR). They have in common that the energy 2Δ has to be provided by the voltage source. Due to energy conservation, processes with higher m set in at lower voltages since each of the transferred particles contributes the energy eV. The height of the current increase depends on the transmission of the channel since the probability of the simultaneous transport of m electrons roughly follows the law τ_i^m (CUEVAS et al. 1996, AVERIN and BARDAS 1995). This sets the basis for the determination of the channel ensemble $\{\tau_i\}$ in contacts with several channels. Because of the independence of the channels (eigenstates) the total current $I(V)$ through a QPC with N channels can be decomposed into the contributions of the individual channels (SCHEER et al. 1997):

$$I(V)=\sum_{i}^{N} i(\tau_i, V) \qquad [2]$$

The superconductivity itself does not influence the development of the channels, but it is only a tool for the determination. A detailed discussion of this point is given in SCHEER et al. (2000).

The measured IVs are fitted with the theory of MAR with N channels und $\{\tau_i\}$ as fitting parameters. The examples in Figure 2*D* are described successfully with three channels (solid lines). Consequently single-atom contacts of Al that contribute to the first maximum around 0.8 G_0 of the histogram in Figure 2*C* accommodate three channels with different $\{\tau_i\}$ that are determined by the central atom and its close environment.

Experiments at Pb single-atom contacts fabricated with a scanning electron microscope show three channels and a total conductance of 1.5 G_0, Nb contacts (notched-wire MCBs) transfer five channels and finally Au breakjunctions with Al leads contribute a single channel in a single-atom configuration (SCHEER et al. 1998). Preliminary results on the divalent, hexagonal metal Zn show one to three channels, presumably depending on the crystalline orientation (HÄFNER et al. 2004).

4. Conductance Channels from Atomic Orbitals

The exact geometry of the contacts on the atomic scale is not known. However, it is very likely that the central part of the constriction consisting of the central atom and its direct neighbors is not a perfectly ordered single crystal. Because of the short Fermi wave length the electrons feel all defects, like voids, dislocations, contamination atoms on this length scale. Therefore the eigenstates of this central part differs markedly from those of the leads, which are well described as Bloch waves. Due to the observed strong variation of the $\{\tau_i\}$ with the elongation it is self-evident to start the solution of this problem with the linear combination of atomic orbitals (LCAO) (CUEVAS et al. 1998, LEVY-YEYATI et al. 1997). Two basic ingredients enter the model:

The central atom has much less neighbors than an atom in the bulk. Consequently, the local bandstructure will differ from that of the bulk. The local Fermi energy will be shifted and has to be recalculated self-consistently. Secondly, all electrons that are transferred *via* the constriction feel – apart from tunnel contributions – the valence orbitals of the central atom. Accordingly an atom can build up at most as many channels as it has valence orbitals. The transmission coefficients of these channels depend on the overlap of the wavefunctions of the neighboring atoms and thus on the exact atomic arrangement. The calculation for different metals in highly symmetric geometries (e. g. two fcc ordered pyramids facing each other and connected *via* one atom) reveals that single-atom contacts of sp-like metals (Al, Pb) with three p-orbitals and one s-orbital close to the Fermi energy are assumed to have three channels with measurable transmission and a fourth one with a transmission lower than 0.01. The exact values of the τ_i do depend on the precise atomic configuration, but the number of channels does not. The transition metal (Nb) (1 s-orbital, 5 d-orbitals) accommodates five channels and monovalent metals (Au) one channel in agreement with the experimental findings. First calculations for Zn predict one dominating channel and two smaller ones for the pyramids oriented along the [001] direction (HÄFNER et al. 2004).

In general, in contacts of the multivalent metals none of the transmission coefficients achieves its saturation value $\tau_i = 1$. This is not a consequence of atomic disorder but of the mismatch between the eigenstates of the QPC and the leads. A necessary condition for perfect transmission is that the Fermi energy is located in the center of the band. This is fulfilled for monovalent metals under the assumption of charge neutrality, as observed for highly symmetric contacts of Au.

5. Conclusions and Future Prospects

The most important conclusions that can be drawn from the reported findings are the following: First, the analysis underlines that the smallest contacts are indeed single-atom contacts, since the number of channels never exceeds the number of valence orbitals of the respective element. The relation of the preferred conductance values of single-atom contacts of different metals is different from the relation of specific resistances of the bulk metals. Thus, the mechanism that gives rise to the electrical resistance on the atomic scale is completely different from the one in macroscopic solids. According to BOLTZMANN'S theory, which describes the resistance by scattering of the electrons at defects, a very small, but perfectly ordered sample would have zero resistance, and thus infinite conductance. Contrary, in the quantum mechanical description the conductance remains finite also if there is no intrinsic scattering and all transmission coefficients are saturated $\tau_i = 1$. The resistance is thus due to the mode filtering of the constriction similar to optical waveguides.

The ensemble of the experimental results is coherently described by the reported quantum chemical LCAO model. As a rule of thumb the number of channels is given by the number of valence electrons, which determines the chemical properties of the element. This observation cannot be explained within a model of free electrons, but a microscopic model that includes the precise atomic arrangement and the orbital structure is required.

Statistically, preferred conductance values are no proof for transmission saturation. One important question is thus left open: What is the reason for the maxima in the histograms? Apparently, certain atomic configurations giving rise to a particular conductance value are preferred. Several mechanisms including Coulomb interaction (KIRCHNER et al. 2001) and the back action of the electrons on the atomic positions (STAFFORD et al. 1997) have been proposed, but answering this question finally requires the investigation of atomic-size contacts with known atomic configuration. Experiments on breakjunctions made of whiskers and clusters with known structure are in progress.

For the use in magneto-electronics, systems with possibly high magnetoresistance ratio $MRR = (R_{ap}-R_p)/R_p$ are intensively studied, where R_{ap} is the resistance at anti-parallel spin configuration of the two leads (maximum resistance) and R_p the resistance when both spin directions are parallel. *MRR* values up to 100.000 % have recently been reported (Hua and Chopra 2003) in Ni contacts and fields of a few 100 mT. However, the mechanism giving rise to such tremendous values is not understood at all. In a recent publication by Viret et al. (2002) magnetoresistance (MR) curves of Ni atomic-size contacts have been reported that show *MRR* values up to 40 % in the single-atom range and much smaller values when the samples are broken to form tunnel contacts. For Co atomic-size contacts we find much higher *MRR* values (up to 70 % for single-atom contacts and more than 500 % in the tunnel regime when oxidizing intentionally the sample tips), but higher magnetic fields are necessary to achieve saturation (see Fig. 3*D*). Typical traces are shown in Figure 3*A* for sample No. 3 in the tunnel regime and in Figure 2*B* for a few-atom contact. Figure 3*C* displays MR curves recorded in different configurations of sample No. 2. The MR curves show a rich and contact-depending behavior, containing discrete resistance jumps as well as continuous developments. The appearance of maxima in both field directions when increasing and decreasing the field as well (Fig. 3*A* and *B*) have been observed for several arrangements of sample Nos. 3 and 4. They

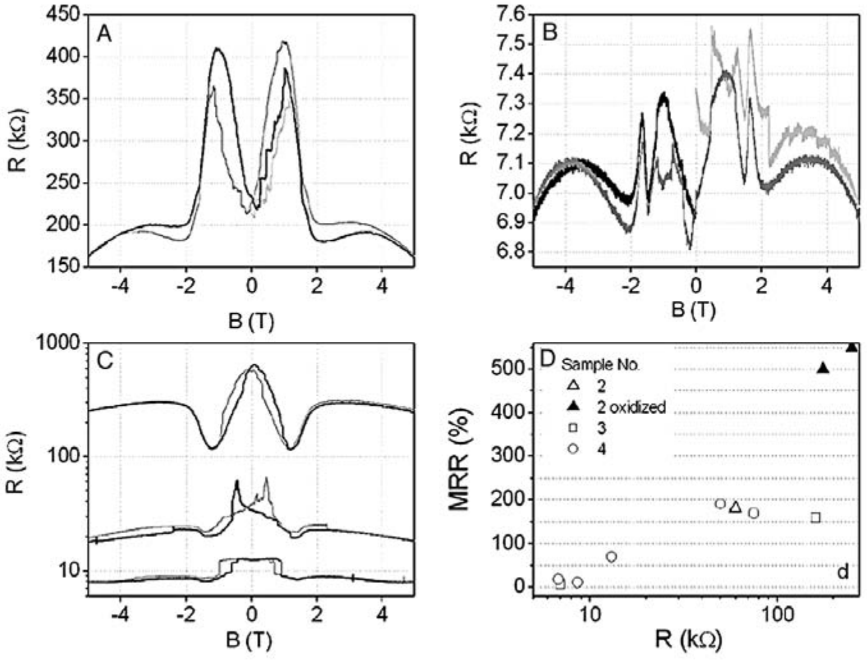


Fig. 3 (*A*)–(*C*) Magnetoresistance curves of different atomic-size contacts of Co, measured at 1.6 K for different, nominally identical samples. Light grey lines: first sweep of the magnetic field from 0 to 5 T, grey: decreasing field from 5 T to –5 T, black: increasing field from –5 T to 0. (*D*) Summary of magnetoresistance ratio *MRR* for samples No. 2, 3, and 4. Since in our experiments we do not arrive at saturated resistance values, we determine R_p at the highest measurement field B = 5 T.

cannot be understood within the simple models of tunneling MR (TMR), giant MR (GMR) or anisotropic MR (AMR) (for a recent overview, see e. g. MAEKAWA and SHINJO 2003). These findings suppose that the local atomic geometry again accounts for the observed behavior. Further experiments, including the determination of the transport channels of magnetic atomic-size contacts are in progress.

Acknowledgement

I thank my colleagues W. BELZIG, J. C. CUEVAS, J. KROHA, A. LEVY YEYATI, H. VON LÖHNEYSEN, U. RÜDIGER, J. VAN RUITENBEEK and C. URBINA for many fruitful discussions and my coworkers R. ARNOLD, P. BRENNER, C. BACCA, P. KONRAD, V. KUNEJ, A. MAYER-GINDNER, and H.-F. PERNAU for their contributions to the work presented here. Financial support by the Alfried Krupp von Bohlen und Halbach foundation and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

AGRAÏT, N., LEVY YEYATI, A., and VAN RUITENBEEK, J. M.: Quantum properties of atomic-sized conductors. Phys. Reports *377*, 81–279 (2003)

AVERIN, D., and BARDAS, A.: AC Josephson effect in a single quantum channel. Phys. Rev. Lett. *75*, 1831–1834 (1995)

COSTA-KRÄMER, J. L.: Conductance quantization at room temperature in magnetic and nonmagnetic metallic nanowires. Phys. Rev. B *55*, R4875–R4878 (1997)

CUEVAS, J. C., LEVY YEYATI, A., and MARTÍN-RODERO, A.: Microscopic origin of the conducting channels in metallic atomic-size contacts. Phys. Rev. Lett. *80*, 1066–1069 (1998)

CUEVAS, J. C., MARTÍN-RODERO, A., and LEVY YEYATI, A.: Hamiltonian approach to the transport properties of superconducting quantum point contacts. Phys. Rev. B *54*, 7366–7379 (1996)

HÄFNER, M., KONRAD, P., PAULY, F., CUEVAS, J. C., and SCHEER, E.: Conduction channels of one atom Zn contacts. Phys. Rev. B *70*, (R) 241404 – 1– 4 (2004)

HUA, S. Z., and CHOPRA, H. D.: 100.000 % ballistic magnetoresistance in stable Ni nanocontacts at room temperature, Phys. Rev. B *67*, (R) 060401–1–4 (2003)

KIRCHNER, S., KROHA, J., and SCHEER, E.: Generalized conductance sum rule in atomic break junctions. In: CHANDRASEKHAR, V., VAN HAESENDONCK, C., and ZAWADOWSKI, A. (Eds.): Kondo Effect and Dephasing in Low-dimensional Metallic Systems; pp. 215–218. Dordrecht: Kluwer Academic 2001

KRANS, J. M., VAN RUITENBEEK, J. M., FISUN, V. V., YANSON, I. K., and DE JONGH, L. J.: The signature of conductance quantization in metallic point contacts. Nature (London) *375*, 767–769 (1995)

MAEKAWA, S., and SHINJO, R.: Spin dependent transport in magnetic nanostructures. Adv. in Cond. Mat. Sci., Gordon and Breach (2003)

LANDAUER, R.: Electrical resistance of disordered one-dimensional lattices. Philos. Magazine *21*, 863–867 (1970)

LEVY YEYATI, A., MARTÍN-RODERO, A., and FLORES, F.: Conductance quantization and electron resonances in sharp tips and atomic size contacts. Phys. Rev. B *56*, 10369–10372 (1997)

SCHEER, E., AGRAÏT, N., CUEVAS, J. C., LEVY YEYATI, A., LUDOPH, B., MARTÍN-RODERO, A., RUBIO BOLLINGER, G., VAN RUITENBEEK, J. M., and URBINA, C.: The signature of chemical valence in the electrical conduction through a single-atom contact. Nature (London) *394*, 154–157 (1998)

SCHEER, E., CUEVAS, J. C., LEVY YEYATI, A., MARTÍN-RODERO, A., JOYEZ, P. DEVORET, M. H., ESTEVE, D., and URBINA, C.: Conduction channels of superconducting quantum point contacts. Physica B *280*, 425–431 (2000)

SCHEER, E., JOYEZ, P., ESTEVE, D., URBINA, C., and DEVORET, M. H.: Conduction channel transmissions of atomic-size aluminum contacts. Phys. Rev. Lett. *78*, 3535–3538 (1997)

STAFFORD, C. A., BAERISWYL, D., and BÜRKI J.: Jellium model of metallic nanocohesion. Phys. Rev. Lett. *79*, 2863–2867 (1997)

VAN RUITENBEEK, J. M., ALVAREZ, A., PINEYRO, I., GRAHMANN, C., JOYEZ, P., DEVORET, M. H., ESTEVE, D., and URBINA, C.: Adjustable nanofabricated atomic size contacts. Rev. Sci. Instrum. *67*, 108–111 (1996)

VAN WEES, B. J., VAN HOUTEN, H., BEENAKKER, C. W. J., WILLIAMSON, J. G., KOUWENHOVEN, L. P., VAN DER MAREL, D., and FOXON, C. T.: Quantized conductance of point contacts in a two-dimensional electron gas. Phys. Rev. Lett. *60*, 848–850 (1988)

VIRET, M., BERGER, S., GABUREAC, M., OTT, F., OLLIGS, D., PETEJ, I., GREGG, J. F., FERMON, C., FRANCINET, G., and LE GOFF, G.: Magnetoresistance through a single nickel atom, Phys. Rev. B *66*(R), 220401-1–4 (2002)

WHARAM, D. A., THORNTON, T. J., NEWBURY, R., PEPPER, M., AHMED, H., FROST, J. E. F., HASKO, D. G., PEACOCK, D. C., RITCHIE, D. A., and JONES, G. A. C.: One-dimensional transport and the quantisation of the ballistic resistance. J. Phys. C *21*, L209–L214 (1988)

YANSON. A. I., and VAN RUITENBEEK, J. M.: Do histograms constitute a proof for conductance quantization? Phys. Rev. Lett. *79*, 2157 (1997)

Prof. Dr. Elke SCHEER
Universität Konstanz
FB Physik
Fach M 681
Universitätsstraße 10
78464 Konstanz
Germany
Phone: +49 7531 884712
Fax: +49 7531 883090
E-Mail: elke.scheer@uni-konstanz.de

350 Jahre Leopoldina – Anspruch und Wirklichkeit

Festschrift der Deutschen Akademie der Naturforscher Leopoldina 1652–2002

Herausgegeben von
Benno Parthier (Halle/Saale) und Dietrich von Engelhardt (Lübeck)
(2002, 816 Seiten, 130 Abbildungen, 8 Tabellen, 54,90 Euro, ISBN 3-928466-45-3)

Die älteste deutschsprachige Akademie prüft »Anspruch und Wirklichkeit« ihrer Vergangenheit und läßt 350 Jahre wechselvoller Geschichte in ihren naturwissenschaftlichen und medizinischen Rahmenbedingungen Revue passieren. Die Festschrift wendet sich an eine interessierte Öffentlichkeit, die allmählich diese besondere Akademie in der deutschen und internationalen Akademienlandschaft mit ihrer spezifischen wissenschaftlich-kulturellen Bedeutung wahrnimmt, nachdem die Wirkungen von 40 Jahren defizitärer Existenz »hinter dem eisernen Vorhang« überwunden werden konnten. (Klappentext)

Inhalt:
Teil I: Geschichte der Leopoldina in Schwerpunkten
Teil II: Die Leopoldina im Spiegel einzelner Wissenschaftsdisziplinen
Teil III: Querschnittsthemen
Teil IV: Anhänge

Mit Beiträgen von:
Gunnar Berg (Halle/Saale), Johanna Bohley (Halle/Saale), Dietrich von Engelhardt (Lübeck), Menso Folkerts (München), Bernhard Fritscher (München), Sybille Gerstengarbe (Halle/Saale), Fritz Hartmann (Hannover), Lothar Jaenicke (Köln), Ilse Jahn (Berlin), Joachim Kaasch (Halle/Saale), Michael Kaasch (Halle/Saale), Kai Torsten Kanz (Lübeck), Andreas Kleinert (Halle/Saale), Eberhard Knobloch (Berlin), Dorothea Kuhn (Marbach), Irmgard Müller (Bochum), Uwe Müller (Schweinfurt), Gisela Nickel (Ober-Olm), Thomas Nickol (Halle/Saale), Benno Parthier (Halle/Saale), Horst Remane (Halle/Saale), Hermann-J. Rupieper (Halle/Saale); Klaus Sander (Freiburg i. Br.), Thomas Schnalke (Berlin), Werner Schroth (Halle/Saale), Eugen Seibold (Freiburg i. Br.), Eduard Seidler (Freiburg i. Br.), Richard Toellner (Rottenburg-Bieringen) und Gudrun Wolfschmidt (Hamburg).

Druck-Zuck GmbH, Seebener Straße 4, 06114 Halle/Saale
Buchbestellung on-line: www.druck-zuck.net

Nova Acta Leopoldina NF *92*, Nr. 340, 47–53 (2005)

Electrical Current through Single Molecules

Heiko B. WEBER[1], Marcel MAYOR[2], and Hilbert VON LÖHNEYSEN[3]

With 3 Figures

Abstract

The electrical current through single molecule junctions is studied. Three different molecules were contacted with the mechanically controlled break-junction technique. The data reflect the transport properties of the molecules with respect to their symmetry and to the different relative positions of the anchor groups on the molecules to the metallic electrodes. The comparison between room temperature and low temperature data displays that vibrational degrees of freedom have important effects on the electronic properties.

Zusammenfassung

Wir untersuchen den elektrischen Strom durch Einzelmolekülkontakte. Drei unterschiedliche Moleküle wurden verwendet, um das Elektrodenpaar eines mechanisch kontrollierten Bruchkontaktes zu überbrücken. In den Meßdaten spiegeln sich die Symmetrieeigenschaften und die relative Position der Ankergruppen am Molekül, welche den Kontakt zur Metallelektrode bilden, wider. Der Vergleich zwischen Raumtemperaturdaten und Tieftemperaturdaten zeigt, daß Vibrationsfreiheitsgrade einen deutlichen Einfluß auf die elektronischen Eigenschaften ausüben.

The idea of *Molecular Electronics* is to use molecules as a basic component of an electronic device. Molecules are the smallest building blocks which can be produced identically in large quantities. When appropriately designed, they may self-assemble to more complex structures like, for example, highly ordered films. Hence molecules are well suited for the frequently desired bottom-up formation of nanostructures. Molecular recognition may be employed for selectively building up even more complex structures. For nanoelectronics, the electron transfer within molecules and their nonlinear electronic response is the basic functionality. It has been investigated thoroughly during many decades in isolated molecules in the gas phase, in solution and in the solid state.

In 1974 AVIRAM and RATNER proposed the idea of a molecular diode (AVIRAM and RATNER 1974): an asymmetric molecule positioned between metallic electrodes may allow for a current in one direction only when the electronic structure is appropriately chosen. Of course, the molecule has to be carefully designed in order to perform a desired function. Because there are infinitely many possibilities, a profound understanding of the underlying physical mechanisms is mandatory to engineer such a complex system. On the other hand, this diversity is also a big advantage of molecular electronics (compared to other concepts of nanoelectronics) because it allows for many variations.

---

[1] Forschungszentrum Karlsruhe, Institut für Nanotechnologie, 76021 Karlsruhe.
[2] Physikalisches Institut, Universität Karlsruhe, 76128 Karlsruhe.
[3] Forschungszentrum Karlsruhe, Institut für Festkörperphysik, 76021 Karlsruhe.

One way to contact molecules electrically is a sandwich-like setup in which a highly ordered molecular film covers a conducting electrode and a second electrode is then evaporated on top of this film (METZGER et al. 1997, CHEN et al. 1999, LUO et al. 2002) or carefully approached to form an electric contact (KUSHMERICK et al. 2002, HOLMLIN et al. 2001). Experiments have shown the functionality of a diode (METZGER et al. 1997), of voltage-pulse programmable switches (LUO et al. 2002), and further conjugated molecular rods have been investigated (KUSHMERICK et al. 2002).

Another direction in experimental research is aimed at measuring the conductance of only one single molecule. To obtain a device which is sufficiently stable to withstand the forces by the applied voltages and the current, the contact to the electrodes must then be a stable covalent bond. REED et al. (1997) performed the first pioneering experiment, using a mechanically controlled break junction (MCB) as a tunable-distance electrode pair which was covered with a self-assembled monolayer of benzene-dithiol molecules. They were able to measure nonlinear current-voltage characteristics (IVs) with reproducible minimum conductance at consistent values and the authors concluded that the number of active molecules could be as few as one. A similar experiment with a different molecule yielded reproducible IVs as well, but reported spontaneous changes in the IVs which were attributed to changes in the contact configuration (KERGUERIS et al. 1999).

The experiment described here is technically similar to the previously described single-molecule experiments (REICHERT et al. 2002, WEBER et al. 2002, MAYOR et al. 2002b, 2003, REICHERT et al. 2003). We adopted the following experimental procedure which allows to collect much more information than previous experiments:

(*i*) We use an improved version of the MCB (VAN RUITENBEEK et al. 1995).
(*ii*) By continuously closing and reopening the contact, the tips are sharpened until atomic-sized tips are obtained as deduced from a conductance of the order of $2e^2/h$ when closed.
(*iii*) Our experiment is run in the rather low coverage regime, which favors contacting of individual molecules.
(*iv*) Systematic comparative studies with different, carefully designed molecules were carried out.
(*v*) By reproducing the experiment a low temperatures (≈ 30 K), the data quality was substantially improved. Note that it is experimentally challenging to form low-temperature data and a special protocol had to be developed to achieve this goal (REICHERT et al. 2003).

Figure 1 shows the molecules that have been investigated. They are all molecular rods consisting of a comparable structural backbone of similar length, which are fitted with thiol groups at both ends. Molecule **1** and **2** are fully conjugated along the rod axis. Their major difference is their symmetry, as can be seen in Figure 1: whereas the junction with molecule **1** is symmetric with respect to the mirror inversion of the two electrodes, **2** is asymmetric. Looking at this simplifying sketch (and neglecting asymmetries induced by disorder in the electrodes and other disordered molecules which may be around), one would anticipate that the conductance is independent of the current direction (REICHERT et al. 2002, WEBER et al. 2002).

The conductance data are shown in Figure 2*A* at room temperature. The junction is stable up to $V \approx \pm 1.1$ V, allowing to trace the same current-voltage characteristics several times. The current level ranges up to 0.21 µA. The IV curve is clearly nonlinear, having a broad step-like feature at $V = \pm 0.35$ V, which presumably corresponds to the onset of conductance when

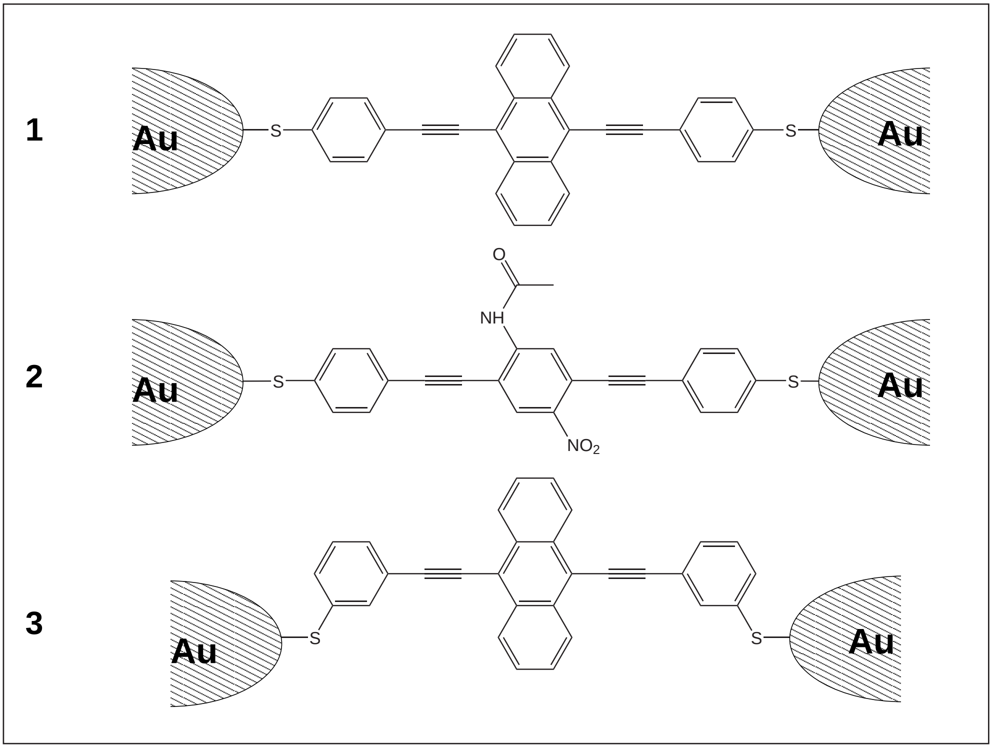


Fig. 1 Scheme of the experimental setup: the three molecules 1–3 between gold electrodes. In solution, the molecules are fitted with acetyl protection groups at both ends which split off upon contact with the gold surface.

the first molecular orbital gets in resonance with the electrochemical potential of the electrodes. The blue curve, obtained by numerical differentiation of *I (V)*, is the differential conductance *dI/dV*. It displays two peaks and the overall structure is to a good approximation symmetric. The corresponding curve for the asymmetric molecules is shown in Figure 2*B*, it is clearly asymmetric. There are two important conclusions that can be drawn from this comparison:

(*i*) The fact that the symmetric molecule gives symmetric IVs and the asymmetric molecule gives asymmetric IVs proves that indeed the molecule is forming the contact (and not water or dust or anything else).

(*ii*) The number of molecules is very small, perhaps even a single one: a large ensemble of molecules, being randomly oriented during the deposition on both electrodes, would result in a symmetric IV.

These findings, together with additional observations described in Reichert et al. (2002) do not unambiguously prove, but indicate strongly that indeed a single molecule or at most a few molecules form the junction.

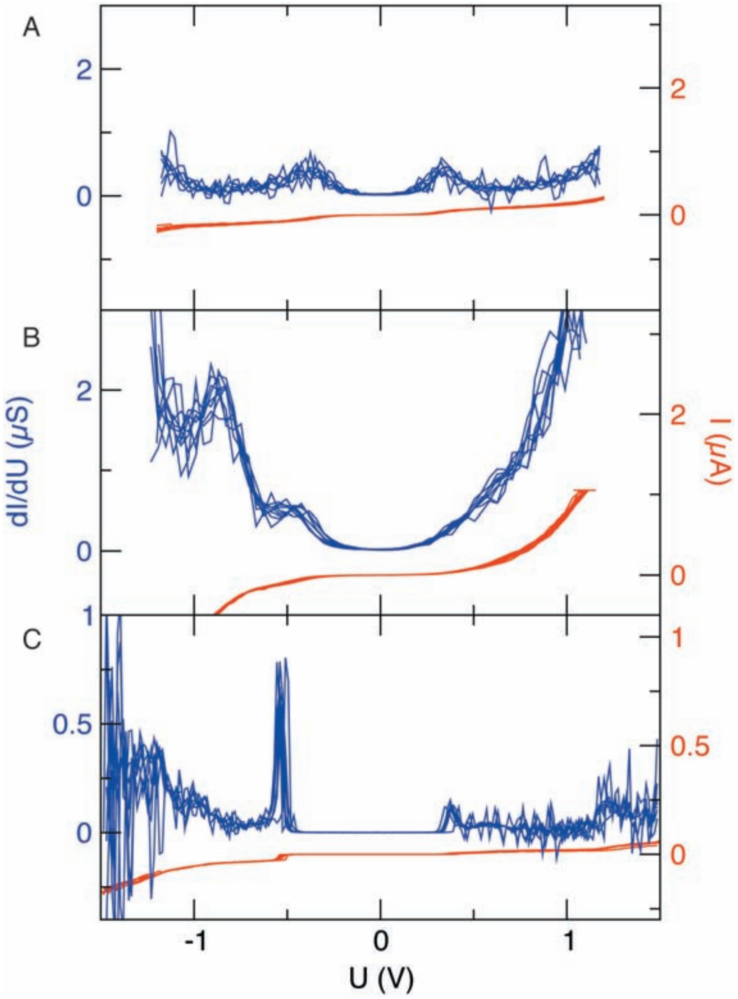


Fig. 2 IV characteristics, reproducibly recorded for a stable junction in a mechanically controlled break junction (red) and their numerical derivative *dI/dU* (blue). (*A*) with molecule **1** at room temperature, (*B*) with molecule **2** at room temperature, (*C*) with molecule **2** at $T \approx 30$ K.

The data shown in Figures 2*A* and *B* are just examples for an IV. If the measurement is repeated, the shape of the IVs changes. The peak position may shift up and down by ≈ 100 mV or it may appear at the opposite voltage sign, the conductance may vary within a factor of 10, the peak height and peak width vary. For the symmetric molecule **1**, sometimes also asymmetric IVs occur, which can be attributed to strongly asymmetric contacts, whereas for **2** the asymmetry is always observed.

These sample-to-sample fluctuations indicate that the molecules can not be considered independent of their local environment. In particular, the interaction with the electrodes is of paramount importance for the electronic properties of the junction. This was also confirmed by theoretical investigations (Yaliraki et al. 1999, Weber et al. 2002), which pointed out that the atomic realization of the contact influences strongly the electronic structure and the transmission. This interaction does not only happen by a modification of the surrounding electrostatic fields, but may also be due to the chemical bond which mixes wave function of the conduction electrons in the electrodes with the molecule's wave function. Because in break junctions the electrode tip is expected to be disordered on the atomic scale, this introduces disorder to the molecular wave function, resulting finally in an unsufficient control over the electronic properties.

We present two approaches to improve the data quality and to achieve a better control over the system. The first is to reduce in a chemically defined way the electronic coupling between the molecule and the electrode. This is expected to reduce also the electronic transparency of the contact, which is desirable because a lower current level corresponds to a higher stability. We employ a suggestion by Yaliraki and Ratner (2002) who proposed that the electronic transparency of a *meta*-connected phenyl ring is reduced compared to that of a *para*-connected one. This reduced coupling is not surprising, it has been observed in electrochemical studies of reducibel subunits as well (Mayor et al. 2002a). We applied this concept to the con-

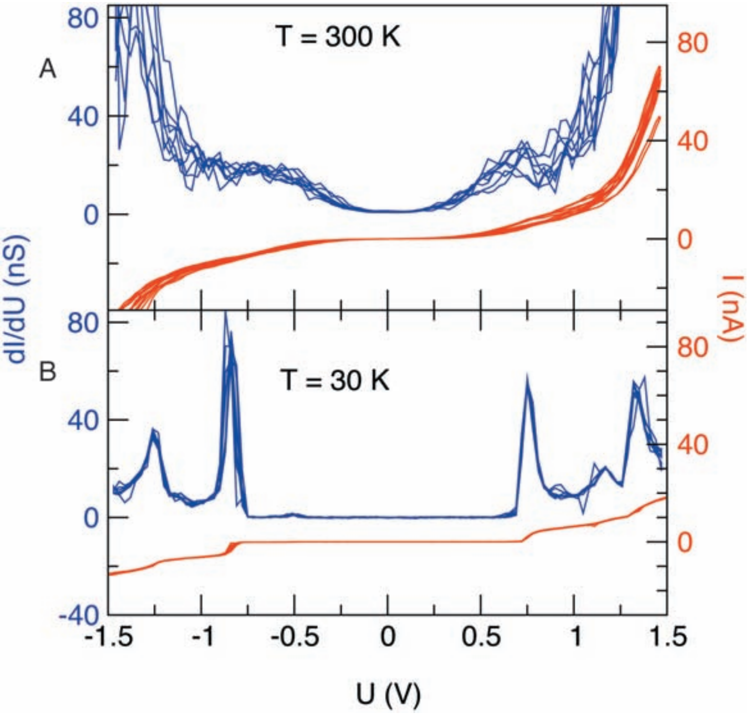


Fig. 3 IV characteristics, reproducibly recorded with molecule **3** (red) and their numerical derivative *dI/dU* (blue). (*A*) at room temperature, (*B*) at $T \approx 30$ K.

tact-forming thiol endgroups and designed molecule **3** (cf. Fig. 1). Its molecular backbone is identical with molecule **1**, but the thiol anchor groups are at different positions (MAYOR et al. 2003). Figure 3*A* shows the IVs obtained with this molecule at room temperature.

Again, the IVs are rather symmetric, as expected for this symmetric molecule. An important observation is that the overall current is substantially reduced. At $V = 1$ V, only 12 nA flow through the contact. So we reached the goal of reducing the electronic transparency. For single molecule contacts, the reduction of the current allows to access a larger bias range (up to $V = 1.5$ V), yielding more informationon the higher-energy electronic structure of the molecule. Further, if molecular rods are used in a molecular film device, a reduced conductance is desirable, because this reduces both the current density and the power dissipation in the contact, which would be significant for molecules **1** and **2**. A future careful statistical evaluation of single-molecule conductance data with molecule **3** will decide whether the reproducibility of the IVs is improved as well due to this decoupling nature of the contact. In an alternative approach, an interruption of the conjugation in the center of the molecule by a Pt II ion resulted in a surprisingly effective increase of the resistance (MAYOR et al. 2002b).

As a second approach to improve the data quality, the temperature is lowered. Electronic excitations, but in particular vibrational degrees of freedom are expected to be frozen out. For the formation of the molecular-electrode bond, on the other hand, room-temperature conditions are required to enable the diffusion of the reaction products and to provide sufficient activation energy (other combinations than acetyl-protected thiol vs. gold might be suitable under different conditions, but have not yet been tested). Hence we establish a molecular junction at room temperature, reopen it (because it is difficult to control the electrode distance during the cool-down process) and when 30 K are reached, the junction is closed again until stable IVs are observed. A detailed description of the experimental protocol can be found in (REICHERT et al. 2003). The data thus obtained with molecules **2** and **3** are displayed in Figure 2*C* and Figure 3*C*, respectively. The comparison with the para-connected molecule **2** as an example shows at low temperatures a blockade of the current around zero bias, in contrast to the broad minimum observed at room temperatures (RT). Looking at the peak-like structure in Figure 2*B*, which is rather shoulder-like in some cases, the peaks have a peak width of several hundred mV. In contrast, the peaks are much better resolved at low *T*. The obvious conclusion is that the molecule is indeed oscillating very fast at RT and the measurement averages over many configurations. The increase in stability can be seen at the accessible stable bias window, which is [–1.5 V, 1.5 V] at low *T*. In addition, the noise, which is not electronic noise induced by insufficient electric stability, but which is originating from the nanocontact, is substantially reduced.

Figure 3*B* shows similar data obtained with the *meta*-connected molecule **3** at low *T* ($T \approx 30$ K). Again, a blockade region around zero bias is visible, which corresponds to a broad minimum at RT. The peaks are much better resolved. The noise is substantially reduced and the peak width is much smaller than at RT. The reasonable symmetry of the IVs with respect to voltage inversion supports the notion that the contact is close to the idealized contact as shown in Figure 1. Any asymmetric configuration, which might in particular result from the cooling down process (where insufficient vacuum might cause an impenetrable solid adsorbate layer) can be ruled out. Similarly, the fact that symmetric molecules cause symmetric IVs, but asymmetric molecules cause asymmetric ones, yields convincing evidence that many “pathological” configurations (like two molecules at the two opposite tips which touch each other, EMBERLY and KIRCZENOW 2001) are definitely not present in our experiments.

Hence we conclude that our experiments give convincing arguments that we measure indeed the electronic characteristics of single-molecule junctions. The data show that the electronic properties reflect some obvious properties of the molecules. This, in turn, encourages the idea that the electronic properties can be tailored by an appropriate choice of the molecule. We have pointed out two ways to improve the data quality. The first is by chosing the contact chemistry such that only weak electronic transparency is realized, which is favourable for the stability of the junction. The other approach is to go to lower temperatures, which allows to reduce undesired fast degrees of freedom and which improves the data quality and the stability. Both strategies open possibilities for many interesting experiments. As an example, in the low temperature regime the interaction with superconducting electrodes or Kondo physics can be realized. Following the synthetic strategies, the pathway is towards a concept of decoupled molecular units, which might act as rather independent modules.

References

AVIRAM, A., and RATNER, M.: Chem. Phys. Lett. *29*, 277–287 (1974)

CHEN, J., REED, M. A., RAWLETT, A. M., and TOUR, J. M.: Science *286*, 1550–1552 (1999)

EMBERLY, E., and KIRCZENOW, G.: Phys. Rev. Lett. *26*, 269701 (2001)

HOLMLIN, R. E., ISMAGILOV, R. F., HAAG, R., MUJICA, V., RATNER, M. A., RAMPI, M. A., and WHITESIDES, G. M.: Angew. Chem. Int. Ed. *40*, 2316–2320 (2001)

KERGUERIS, C., BOURGOIN, J.-P., PALACIN, S., ESTEVE, D., URBINA, C., MAGOGA, M., and JOACHIM, C.: Phys. Rev. B *59*, 12505–12513 (1999)

KUSHMERICK, J. G., HOLT, D. B., YANG, J. C., NACIRI, J., and SHASHIDAR, R.: Phys. Rev. Lett. *89*, 086802-1–4 (2002)

LUO, Y., COLLIER, C. P., JEPPESEN, J. O., NIELSEN, K. A., DELONNO, E., HO, G., PERKINS, J., TSENG, H.-R., YAMAMOTO, T., FRASER STODDART, J., and HEATH, J. R.: ChemPhysChem *3*, 519–525 (2002)

MAYOR, M., BÜSCHEL, M., FROMM, K. M., LEHN, J.-M., and DAUB, J.: Ann. New York Acad. Sci. *960*, 16–28 (2002)

MAYOR, M., HÄNISCH, C. VON, WEBER, H. B., REICHERT, J., und BECKMANN, D.: Angew. Chem. Int. Ed. *41*, 1183–1186 (2002)

MAYOR, M., WEBER, H. B., REICHERT, J., ELBING, M., HÄNISCH, C. VON, BECKMANN, D., and FISCHER, M.: Angew. Chem. Int. Ed., accepted for publication (2003)

METZGER, R. M., CHEN, B., HÖPFNER, U., KAKSHMIKANTHAM, M. V., VUILLAUME, D., KAWAI, T., WU, X., TACHIBANA, H., HUGHES, T. V., SAKURAI, H., BALDWIN, J. W., HOSCH, C., CAVA, M. P., BREHMER, L., and ASHWELL, G. J.: J. Amer. Chem. Soc. *119*, 10455–10466 (1997)

REED, M. A., ZHOU, C., MULLER, C. J., BURGIN, T. P., and TOUR, J. M.: Science *278*, 252–254 (1997)

REICHERT, J., OCHS, R., BECKMANN, D., WEBER, H. B., MAYOR, M., and LÖHNEYSEN, H. VON: Phys. Rev. Lett. *88*, 176804-1–4 (2002)

REICHERT, J., WEBER, H. B., MAYOR, M., and LÖHNEYSEN, H. VON: Appl. Phys. Lett. *82*, 4137–4139 (2003)

VAN RUITENBEEK, J. M., ALVAREZ, A., PINEYRO, I., GRAHMANN, C., JOYEZ, P., DEVORET, M. H., ESTEVE, D., and URBINA, C.: Rev. Sci. Instrum. *67*, 108–111 (1995)

WEBER, H. B., REICHERT, J., WEIGEND, F., OCHS, R., BECKMANN, D., MAYOR, M., AHLRICHS, R., and LÖHNEYSEN, H. VON: Chem. Phys. *281*, 113–125 (2002)

YALIRAKI, S. N., and RATNER, M. A.: Ann. New York Acad. Sci. *960*, 153–162 (2002)

YALIRAKI, S. N., ROITBERG, A. E., GONZALEZ, C., MUJICA, V., and RATNER, M. A.: J. Chem. Phys. *111*, 6997–7002 (1999)

Dr. Heiko B. WEBER
Forschungszentrum Karlsruhe
Postfach 36 40
76021 Karlsruhe
Germany
Tel.: +49 7247 826376
Fax: +49 7247 826369
E-Mail: heiko.weber@int.fzk.de

Festliche Übergabe des Präsidentenamtes von Benno Parthier an Volker ter Meulen

am 13. Februar 2003 im Freylinghausen-Saal der Franckeschen Stiftungen zu Halle (Saale)

Nova Acta Leopoldina N. F., Bd. *89*, Nr. 335
Herausgegeben vom Präsidium der Akademie
(2003, 54 Seiten, 17 Abbildungen, 22,80 Euro, ISBN 3-8047-2039-0)

Die Übergabe des Präsidentenamtes in der Deutschen Akademie der Naturforscher Leopoldina lieferte die Gelegenheit für eine erneute Standortbestimmung der Akademie, nachdem die Leopoldina erst 2002 ihr 350. Gründungsjubiläum begangen hatte. Nach der Begrüßung durch Leopoldina-Vizepräsident Ernst-Ludwig WINNACKER (Bonn/München) beschäftigte sich der scheidende Präsident Benno PARTHIER (Halle/Saale) mit den erforderlichen Weichenstellungen und Entwicklungen der Wirkungsfelder der Akademie in den zurückliegenden Jahren seiner Präsidentschaft. In seiner Antrittsrede umriß der neue Präsident Volker TER MEULEN (Würzburg) die weiteren Aufgaben der Leopoldina und ging dabei auch auf die heißdiskutierte Frage einer nationalen Akademie für Deutschland ein. In seinem Festvortrag sprach Wolfgang FRÜHWALD (München) zum Thema »Eine liebenswerte Wissenschaft und ein glücklicher Sisyphos. Zum Leben und zur Arbeit einer nationalen Akademie«.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 55–60 (2005)

Interlayer Exchange Coupling of Fe Films across Si Tunnel Barriers

Rashid R. Gareev[1], Lars L. Pohlmann, Daniel E. Bürgler, and
Peter A. Grünberg[2]

With 2 Figures and 1 Table

Abstract

Fe (5 nm)/Si (0.8–2 nm)/Fe (5 nm) structures were grown by molecular-beam epitaxy on Ag(001) buffered GaAs substrates. Tunneling junctions with crossed electrodes and areas ranging from 22 to 225 µm^2 were patterned using photolithography. Antiparallel alignment of the magnetizations due to antiferromagnetic interlayer coupling, which was confirmed by longitudinal MOKE hysteresis loops, exists for the whole range of spacer thicknesses. Transport properties in CPP geometry were examined by the four-point method in the temperature range from 4 K to room temperature. As a function of spacer thickness, the junctions show a strong increase of the resistance times area product from ≈ 1 Ω µm^2 to more than 10 kΩ µm^2. The *dI/dV-V* curves are parabolic and asymmetric and thus characteristic for trapezoidal tunneling barriers. The mean barrier heights derived from Brinkman fits range from 0.3 to 0.8 eV. The zero-bias resistance of the tunneling junctions moderately decreases with temperature by less than 10 % over the whole measured temperature range. All these transport properties fulfil the necessary and sufficient criteria for elastic tunneling proofing that strong AF interlayer coupling is possible across tunnel barriers.

Zusammenfassung

Fe(5 nm)/Si(0,8–2 nm)/Fe(5 nm)-Schichtungen wurden mit Hilfe von thermischem Verdampfen auf Ag(001) gepufferten GaAs-Substraten hergestellt. Durch laterale Strukturierung wurden hieraus Tunnelstrukturen mit gekreuzten Zuleitungen und Kontaktflächen zwischen 22 und 225 µm^2 hergestellt. Für den gesamten untersuchten Bereich der Zwischenschichtdicken ergab sich antiparallele Ausrichtung der Magnetisierungen als Folge von antiferromagnetischer Zwischenschichtkopplung. Dies wurde mit Hilfe von Ummagnetisierungsmessungen unter Zuhilfenahme des magnetooptischen Kerr-Effektes (MOKE) festgestellt. Messungen des elektrischen Widerstandes wurden in der CPP-Geometrie mit der Vierpunktmethode im Temperaturbereich zwischen 4 K und Raumtemperatur durchgeführt. Als Funktion der Zwischenschichtdicke zeigten die Proben einen starken Anstieg des Flächenwiderstandes von ≈ 1 Ω µm^2 zu mehr als 10 kΩ µm^2. Die *dI/dV-V*-Kurven sind parabolisch und asymmetrisch und daher typisch für trapezoidale Tunnelbarrieren. Die aus Brinkman-Fits bestimmten mittleren Barrierehöhen liegen zwischen 0,3 und 0,8 eV. Der Widerstand bei sehr kleinen Spannungen verkleinert sich als Funktion der Temperatur über den gemessenen Bereich um weniger als 10 %. Diese Transporteigenschaften erfüllen die notwendigen und hinreichenden Kriterien für elastisches Tunneln und zeigen damit, daß starke antiferromagnetische Kopplung über Tunnelbarrieren möglich ist.

---

11 E-Mail: r.gareev@fz-juelich.de.

12 Presenting author, E-Mail: p.gruenberg@fz-juelich.de.
Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-3l-l09-Eng-38.

1. Introduction

Epitaxial Fe/Si/Fe structures are interesting due to strong antiferromagnetic (AF) interlayer coupling and its interplay with transport properties, which both are sensitive to preparation conditions (Fullerton et al. 1992, Inomata et al. 1995, de Vries et al. 1997, Endo et al. 2000). Recently, we have found that insulating-type, highly resistive spacers can be prepared by a certain deposition procedure (Gareev et al. 2002a,b,c). Corresponding Fe/Si/Fe structures reveal very strong AF interlayer coupling with a total coupling strength in excess of 5 mJ/m^2 (Gareev et al. 2002b), which could be further increased to 8 mJ/m^2 by inserting thin epitaxial and metallic FeSi boundary layers at interfaces (Gareev et al. 2001, 2002a). For combined semiconducting/metallic epitaxial spacers (i.e. nominally pure Si/Fe$_{0.5}$Si$_{0.5}$), the main impact to AF coupling arises from the semiconducting part of the spacer (Gareev et al. 2002c). Hence, we came to the conclusion that the strong and exponentially decaying AF coupling arises from Si-rich spacers in qualitative agreement with the quantum interference model of exchange coupling across insulating spacers as described by Bruno (1995).

The behavior of interlayer coupling indicates that nominally pure Si spacers are effectively not homogeneous. For a nominal spacer thickness t less than several monolayers, the interlayer coupling becomes ferromagnetic (FM) very likely due to conducting pin-holes formed by interdiffusion at the interfaces (Gareev et al. 2002a,b). For thicker spacers, the effect of pin-holes and – accordingly – FM coupling are suppressed.

The resistivity in CPP (current perpendicular to the sample plane) geometry is expected to yield additional and clear information whether a Si-rich spacer is metallic or insulating. Hence, the question is whether the transport in highly resistive spacers is due to elastic tunneling, or whether it arises from additional channels of conductivity across submicron-sized pin-holes, as it was pointed out by Rabson et al. (2001) and Åkerman et al. (2002). For this reason we examined for our structures the validity of the necessary and sufficient criteria for direct elastic tunneling (Åkerman et al. 2002), i.e. (*i*) strong and exponential increase of the resistance with t, (*ii*) parabolic dependence of conductivity *versus* bias voltage, and – most decisive – (*iii*) small and negative temperature coefficient of the zero-bias resistance.

2. Experimental Procedures

The preparation procedure of Fe(5 nm)/Si(0.8–2 nm)/Fe(5 nm) wedge-type epitaxial samples on Ag(150 nm)/Fe(1 nm)/GaAs(100) buffer systems has been described by Gareev et al. (2002a) and Gareev et al. (2001). We measured longitudinal magneto-optical Kerr effect (MOKE) hysteresis loops to verify the presence of AF coupling, which is reflected by zero remanent magnetization. The external magnetic field is applied along an easy-axis of the Fe layers. Additionally, we prepared structures with constant spacer thickness and checked the antiparallel alignment by SQUID magnetometry, where we can apply higher magnetic fields and saturate the samples. After these magnetic characterizations, 10×10 mm^2-sized, wedge-type samples were patterned using photolithography, ion-beam etching, and lift-off technique to obtain CPP junctions with different spacer thicknesses, which are all deposited under the same growth conditions. We use crossed contacts, where the upper electrode is formed by deposition of a 300 nm-thick Cu layer. The patterned 150 nm-thick silver buffer layer serves as a bottom electrode. The sheet resistances RA of both electrodes are about 0.1 Ωcm^2 and thus significantly smaller than the resistance of the tunneling junctions in CPP geometry (Tab. 1), such that current distribution effects are diminished (VAN DE VEERDONK et al. 1997). Insulation of the electrodes was achieved by deposition of a 250 nm-thick Si-oxide layer. Finally, we fabricated junctions of rectangular shape ranging in area A from 22 to more than 200 µm^2. The layout of the patterned sample is shown in Figure 1*A*. A typical patterned junction is shown in the inset. After patterning, voltage and current leads suitable for four-point transport measurements were connected by ultrasonic bonding. We measured the I-V characteristics of junctions with different areas A and nominal spacer thicknesses t (see Tab. 1).

Tab. 1 Junction area *A*, nominal spacer thickness *t*, junction resistance *R*, and the parameters derived from Brinkman fits: mean barrier height ø, barrier asymmetry Δø, and the fitted barrier thickness t_{eff} for various junctions labelled J1 to J6.

Junction	A (µm^2)	t (nm)	R (Ω)	ø (eV)	Δø (eV)	t_{eff} (nm)
J1	22	1.54	307	0.35	−0.35	1.83
J2	22	1.70	23.4	0.54	−0.36	1.22
J3	100	1.48	26.0	0.33	0.05	1.74
J4	100	1.54	5.6	0.43	−0.18	1.35
J5	100	1.64	223	0.78	−0.30	1.44
J6	225	1.70	5.3	0.36	−0.10	1.55

3. Results and Discussion

The thickness dependence of the AF interlayer coupling strength J_1 of our structures with different Si content is shown in Figure 2. For nominally pure Si spacers $|J_1|$ decays exponentially with *t* with a decay length of about 0.3 nm. Finally, for $t \approx 2$ nm the AF coupling strength decreases to $|J_1| \approx 0.1$ mJ/m^2. The zero-field antiparallel alignment is observed in the whole range of temperatures and for all spacer thicknesses.

A representative *I-V* curve taken at room temperature and the corresponding *dI/dV-V* curve is presented in Figure 1*B* and shows the typical tunneling-type behavior. The *dI/dV-V* curve is parabolic with its minimum away from $V = 0$. These features are characteristic for tunnel junctions with asymmetric barriers and indicate different conditions at the diffused Fe/Si and Si/Fe interfaces, probably due to different interfacial densities of states and/or transmission probabilities of the carriers. There is no evidence for a conductivity anomaly near $V = 0$, as previously reported MOODERA and MATHON (1999) for ferromagnetic junctions with Al-oxide spacers and related to inelastic scattering assisted by magnons and impurities.

Similar *I-V* curves can occur when transport is due to another conductivity channel, namely submicron-sized pin-holes, which can mimic elastic tunneling (RABSON et al. 2001). As we will show below based on an analysis of the temperature dependence of the resistance, this metallic-type channel here gives no significant contribution.

In Figure 1*C* we show the resistance times area product *RA* versus *t* on a semi-logarithmic scale. The value of *RA* increases at room temperature strongly with *t* by more than 4 orders of magnitude, while *t* only approximately doubles. The decay length $t_0 \approx 1$ Å (dashed line in Fig. 1*C*) is significantly shorter compared to corresponding decay lengths for structures with amorphous Si spacers as reported by XU et al. (1995). Note, that the AF exchange coupling

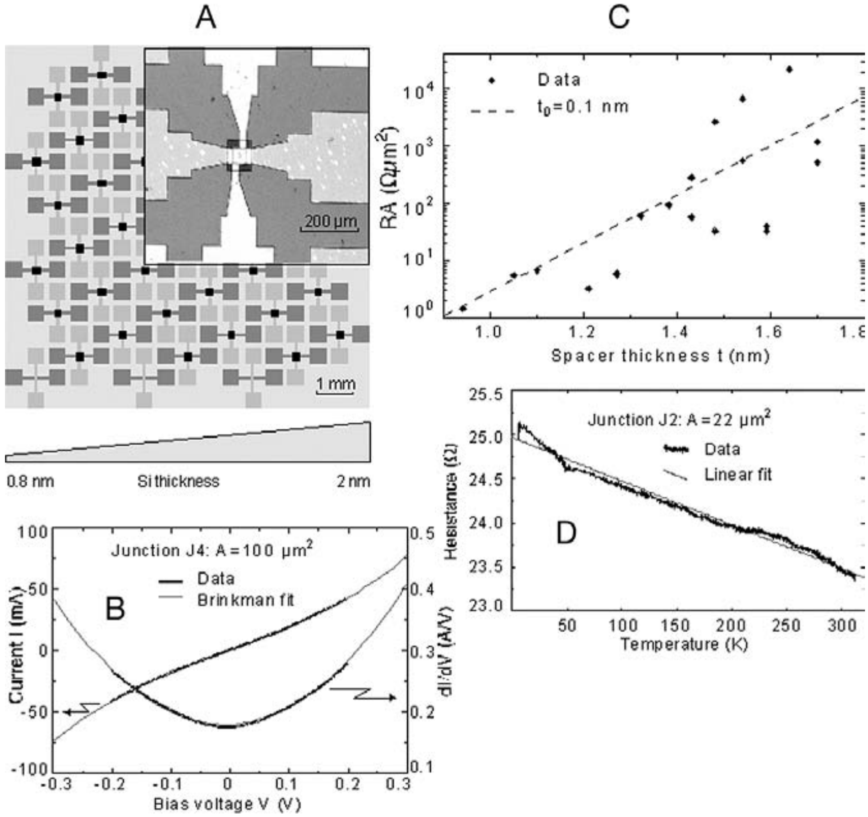


Fig. 1 Part (*A*): Layout of the sample with a wedge-type Si spacer layer resulting in junctions with different spacer thickness. The inset shows a photograph of a typical patterned junction. Part (*B*): Measured (black) and fitted (grey) *I-V* and *dI/dV* curves of junction J4. Part (*C*): Dependence of the resistance times area product *RA* on the nominal spacer thickness *t* obtained from a wedge-type Fe/Si/Fe structure. The dashed line corresponds to a decay length $t_0 = 1$ Å. Part (*D*): Dependence of the resistance on temperature for junction J2. The solid line is a linear fit yielding a temperature coefficient of -5×10^{-3} ΩK^{-1}

across epitaxial, Si-rich spacers is also a short-range interaction and decays with a very similar decay length as the tunneling (Gareev et al. 2002b).

At present, we observe tunneling-type *I-V* curves only for $t > 1.5$ nm, where the voltage drop is sufficient to reveal the non-linear part of *I-V* characteristics.

In Table 1 we present values of maximal resistance *R* at room temperature and show the corresponding parameters of the tunneling barrier derived from Brinkman fits (Brinkman et al. 1970) commonly used for trapezoidal barriers. The calculated barrier heights ø vary from 0.33 to 0.78 eV for different junctions, which all show a definite barrier asymmetry. The variation of the barrier heights could be related to locally different Si contents in the Si-rich spacer. Actually, as it was shown previously, an increase of the nominal Si content in a spacer layer to more than 70 % leads to an increase of the mean barrier height ø from 0.15 to 0.7 eV

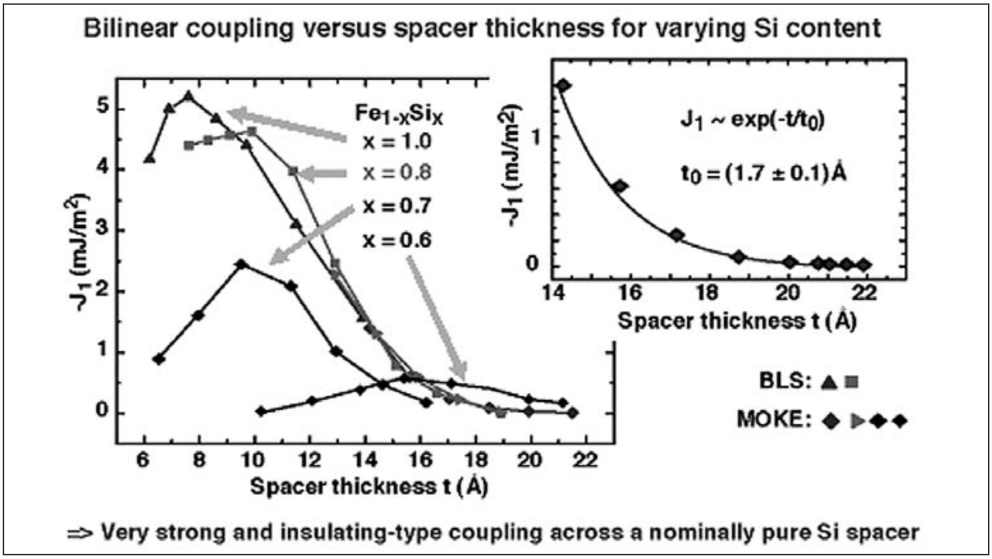


Fig. 2 AF coupling constant J_1 versus spacer thickness t. The fitted curve yields a decay length of 0.33 nm (see inset).

(Endo et al. 2000). The observed barrier asymmetry is most likely caused by different rates of diffusion at Fe/Si and Si/Fe interfaces (Gareev et al. 2002a, b, Kläsges et al. 1997). In the case of interdiffusion, the effective thickness t_{eff} of the tunneling barriers should become smaller than the nominal value t. However, for junctions J1 and J3 the Brinkman fits result in $t_{eff} > t$, which according to Åkerman et al. (2002), is an indication of a small amount of pin-holes in the spacer layer. In this case, the transport across the pin-holes coexists with the dominating tunneling process and leads to a slightly decreased value of the fitted barrier height (Åkerman et al. 2002). Actually, for junctions J1 and J3 the fitted mean barrier heights turn out to be comparatively small (Tab. 1).

A typical temperature dependence of the zero-bias resistance for junctions with $t_{eff} < t$ is presented in Figure 1*D*. The resistance slightly decreases with temperature and shows tunneling-type behavior. The corresponding total change of resistance does not exceed 5–7 %. We relate the change of resistance to prevailing direct elastic tunneling, which yields a weak temperature dependence due to the broadening of Fermi distributions. The elastic but resonant tunneling channel is much weaker than the direct one and obeys a decay length, which is twice as large as the decay length of direct tunneling. However, resonant elastic tunneling cannot definitely be excluded for our junctions with t lying between 1.4 and 1.7 nm. Different weights of the contributions from elastic direct and elastic resonant tunneling could lead to the scatter of the *RA* values in Figure 1*C*. Next, we consider inelastic tunneling based on thermo-activated hopping across impurity states in the barrier. According to Xu et al. (1995), for this channel a strong decrease of resistance with temperature is expected. Thus, this channel is not dominant in our junctions. Finally, the third criterion for direct tunneling – the negative temperature coefficient of the resistance observed in Figure 1*D* allows us to exclude a significant metallic contribution to the electron transport through pin-holes for a subset of our junctions (J2, J4, J5, and J6).

4. Conclusion

We conclude that epitaxial, AF coupled Fe/Si/Fe junctions fulfill the necessary and sufficient criteria for direct elastic electron tunneling: The junctions show (*i*) a strong increase of area times resistivity product with spacer thickness, (*ii*) parabolic conductivity versus voltage dependencies, and (*iii*) small negative temperature coefficients of the resistance. Thus, we could show for a set of AF coupled Fe/Si/Fe junctions, that there is no significant contribution to the conductivity caused by pin-holes. The experimentally proven coexistence of both strong AF coupling and electron transport via elastic tunneling across nominally pure Si spacers is an important piece of information for a better understanding of the mechanism of strong AF interlayer exchange coupling across Si spacers.

References

Åkerman, J. J., Escudero, R., Leighton, C., Kim, S., Rabson, D. A., Dave, R. W., Slaughter, J. M., and Schuller, I. K.: J. Magn. Magn. Mater. *240*, 86–91 (2002)

Brinkman, W. F., Dynes, R. C., and Rowell, J. M.: J. Appl. Phys. *41*, 1915–1921 (1970)

Bruno, P.: Phys. Rev. B *52*, 411–439 (1995)

Endo, Y., Kitakami, O., and Shimada, Y.: J. Appl. Phys. *87*, 6836–6838 (2000)

Fullerton, E. E., Mattson, J. E., Lee, S. R., Sowers, C. H., Huang, Y. Y., Felcher, G., and Bader, S. D. J.: Magn. Magn. Mater. *117*, L301–L306 (1992)

Gareev, R. R., Bürgler, D. E., Buchmeier, M., Olligs, D., Schreiber, R., and Grünberg, P.: Phys. Rev. Lett. *87*, 157202(1)–157202(4) (2001)

Gareev, R. R., Bürgler, D. E., Buchmeier, M., Schreiber, R., and Grünberg, P.: Appl. Phys. Lett. *81*, 1264–1266 (2002a)

Gareev, R. R., Bürgler, D. E., Buchmeier, M., Schreiber, R., and Grünberg, P.: J. Magn. Magn. Mater. *240*, 235–237 (2002b)

Gareev, R. R., Bürgler, D. E., Buchmeier, M., Schreiber, R., and Grünberg, P.: Trans. Magn. Soc. Jpn. *2*, 205–206 (2002c)

Inomata, K., Yusu, K., and Saito, Y.: Phys. Rev. Lett. *74*, 1863–1866 (1995)

Kläsges, R., Carbone, C., Eberhardt, W., Pampuch, C., Rader, O., Kachel, T., and Gudat, W.: Phys. Rev. B *56*, 10801–10804 (1997)

Moodera, J. S., and Mathon, G.: J. Magn. Magn. Mater. *200*, 248–273 (1999)

Rabson, D. A., Jönsson-Åkerman, B. J., Romero, A. H., Escudero, R., Leighton, C., Kim, S., and Schuller, I. K.: Appl. Phys. *89*, 2786–2790 (2001)

van de Veerdonk, R. J. M., Novak, J., Meservey, R., Moodera, J. S., and Jonge, W. J. M. de: Appl. Phys. Lett. *71*, 2839–2841 (1997)

Vries, J. J. de, Kohlhepp, J., den Broeder, F. J. A., Coehoorn, R., Jungblut, R., Reinders, A., and Jonge, W. J. M. de: Phys. Rev. Lett. *78*, 3023–3026 (1997)

Xu, Y., Ephron, D., and Beasley, M. R.: Phys. Rev. B *52*, 2843–2859 (1995)

Prof. Dr. Peter Grünberg
Forschungszentrum Jülich GmbH
Institut für Festkörperforschung
Wilhelm-Johnen-Straße
52425 Jülich
Germany
Phone: +49 2461 613286
Fax: +49 2461 614443
E-Mail: p.gruenberg@fz-juelich.de

Nova Acta Leopoldina NF *92*, Nr. 340, 61–68 (2005)

Spin-polarized Scanning Tunneling Microscopy of Antiferromagnetic Surfaces

Matthias Bode, Robert Ravlić, Michael Kleiber, and
Roland Wiesendanger, Member of the Academy (Hamburg)

With 4 Figures

Abstract

Within the recent decade spin-polarized scanning tunneling microscopy (SP-STM) became a mature tool for the microscopic investigation of surface magnetic domain structures. SP-STM is especially valuable for studying antiferromagnetic surfaces. The imaging of these sample systems is particularly difficult with other magnetically sensitive microscopic techniques since the net magnetization of antiferromagnets vanishes on a length scale larger than the atomic scale. In this contribution we present SP-STM data which reveal the spin structure of defect-free and non-perfect Cr(001) surfaces. Theoretical predictions suggested that the (001) surface of Cr exhibits extremely interesting properties as the so-called “topological antiferromagnetism”. Measurements performed on perfect Cr(001) surfaces confirm this prediction. Topological defects, however, lead to a magnetic frustration which is compensated by the formation of domain walls. At low coverage Fe islands of monolayer height are aligned antiferromagnetic with respect to the underlying substrate.

Zusammenfassung

Die spinpolarisierte Rastertunnelmikroskopie (sp-RTM) hat sich während der vergangenen Dekade in eine ausgereifte Methode zur mikroskopischen Untersuchung magnetischer Domänenstrukturen von Oberflächen entwickelt. Insbesondere ist sie für das Studium antiferromagnetischer Oberflächen geeignet. Diese sind mit anderen magnetisch sensitiven Mikroskopiemethoden nicht abzubilden, da die Magnetisierung von Antiferromagneten auf Längenskalen jenseits der atomaren Skala verschwindet. In diesem Beitrag präsentieren wir sp-RTM-Daten, welche die Spinstruktur perfekter und defekthaltiger Cr(001) Oberflächen aufzeigen. Theoretische Arbeiten legten nahe, daß die (001)-Oberfläche von Cr interessante magnetische Eigenschaften wie etwa den sogenannten »topologischen Antiferromagnetismus« aufweisen. Tatsächlich wird die Vorhersage durch Messungen an perfekten Cr(001)-Oberflächen bestätigt. Topologische Defekte führen allerdings zu magnetischen Frustrationen und der Bildung von Domänenwänden. Bei hinreichend niedriger Bedeckung koppeln Fe-Inseln mit der einer atomaren Monolage entsprechenden Höhe antiferromagnetisch bezüglich der unterliegenden Terrasse.

1. Introduction

The detailed understanding of antiferromagnetic surfaces and the coupling between antiferro- and ferromagnets becomes more and more important. Especially, the exchange bias effect, i.e. the pinning of a ferromagnet due to exchange-coupling to an antiferromagnet, is of great economic interest, because it is used to pin the magnetization of one magnetic thin film in planar tunnel junctions which are the sensing element in read heads of magnetic hard drives. Due to the fact, however, that the magnetic moments of antiferromagnets cancel out on lateral dimensions above the atomic scale the measurement of their magnetic properties is particularly challenging. Therefore, a magnetic imaging technique which combines high lateral resolution with high surface sensitivity is desirable and its availability may lead to a better understanding of antiferromagnetic surfaces and of details of the exchange-bias effect.

Chromium is the prototypical antiferromagnetic material. It has been intensively investigated in the past and is still the subject of numerous experimental and theoretical studies (FAWCETT 1988, ZABEL 1999). Several magnetic effects as, e.g., the giant magnetoresistance effect and the interlayer exchange coupling, have been discovered in Fe/Cr multilayers. In spite of its importance only little was known about the domain structure of Cr. Cr exhibits a transversal and a longitudinal spin-density wave below $T_T = 311$ K and $T_L = 121$ K, respectively, which propagate along the three equivalent [001]-directions leading to a ferromagnetic couplin within single (001)-planes but to an antiferromagnetic coupling between adjacent (001)-planes. Although it was shown theoretically that even the (001) *surface* of Cr couples ferromagnetically and exhibits an enhanced magnetic moment (FU and FREEMAN 1986), no net magnetic moment could be found by spin-resolved photoemission (KLEBANOFF et al. 1984).

As first pointed out by BLÜGEL et al. (1989) this is caused by the fact that surfaces cannot be prepared atomically flat. Instead, real surfaces always exhibit step edges which separate different atomically flat terraces from each other. Thereby, different (001)-planes with opposite magnetization directions are exposed to the surface leading to the so-called “topological antiferromagnetism” of the Cr(001) surface. Typically, these terraces have a width of about 10 nm up to several hundred nanometers. Furthermore, the magnetization of the first subsurface layer points opposite to the surface. Therefore, all experimental methods with insufficient lateral resolution (> 10 nm) or surface sensitivity (> 1 ML) average over regions of opposite magnetization which leads to the cancellation of magnetic signals.

2. Results

SP-STM/STS does not suffer from these limitations. Both, the lateral resolution as well as the surface sensitivity, are well beyond the requirements mentioned above. Indeed, by using constant-current SP-STM WIESENDANGER et al. found first experimental evidence of topological antiferromagnetism on the Cr(001) surface (WIESENDANGER et al. 1990). In this experiment, CrO_2 tips with a high degree of spin polarization were successfully used to detect periodic alternations of the measured monoatomic step heights in constant-current images. The deviations of the measured step height values from the topographic monoatomic step height could be related with the effective spin-polarization of the tunnel junction.

A significant drawback of this experimental approach was, however, the superposition of topographic and magnetic structure information. To solve this problem, we have performed spectroscopic measurements of the differential conductivity dI/dU which is basically proportional to the density of electronic sample states. Figure 1*A* shows an averaged spectrum as measured with a non-magnetic W tip. A peak which is known to stem from a *d*-derived and spin-polarized surface state (STROSCIO et al. 1995) can be recognized very close to the Fermi level ($U = 0$ V). The inset shows the topography and a map of the dI/dU signal at the peak position. The correlation of both images reveals that the (spin-averaged) differential conductivity does not change across a step edge if the measurement is performed with a non-magnetic tip. As shown in Figure 1*B* spatial variations of the dI/dU signals could only be detected

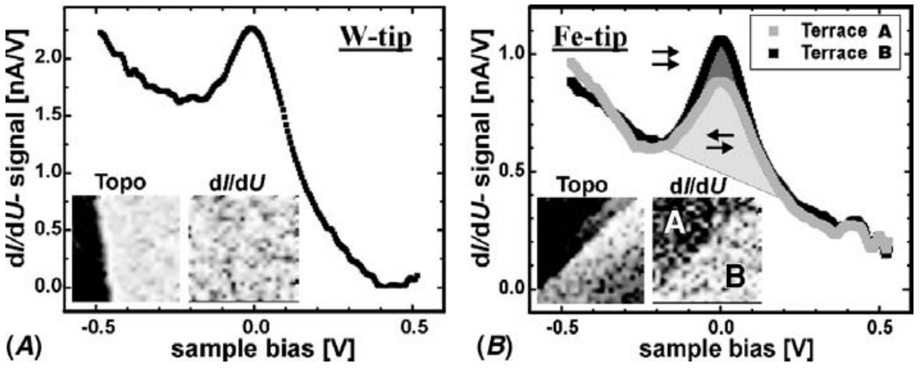


Fig. 1 Typical tunneling spectrum of Cr(001) as measured (*A*) with a non-coated W-tip and (*B*) with a Fe coated tip. All spectra are dominated by a strong peak at $U = -20$ mV which represents the *d*-like surface state (STROSCIO et al. 1995). The insets show the topography (*left*) and maps of the d*I*/d*U* signal at the surface state peak position (*right*). In both cases the topography shows two atomically flat terraces which are separated by a monoatomic step edge. While the spectra measured with the W tip are identical on both terraces the spatially resolved d*I*/d*U* signal as measured with the Fe coated tip reveals significant differences between the two terraces due to the vacuum-tunneling magnetoresistance effect.

after using Fe coated tips which exhibit the required in-plane anisotropy: due to different relative magnetization directions between the tip on one side and terraces **A** and **B** on the other side the d*I*/d*U* signal changes at the position of the step edge.

We can reduce the measurement time considerably by restricting the measurement to a single bias voltage which gives high magnetic contrast. The data presented in Figure 1*B* might suggest that a high magnetic contrast can be achieved at the Cr(001) surface state peak position, i.e. very close to the Fermi level. We have, however, to take into account that the tip-sample distance is not constant but, as a result of the constant current mode of operation, depends on the local differential conductivity which is not only an intrinsic property of the sample surface but which in spin-polarized experiments is also influenced by the relative magnetization direction of tip and sample. If the Cr(001), which is chemically homogeneous, is scanned in the constant current mode of operation with a magnetic tip at a bias voltage corresponding to the energetical position close to the surfaces state the tip-sample distance is increased (decreased) above Cr terraces magnetized (anti)parallely with respect to the tip. As already mentioned above this variation of the tip-sample distance shows up as deviations of the measured step height values from the topographic step height (KLEIBER et al. 2000, WIESENDANGER et al. 1990). This, however, leads to a strong reduction of the variation of the differential conductivity d*I*/d*U* above oppositely magnetized Cr(001) terraces. A high (magnetic) d*I*/d*U* contrast can only be achieved if non-spin-polarized electronic states contribute to the tunneling current, a situation which is fulfilled at enhanced sample bias. To our experience on Cr(001) the highest d*I*/d*U* contrast is obtained at $U \approx \pm(250 \pm 50)$ mV. Figure 2*A* shows the defect free topography of a Cr(001) surface as measured with a Fe coated tip at $U \approx -230$ mV. Figure 2*B* reveals that the terraces are separated by steps of monoatomic height. At this bias voltage the

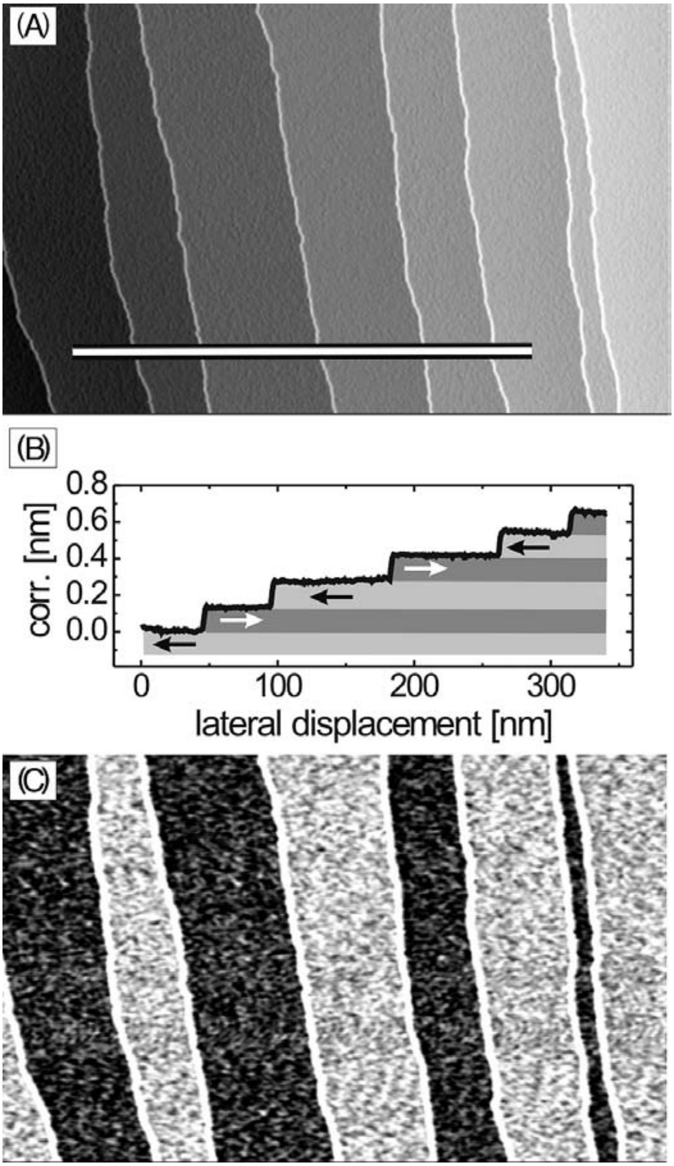


Fig. 2 (*A*) STM topograph of the Cr(001) surface (scan range: 500 nm × 300 nm). (*B*) The line section which has been drawn along the white line reveals that the terraces are separated by step edges of monatomic height. According to Blügel’s model of “topological antiferromagnetism” (Blügel et al. 1989) this topography should lead to a surface magnetization which alternately switches between opposite directions from terrace to terrace. (*C*) In fact, using a Fe coated probe tip alternately magnetized Cr terraces are observed by SP-STS (U = –230 mV).

measured step height is equal to the topographic step height for all step edges. According to BLÜGEL'S model this topography should lead to a magnetization which alternates between adjacent terraces. This is indeed observed experimentally in the magnetic d*I*/d*U* signal which alternates from terrace to terrace between high (bright) and low (dark) thereby proving the idea of "topological antiferromagnetism" (Fig. 2*C*).

The data presented so far confirm the theoretically expected behavior. A more interesting domain configuration can be seen in Figure 3 showing the topography of a location where two screw dislocations cross the surface plane. They are both marked by arrows. At the position of either screw dislocation an additional, semi-infinite step edge appears. In a "topological antiferromagnet" the presence of screw dislocations and the related appearance of semi-infinite step edges must lead to magnetic frustrations since the magnetic order of the undistorted surface cannot be perfectly maintained on both sides of the dislocation. As can be recognized in the magnetic image of Figure 3*B* in this particular case a domain wall is created at one dislocation and annihilated at the other dislocation. Similar configurations were found frequently. We believe that it is energetically favourable since it allows the minimization of the domain wall energy by making the domain wall as short as possible. As indicated by two lines in Figure 3*B* we have drawn line profiles of the d*I*/d*U* signal across the domain wall in two adjacent Cr terraces. The result is plotted in Figure 3*C*. We found that the line profiles can nicely be fitted by a tanh function which describes a 180° wall in the framework of micromagnetic theory (HUBERT and SCHÄFER 1998):

$$y(x) = y_0 + y_{sp}\tanh\left(\frac{x - x_0}{w/2}\right) \qquad [1]$$

where $y(x)$ is the d*I*/d*U* signal measured at position x, x_0 is the position of the domain wall, w is the wall width, and y_0 and y_{sp} are the spin-averaged and spin-polarized d*I*/d*U* signal, respectively. Averaging over a large number of Cr(001) surface domain walls we can summarize that the domain wall width amounts to 120–170 nm.

One may ask why the domain wall width of Cr has not been determined earlier by another experimental method than SP-STM. As already mentioned above this is either caused by an insufficient surface sensitivity or by a rather poor lateral resolution which effectively leads to an average signal from several adjacent Cr(001) terraces. Both possibilities lead to the fact that the net polarization in the measured signal is close to zero. For example, scanning electron microscopy with polarization analysis (SEMPA) has a probing depth which is much larger than the separation of the alternately magnetized (001) planes of Cr. On the other hand, magnetic force microscopy (MFM) fails to reveal domains and domain walls in antiferromagnetic samples due to the lack of a measurable magnetic stray field of the sample which the magnetic probe tip can interact with.

It is widely believed that the exchange coupling at the interface between two semi-infinite Cr and Fe crystals is negative, i.e. Fe and Cr couple antiferromagnetic (AFM). Figure 4 shows a series of topographic images (*left*) and spin-resolved d*I*/d*U* maps (*right*) at different Fe coverages on Cr(001). Up to a total Fe coverage of $\theta = 0.2$ ML the well-known alternating contrast from adjacent Cr(001) terraces indicates that the topological antiferromagnetic order of the substrate is maintained. Additionally, a clear contrast between islands on different terraces can be recognized: Dark islands are found on bright terraces and *vice versa*. This is a clear indication of antiferromagnetic coupling between the Cr substrate and the Fe adislands. The magnetic contrast amounts up to 10–12 %, the same value as found on clean Cr(001).

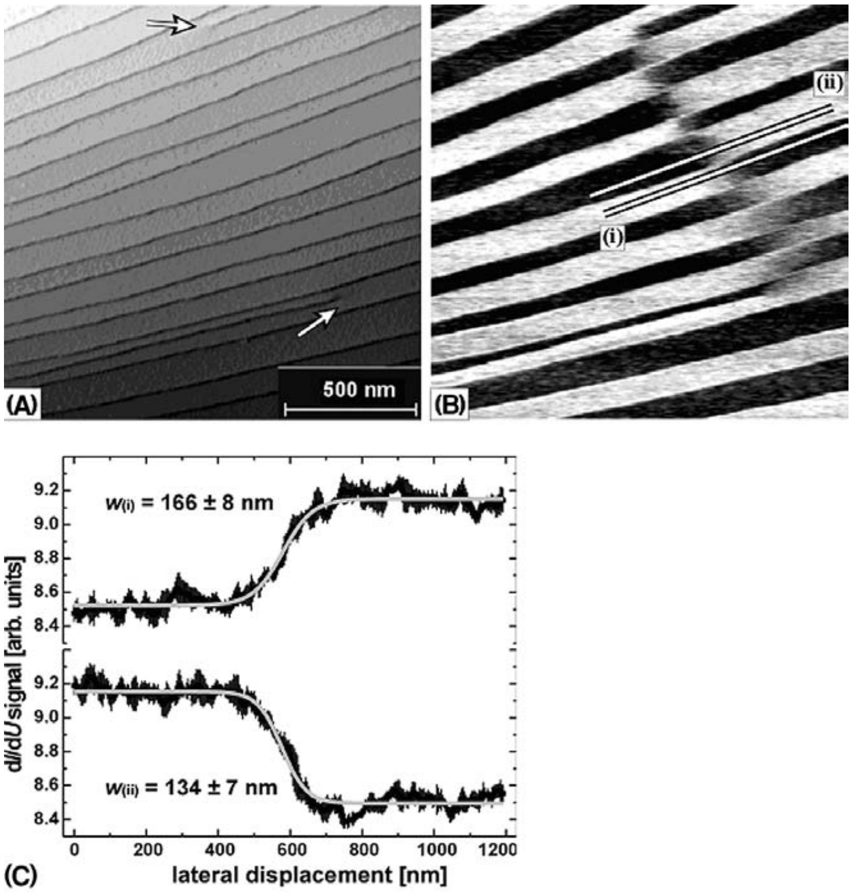


Fig. 3 (*A*) Topography and (*B*) d*I*/d*U* signal at U = 190 mV of a Cr(001) surface. The surface is magnetically dominated by a magnetization which alternates between adjacent Cr(001) terraces. Within the scan range of 2 µm × 2 µm the sample exhibits two screw dislocations. Spin frustration leads to the formation of a magnetic domain wall between these dislocations. Line section drawn along the lines will be shown in Fig. 4. (*C*) Two domain wall profiles taken along the white lines in (*B*). The wall profiles can nicely be fitted by micromagnetic theory resulting in domain wall widths of $w_{(i)}$ = 134 ± 7 nm and $w_{(ii)}$ = 66 ± 8 nm.

3. Summary

We have discussed the working principle of SP-STM by the example of a spin-polarized surface state of Cr(001). Depending on the relative magnetization directions of tip and sample the local tunnel-magnetoresistance effect leads to a characteristic variation of the differential conductivity. This can be used to map the surface spin-structure simultaneously with the topography. Experiments on defect-free Cr(001) surfaces confirm the theoretically predicted

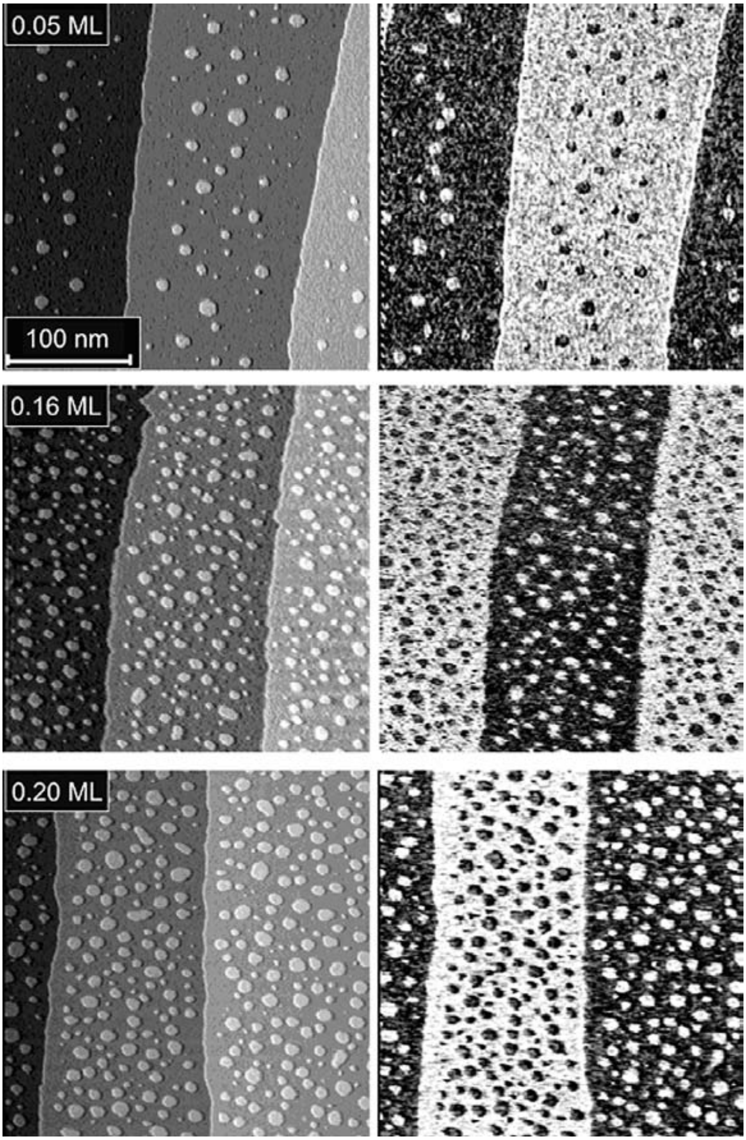


Fig. 4 Fe coverage-dependent series of images (250×250 nm^2) showing the topography (*left*) and the simultaneously recorded spin-resolved dI/dU map (*right*). An AFM coupling of the first Fe layer to the Cr surface is found.

topological antiferromagnetism. Measurements on Cr(001) surfaces which exhibit screw dislocations reveal defect-induced magnetic frustrations which are compensated by the formation of domain walls. The domain wall width of Cr(001) is determined to 120–170 nm. The high resolution of SP-STM reveals that Fe monolayer islands couple antiferromagnetic to the Cr(001) substrate at sufficiently low coverage (< 0.2 ML).

References

BLÜGEL, S., PESCIA, D., and DEDERICHS, P. H.: Ferromagnetism versus c(2×2) antiferromagnetism of the Cr(001) surface. Phys. Rev. B *39*, 1392 (1989)

FAWCETT, E.: Spin-density-wave antiferromagnetism in chromium. Rev. Mod. Phys. *60*, 209 (1988)

FU, C. L., and FREEMAN, A. J.: Surface ferromagnetism of Cr(001). Phys. Rev. B *33*, 1755 (1986)

HUBERT, A., and SCHÄFER, R.: Magnetic Domains. Berlin: Springer 1988

KLEBANOFF, L. E., ROBEY, S. W., LIU, G., and SHIRLEY, D. A.: Observation of a surface magnetic phase transition on Cr(100). Phys. Rev. B *30*, 1048 (1984)

KLEIBER, M., BODE, M., RAVLIĆ, R., and WIESENDANGER, R.: Topology-induced spin frustrations at the Cr(001) surface studied by spin-polarized scanning tunneling spectroscopy Phys. Rev. Lett. *85*, 4606 (2000)

STROSCIO, J. A., PIERCE, D. T., DAVIES, A., CELOTTA, R. J., and WEINERT, M.: Tunneling spectroscopy of bcc(001) surface states. Phys. Rev. Lett. *75*, 2960 (1995)

WIESENDANGER, R., GÜNTHERODT, H.-J., GÜNTHERODT, G., GAMBINO, R. J., and RUF, R.: Observation of vacuum tunneling of spin-polarized electrons with the STM. Phys. Rev. Lett. *65*, 247 (1990)

ZABEL, H.: Magnetism of chromium at surface, interfaces, and thin films. J. Phys. Cond. Matter *11*, 9303 (1999)

Dr. Matthias BODE
Universität Hamburg
Institut für Angewandte Physik
Jungiusstraße 11
20335 Hamburg
Germany
Phone: +49 40 428382041
Fax: +49 40 428385311
E-Mail: mbode@physnet.uni-hamburg.de

Nova Acta Leopoldina NF *92*, Nr. 340, 69 – 74 (2005)

A Nanotechnology Approach to Data Storage

Bernd GOTSMANN, Thomas R. ALBRECHT, Gerd K. BINNIG, Michel DESPONT, Ute DRECHSLER, Urs DÜRIG, Daniel JUBIN, Walter HÄBERLE, Mark A. LANTZ, Hugo ROTHUIZEN, Richard STUTZ, Peter VETTIGER, Dorothea WIESMANN (*Micro-/Nanomechanics Group*), and
Peter BÄCHTOLD, Giovanni CHERUBINI, Ajay DHOLAKIA, Evangelos ELEFTHERIOU, Christoph HAGLEITNER, Teddy LOELIGER, Aggeliki PANTAZI, Haris POZIDIS (*Advanced Storage Technologies Group*)

With 4 Figures

Abstract

Ultrahigh storage densities of up to 1 Tbit/in.^{2} or more can be achieved using local-probe techniques to write, read back, and erase data in very thin polymer films. The thermomechanical scanning-probe-based data-storage concept, internally dubbed “Millipede”, combines ultrahigh density, small form factor, and high data rates. High data rates are achieved by parallel operation of large two-dimensional arrays with thousands of micro/nanomechanical cantilevers/tips that can be batch-fabricated by silicon surface-micromachining methods. The inherent parallelism, the ultrahigh areal densities, and the small form factor may open up new perspectives and opportunities for applications in areas beyond those envisaged today.

Zusammenfassung

Hohe Speicherdichten von bis zu 1 Tbit/in^2 oder mehr können bei Verwendung von Lokal-Probe-Techniken zum Schreiben, Abrufen und Löschen von Daten in sehr dünnen Polymerfilmen erreicht werden. Das thermomechanische *Scanning-probe*-basierte Datenspeicherkonzept, intern als „Millipede“ bezeichnet, verbindet hohe Speicherdichte, Kleinformatigkeit und hohe Datenübertragungsraten. Hohe Datenübertragungsraten werden durch paralleles Operieren großer zweidimensionaler Musterfelder mit Tausenden von mikro/nanomechanischen Trägern/Tips erreicht, die im Batch-Verfahren durch Silikon-Oberflächen-mikromaschinelle Methoden gefertigt werden, erreicht. Die inhärente Parallelität, die hohe Arealdichte und die Kleinformatigkeit könnten neue Perspektiven und Möglichkeiten für Anwendungen in Bereichen, die weit über unser heutiges Vorstellungsvermögen hinausgehen, eröffnen.

1. Introduction

Data storage is a key element in current and future information technology. The ever-increasing demand for more storage capacity in an ever-shrinking form factor as well as the pressure to decrease the price per storage unit ($/MByte) have been the driving force behind worldwide research efforts and development activities. For many decades, silicon-based semiconductor memory chips and magnetic hard drives (HDD) have dominated the data-storage market. Both technologies have achieved storage-density increases of about 60 – 100 % per year, at more or less constant cost. However, both technologies are approaching their limits in terms of current concepts, materials, and fabrication techniques. For semiconductor memories, such as DRAM, SRAM, and Flash, the challenges are predominantly in lithography and very thin gate oxide materials. For HDDs, the main challenge is the so-called superparamagnetic effect, which predicts that the bit stability over temperature and time will decrease with increasing densities because the volume of the magnetic grains tends to shrink with the bit size. A substantial worldwide effort in semiconductor and HDD technologies as well as in the equipment industry (e.g. lithography tools) is focused on all these challenges in order to maintain the performance-improvement rate.

The invention of scanning-probe techniques (SPT), such as scanning tunneling (STM), atomic force (AFM) and scanning near-field optical (SNOM) microscopy, gave birth to the field of nanometer- and atomic-scale imaging. SPT even made atomic- and molecular-scale manipulation possible, leading to quite complex atomic functionality such as atomic/molecular switches and logic building blocks. Originally a tool for nanoscience, SPT is currently being investigated for its potential use in data storage. For this purpose, various storage media, such as phase-change, magnetic, ferroelectric and polymer materials, are being considered.

A major drawback of SPT for data storage is the low data rate of a single probe, which is limited by the achievable mechanical resonance frequencies of the microfabricated cantilevers and their write/read speed. The latter is strongly influenced by the storage medium and by the write/read functionality required by the probe. Single-probe storage approaches currently operate – at best – on the low microsecond time scale, whereas semiconductor and HDD technologies operate at least three orders of magnitude faster.

It is our vision and conviction that very large-scale-integrated (VLSI) micro/nanomechanics will greatly influence future micro- and nanoelectronics. Therefore, in 1995, the Micro/Nanomechanics team at IBM's Zurich Research Laboratory started a research project called "Millipede". The aim was to employ large two-dimensional (2D) arrays of cantilevers, fabricated using micro/nano-electro mechanical system (MNEMS) techniques and operating in parallel, and to have each cantilever perform write/read/erase operations in an individual storage field (see, for example, VETTIGER et al. 2002, VETTIGER and BINNIG 2003). The "Millipede" concept presented here is a novel approach to store data at ultrahigh or, ultimately, even atomic-level density with competitive data rates and access time. The ultimate in localization is provided by a very sharp tip, and high data rates result from a massive, parallel operation of such tips. As storage medium, polymer films are being considered, although the use of other media is not ruled out.

While a MEMS-based electro magnetically-activated micro scanner moves the polymer medium in the *x*/*y* directions underneath the array chip, the individual tips can be addressed for parallel write/read operations. The high areal storage density and small form factor make this concept very attractive as a potential future storage technology in mobile applications, offering gigabytes of capacity and low power consumption at data rates of megabytes per second. Moreover, these features, coupled with the inherent massive parallelism, may open up new perspectives and opportunities for application in areas beyond those we envisage today.

The millipede concept is illustrated in Figure 1: It basically consists of a large 2D array of cantilevers and a MEMS-based *x*/*y* storage-medium scanner (VETTIGER et al. 2002). The electro magnetically actuated scanner moves the storage medium with nanometer precision in both the *x*- and the *y*-direction underneath the cantilever-array chip, so that each tip reads and writes in its own storage field. Independent and parallel cantilever operation is achieved by a vertically interconnected CMOS read/write channel array chip. In the following, we will describe some key aspects of this technology.

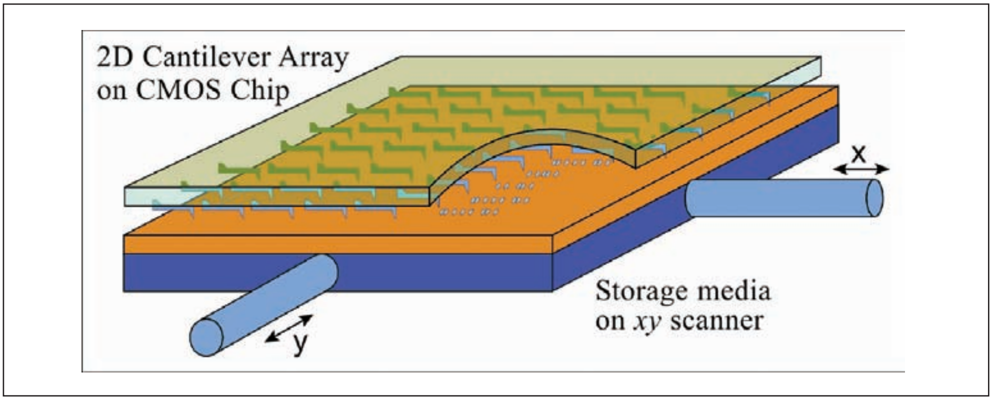


Fig. 1 The millipede concept. From Despont et al. 2003, © 2003 IEEE.

2. The Thermo-Mechanical Read/Write and Erase Mechanisms

For operation of the device (write, read, and erase), the tips are in contact with the thin polymer-film medium. Bits are written by heating an integrated resistor in the cantilever to a temperature of typically 400 °C. Thus the heater and tip soften the polymer while a simultaneously applied force on the cantilever generates a nanometer-sized indentation in the polymer. For reading, the resistor is operated at a lower temperature, typically 300 °C, which does not soften the polymer. When the tip drops into an indentation, the resistor is cooled by the improved heat transport within the medium/heater air gap, resulting in a measurable change of the heater resistance. To overwrite data, the tip makes a series of offset indentations that overlap so closely that their edges fill in the old pits, effectively erasing the unwanted data. Figure 2 shows a data section written and read back by a single cantilever using the thermo mechanical write/read concept described here as well as a single line-scan read-back signal. So far, densities approaching 1 Tbit/in.^{2} have been demonstrated. Current research topics include the nano-scale heat transfer between tip and medium surface (Lantz et al. 2003) as well as tip and medium wear.

2.1 The Scanner

A key issue for our millipede concept is the need for a low-cost, miniaturized scanner with *x*/*y*-motion capabilities on the order of 100 µm (i.e. the pitch between adjacent cantilevers in the array). We have developed a micro scanner with these properties based on electromagnetic actuation. See Figure 3. It consists of a mobile platform (that carries the polymer medium) supported by springs and is fabricated from single-crystal silicon. Actuation in the *x*- and the *y*-direction is achieved by applying a current to a coil positioned between a pair of miniature permanent magnets attached to the silicon scanner. One such coil and its pair of magnets for actuation in one direction are shown in Figure 3. When the scanner is actuated, two masses move in opposite directions. By this, the scanner is carefully mass-balanced in order to reduce the sensitivity to external vibration and shock.

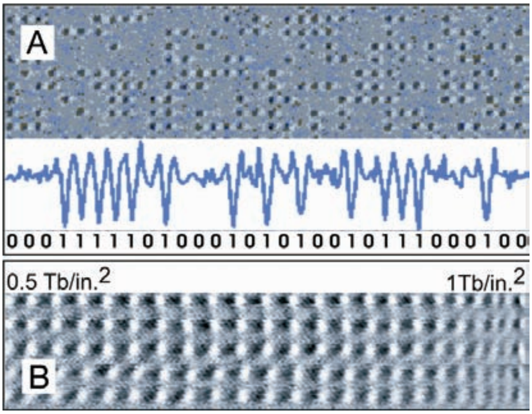


Fig. 2 (*A*) Data-bit section written and read back using the thermomechanical concept as well as a single line-scan read-back signal. (*B*) Data bits at areal densities up to 1 Tbit/in.^{2}. From ELEFTHERIOU et al. 2003.

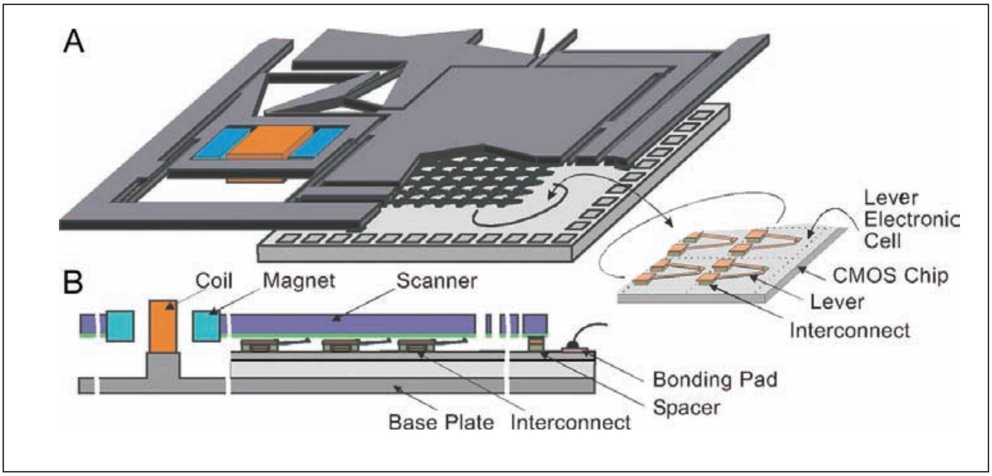


Fig. 3 (*A*) 3D schematic of miniaturized scanner and cantilever-array chip with integrated electronics. (*B*) Side view of scanner, cantilever array, and CMOS electronics. From ELEFTHERIOU et al. 2003.

2.2 CMOS-MEMS Interconnect

Another key technological aspect is the vertical interconnect between the cantilever array and the CMOS channel array chip. DESPONT et al. (2003) have developed a novel approach to transfer/interconnect the cantilever arrays to their CMOS counterpart chips on a full wafer-to-wafer basis. We demonstrated the wafer-level transfer and interconnect of arrays consisting of 4096 (64 × 64) freestanding cantilevers. The cantilevers transferred exhibited high yield in terms of electrical functionality and mechanical integrity (see Figs. 3 and 4). More than 300 solder joints/mm^2 have been achieved, demonstrating the potential for very dense vertical interconnects. This technique holds great promise for system-on-chip (SOC) applications such as heterogeneous device integration (mixed technology), 3D integration and chip stacking.

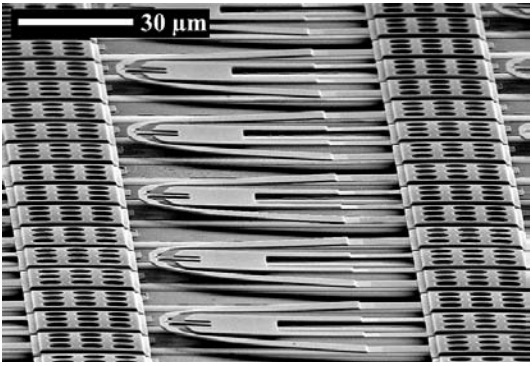


Fig. 4 Scanning electron micrograph of a section of the cantilever array transferred and interconnected to its carrier wafer.

2.3 Servo and Tracking

Each cantilever can write and read data to and data from a dedicated area of the polymer substrate, called storage field. As mentioned above and shown in Figure 2, in each storage field the presence (absence) of an indentation corresponds to a logical “1” (“0”). All indentations are nominally of equal depth and size. The logical marks are placed at a fixed horizontal distance from each other along a data track.

The purpose of the servo system is to maintain the position of the read/write probe on the center of the target track during normal read/write operation. This is achieved by the so-called track-follow procedure. Track following controls the fine positioning of the read/write probe in the cross-track direction and is critical for reliable storage and retrieval of user data. It is typically performed in a feedback loop driven by a position-error signal, which indicates the deviation of the current position from the track centerline. A robust way to achieve synchronization and servo control in an *x*/*y*-actuated large 2D array is to reserve a small number of storage fields exclusively for timing recovery and servo-control purposes as described by ELEFTHERIOU et al. (2003).

Because of the large number of levers in our arrays, this solution is advantageous in terms of overhead compared with the alternative of embedding timing and servo information in all data fields. It has been estimated that the dedicated servo- and timing-field strategy incurs a very 5 %.

3. Conclusion

A very large two-dimensional array of AFM probes has been operated in a multiplexed and parallel fashion. Write/read/erase operations in a thin polymer medium have been successfully demonstrated at densities significantly higher than those achieved with current magnetic-storage systems.

The millipede array has the potential to achieve ultrahigh areal storage densities on the order of 1 Tbit/in.^{2} or higher. The high areal storage density, small form factor, and low power consumption make this concept a very attractive candidate as a future storage technology for mobile applications because it offers several gigabytes of capacity at data rates of several megabytes per second.

Although many of the basic building blocks of this novel technology have already been demonstrated (including the fabrication of large arrays and demonstration of high-density thermomechanical writing and reading), there are a number of issues that need further investigation, such as overall system reliability, including long-term stability of written indentations, tip and medium wear, limits of data rates, array and cantilever size as well as tradeoffs between data rate and power consumption.

References

DESPONT, M., DRECHSLER, U., YU, R., POGGE, H. B., and VETTIGER, P.: Wafer-scale microdevice transfer/interconnect: From a new integration method to its application in an AFM-based data-storage system. In: Transducers ’03 The 12th International Conference on Solid-State Sensors, Actuators and Microsystems, Boston, MA, USA. Digest of Technical Papers, Vol. *2*, pp. 1907–1910. Piscataway, NJ: IEEE 2003

ELEFTHERIOU, E., BÄCHTOLD, P., CHERUBINI, G., DHOLAKIA, A., HAGLEITNER, C., LOELIGER, T., PANTAZI, A., POZIDIS, H., ALBRECHT, T., BINNIG, G. K., DESPONT, M., DRECHSLER, U., DÜRIG, U., GOTSMANN, B., JUBIN, D., HÄBERLE, W., LANTZ, M. A., ROTHUIZEN, H., STUTZ, R., VETTIGER, P., and WIESMANN, D.: A Nanotechnology-based approach to data storage. In: Proceedings of the 29th International Conference on Very Large Databases (VLDB 2003), Berlin, Germany, 2003, in press

LANTZ, M. A., GOTSMANN, B., DÜRIG, U. T., VETTIGER, P., NAKAYAMA, Y., SHIMIZU, T., and TOKUMOTO, H.: Carbon nanotube tips for thermomechanical data storage. Appl. Phys. Lett. *83*, 1266–1268 (2003)

VETTIGER, P., and BINNIG, G. K.: The nanodrive project. Scientific American, January issue, 34–41 (2003)

VETTIGER, P., CROSS, G., DESPONT, M., DRECHSLER, U., DÜRIG, U., GOTSMANN, B., HÄBERLE, W., LANTZ, M. A., ROTHUIZEN, H., STUTZ, R., and BINNIG, G. K.: The “millipede” – nanotechnology entering data storage. IEEE Trans. Nanotechnology *1*, 39–55 (2002)

Dr. Bernd GOTSMANN
IBM Research
Zurich Research Laboratory
8803 Rüschlikon
Switzerland
Phone: +41 1 7248529/8223
Fax: +41 1 7248958
E-Mail: bgo@zurich.ibm.com

Nova Acta Leopoldina NF *92*, Nr. 340, 75 (2005)

Nanocrystals as a New Class of Macromolecules

Paul ALIVISATOS (Berkeley)

The shape of a nanocrystal can be controlled by growing the crystal in the presence of an organic molecule that selectively adheres to one crystallographic facet, effectively reducing the growth rate of the facet compared to others. This method of shape control has been applied to CdSe, CdTe, Co, iron oxides and titanium dioxide. In each case, a variety of shapes can be prepared, including rods, disks, and branched structures.

Common principles about how to create the different shapes are emerging based on the comparisons between the several systems.

The resulting materials can find a wide range of applications, from components in new solar cells, to reporters in cell tracking and cancer diagnostics.

Prof. Dr. Paul ALIVISATOS
University of California Berkeley
Department of Chemistry
Berkeley, CA 94720
USA
Phone: +1 51 06435128/2050
Fax: +1 51 06426911
E-Mail: hlcameron@lbl.gov

Energie

Vorträge anläßlich der Jahresversammlung vom 17. bis 20. Oktober 2003
zu Halle (Saale)

Nova Acta Leopoldina N. F., Bd. *91*, Nr. 339
Herausgegeben von Harald zur Hausen (Heidelberg)
(2004, 378 Seiten, 175 Abbildungen, 25 Tabellen, 39,95 Euro, ISBN 3-8047-2171-0)

Während früher naturwissenschaftliche und technische Argumente in Diskussionen über Energiebedarf, -erzeugung und -nutzung bestimmend waren, werden diese heutzutage auf vielfältige Weise durch ökologische, soziale und kulturelle Aspekte verdrängt. Bürgerinitiativen, Umweltgruppen, Medien, Gewerkschaften, Parteien und auch Kirchen sind am Energiediskurs beteiligt. Daß Energie eine naturwissenschaftliche Basis hat, wird in der Öffentlichkeit häufig kaum noch wahrgenommen. Aus einem naturwissenschaftlich-technischen ist ein gesellschaftswissenschaftlich-kultureller Diskurs geworden. Angesichts der Vielzahl unterschiedlicher Prognosen zum Weltenergiebedarf und der Energienutzung, die Experten und Politik der Öffentlichkeit vorlegen, kann das nicht verwundern. Die Leopoldina nahm das zum Anlaß, um auf ihrer Jahresversammlung verschiedene Energieszenarien zu erörtern. Ausgehend von den naturwissenschaftlichen Grundlagen werden sowohl die Auswirkungen der verschiedenen Formen von Energieträgernutzung auf die Umwelt, aber auch Leitbilder, Zielvorstellungen und ethische Prinzipien der Energieversorgung hinterfragt. Im Hinblick auf Komplexität, Globalität und Langfristigkeit des Energiebereiches liefern die Beiträge des Bandes eine auf dem heutigen Erkenntnisstand gegründete wissenschaftliche Standortbestimmung zu Fragen der Energieerzeugung und Energienutzung. Dabei werden Windkraft und Biomasse ebenso ausführlich betrachtet wie Kernenergie und Kernfusion. Die Tendenzen in der Nutzung fossiler Energieträger unterliegen einer kritischen Analyse. Außerdem werden technische Fragen (Solarzellen, Brennstoffzellen, Aufwindkraftwerke, energieeffizientes Gebäudemanagement) und ökonomische Probleme (z. B. der Strommarktliberalisierung) umfassend dargestellt. Ein Positionspapier faßt die Sicht der Leopoldina auf die für zukünftige politische, ökonomische und wissenschaftliche Weichenstellungen aktuell bedeutsame Energieproblematik zusammen.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 77 (2005)

Carbon Nanotubes – from Science to Applications

Siegmar Roth (Stuttgart)

Carbon nanotubes are seamless tubes of graphitic carbon, typically 1 nanometer in diameter and several micrometers or even millimeters long. There are single-walled and multi-walled nanotubes, semiconducting and metallic nanotubes. Because of the small cross section the nanotubes behave radially like molecules, in the direction of the tube axis they behave like extended solids. Most of the physics of carbon nanotubes can be derived from the physics of (hypothetic) graphitic monolayers and the confinement of the electrons to a nano-cylinder. This confinement leads to several peculiarities, like van Hove spikes in the electronic density of states, ballistic electron transport along the cylinder, conduction quantization etc.

Technical applications of individual nanotubes and nanotube bundles aim at nanotube-based field effect transistors and single electron transistors (in particular the “all-carbon transistor”) and to bias and interconnects in silicon technology integrated circuits. Because of the field enhancement at the sharp tips of the tubes electrons can be fairly easily extracted (field emmission). Thus carbon nanotubes act as cold electron sources, which are useful in light emmitting devices, microwave amplifiers, multibeam electron lithography, and miniaturized portable X-ray tubes.

As fillers in nanocomposites carbon nanotubes can be used for mechanical reinforcement of plastics and to render polymers electrically conducting. A special application would be transparent electrodes for light emitting diodes and for solar cells. Electrically charged nanotubes change their shape (they stretch or contract). Consequently they can be used as nanoscale actuators (NEMS = nanoelectromechanical systems). In the form of bucky paper or bucky yarn nanotubes can be used for macroscopic actuators (“artificial muscles”). Finally, the large surface area per gram of macroscopic nanotube samples (powders, papers, networks) can be used in supercapacitors, for catalyst support, and for hydrogen storage.

The talk will summarize the physics of carbon nanotubes and give an overview of technical applications.

Prof. Dr. Siegmar Roth
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
70569 Stuttgart
Germany
Phone: +49 71 16891434
Fax: +49 71 16891010
E-Mail: s.roth@fkf.mpg.de
www.mpi-stuttgart.mpg.de/KLITZING/research/nano/nano.html

Das Leopoldina-Postdoc-Stipendium

Wir bieten in einem Förderprogramm ausgewählten **Wissenschaftlerinnen** und **Wissenschaftlern** aus Deutschland, Österreich und der Schweiz mit einem Postdoc-Stipendium Unterstützung in ihrer beruflichen Entwicklung. In das Förderprogramm werden herausragende **promovierte Nachwuchswissenschaftler** unter 36 Jahren aus naturwissenschaftlichen und medizinischen Fachgebieten aufgenommen. Die Förderung umfaßt:

- ein monatliches Stipendium während der Gastaufenthalte (orientiert an Sätzen und Zuschlägen der DFG bzw. der AvH-Stiftung),
- Beihilfe zu Reisekosten,
- beschränkte Mittel für Laborbedarf.

Sie wird von Zuwendungen des bmb+f (Bundesministerium für Bildung und Forschung) getragen.

Die Förderung ermöglicht die vollständige Bearbeitung eines eigenständigen Forschungsprojektes von zwei- bis dreijähriger zusammenhängender Dauer an renommierten Forschungsstätten im Ausland. Sie hat eine Vertiefung von Kenntnissen und Befähigungen in der jeweiligen Spezialdisziplin zum Ziel, nicht jedoch die Habilitation. Eine Bewerbung kann jederzeit durch ein Mitglied der Akademie, die Institutsleitung der Bewerber oder mit zwei Referenzen durch die Bewerber selbst eingebracht werden. Richten Sie diese an:

Deutsche Akademie der Naturforscher Leopoldina
Postfach 11 05 43
06019 Halle (Saale)

Eine Bewerbung sollte enthalten:

- die formlose Antragstellung an den Präsidenten der Akademie, Herrn Prof. Dr. Volker TER MEULEN,
- einen tabellarischen Lebenslauf,
- Ihre Zeugnisse und Referenzen,
- Listen Ihrer Publikationen, Vorträge, ...,
- gewünschte Gastinstitute und Betreuer,
- eine Projektskizze und den Arbeitsplan.

Die eingehenden Anträge werden von einer Vergabekommission unter Einbeziehung von Fachgutachten bewertet und entschieden. Ein Rechtsanspruch auf Förderung besteht nicht.

Weitere Informationen erhalten Sie bei:

Dr. Andreas CLAUSING,
Tel.: (03 45) 4 72 39 50, Fax: (03 45) 4 72 39 59,
E-Mail: stipendium@leopoldina-halle.de oder unter http://www.leopoldina-halle.de

Nova Acta Leopoldina NF *92*, Nr. 340, 79 (2005)

Synthesis, Properties and Self-Assembly of Nanoparticles

Horst Weller (Hamburg)

This talk describes recent developments in the synthesis and characterization of semiconductor and metal nanoparticles. Results on the growth kinetics and the control of size, shape and surface chemistry will be addressed. We present Monte Carlo simulations of an ensemble of growing particles showing that optimal conditions for the synthesis of highly luminescent semiconductor nanoparticles are maintained if the exchange rate of monomers at the particles' surface is high during the growth. Polarized absorption and emission is observed in quantum-dot-quantum-rod hybrid systems which consist of a spherical CdSe particle coated by a rod-like CdS shell. Examples for 2D and 3D self assembly of nanoparticles are given. We report on the formation of colloidal crystals from semiconductor and magnetic nanoparticles. In mixtures of differently sized particles complex 3D structures are formed which are analog to inter-metallic phases. Self assembly of ZnO nanoparticles in solution finally leads to the formation of single crystalline nanorods *via* oriented attachment.

Prof. Dr. Horst Weller
Institute of Physical Chemistry
University of Hamburg
Grindelallee 117
20146 Hamburg
Germany
Phone: +49 404 28383463
Fax: +49 404 28383452
E-Mail: weller@chemie.uni-hamburg.de

»Bewahren und Verändern im Kontext biologischer und kultureller Evolution« Gaterslebener Begegnung 2003

Gemeinsame Tagung des Instituts für Pflanzengenetik und Kulturpflanzenforschung (IPK) Gatersleben und der Deutschen Akademie der Naturforscher Leopoldina vom 22. bis 24. Mai 2003 in Gatersleben

Nova Acta Leopoldina N. F., Bd. *90*, Nr. 338
Herausgegeben von Anna M. Wobus (Gatersleben), Ulrich Wobus
(Gatersleben) und Benno Parthier (Halle/Saale)
(2004, 244 Seiten, 15 Grafiken, 34 Abbildungen, 10 Tabellen, 29,95 Euro,
ISBN 3-8047-2170-2)

Zum nunmehr zehnten Mal trafen sich in Gatersleben Natur- und Geisteswissenschaftler, Schriftsteller, Künstler, Journalisten und Politiker zum interdisziplinären Dialog über Fragen, die sich aus den Entwicklungen von Naturwissenschaft und Technik für die Gesellschaft ergeben. Naturwissenschaftler und Biologen sind dem Erhalt der in der Evolution entstandenen biologischen Vielfalt, aber auch dem Anspruch verpflichtet, dieses Potential verantwortungsvoll zum Wohle des Menschen einzusetzen und zu gestalten. Der Band enthält neben den *Anfragen an Wissenschaftler* (diesmal von der Schriftstellerin Helga Schütz, Potsdam) Beiträge zur Evolutionsbiologie (Konrad Bachmann, Gatersleben, Evolution und Information; Jörg Hacker, Würzburg, Evolutionäre Infektionsbiologie), Ethologie (Wulf Schiefenhövel, Andechs, Vom Instinkt zur Kultur: Zur Evolution geistiger Fähigkeiten Beispiele aus traditionalen Kulturen Melanesiens), Humangenetik (Peter Propping u. a., Bonn, Humane Reproduktionsbiologie: Eingriff in die natürliche Evolution des Menschen?), Kulturwissenschaft (Sigrid Weigel, Berlin, Evolution der Kultur oder Kulturgeschichte der Evolutionstheorie – Epistemische Probleme am Schnittpunkt der zwei Kulturen) und Ethik (Klaus Tanner, Halle/Saale, Zwischen »Heuristik der Furcht« und Hoffnung auf Veränderung). Er spannt damit den Bogen von naturwissenschaftlichen Problemen über die Reflexion wissenschaftshistorischer und -philosophischer Zusammenhänge bis hin zur Debatte ethischer Standpunkte. Verbunden mit Gedichten der beteiligten Schriftsteller und Abbildungen der Werke der in Gatersleben zur Begegnung ausstellenden Künstler vermittelt der Band einen unkonventionellen Blick auf ein nach wie vor brisantes Thema.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 81–82 (2005)

Molecular Self-Assembly – A Key Technology in Nanoscience and Templating

Wolfgang M. Heckl (Munich)

Directed molecular self-assembly plays an important role in biological systems, such as DNA, where the complementary base pairing *via* hydrogen bonds ensures the correct transfer of genetic information. Similar principles of stereospecific interactions lead to two-dimensional supramolecular structures upon adsorption of molecules onto templating surfaces.

The formation of highly ordered monolayers of organic molecules through physisorption mediated molecular self-assembly at the solid-liquid interface is an example for the spontaneous creation of order. The resulting two-dimensional molecular crystal structures can be determined using the combination of scanning tunneling real space analysis and diffraction methods together with molecular modeling. Here we present examples ranging from liquid crystals to heterocyclic organic molecules like trimesic acid, representative for a molecular host-guest system. In the case of DNA-molecules we have proposed a functional role of this process of spontaneous self-organization for the emergence of terrestrial life, which may also lead towards the construction of genetically based supramolecular architectures for modern technical applications, such as heterogeneous catalysis.

Self-assembly as a parallel process of fabrication down to the molecular level is of outmost importance in nanoscience, where spacially controlled fixation and precise manipulation of matter down to the single molecule level is an essential requirement for nanotechnology applications, e.g. in molecular electronics, where single molecule switches comprise the ultimate limit in processor design. Although futuristic at the contemporary level of technical manufacturing, the single molecule concept is widely realized in natural biological systems, where molecular assemblers, motors and machines are key to live. In molecular storage and quantum computing molecules or atom clusters comprising quantum dots must be arranged in a highly repetitive spatially ordered way over a huge area in comparison to the elementary building blocks. Additionally, controlled manipulation of the species must be possible. In the future biotechnology will use such concepts for biochip design, in order to raise the throughput. Often an ordered array of molecules acting as specific binding sites or receptors addressable one by one is highly desirable. Ambient condition and room temperature work environment is another challenge.

In my talk I will present our efforts for a cheap and easy to use ambient condition method based on a two-dimensional molecular organic template acting as a host architecture for the fixation of spacially highly ordered guest molecules. This method makes the precise manipulation of single molecule species possible at room temperature. As a demonstration we kick a carbon 60 buckyball with an STM tip between two goals each built from six benzene derivative molecules and separated by only 1.2 nanometers.

Molecular self-assembly, templating and STM-induced manipulation techniques such as re-arrangement of single molecules, rotation, change of coordination sites etc. strongly depend on the local bonding configuration the molecules. However, their availability is a prerequisite for the construction of man-made structures in the nano-regime in the near future.

References

HECKL, W. M.: Molecular self-assembly. In: FIGGER, H., MESCHEDE, D., and ZIMMERMANN, C. (Eds.): Laser Physics at the Limits; pp. 505–517. Berlin, New York: Springer Verlag 2002

HECKL, W. M.: Molecular self-assembly and the emergence of life. In: HORNECK, G., and BAUMSTARK-KHAN, C. (Eds.): Astrobiology, The Quest for the Conditions of Life; pp. 361–371. Berlin, Heidelberg: Springer 2002

GRIESSL, S., LACKINGER, M., EDELWIRTH, M., HIETSCHOLD, M., and HECKL, W. M.: Self-assembled two-dimensional molecular host-guest architectures from trimesic acid. Single Mol. *3.1*, 25–31 (2002)

Prof. Dr. Wolfgang HECKL
Ludwig-Maximilians-Universität München
Department für Geo- und Umweltwissenschaften
Bereich Kristallographie
Raum 249 (2. OG)
Theresienstraße 41
80333 München
Germany
Phone/Fax: +49 89 21804331
E-Mail: heckl@lmu.de
Website: http://www.nano.geo.uni-muenchen.de
Website: http://www.nanoanalytik-muenchen.de

Nova Acta Leopoldina NF *92*, Nr. 340, 83 (2005)

Brainchips – from Nano to Milli

Peter Fromherz (Martinsried/München)

Electrical information processing in brains and computers relies on different charge carriers – ions and electrons. It is a challenge to join neuronal networks and computer chips on a microscopic electrical level, with the goal to get better insight of brain dynamics and to built neuroelectronic processors. The research has two directions: (*A*) Elucidation of the electrical dynamics of the cell-silicon interface on a nanoscopic level. (*B*) Assembly of hybrid systems made of neuronal nets and semiconductor devices on a microscopic level.

(*A*) In the first area we analyzed the structure of the neuron-silicon contact using fluorescent dyes: (*i*) Taking advantage of the optical microcavity effect in front of silicon we determined the distance of cells and chips. We found that the insulating core of cell membranes is separated from the insulating silicon dioxide of chips by a cleft of about 50 nm. (*ii*) Taking advantage of the molecular Stark effect of dyes we observed the electrical response of cells to ac stimuli at the chip. We measured a sheet resistance around 10 megohm-square. The electrical interfacing of cells and chips is achieved by a current-voltage mechanism: ionic and capacitive currents through the cell membrane give rise to an extracellular voltage along the cleft that affects the electrons in the chip. Capacitive current through the silicon/electrolyte interface gives rise to a voltage along the cleft that affects ion conductances of the cell. We optimized the cell-silicon junction by lowering the conductance of the cleft, by enhancing the current through the membrane by recombinant ion channels and the current through the silicon/electrolyte interface by materials with high dielectric constant.

(*B*) In the second area we proceeded in three directions: (*i*) Using large identified neurons from molluscs, we built small neuroelectronic devices. A signal loop was assembled with capacitive stimulation from silicon to neuron, with a chemical synapse and with transistor recording of the second neuron. A complementary loop was created with transistor recording of neuronal excitation, with signal recognition on the chip and with capacitive stimulation of a second disconnected neuron. (*ii*) Using organotypic slices from rat brain we studied the interfacing of neuronal tissue to silicon. With capacitors for stimulation and transistors for recording a signal loop silicon-CA1-synapse-CA3-silicon was assembled that implemented neuronal learning on a silicon chips. (*iii*) A highly integrated CMOS chip was developed in order to achieve simultaneous interfacing at thousands of contact sites.

Prof. Dr. Peter Fromherz
Max-Planck-Institut für Biochemie
Abteilung Membran- und Neurophysik
Am Klopferspitz 18a
82152 Martinsried
Germany
Phone: +49 89 85782821/2820
Fax: +49 89 85782822
E-Mail: fromherz@biochem.mpg.de

Nonlinear Dynamics and the Spatiotemporal Principles of Biology

Leopoldina-Symposium
gemeinsam veranstaltet von der Deutschen Akademie der Naturforscher Leopoldina
und dem Graduiertenkolleg 340 »Kommunikation in biologischen Systemen«
sowie der Jungen Akademie
vom 13. bis 15. Mai 2002 in Darmstadt

Nova Acta Leopoldina N. F., Bd. *88*, Nr. 332
Herausgegeben von Friedrich BECK (Darmstadt), Marc-Thorsten HÜTT (Darmstadt)
und Ulrich LÜTTGE (Darmstadt)
(2003, 406 Seiten, 138 Abbildungen, 5 Tabellen, 37,80 Euro, ISBN 3-8047-2077-3)

Schwerpunkte der Veranstaltung bildeten nichtlineare Dynamik im allgemeinen, stochastische Resonanz und Synchronisation. Alle diese Themen wurden mit engem Bezug zu aktuellen Anwendungen in der Biologie im Wechselspiel von Theorie und Empirie behandelt. Sobald man bei dem Versuch, ein mathematisches Modell eines biologischen Phänomens zu entwerfen, die dynamischen Variablen über lineare Flüsse miteinander verbindet, findet die Beschreibung im Rahmen der linearen Systemtheorie statt. Wenn dann nichtlineare Wechselwirkungen einbezogen werden, gelangt die Modellierung in den Bereich der nichtlinearen Dynamik. Die Beiträge behandeln als Kernthemen Oszillationen, zeitliche und räumliche Synchronisation und Rauschen. Die im Rahmen des Symposiums diskutierten Oszillationen in der Natur reichen von ultradianen zu circadianen Rhythmen, von der Dynamik einzelner Enzyme zu Zellen, Organismen und Populationen. Die Diskussion von Synchronisation reicht von springenden Brownschen Teilchen, Ionenkanälen, Mikroalgen, Wasserflöhen (Daphnien), Zellen in einem Organ, Neuronen, entwicklungsbiologischen Organisations- und Signalzentren, Fischen in einem Vortex bis hin zu Planktonpopulationen. Rauschen wird als Umwelteinfluß oder als interner Beitrag schneller Dynamiken beschrieben. Biologische Variabilität in nichtlinearen Systemen vermag, ähnlich wie Rauschen, raumzeitliche Muster zu induzieren. Mit dem Auftreten nichtlinearer Phänomene in der Biologie stellt sich die Frage eines evolutionär wirksamen Nutzens für das biologische System. So können Oszillationen etwa den evolutionären Vorteil einer Zeitreferenz und einer inneren Uhr mit sich bringen. Die Beiträge machen solche funktionellen Vorteile in der Synchronisation biologischer Prozesse und im auf Brownsche Motoren wirksamen Rauschen bzw. in der Kontrolle von Krankheiten aus. Die nichtlineare Struktur ihrer Dynamik verleiht lebenden Systemen Robustheit.
Alle Beiträge sind in englischer Sprache abgefaßt.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 85 (2005)

Magnetic Structures and Magnetization Processes in Small Particles and Thin Films

Helmut Kronmüller (Stuttgart)

The micromagnetic backgrounds for the investigation of magnetic configurations and magnetization processes are reviewed for thin platelets and small particles applying the Finite Element Method (FEM). It is shown that magnetization patterns as well as magnetization processes are determined by the exchange lengths of the dipolar fields, and of the crystal anisotropy, (A = exchange constant, K_1 = first anisotropy constant).

The conditions for the formation of different types of spin configurations in thin platelets and small particles, including low- and high-remanence states are discussed. The intrinsic magnetization processes of these different configurations are characterized by reversible spin rotations, reversible domain wall displacements and irreversible nucleation and annihilation processes.

In cubic particles it is shown that with increasing edge length the spin configurations with lowest energy change from the so-called Flower State *via* the Twisted Flower State to the Vortex State. A similar situation holds in square and rectangular platelets. The numerical results obtained for the critical sizes of single domain particles of cubic, spherical and platelet shapes are compared with analytical results. The role of vortex and stray field free configurations is discussed.

For the application of nano-elements for recording systems besides the critical thickness parameters also small switching times are an important pre-requisite. Dynamic magnetization processes are investigated on the basis of Gilbert's equation using a damping term of the type $\alpha\ [\mathbf{M} \times d\mathbf{M}/dt]$. It is shown that optimal switching times below the ns range require an optimisation of the damping constant as well as of the shape of the magnetic elements. Including the effects of thermal fluctuations it is shown that smaller switching times can be achieved by thermally excited spin waves.

Prof. Dr. Helmut Kronmüller
Max-Planck-Institut für Metallforschung
Heisenbergstraße 3
70569 Stuttgart
Germany
Phone: +49 711 6890
Fax: +49 711 6891010
E-Mail: kronm@physix.mpi-stuttgart.mpg.de

Deutsche Akademie der Naturforscher Leopoldina Jahrbuch 2003

Leopoldina (Reihe 3), Jahrgang *49* (2003)

Herausgegeben von Volker TER MEULEN (Halle/Saale – Würzburg)
(2004, 672 Seiten, 99 Abbildungen, 10 Tabellen, 30,00 Euro, ISBN 3-8047-2168-0)

Das Jahrbuch berichtet über die wissenschaftlichen und wissenschaftspolitischen Aktivitäten der Leopoldina im Jahre 2003. Der Band enthält, neben Angaben zu Präsidium, Senatoren und Mitgliedern, Berichte über die Jahresversammlung 2003 »Energie« und die Symposien, Meetings bzw. Workshops »Epithelial Transport of Ions in Health and Disease«, »Bildgebung und Tumorheilung«, Gaterslebener Begegnung 2003 (»Bewahren und Verändern im Kontext biologischer und kultureller Evolution«), »Christian Gottfried Nees von Esenbeck – Politik und Naturwissenschaften in der ersten Hälfte des 19. Jahrhunderts«, »Psychological Thought and Practice: Historical and Interdisciplinary Perspectives«, »Medizin – Ethik – Recht. Die Zukunft der Transplantation von Zellen, Geweben und Organen«, »From Nanoscience to Nanotechnology«, »Struktur und Wirkung in der Katalyse«. Berichte über die monatlichen Sitzungen der Akademie sowie Mitteilungen aus Archiv, Bibliothek und Redaktion der Akademie ergänzen die Jahresübersicht.

Interessenten: Naturwissenschaftler und Mediziner, Wissenschaftshistoriker, Journalisten, Politiker, wissenschaftlich interessierte Öffentlichkeit.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 87 (2005)

Novel Methods for Fabrication of Nanostructures

Mark WELLAND (Cambridge)

Conventional techniques for nanofabrication based on semiconductor processing methods, such as electron and optical lithographys, are not able to fully exploit all facets of nanotechnology. There is therefore an increasing interest in alternative methods that range from scanned probe methods to directed self-assembly. We have recently been developing two technologies that aim to solve some of the complexity issues associated with fabrication of 3D nanostructures.

The first technique has been developed through an EU funded programme, ATOMS. The principle is that a specially modified atomic force microscope can both image and fabricate nanostructures. The cantilever of the AFM is specially fabricated and contains a silicon nitride membrane that is patterned with holes of varying shape and size. As the cantilever is scanned across the surface material is selectively evaporate through the holes to build up complex patterns form up to 4 different materials. By altering the velocity and direction of motion of the cantilever 3D hetrostructures can be fabricated directly. The added advantage of imaging with the AFM tip means that the position of a nanostructure can be predetermined relative to an existing surface structure. For example, connections can be made to a single wall nanotube by firstly imaging the SWNT and then by precisely positioning one of the cantilever apertures over the SWNT evaporate an electrode.

The second quite different technique used spinodal dewetting to make ordered structures from a single phase polymer. Under specific conditions an initially uniform thin polymer film coated on a substrate can become unstable and random patterns will appear on its surface. Such an induced structure obtained by topographic instability is of great interest as its size can be controlled to the order of sub-hundred nanometers. To make these patterns technologically applicable for the purpose of nanofabrication, two important issues must be resolved. Firstly, can a structure of high degree of ordering be produced on the surface and if yes, how? The other challenge is to find a way to transfer the structure formed by a single-phase polymer, particularly when the thickness variation of the patterned film is on the nanometer scale. Here we show that (*i*) it is possible to guide the random structures induced by topographic instability and form highly regular and periodic arrays or even rather complicated patterns by engineering the film stress, and (*ii*) that the pattern transfer can be achieved by a simple surface wave template that allows for the fabrication of highly ordered nanomagnetic structures.

Mark E. WELLAND FRS FREng
Professor of Nanotechnology
Director of IRC in Nanotechnology
Nanoscience
University of Cambridge
11. J J Thomson Ave
Cambridge
CB3 0FF

Phone: +44 1223 760305
Fax: +44 1223 760306
E-Mail: mew10@eng.cam.ac.uk

Ergebnisse des Leopoldina-Förderprogramms III

Meeting und Berichte der Stipendiaten

am 8. und 9. November 2002
Halle/Saale

Nova Acta Leopoldina N. F. Supplementum 18
Herausgegeben von Gunter S. Fischer (Halle/Saale), Benno Parthier (Halle/Saale) und Roland Riedel (Halle/Saale)
(2004, 284 Seiten, 118 Abbildungen, 12 Tabellen, 26,80 Euro, ISBN 3-8047-2176-1)

Ergebnisse des Leopoldina-Förderprogramms IV

Tagung und Berichte der Stipendiaten

am 14. und 15. Oktober 2004
Halle/Saale

Nova Acta Leopoldina N. F. Supplementum 19
Herausgegeben von Gunter S. Fischer (Halle/Saale), Andreas Clausing (Halle/Saale) und Volker ter Meulen (Halle/Saale – Würzburg)
(2004, 208 Seiten, 101 Abbildungen, 21,80 Euro, ISBN 3-8047-2177-X)

Die älteste deutsche Akademie, die Deutsche Akademie der Naturforscher Leopoldina, bemüht sich in besonderem Maße um Förderung von Nachwuchswissenschaftlern. Seit 1992 vergibt sie zur Unterstützung der beruflichen Weiterentwicklung herausragender junger Wissenschaftlerinnen und Wissenschaftler ein Stipendium, das es den Ausgezeichneten ermöglicht, innerhalb von zwei bis drei Jahren eigenständig ein außergewöhnlich innovatives Forschungsprojekt an ausländischen Wissenschaftseinrichtungen umzusetzen. Über 240 Forscherinnen und Forscher konnten seit Beginn des Programms gefördert werden. Die vorliegenden Bände zeigen die Vielfalt der Projekte und liefern Beispiele für die erreichten Ergebnisse in den letzten Jahren. Damit werden Chancen und Ansprüche des Förderprogramms für künftige Bewerber deutlich.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 89 (2005)

Nanosilicon

Ulrich GÖSELE (Halle/Saale)

Crystalline silicon is the base material of microelectronics. The intense interest in the fabrication and properties of nanoscale silicon comes from various sides:

(*i*) Scaling of microelectronics has now arrived at the sub-100 nm level.
(*ii*) Si layers of a few nanometers are used as strained silicon layers for higher mobility devices.
(*iii*) Silicon nanowires with a diameter of 5 – 10 nm are considered as one possibility to replace conventional silicon devices in the future.
(*iv*) Silicon itself is a poor light-emitter due to its indirect bandgap. However, silicon structures with dimensions below about 4 nm show efficient light emission.

Different ways to generate silicon nanostructures (nanosized layers, nanowires, nanowire-sponges and nanodots) will be presented. The properties of these nanostructures and their actual or potential applications will be discussed.

Prof. Dr. Ulrich M. GÖSELE
MPI of Microstructure Physics
Weinberg 2
06120 Halle (Saale)
Germany
Phone: +49 345 5582657
Fax: +49 345 5582557
E-Mail: goesele@mpi-halle.de

Chemistry and Mathematics: Two Scientific Languages of the 21st Century

Leopoldina-Symposium
gemeinsam veranstaltet von der Deutschen Akademie der Naturforscher Leopoldina, der Göttinger Akademie der Wissenschaften und der Académie des Sciences, France vom 11. bis 13. Oktober 2001 in Göttingen

Nova Acta Leopoldina N. F., Bd. *88*, Nr. 330
Herausgegeben von Hans Föllmer (Berlin), François Mathey (Palaiseau),
Herbert W. Roesky (Göttingen) und Jürgen Troe (Göttingen)
(2003, 160 Seiten, 106 Abbildungen, 2 Tabellen, 28,80 Euro, ISBN 3-8047-2038-2)

Die Mathematik erlangt in der Chemie immer größere Bedeutung. In den Beiträgen wird u. a. gezeigt, wie nützlich mathematische Verfahren für Bestimmung und Vorhersage chemischer Strukturen sind. Behandelt werden der Informationsgehalt chemischer Namen und Formeln, insbesondere die umfassende Information, die von chemischen Molekülformeln geliefert wird. Dabei zeigt sich die Chemie als eine Theorie, die induktive Gesetze, Experimente und Intuition verbindet. Sie weist eine Vielzahl interessanter Berührungsfelder mit der Mathematik auf, in die sich u. a. durch Modellvergleiche interessante Einblicke gewinnen lassen. Diese reichen von der Computerchemie bis zu Anwendungen in der virtuellen Kristallographie und im Verbrennungsmotorenbau, aber auch auf dem Gebiet der Biologie. Darüber hinaus wird historischen Beziehungen in den Sprachen von »Chemie« und »Mathematik« nachgegangen, die auch eine Brücke zu Poesie und Musik schlagen können.
Alle Beiträge sind in englischer Sprache abgefaßt.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 91 (2005)

Bioreceptors as Model Systems for Functional Nanostructures

Horst Hahn (Karlsruhe) and Branko Stahl (Karlsruhe)

In the area of mechanical properties the imitation of biological structures has been successfully applied. As an example, this has led to the understanding of the increased fracture strength of biological systems and to the transfer to complex ceramic structures. This bio-inspired approach to materials science and the development of novel structures has been actively followed by many groups worldwide. The different forms of sensory perception in nature are based on a diversity of receptor mechanisms. In many cases the receptors are highly integrated complex structures consisting of different materials which receive optical, magnetic or chemical signals. Recently, biologists discovered a magnetic nanostructure in the upper beak of the homing pigeon which is related to the magnetic orientation. The identification of the structures consisting of several inorganic compounds in complex spatial arrangements, the understanding of the receptor mechanisms and the successful transfer of the biological principle to a technical component are the main challenges. Based on the details of the nano- and microstructures in the beak of the homing pigeon the connection to artificial nanostructures will be given. This includes nanoparticles containing iron such as FePt, amorphous Fe-C-P alloys, magnetite and others, which are synthesized by various wet chemical or gas phase processes. Due to the narrow size distribution of the nanoparticles and the functionalization of the surface by organic molecules complex structures can be build by self organisation. The magnetization processes and the anisotropy of these surface and interface controlled materials which can be influenced by the environment and the functionalization are studied.

Prof. Dr. Horst Hahn
Forschungszentrum Karlsruhe
Institut für Nanotechnologie/Institute of Nanotechnology
Postfach 3640
76021 Karlsruhe
Germany
Phone: +49 7247 826350
Fax: +49 7247 826368
E-Mail: horst.hahn@int.fzk.de

Das Allgemeine und das Einzelne – Johann Wolfgang von Goethe und Alexander von Humboldt im Gespräch

Acta Historica Leopoldina Nr. 38
Leopoldina-Meeting, gemeinsam veranstaltet von der Deutschen Akademie der Naturforscher Leopoldina und der Martin-Luther-Universität Halle-Wittenberg am 29. und 30. Oktober 1999 in Halle (Saale)
Herausgegeben von Ilse Jahn (Berlin) und Andreas Kleinert (Halle/Saale).
(2003, 199 Seiten, 11 Abbildungen, 24,80 Euro, ISBN 3-8047-2050-1)

Als dieses Meeting Ende Oktober 1999 stattfand, waren schon zahlreiche nationale und internationale Veranstaltungen zum Gedenken einerseits an den 250. Geburtstag von Johann Wolfgang von Goethe (28. August 1749) und andererseits an die Abreise Alexander von Humboldts nach Amerika vor 200 Jahren (5. Juni 1799) vorangegangen.

Beide Persönlichkeiten waren Mitglieder der Deutschen Akademie der Naturforscher Leopoldina, Humboldt bereits ab 1793, Goethe ab 1818. So nahm die Leopoldina diese zwei Jubiläen zum Anlaß, nach den Beziehungen und dem gegenseitigen Gedankenaustausch beider zu Problemen und Methoden der zeitgenössischen Naturwissenschaften zu fragen und noch nicht geklärte Aspekte in Vorträgen und im Wechselgespräch zu beleuchten.

Nach den Grußworten des Präsidenten der Leopoldina (Benno Parthier, Halle/Saale) und des Rektors der Martin-Luther-Universität (Reinhard Kreckel, Halle/Saale) führte Dorothea Kuhn (Marbach) in das interdisziplinär weit gespannte Thema ein. Wolf von Engelhardt (Tübingen) stellte neue Einsichten zu »Goethe und Alexander von Humboldt – Bau und Geschichte der Erde« vor (Neptunismus-Vulkanismus-Streit), Xosé A. Fraga (A Coruña, Spanien) erforschte Humboldts und Goethes Rezeption und Wirkung in der spanischen Naturwissenschaft des 19. Jahrhunderts, Manfred Wenzel (Marburg) analysierte die Problemkreise um Galvanismus und vergleichende Anatomie in den Korrespondenzen zwischen Goethe, Alexander von Humboldt und Samuel Thomas Soemmerring. Das Verhältnis beider »Zentralfiguren europäischer Kultur« zur physischen Anthropologie verglich Renato G. Mazzolini (Trient) mit den zeitgenössischen Diskursen über Rassentheorien, rassistische Literatur und der »Konstruktion einer europäischen somatischen Identität«. Goethes Einfluß auf den jungen Humboldt verdeutlichte Shu Ching Ho (Freiburg i. Br.) (»Vom atomistischen Weltbild zum organischen Universum«). Gisela Nickel (Ober-Olm) stellte beide als Wetterkundler in ihren völlig unterschiedlichen Herangehensweisen vor (»wechselseitige Anregung oder Nichtbeachtung?«), Otto Krätz (München) behandelte ihr Verhältnis zur Chemie (»Inwiefern es möglich sei, der organisch chemischen Operation des Lebens beizukommen«), und Ludolf von Mackensen (Kassel) plädierte anhand von eindrucksvollen optischen Experimenten für Weiterungen aus Goethes Farbenlehre und zeigte die nachvollziehbaren Gründe auf für ihre Ablehnung bzw. das Nichtverstehen durch Humboldt (wie der meisten zeitgenössischen Physiker), während Ulrike Leitner (Berlin) in Humboldts Schriften Anregungen und Reflexionen Goethes aufspürte. Dietrich von Engelhardt (Lübeck) stellte beide Geistesgrößen unter dem Titel »Das Allgemeine und das Einzelne, der Begriff und die Erscheinung« in den »Kontext der Philosophie und Wissenschaft der Natur um 1800«.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart

Nova Acta Leopoldina NF *92*, Nr. 340, 93–94 (2005)

Current and THz Spectroscopy of Quantum States

Erich GORNIK (Wien)

Ballistic Electron Spectroscopy (KAST et al. 2001, 2002) is used to measure the energy splitting and the progressive localization of the Wannier-Stark states in short period superlattices. The main problem to determine the Wannier-Stark splitting in a semiconductor superlattice is the electric field induced localization. The localization length inside the superlattice is inversely proportional to the applied electric field which leads to a quenching of the coherent electron transport through the individual states. By using LO-phonon scattering inter-Wannier-Stark state transitions can be induced. This way incoherent transmission channels are opened which enable carrier transport throught the superlattice. Two different superlattices with 4 and 5 periods have been designed. The miniband width of the 5 period SL equals the optical phonon energy (36 meV) whereas the miniband width of the 4 period SL (23 meV) is well below the optical phonon energy. Due to the high resolution (KAST et al. 2001) of the spectrometer the energy splitting and the transmission behavior of the individual Wannier-Stark states are observed separately. The basic transport through Wannier-Stark states is identified to be coherent. Individual transport channels induced by LO-phonon scattering sets in when the Wannier-Stark states spacing tunes into the optical phonon energy.

A magnetic field parallel to the current direction reduces the phase space for all scattering processes in the device. As a consequence the ballistic electron beam is focused which is directly observed as a decrease in the energetic widths of the individual peaks in the transfer ratios. Moreover, a clear magnetic field dependence of the strength of the LO-phonon induced inter-Wannier-Stark state transitions is observed. The transmission of the incoherent part in the measured transfer ratio which directly represents the strength of the LO-phonon scattering process increases with the applied magnetic field.

Efficient electron capture into electronic states in self-assembled quantum dots (QDs) is a basic requirement for applications as MIR photodetectors (REBOHLE et al. 2002), emitters (ANDERS et al. 2003) or even candidates for q-bit operations. In contrast to subband transitions in two-dimensional structures the density of states is sharply peaked at the transition energy, which reduces the phase space for scattering. Therefore, longer relaxation and dephasing rates are expected in QDs as compared to quantum wells. A strong requirement for q-bit applications is a controlled way of radiative coupling between the electronic levels.

The experimental procedure is to superimpose a pulsed NIR excitation laser field with a low intensity cw THz field on a single quantum dot. The exciton recombination is recorded with a micro luminescence setup for NIR excitation as well as for combined NIR/THz excitation. First results show an electron transfer from the lower excitonic levels into higher levels, which changes the count rates for the emission lines. The efficiency of this process seems to depend on the NIR pump intensity and is object of further studies. Furthermore ultrabroadband MIR time-domain spectroscopy (Müller et al. 2001) allows to study the dynamical properties within the electronic dot levels. In a first approach the electron capture respectively injection into the electronic levels of dot ensembles is studied. Combined with the µPL system the dynamics of electrons in single dots are investigated. The main motivation is to control the relaxation and dephasing processes and to achieve coherent excitations within the electronic dot levels, which would allow very fast control of QD based devices.

References

Anders, S., Rebohle, L., Schrey, F. F., Unterrainer, K., and Strasser, G.: Appl. Phys. Lett. *82*, 3862 (2003)
Kast, M., Pacher, C., Strasser, G., and Gornik, E.: Appl. Phys. Lett. *78*, 3639 (2001)
Kast, M., Pacher, C., Strasser, G., and Gornik, E.: Phys. Rev. Lett. *89*, 136803 (2002)
Müller, T., Bratschitsch, R., Strasser, G., and Unterrainer, K.: Appl. Phys. Lett. *79*, 2755 (2001)
Rebohle, L., Schrey, F. F., Hofer, S., Strasser, G., and Unterrainer, K.: Appl. Phys. Lett. *81*, 2079 (2002)

Prof. Dr. Erich Gornik
Technische Universität Wien
Institut für Festkörperelektronik
Floragasse 7
A-1040 Wien
Austria
Phone: +43 1 5880136200
Fax: +43 1 5880136299
E-Mail: erich.gornik@tuwien.ac.at

Nova Acta Leopoldina NF *92*, Nr. 340, 95 (2005)

Dislocation and Grain-Boundary Deformation Processes in Nanocrystalline Materials by Multiscale Computer Simulation[1]

Dieter Wolf (Argonne)

We review the results of recent molecular-dynamics simulations of plastic deformation and grain growth in nanocrystalline fcc metals (i.e., of polycrystals with a grain size of less than 100 nm). These simulations have now become large and sophisticated enough where they begin to cover the entire range of grain sizes in which the experimentally suggested transition from a dislocation-based deformation mechanism to one involving grain-boundary processes takes place as the grain size becomes ever smaller. Their atomic-level resolution provides novel insights into the intricate interplay between dislocation and GB processes responsible for this crossover.

As an outlook, we use the example of grain growth to describe a hierarchical multiscale approach for the simulation of polycrystalline materials that can overcome the inherent length- and time-scale limitations of these atomic-level simulations. This approach includes the three most relevant scales: the atomic level, the microstructural length and time scales (the "mesoscale") and the continuum level. The objects of the mesoscale simulation evolving, by dissipative processes, in time and space are the grain boundaries rather than the atoms. Instead of the vibration periods of the atoms and their distances, the related microstructural time and length scales are therefore governed by the mobilities of the GBs and grains and by the grain size. The connection to the continuum level is established by meshing the grain interiors in a way that connects with the already discretized grain microstructure; this enables determination of the inhomogeneous stress distribution within the microstructure.

Dr. Dieter Wolf
Materials Science Division
Argonne National Laboratory
Blgd. 212
Argonne
IL 60439
USA
Phone: +1 630 2525205
Fax: +1 630 2524289
E-Mail: wolf@anl.gov

---

[1] Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-3l-l09-Eng-38.

Christian Gottfried NEES VON ESENBECK: Briefwechsel mit Johann Wolfgang von Goethe nebst ergänzenden Schreiben

Acta Historica Leopoldina Nr. *40*
Bearbeitet von Kai Torsten KANZ (Lübeck)
(2003, 470 Seiten, 12 Abbildungen, 34,80 Euro, ISBN 3-8047-2001-3)

Der Band enthält die zwischen dem Botaniker und Präsidenten der heutigen Deutschen Akademie der Naturforscher Leopoldina, Christian Gottfried NEES VON ESENBECK (1776–1858), und dem Dichter und Naturforscher Johann Wolfgang VON GOETHE (1749–1832) in den Jahren 1816 bis 1831 gewechselten mehr als 150 Schreiben. Damit wird eine der bedeutendsten naturwissenschaftlichen Korrespondenzen des alten GOETHE erstmals vollständig und in kommentierter Form zugänglich gemacht. Ergänzend werden die Korrespondenz zwischen NEES VON ESENBECK und GOETHES Sekretär ECKERMANN sowie weitere Briefe ediert. Neben einer Einführung in die Ausgabe sind die Texte vollständig durch Register (Personen, Sachen, Orte) erschlossen.

Die historische Bedeutung Christian Gottfried Daniel NEES VON ESENBECKS liegt neben seiner vierzigjährigen Amtszeit als XI. Präsident der Leopoldina (1818–1858) in seinem wissenschaftlichen Lebenswerk als Botaniker, Naturphilosoph und Wissenschaftsorganisator, in seiner Tätigkeit als Hochschullehrer an den Universitäten Erlangen, Bonn und Breslau sowie in seinem engagierten sozialpolitischen Wirken. Sein Leben und Werk ist in vielfacher Weise ein Spiegel der Wissenschafts- wie auch der allgemeinen Geschichte der ersten Hälfte des 19. Jahrhunderts.

Seine umfangreiche Korrespondenz, die sich über weit mehr als 4000 Briefe ausdehnt, stellt einen Schlüssel zum Verständnis seines Wirkens dar. Darüber hinaus sind die Briefe für eine Vielzahl weiterer Fragestellungen aus der Wissenschafts-, Literatur- und Kulturgeschichte sowie der politischen Geschichte (Arbeiterbewegung, Christkatholizismus, Revolution von 1848) von herausragendem Quellenwert. Der vorliegende Band eröffnet die schwerpunktmäßig ausgewählten Editionen dieser Korrespondenzen in der Reihe *Acta Historica Leopoldina*.

In Kommission bei Wissenschaftliche Verlagsgesellschaft mbH Stuttgart