\[ \tau_{\text{inc}} \propto (T_s - T_f)^{-2} \]
Cover pictures (from top):

- Carrier lifetimes of a RGS silicon solar cell (p. 36)
- Isomer-resolved photoelectron spectra of C$_{11}$ clusters (p. 40)
- Mechanically controllable break-junction made of Co with leads (p. 5)
- Incubation time for the onset of ordering in an A$_3$B alloy (p. 58)
- Magnetic domains of a Co/Cr multilayer surface (p. 12)
- Surface damage caused by water droplets in the SLC process (p. 27)
I. Preface

This annual report gives a short and comprehensive overview about ongoing research and recent results of our department in the field of solid state and cluster physics. The annual report of the year 2001 about “Soft condensed matter” and the biannual report (2000 and 2001) of the “Optik-Zentrum” accomplish this series about our main research activities. Of course, this compacted survey cannot replace the complete work that can be found in the literature.

As before, our activities and interests are widespread and include fundamental properties of solids and clusters as well as applied physics, theoretical physics as well as experimental physics. Special emphasis lies in the research on nanostructures on surfaces and interfaces, that is funded by the German Research Society (DFG) through the Sonderforschungsbereich 513. This SFB in which many groups of the department collaborate, has successfully been evaluated in September 2001 and approved for the next three years.

We could congratulate Prof. P. Leiderer who was elected as a member of the Heidelberger Akademie der Wissenschaften. Dr. Giso Hahn was awarded the Förderpreis of the “Foundation Environment and Living (LBS)”. It is a pleasure to announce that Dr. J. Müller received the Dornier-Award for his PhD thesis.

We are glad to have had a number of guests for long term visits. Two of us profited from their own sabbaticals – W. Dieterich during the summer term and G. Ganteför in the winter term 2001/2002. Our emeriti Prof. Dr. Klaus Dransfeld and Prof. Dr. Ekkehard Recknagel celebrated their 75th and 70th birthdays, respectively.

Our research activities would not have been possible without the dedicated and hard work of the scientific and technical staff, and the doctorate and diploma students.

14 students finished their diploma studies with a thesis work in solid state or cluster physics, 12 young researchers were promoted to a Dr. rer. nat. of our university with research topics in solid state and cluster physics.

We would like to thank all co-workers from the secretaries’ offices, central services, laboratories, workshops, and the helium liquification of the university contributing to the results of the previous year.

We gratefully acknowledge the generous support given by several research funding institutions and institutes, in particular the before-mentioned German Research Society (DFG), the European Union through the scientific projects ACE, ASCEMUS, HIT, Fast-IQ, and SIMU, the State of Baden-Württemberg, the German Ministry of Education, Science, Research and Technology (BMBF), the East European Office of the BMBF, German Ministry of Economy (BMWi), the Deutscher Akademischer Austauschdienst (DAAD), the Krupp Foundation, the German-Israeli-Foundation (GIF, Jerusalem), the Paul-Scherrer-Institute (Villigen/Switzerland), the ISOLDE/CERN (Geneva/Switzerland), and the companies ASE, Bayer, centrotherm, Ersol, EKRA, Merck, sunways, Winter, Zeiss and BP Solarex (USA/GB), DISCO HiTec (J), Elkem (N), Evergreen Solar (USA), Eurosolare (I), GT Solar (USA), Photowatt (F), Shell Solar (NL).

Konstanz, October 2002

Elke Scheer
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II. Research Reports

1. Aharonov-Bohm oscillations in mesoscopic rings: Microscopic versus global phase

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One of the most prominent manifestations of quantum coherence in metallic nanostructures is the so-called Aharonov-Bohm (AB) effect 1), i.e. periodic oscillations of the conductance as a function of an external control parameter as e.g. the magnetic field $B$ or energy $E$ in ring or loop geometries. The oscillations are observable as long as the transport in a device is phase coherent. This means that the dimensions have to be smaller than the phase coherence length, which is approximately $L_q \approx 1 \mu$m at very low temperatures for samples made of disordered metallic thin films in which the transport is diffusive. Since the first experimental observation in 1985 2) they have been developed to a powerful tool for studying the mechanisms that are responsible for the loss of electronic phase coherence in mesoscopic devices. The oscillations are caused by interference between the individual electronic paths along a mesoscopic sample. External fields cause phase shifts between the paths. For diffusive wires in a perpendicular magnetic field, a dependence of the magnetoconductance (MC) according to 3)

$$\Delta G = g(B, E) \cos \left[ 2\pi \frac{BA}{\Phi_0} + \varphi(B, E) \right]$$

is expected where $A$ denotes the enclosed area of the ring and $\Phi_0 = \hbar/e$ the fundamental flux quantum. The amplitude $g$ and the phase $\varphi$ are sample specific as they depend on the microscopic arrangement of the scattering centers in the ring. The typical scales in $B$ and $E$ for a variation of $g$ and $\varphi$ are the correlation field $B_c \approx \Phi_0/(2\pi L)$ and the Thouless energy $E_c = \hbar D/(0.7 L_q)^{1.3}$ where $w$ is the width of the ring arms, $L$ the half perimeter of the ring, and $D$ the electronic diffusion constant. For a fully phase coherent sample the amplitude of the AB oscillations achieves the order of the conductance quantum $e^2/h$. For sample dimensions exceeding $L_q$ the amplitude is exponentially damped. The average resistance of our samples is in the order of 30 to 60 $\Omega$, corresponding to a conductance of 400 to 900 $e^2/h$. With $D \approx 0.5-1 \times 10^{-2} \text{m}^2/\text{s}$ and $L_q$ of order 1 $\mu$m this implies AB oscillations with relative amplitude of $\Delta G/G \approx 10^{-5}$ to $10^{-4}$.

Fig. 1: Electron microscope photograph of (a) a ring in 2-point geometry and (b) in 4-point geometry. The diameter of the rings is 1 $\mu$m, the linewidth is (a) 80 nm, (b) 60 nm and the thickness of the films is 15 nm.

Fig. 2: Conductance oscillations $\Delta G$ vs. magnetic field $B$ for a sample in 2-point geometry at currents $I_{dc} = 0, 0.4$, 0.8, ..., 6.8 $\mu$A (from top to bottom) and at a temperature of $T < 100$ mK. The data were digitally Fourier filtered. The data are offset for clarity. The effective zero field is at $B = 4.5$ mT. The arrows indicate maxima positions of subsequent oscillation traces.

In this work, we have investigated the influence of the sample geometry on the symmetry of the MC. According to fundamental symmetry relations the MC of a mesoscopic sample in a 2-point geometry (current and voltage leads split outside the phase-coherent region, see Fig. 1a) is expected to be symmetric upon magnetic-field reversal 4): $G(B) = G(-B)$. This implies that at zero magnetic field the phase of the AB oscillations has to be zero (maximum conductance) or $\pi$ (minimum conductance). This prediction is in contrast to the naive picture that elastic scattering of impurities (what happens in our diffusive wires at a distance of the mean free path $l \approx 10-20$ nm) gives rise to arbitrary phase shifts of the AB oscillations. In a mesoscopic 4-point geometry (current and voltage leads split inside the phase coherent region, see Fig. 1b) the symmetry rules predict a symmetric MC only when simultaneously exchanging the role of current and voltage leads 4): $G_{U,I}(B) = G_{I,U}(-B)$. Reversing the magnetic field alone gives no particular symmetry. Consequently, arbi-
Conductance oscillations

We have checked these predictions by forcing the microscopic phases of the electronic paths to shift by applying a high dc bias voltage \( \delta \varphi = eU \tau_0 / h \), where \( \tau_0 \) is the diffusion time through the sample.

Fig. 2 displays the results for a sample in 2-point geometry for different values of \( I_{dc} = U_{dc} G \) at \( T < 100 \) mK. The oscillation period is \( B_{per} = 5.2 \pm 0.5 \) mT, in good agreement with the expected value \( \Phi_0 / A = 5.3 \) mT. The amplitude and its modulations are strongly influenced by \( I_{dc} \) while the overall MC remains always symmetric with respect to \( B = 4.5 \) mT which is the offset field of the superconducting solenoid used for applying the magnetic field.

Fig. 2: Conductance oscillations \( \Delta G \) vs. magnetic field \( B \) for a sample in 4-point geometry at currents \( I_{dc} = 0, 0.15, 0.3, …, 3.3 \) \( \mu \)A (from top to bottom) and at a temperature of \( T < 100 \) mK. The data were digitally Fourier filtered. The data are offset for clarity. The effective zero field is at \( B = 4.5 \) mT. The arrows indicate maxima positions of subsequent oscillation traces.

For a ring with the same diameter but in 4-point geometry we observe the MC curves displayed in Fig. 3 without any observable symmetry but arbitrary phase at zero field. Due to the diffusive nature of the transport within the ring arms the shift is not continuous for all values of the bias, but only within certain limits given by the Thouless energy \( E_T \approx 14 \) \( \mu \)eV of the ring corresponding to a correlation current \( I_c \approx 0.3 \) \( \mu \)A. From a detailed analysis of the phase shifts for MC curves with bias currents up to \( 50 \) \( \mu \)A we obtain a typical current scale of \( 1 \) \( \mu \)A for shifting the phase by \( 2 \pi \) in reasonable agreement with the estimation of the Thouless energy.

The different behavior in 2- and 4-point geometry can be accounted for by calculating the cross-correlation function (CCF) between the MC measured at two different bias currents:

\[
C(I_1, I_2, \Delta B) = \int \Delta G_{I_1}(B) \Delta G_{I_2}(B + \Delta B) dB
\]

The CCF between two periodic functions with the same period is again a periodic function. A shift of \( \Delta B \) between these functions manifests itself in a shift of the maxima of the CCF by \( \Delta B \).

The phase shifts of the oscillations \( \delta \varphi \) is related to \( \Delta B \) by the relation \( \delta \varphi = 2 \pi \Delta B / B_{per} \). The observed shift of the CFF’s results in \( \delta \varphi = 0 \) or \( \delta \varphi = \pi \) for a 2-point geometry whereas \( \delta \varphi \) is arbitrary for the 4-point geometry [cf. Fig. 4]. This behavior demonstrates convincingly the expected symmetry relations.

Fig 4: Phase shifts referred to \( I_{dc} = 0 \) for a sample in (a) 2-point and (b) 4-point geometry. Some of the MC traces are displayed in Figs. 2 and 3. The data were evaluated in a magnetic-field range from \(-30 \) to \( 30 \) mT. The dashed line is a guide to the eye.

In conclusion, although the microscopic phase of the electronic wave function is varied continuously by a modification of \( I_{dc} \), the macroscopic phase of the conductance oscillations varies in quantized manner for 2-point geometries. However, there is no abrupt change in the MC. Rather, the macroscopic phase flip is accompanied by a rearrangement of the individual electron phases to produce an interference pattern leading to a minimum in the oscillation amplitude. This continuous variation of the interference on the microscopic level is also visible as a slight shift of the oscillation frequency whenever a phase slip occurs (see Fig. 2). Thus the suppression at macroscopic phase flips indicates the rearrangement at the microscopic level. This confirms the notion that the current induced variation of the energy of the electrons leads to an altered microscopic interference pattern. In the case of a 4-point geometry, this variation of the interference does not need to be correlated in both arms of the ring, as can be seen in the arbitrary values of the phase shift of the oscillations (see Fig. 3).

(1) Y. Aharanov and D. Bohm, Phys. Rev. 115 (1959) 485
2. Experimental setup for conductance measurements on DNA molecules under mechanical stress

R. Hackl, R. Lehner, T. Gisler, G. Maret and E. Scheer

DNA plays a central role in biology as the carrier of genetic information. During the last years DNA has also been discussed as possible building block for molecular electronics since its well known self-assembly properties can be exploited to make a variety of structures including multi-terminal devices useful for nanoelectronics. It combines unique recognition accuracy with distinct optical characteristics, chemical stability and adaptability. However, at present one of the key properties for the use of DNA in electronics is still under debate, namely its electronic conductivity. Several contradictory experimental results ranging from good metallic behavior via wide-gap semiconducting up to clearly insulating behavior as well as proximity superconductivity have been reported. Problems in the comparison of the different experiments arise from the use of different types of DNA (e.g. λ-DNA vs. polyG-polyC-DNA), different contact and measurement setups, different electrochemical environments (aqueous solution, ambient conditions, UHV conditions), statistics of the experiment (single-molecule vs. ensemble average) and possibly many more so far uncontrolled parameters. In particular the structural properties of the molecules under test are unknown in most of the experiments. The control of the structure is the starting point of the present experiment.

Fig. 1: Schematic structure of the double stranded DNA in B-conformation.

It is widely assumed that if DNA has an intrinsic electrical conductivity the conduction takes place through the \( \pi \)-orbitals of the base pairs.

In the usual conformation (see Fig. 1), the so-called B-conformation the base pairs are coupled via hydrogen bonds, which occur only in the combination C-G (cytosine-guanine) and A-T (adenine-thymine) form the rungs of a helical ladder. The \( \pi \)-orbitals of the base pairs are then directed perpendicularly to the rungs and thus parallel to the helix axis. Orbitals of neighboring base pairs have a large overlap and should thus be able to conduct current over long distances.

From force measurements it is known that DNA can be stretched to a length exceeding the contour length - i.e. the length when the helix axes builds a straight line but no further mechanical stress is applied - by a factor of 1.6. The molecule is then in the so-called S-conformation in which the rungs are turned around up to an angle of 90°. The \( \pi \)-orbitals are now directed perpendicularly to the helix axis and have a reduced overlap to the neighboring base pair. If the current transport in DNA is dominantly carried by the \( \pi \)-orbitals, the conductivity should drastically be reduced when switching into the S-conformation.

Spectroscopic investigations of electron-transfer rates show a long-lived excited state of the base pairs, which is interpreted as being due to an anharmonic structural fluctuation of the base pairs in the gigahertz range. The relaxation of the excited state would be blocked whenever the base pairs are in the “wrong” configuration.

The outline of the experiment is the following: An ensemble of 1000 to 10000 DNA molecules (λ-DNA, contour length 16 µm) is attached to gold electrodes on a glass substrate separated by varying distance ranging from 1 to 1.6 times the contour length. The conductivity of the circuit is measured as a function of the distance of the electrode pairs and thus of the elongation of the molecules.

The electrodes are prepared by a combination of optical and electron beam lithography since the required dimensions range from the nanometer to the millimeter regime. First the contact pads and wide interconnects are fabricated with optical lithography. Subsequently the fine electrodes are patterned aligned to the coarse structures with electron beam lithography.

Fig. 2: Coarse contact structure of gold on a glass substrate patterned by optical lithography. Dimensions are: substrate 24 mm x 24 mm, contact pads 2 mm x 2 mm, width of the narrow interconnects leading to the center of the substrate 100 µm.
In a first step the glass substrates are covered with a polyimide layer that improves the quality of the optical lithography and the adhesion of the gold electrodes. The photoresist is then spin-coated and exposed with a 365 nm UV lamp through a homemade mask from a small picture slide in contact with the photoresist. After development of the photoresist the substrates are coated with a 50 nm thick gold layer by thermal evaporation in high vacuum. The photo mask is finally lifted-off in warm acetone. The layout of the coarse contact leads prepared by this step are shown in Fig. 2.

The contact pads have dimensions of 2 mm x 2 mm and the smallest structures ending within a surface of 1 mm x 1 mm have a width of 100 µm. The resolution of this simplified optical lithography process is limited to about 10 µm by the contrast and the granularity of the photographic film, its planarity and the divergence of the UV lamp.

For the electron beam lithography the substrates are covered with a PMMA bilayer resist and the fine structures are written in a scanning electron microscope (see report by Kunej et al.). The metallization is again performed by thermal evaporation of gold and lift-off in acetone. The geometry of the fine structure is shown in Fig. 3. The electrodes form 1 mm long and 1 µm wide lines with distances of 15 µm, 18 µm, 21 µm, and 24 µm.

Before the DNA molecules are assembled with the electrodes they are chemically prepared with a fluorescent for later optical inspection and with thiol-modified oligonucleotides as endgroups in order to build a chemical bond with the gold of the electrodes.

The attachment and stretching is performed by repeated dipping of the substrate into a solution containing the prepared DNA molecules. Possible parameters for controlling the elongation factor are the dipping speed and the surface tension of the solvent that can be varied by addition of suitable salts.

By this procedure molecules attach with a certain prob-
3. Fabrication of metallic nanostructures with electron beam lithography

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Our work on mesoscopic physics includes the study of transport properties of diffusive metals, atomic-size point contacts, clusters and organic molecules. The physical phenomena under investigation are Andreev reflection and proximity effect in superconductor-normal metal or superconductor-ferromagnet structures, universal conductance fluctuations, nonequilibrium transport properties, charging effects and effects of external forces or deformation on the conductivity. Most of the experiments are performed at very low temperatures \( T < 1 \text{ K} \).

The different experiments require samples with smallest structure sizes below 100 nm, well-controlled interfaces between different metals as well as unusual substrate materials. In addition, contact pads in the millimeter range are necessary for performing electrical contact to the measurement setup.

![Fig. 1: Standard lift-off process: a) Substrate (yellow) with bilayer resist (pink: buffer layer, red: mask layer); b) after electron beam writing and development; c) after deposition of metal layer (blue); d) after lifting-off the mask.](image)

Our samples are fabricated by electron-beam lithography in a lift-off process with a bilayer resist (see Fig. 1). For some purposes the combination with optical lithography is required (see report by R. Hackl et al.).

The electron-beam lithography is performed with a Philips XL30 scanning electron microscope with a Raith Elphy Quantum lithography system. Smallest structure sizes of \( \approx 50 \text{ nm} \) have been achieved on a standard silicon substrate. The metals are deposited by thermal evaporation under ultra high vacuum conditions at room temperature or substrate temperatures down to \(-80^{\circ}\text{C}\).

For the fabrication of atomic-size contacts with the help of the mechanically controllable break-junction technique (MCB) \(^1\), the use of a flexible substrate is necessary. We use carefully polished 0.3 mm thick bronze wafers covered by a 2 \(\mu\text{m}\) thick polyimide layer for electrical insulation and planarization of the remaining roughness. Subsequently, the standard lift-off procedure can be performed. The resolution on these non-standard substrates is slightly reduced to \( \approx 80 \text{ nm} \).

The design for the electron-beam writing is a narrow constriction of length and width 100 nm between two funnel-shaped leads. After metalization and lifting off the mask, an isotropic dry etch process in an oxygen plasma is performed for suspending the narrow region and forming a freestanding nanobridge (see Fig. 2).

![Fig. 2: MCB fabrication: a) bronze substrate with polyimide sacrificial layer (green) and bilayer resist (red, for simplicity shown as a single layer); b) after electron beam writing (pink: exposed areas); c) after development, d) after metal (blue) deposition; e) after lift-off; f) after plasma etching.](image)

![Fig. 3: Micrograph (observation angle 65°) of a MCB made of Al (blue) after reducing the polyimide (green) thickness by \( \approx 700 \text{ nm} \) in a plasma etch process. The Al layer thickness is 150 nm; the separation between the two rectangular electrodes is 2 \(\mu\text{m}\). The thickness in the constriction is reduced presumably due to an error during electron beam writing.](image)

Fig. 3 shows an example of an Al nanobridge. The samples are then mounted onto a three-point bending mechanism that allows for a controlled elongation of the
nanobridge with a precision of a few femtometer under ultrahigh vacuum conditions and at very low temperatures (Fig. 4).

The same sample design can be used for the fabrication of electrodes for transport measurements through clusters (see report no. 29)

For the study of Andreev reflection, proximity effect and charging effects, clean and/or well-controlled tunnel contacts between two or more metals with an alignment accuracy of a few nm are required. These can be achieved by different methods: For most of our purposes the shadow evaporation technique \(^2\) is sufficient (Fig. 5).

It uses a single suspended lithographic mask through which the metals are deposited from different angles. The advantages of this method are the self-alignment by the use of the same mask and the possibility to control the interface between the metal layers since they are all deposited within the same vacuum step. A drawback however is the restriction to particular layouts since all structures appear multiply on the substrate. An example for a lithographic mask used for the fabrication of atomic-size contacts of ferromagnets with superconducting leads is shown in Fig. 6 and an Al-Co-Al sample, prepared with a similar mask in shadow evaporation technique in Fig. 7.

4. Computations of structures and conductance in nano-wires

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The stability and electronic properties of wires on nanometer length scales have been studied by experimental and theoretical methods recently \(^1\)\(^-\)\(^7\). Atomic size Au-wires are studied by experimental methods in Konstanz in the group of E. Scheer \(^8\)\(^-\)\(^10\). In such studies the wires are stretched down to single-atom contacts.

The electronic and structural behavior of these systems is not yet understood entirely on a microscopic level. In our group we have studied \(^1\)\(^1\) the stretching of Au-wires by molecular dynamics methods applying stretching forces in one spatial direction. In computations with Lennard-Jones particle-interactions single atom contacts and shifts of atomic layers were found, but no formation of atomic chains. Stretching wires with “effective medium”-particle interactions (EMT) however resulted in structures with single atom contacts as well as atomic chains, see Fig. 1. This feature of the EMT potentials in the literature is sometimes attributed to the fact that the binding energy per particle is dependent on the number of neighboring atoms. In the molecular dynamics simulations a Nose-Hoover thermostat was used to avoid the heating of the wire during the stretching process.

The conductance in these systems was then studied by a combination with “tight-binding”-methods \(^1\(^2\). In the computations the electric current through a nanocontact can be decomposed in single channels and conductance

*Fig. 1: Structures in Au-wires upon stretching in z-direction and resulting conductance \(^1\(^1\).*
curves can be found for different stretching distances of the electrodes. During the stretching process the wire is thinning and the smallest effective diameter along the wire can be computed. The conductance in units of the "conductance quantum" $G_0 = 2e^2/h$, the contributions of different channels to the conductance and the smallest diameter (dotted red line) are shown in Fig. 1 for different stretching lengths of the wire. The conductance "plateaus" at $G/G_0 \approx 1, 1.6, 2.6, 3.6$ are close to the experimental values $^9)$. The conductance fluctuations however seem to be slightly larger compared to the experiment.

The current through the contact depends mainly on the wire atoms and the atomic configurations at the smallest diameter. Interestingly however the atomic configurations in the vicinity of the location of the smallest diameter have a significant contribution to the conductance as well. Further studies are planned.

(11) M. Dreher, Diplomarbeit, Universität Konstanz (2002)
5. Thickness dependence of the magnetic anisotropy in CoPt$_3$-films on WSe$_2$

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A promising approach to overcome the areal density limit for magnetic recording imposed by superparamagnetism in conventional longitudinal magnetic media is the use of perpendicular media with high perpendicular magnetic anisotropy (PMA). In particular, Co-Pt alloys are very interesting materials showing the required properties.

The relations between structural and magnetic properties of nanostructured CoPt$_3$(111)-films has been shown in previous articles. The main result is, that the magnetic anisotropy can be tuned by modifying the structural parameter of long-range ordering (LRO). Strictly speaking, the recommended perpendicular magnetic anisotropy can be achieved even at room temperature (RT) on the substrate WSe$_2$. In this case we found no LRO but strong PMA which might be explained by Co clustering induced by the substrate surface. On the other hand, codeposition at temperatures higher than 150°C cause LRO that leads to an easy axis in the film plane.

In this report the dependence of LRO, PMA on film thickness will be discussed. For this purpose we produced several CoPt$_3$-films on WSe$_2$ with different thicknesses (10 Å, 30 Å, 50 Å and 100 Å) at RT and 200°C.

Whereas a CoPt$_3$-film deposited at RT shows no LRO, independent of film thickness, the LRO-parameter for a CoPt$_3$-film deposited at 200°C decreases slowly with thickness (see Fig. 1).

\[ H \text{[kOe]} \]

**Fig. 1:** Thickness dependence of the chemical ordering parameter for CoPt$_3$(111) films on WSe$_2$ deposited at 200°C.

Fig. 2 shows hysteresis loops, measured by MOKE for different thicknesses and deposition temperatures, RT and 200°C. Note that films with a thickness of 10 Å show no Kerr-rotation due to the limited sensitivity of the used microscope. For the RT samples the easy axis of magnetization switches from out-of-plane to in-plane for a critical film thickness of about 60 Å.

The easy axis for films deposited at 200°C rotate from in-plane to out-of-plane directly correlated to the decrease in LRO (see Fig. 1).

![Hysteresis Loop](image)

**Fig. 2:** MOKE- hysteresis loops for films with different thicknesses deposited at a) room temperature and b) 200°C.

To determine the magnetic anisotropy energy, SQUID-measurements have been performed for 30 Å and 90 Å thick CoPt$_3$-films deposited at RT. We found an anisotropy energy \( K_{\text{eff}} = K_u - 0.5\mu_0M_S^2 \) (\( K_u \): uniaxial anisotropy, \( M_S \): saturation magnetization) of +0.15 MJ/m$^3$ and −0.04 MJ/m$^3$ for the 30 Å and 90 Å film as shown in Fig. 3. In this case positive values indicate out-of-plane while negative values indicate in-plane magnetization. So far the SQUID measurements confirmed the results obtained by MOKE. In order to study the influence of the used substrate surface, we produced simultaneously 30 Å CoPt$_3$ film on WSe$_2$ (0001) and on Pt(111) at RT. As expected the CoPt$_3$ film grown on Pt does not show any magnetic anisotropy, which proves that the growth conditions on WSe$_2$ play a decisive role for the observed magnetic properties (see inset in Fig. 3).

Furthermore Fig. 4 shows the uniaxial magnetic anisotropy energy as a function of deposition temperature for
30 Å thick CoPt$_3$-films grown on WSe$_2$ and for comparison a thick CoPt$_3$ film grown on Pt (111). We found that the maximum of the anisotropy energy is shifted by at least 400°C by simply changing the substrate. Above 200°C the uniaxial magnetic anisotropy in thin CoPt$_3$-films grown on WSe$_2$ vanishes completely.

![Fig. 3: SQUID-hysteresis loops for an 30 Å and 90 Å thick CoPt$_3$-film, deposited at RT on WSe$_2$. The films have been measured in parallel and perpendicular geometry.](image1)

![Fig. 4: Temperature dependence of the uniaxial magnetic anisotropy energies for 30 Å thick CoPt$_3$-films and for comparison 3000Å thick CoPt$_3$-films grown on Pt(111).](image2)

PEEM experiments (photo electron emission microscopy) give access to the morphology of the magnetic domains. Fig. 5 shows the magnetic domain pattern of 30 Å and 60 Å thick CoPt$_3$-films, both deposited at RT on WSe$_2$.

![Fig. 5: PEEM-images of a 30 Å and 60 Å thick CoPt$_3$-film grown on WSe$_2$(0001) at RT.](image3)

Only two different brightness steps can be observed in the images indicating again out-of-plane magnetization in agreement with the SQUID data. For the thicker film the smaller domains superimpose the larger domains. The reduction of the domain size reduces the magnetic energy in a way that the out of plane magnetization is stabilized.

6. Alloy formation by laser annealing of Co/Cr-multilayer systems

A. Barth, M. Albrecht, F. Treubel, M. Maret, U. Mazur and G. Schatz

Perpendicular magnetic anisotropy is a property occurring in certain magnetic thin film materials that is a promising way to permit higher areal storage densities of hard disks than conventional longitudinal recording. Alloys consisting of magnetic materials showing perpendicular magnetization have been investigated intensively in the past few years in our group. CoPt3 [1], Co3Cr [2] and CrPt3 [3] have been grown epitaxially on WSe2 and their magnetic properties examined.

In this experiment the formation of alloys in a thin film by irradiation of multilayered structures with a laser beam of high intensity was investigated. The technique of laser annealing is well known and is commercially used for more than 10 years now, mainly in order to smoothen Si-annealing is well known and is commercially used for more than 10 years now, mainly in order to smoothen Si-surfaces. Very short pulses (FWHM: several ns) of a high intensity laser beam lead to high heating and cooling rates (in the order of 10¹¹ K/s) melt the thin film, which recrystallizes epitaxially afterwards.

Multilayer structures were deposited at room-temperature on a (4x4)-reconstructed Pt(111) buffer, that was grown epitaxially before at 650 K on a Al₂O₃(0001)-substrate. The deposition rates ranged from 0.5 Å/s to 1.0 Å/s. The overall film thickness was in a range of 200 Å to 260 Å. The thickness of the single layers was chosen in a way to get the same ratio of atoms of Co and Cr as in the Co₃Cr-alloy, usually 9 monolayers (ML) Co and 3 ML Cr, repeated 10 times. Moreover, Cr/Co multilayers with 15 or 20 bilayers of 1 ML Cr and 3 ML Co have also been prepared.

During deposition the growth was followed by RHEED (Reflection High Energy Electron Diffraction) analysis and a fast relaxation of the lattice parameter was observed (s. Fig. 1) while depositing the Cr-layers indicating a high mechanical stress in these layers. This is in accordance with the relatively high lattice mismatch of 12.8 %. It is also an indication for growth in the Kurdjumov-Sachs-orientation of the pseudo-hexagonal bcc(110)-surface of the Cr on a hexagonal hcp(0001) surface of the underlying Co-layer.

In Fig. 2 a typical AFM-image of the surface is shown together with a height profile across two grains. The films show a granular surface with grain sizes of about 10 nm. The overall roughness amounts less than 1 nm. Both observations are in accordance with the diffraction patterns received by RHEED.

![Fig. 2: Surface structure of a Co/Cr-multilayer grown on a Pt(111)-buffer on Al₂O₃. The height profile on the right is taken along the short line the upper left corner in the AFM-picture.](image)

The granular structure is a result of the high lattice mismatch and the low deposition temperatures. From x-ray diffraction (XRD) measurements it was found that the multilayer structure is not of a good quality, i.e. the interfaces are relatively rough and thereby the diffraction patterns due to the superstructure are weak. Another reason for the granular structure is that Cr prefers to grow in the Volmer-Weber mode on Co [4].

The magnetic behavior and the magnetic domains of the unirradiated samples were examined by SQUID and MFM and later on compared to results after laser annealing.

The multilayers show an in-plane magnetization and an anisotropic behavior. The coercivities range from Hₑ = 110 Oe to 281 Oe with the applied field pointing perpendicular to the surface and Hₚ = 95 Oe to 112 Oe in parallel orientation, depending on the overall film thickness. The magnetic domains form an irregular stripe structure, similar to films of pure Co. The stripe domains are about 80 nm to 100 nm wide (s. Fig. 3).

The samples were irradiated with short laser pulses at high intensities and then the measurements by AFM, MFM, SQUID and XRD were repeated. The granular structure of the surface shown in Fig. 2 vanishes and flat areas are observed with trenches of up to 5 nm depth. This indicates that the surface was melted and then recrystallized again. This is a typical effect of laser annealing. Possible reasons for the appearance of the trenches are evaporation of material or that the recrystallization does not proceed equally fast all over the surface. The magnetic do-
main structure changes dramatically. The initially irregular stripes (Fig. 3a) form hexagonal patterns (Fig. 3c) that might be induced by the hexagonal structure of the substrate. Their width declines to 60 nm to 80 nm, what corresponds to a reduction of 20%.

If the change of the magnetic domain structure is driven by the influence of the hexagonal surface of the substrate it must be checked in further experiments on substrates that own i.e. a cubic surface symmetry.

Measurements by SQUID were performed in order to investigate the change in the magnetic behavior of the irradiated sample (Fig. 4). For this, small samples with 3.5 x 3.5 mm² surface area were produced and then illuminated by a laser beam with a diameter of 3 mm, so most of the sample was covered. The dependence on the intensity was investigated and has shown that until a critical intensity from which on the film gets destroyed the anisotropy changes gradually towards the behavior of an alloy film. The Co₃Cr alloy shows an isotropic magnetic behavior ²), while the multilayer system has an in-plane easy axis. Fig. 4 shows a typical hysteresis loop recorded before and after Laser annealing. The field was applied perpendicular and parallel to the film plane.

Fig. 3: (a) Magnetic domains of an as-prepared Co/Cr-multilayer surface. The height profile is taken along the black line. (b) Typical surface topography of an annealed Co/Cr-Multilayer. The height difference on a scale of 500 nm amounts less than 8 Å (see graph on the right). (c) Magnetic domains of an annealed surface.

Fig. 4: Hysteresis loops of a Co/Cr-multilayer before and after laser annealing. The sample was treated with two laser pulses with the intensities 310 mJ/cm² and 290 mJ/cm².

In further experiments samples consisting of Co/Pt multilayers were investigated, with an aspect ration Co/Pt of 1:3 monolayers. This composition is very interesting, because the multilayer system shows a very strong perpendicular magnetic anisotropy. Again a flattening of the surface is observed, with a magnetic anisotropy similar to an alloy film after Laser annealing. Again the magnetic anisotropy changes stronger with increasing laser intensity. Similar samples of 3 ML Cr and 9 ML Pt were prepared and changes after laser annealing investigated. The nonmagnetic multilayer system shows after the irradiation with the high intensity laser pulses an in-plane magnetization. This indicates clearly that the materials at least partially mix and form a ferrimagnetic CrPt₃ alloy ³).

(1) M. Albrecht et al., Europhys. Lett. 56 (2001) 884
(2) Annual report 2000, Universität Konstanz, p. 12
7. **CoPt$_3$-films on PTFE (polytetrafluoroethylene)**

*N. Apetroaie, U. Mazur, A. Liebig, B. Riedlinger, A. Barth, H. Wider and G. Schatz*

Homogenous CoPt$_3$-films have been investigated for some time and used for magnetic data storage for years. Granular CoPt$_3$ films on the other hand can be grown on van-der-Waals surfaces utilizing Vollmer-Weber growth mode. WSe$_2$ is a very appropriate substrate to obtain interesting granular films $^1$. In our experiment a new substrate is tested, polytetrafluoroethylene (PTFE), commonly known as Teflon.

PTFE is, due to the very stable F-C-bonds, nearly completely chemically inert and has therefore found a lot of applications as insulator and lubricant. However, PTFE surfaces are - as expected - by far not atomically flat as WSe$_2$. Since PTFE is an insulator, STM measurements are not possible. Also the PTFE surface is very rough, so topography measurements with an AFM are not very informative - it is not so easy to distinguish between substrate and deposited material. Nevertheless it is possible to get results using the AFM phase information.

CoPt$_3$ was deposited by co-evaporation of one part cobalt and three parts platinum with an average thickness of 30 at 150 and a flux of $\approx 0.1$ Å/s.

Fig. 1 shows an AFM phase image of the covered sample. Comparison with the pictures of the uncovered substrate allows to identify the grainy areas as uncovered PTFE. The Co/Pt material seems to accumulate in the depressions of the substrate and flattens therefore the surface.

![AFM phase image indicating two different phases.](image)

**Fig. 1:** AFM phase image of the partially covered surface at a nominal coverage of 30 Å. The covered area appears dark.

Figure 2 shows on an enlarged scale - at a scan range of 1 μm - the granular structure of the Co/Pt-film. As already mentioned, such a growth was expected due to the chemical inertness of the substrate. It is similar to the nanostructures and granular films on WSe$_2$ $^1$.

However, higher resolution phase images of the covered areas (figure 3) show a different behavior as the films on the layered semiconductor. The phase information shows different domains, in contrast to the topography, which is very smooth. This points to a phase-separation in Co and Pt rich phases.

![Granular surface morphology of the Co/Pt-film.](image)

**Fig. 2:** Granular surface morphology of the Co/Pt-film.

The phase diagram $^2$ shows only a composition range of about 10% where CoPt$_3$ is stable. Thermodynamically stable are both the CoPt$_3$ phase and a mixture of CoPt and Pt. Ordered CoPt$_3$ on WSe$_2$ at temperatures 400 below the ordering temperature of the bulk material is surprising and it is now interesting to find a better understanding of the different behavior for the different substrates.

![AFM phase image indicating two different phases.](image)

**Fig. 3:** AFM phase image indicating two different phases.

SQUID measurements of the magnetic properties of the film are currently under way. A comparison with the films on WSe$_2$ should give some information whether the hypothesis of the phase separation between CoPt and Pt is correct.

It would also be interesting to study the CrPt$_3$ system on PTFE to have a comparison to the systems on WSe$_2$.

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2. T. Massalski (ed.), *Binary alloy phase diagrams* (ASM international, 1996)
8. Magnetization dynamics of thin Co films under ns laser annealing

B. Böck, P. Leiderer and B.-U. Runge

Recently there have been several attempts to observe ferromagnetism in the liquid phase. In nature ferromagnetism is found only in solids, since for all the systems known so far the melting temperature \( T_m \) is always higher than the Curie temperature \( T_C \). It might be possible, however, to obtain ferromagnetism in a liquid by sufficiently deep supercooling of the melt. All previous studies in that direction have been carried out using an electromagnetic levitation technique, and magnetic ordering could be observed indeed in sufficiently undercooled melts of cobalt alloys close to the critical point. However up to now there are only limited possibilities to make measurements below \( T_C \), mainly because high cooling rates are required for substantial supercooling, whereas for levitated samples cooling rates above 100 K/s are hard to achieve.

We use here an alternative approach by applying intensive nanosecond laser pulses to melt thin (40 nm) cobalt films on glass or sapphire. Because of the high heating and cooling rates on the order of \( 10^{11} \) K/s it is possible to reach the regime of a highly (more than 400 K) undercooled melt. In our measurements the melting and re-solidification as seen in reflectivity and magnetization are studied on a nanosecond time scale. Simultaneously the thermal radiation is recorded to relate the magnetic properties to the temperature of the sample.

The experimental setup is shown in Fig. 1. The sample was a 40 nm thick Co film on quartz glass with a 3 nm Ti buffer layer. The temperature was calculated from the thermal radiation measurement assuming Planck’s black body radiation and constant emissivity of the Co film. The plateau in the falling slope relates to the phase transition from liquid to solid. At sufficiently low pulse energies the plateau appears at a temperature smaller than the melting temperature \( T_m = 1768 \text{ K} \). This corresponds to undercooling.

In Fig. 2 the temperature of the sample during laser annealing is shown for various intensities of the heating pulse, which has a FWHM of 15 ns and reaches the sample at the time \( t = 0 \). The sample was a 40 nm thick Co film on quartz glass with a 3 nm Ti buffer layer. The temperature was calculated from the thermal radiation measurement assuming Planck’s black body radiation and constant emissivity of the Co film. The plateau in the falling...
slope corresponds to the phase transition from liquid to solid and occurs due to the latent heat of this phase transition. For high pulse energies the temperature of the substrate increases significantly. Therefore the cooling rate is reduced, there is no undercooling and the plateau appears at the melting temperature ($T_m = 1770$ K). This known temperature was used as a fixpoint for the conversion between thermal radiation and temperature. At sufficiently low pulse energies, if the energy is just high enough to melt the Co film, the plateau appears at a lower temperature. This relates to undercooling of the liquid Co film.

Reflectivity:

Kerr signal:

Thermal radiation:

Fig. 4: Reflectivity, Kerr signal and thermal radiation for various intensities of the heating pulse. For a clearer representation the Kerr curves are inverted as compared to Fig. 3. Melting sets in at about 200 mJ/cm².

Fig. 3 shows reflectivity, Kerr signal and thermal radiation in a typical annealing experiment. The reflectivity drops with rising temperature. As the film cools down again there is a small jump in the reflectivity at the phase transition from liquid to solid. Simultaneously there is a plateau in the thermal radiation. The magnetization vanishes as long as the film is above the Curie temperature. Therefore the temperature at the reappearance of the magnetization is the Curie temperature.

The behavior of reflectivity, Kerr signal and thermal radiation for various intensities of the heating pulse is shown in Fig. 4. For a clearer representation the Kerr curves are inverted in this graph. The reflectivity curves exhibit a minimum and the thermal radiation a maximum which becomes more and more pronounced as the pulse energy and therefore the maximum temperature of the sample rises. At high pulse energies the jump in the rising slope of the reflectivity curve and the plateau in the thermal radiation relate to the phase change from liquid to solid. For low pulse intensities a peak in the Kerr signal emerges, which grows with rising energy. As soon as the energy is sufficient to reach the Curie temperature ($T_C = 1388$ K) the heated film is fully demagnetized and the Kerr signal is maximal. Further increase of the pulse energy increases the time during which the film remains above the Curie temperature.

In Fig. 5 the temperature at the reappearance of the magnetization (Curie temperature) and the temperature at the phase transition from liquid to solid as defined in Fig. 3 are compared for various intensities of the heating pulse. For high pulse energies the phase transition occurs at the melting temperature $T_m$. For sufficiently low pulse energies it occurs for temperatures lower than the Curie temperature $T_C$. We take this as a first indication of ferromagnetism in supercooled liquid Co. Experiments to corroborate this hypothesis are under way.

(2) C. Bührer, M. Beckmann, M. Fähnle, U. Grünewald and K. Maier, JMMM 212 (2000) 211
9. Setup of a Kerr magnetometer (MOKE)

U. Mazur, B. Riedlinger and G. Schatz

Magnetic thin films are produced in a MBE apparatus and are characterized with methods like scanning tunneling microscopy (STM), atomic force microscopy (AFM) and magnetic force microscopy (MFM). For measurements of the magnetic properties a superconducting quantum interference device (SQUID) is used, but those measurements are time consuming and are technically complex, furthermore the sample cannot be transferred to the SQUID under vacuum conditions and has to be covered by a protective layer. Therefore we decided to integrate a MOKE apparatus into the vacuum chamber in order to measure the magnetic properties of our films in situ.

To obtain absolute values we have to calibrate the MOKE measurements using the saturation magnetization obtained by SQUID-measurements.

The magnetic field $B_L$ is calculated by

$$B_L = \frac{NI\mu_0}{d + \frac{k_S}{\mu} \left(2l_p + l_y\right) A_y A_p}$$

with $NI = \text{ampere-turn}$; $\mu = \text{susceptibility}$; $d = \text{pole gap}$; $k_S = \text{correction factor}$; $l_p$, $A_p$, $l_y$, $A_y = \text{length and area of pole tip and yoke}$, respectively.

The magnetic field is determined mainly by the ampere-turn and the gap between the pole tips. Our setup has a pole gap of 20 mm and an area of the tips of 3.14 cm². Therefore we estimate a maximum field of 1.4 Tesla. The solenoids consist of an aluminum body furnished with 1200 turns. The wire is WSO of three millimeter in diameter, allowing a working temperature of up to 200°C. Therefore no cooling is necessary.

The measuring chamber is designed as a cube with DN 63 CF flanges. To pick up the weight of the solenoids, cores and the yoke – totaling around 300 kg – special flanges had to be designed to relieve the braze joint between the V2A CF flanges and the soft-iron (armec) core. At the end of the core, which has a centrical hole, a DN 16 CF flange is hard soldered. On this a V/P suprasil view port is mounted using a reducer flange 16/40. We decided not to use a DN 16 viewport in order to prevent problems due to the heat of the coils. Inhomogenities of the glass are reduced by the greater diameter.

The apparatus is assembled separately to adjust the optical pathways. As a light source a 10 mW laser diode is used. We will use a Lock-in amplifier, the details of the modulator and detector design are in progress.
10. Muon-spin-relaxation study of the magnetic penetration depth in MgB$_2$

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The recent discovery of superconductivity at 39 K in the binary compound MgB$_2$\textsuperscript{1)} has triggered an enormous scientific effort in order to understand the mechanism that leads to such a high critical temperature in a seemingly classical superconductor. Based on band structure calculations Kortus et al.\textsuperscript{2)} conclude that a sizeable electron phonon coupling in combination with the high phonon frequencies due to the light mass of boron can reproduce the high critical transition temperature. The observation of a large B isotope effect confirms the important role of the phonons for superconductivity in this compound\textsuperscript{3,4).}

Subsequently, a large body of experimental work focused on the study of the symmetry of the superconducting order parameter. Measurements of the $^{11}$B nuclear spin lattice relaxation rate, inelastic neutron scattering measurements, specific heat, high resolution photoemission and scanning tunneling spectroscopy are strongly in favor of a conventional BCS s-wave pairing state with moderately strong electron phonon coupling. Even if superconductivity is phonon mediated an analysis beyond a simple isotropic model may be required. Two different order parameters arising from two different sheets of the Fermi surface were calculated by Liu et al.\textsuperscript{5)} and these predictions are in good agreement with the analysis of specific heat and Raman data in terms of a two-gap model (see e.g. Ref. 6).

Here we report our experimental data on the magnetic penetration depth $\lambda$, which is inversely proportional to the square root of the superfluid density. The temperature dependence of $\lambda$ is a measure of low-lying superconducting quasiparticle excitations and therefore contains information about the symmetry of the superconducting order parameter. We measured $\lambda$ using the transverse field muon spin rotation technique (TF-$\mu$SR). The depolarization of the muon spin precession provides a measure of the field distribution within the vortex state and hence of the magnetic penetration depth $\lambda$. Figure 1 displays the temperature dependent TF-$\mu$SR depolarization rate $\sigma$ (~$1/\lambda^2$) at $H_{ext} = 0.6$ T. It occurs that $\sigma(T)$ is almost temperature independent below 5 K, while it exhibits a kink around 7 K where it suddenly begins to decrease with increasing temperature. Such a trend can be rather well reproduced with a two-gap model that assumes that the superconducting carriers reside in two different energy bands. The coupling between these bands needs to be sufficiently weak such that the magnitude of the energy gaps is different while they both appear simultaneously at the $T_c$ that is determined by the larger gap. Evidence in favor of the two-gap model has been recently obtained by specific heat and by Raman measurements. The thick solid line shows the best fit to our experimental data using the two-gap model. The obtained values of the fitting parameters are $\Delta_1 = 6.0$ meV ($2\Delta_1/k_BT_c = 3.6$), $\Delta_2 = 2.6$ meV ($2\Delta_2/k_BT_c = 1.6$) and $\gamma = 1.5 - 2$. These values are in reasonable agreement with previous results that have been obtained by applying the two-gap model to experimental data (see e.g. Bouquet et al. and references therein). Taking the fitted low temperature value for $\sigma(T\rightarrow0) = 7.9$ $\mu$s$^{-1}$ we derive a value of about 100 nm for the magnetic penetration depth.

![Fig. 1: Temperature dependence of $\sigma$ for an applied external field of 0.6 T. The solid line shows the best fit using a two-gap model. Also shown by the dotted line is a fit assuming an isotropic single gap.](image)

(4) D. G. Hinks et al., Nature 411 (2001) 457
(5) A.Y. Liu, I.I. Mazin and J. Kortus, cond-mat/0103570
(6) F. Bouquet et al., cond-mat/0107196
11. Slow muon experiments on a superconductor/ferromagnet YBa$_2$Cu$_3$O$_y$/SrRuO$_3$ superlattice

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It has previously been shown that the competition between ferromagnetic (FM) and superconducting (SC) order in superlattices of a YBa$_2$Cu$_3$O$_y$ high-$T_c$ cuprate superconductor and ferromagnetic SrRuO$_3$ or La$_{2/3}$Ca$_{1/3}$MnO$_3$ involves a surprisingly large length scale of several hundred Ångstroems far in excess of the SC coherence length $\lambda$. Furthermore, the mutual interaction between SC and FM not only leads to a strong suppression of both phenomena but also gives rise to a metal/insulator transition that is rather unexpected since the individual layers are metals. Field cooled and zero field cooled DC magnetization measurements obtained at 5 Oe for the YBa$_2$Cu$_3$O$_y$ (400 Å) / SrRuO$_3$ (200 Å) superlattice used in our study are displayed in Figure 1. The zero field curve shows a large diamagnetic shift below $T_c \approx 65$ K, whereas the ferromagnetic transition at $T_{\text{curie}} \approx 120$ K is more clearly seen in the field cooled curve.

![Figure 1](image1.png)

**Fig. 1:** Temperature dependence of the magnetization in an external field of 5 Oe. The zero field curve shows a large diamagnetic shift below $T_c \approx 65$ K, whereas the ferromagnetic transition at $T_{\text{curie}} \approx 120$ K is more clearly seen in the field cooled curve.

Another remarkable observation concerns the temperature dependence of the magnetization which exhibits a dramatic increase in the SC state. (see Figure 2). In marked contrast to the naive expectation that the FM order parameter should be (at least) partially suppressed at the onset of SC inside the YBa$_2$Cu$_3$O$_y$ layers, the field-cooled magnetization exhibits a very strong and sudden increase below $T_c$.

In order to shed more light on this interesting phenomenon we have employed the technique of low-energy muon-spin-rotation (LE-µSR) and investigated the distribution of local magnetic fields inside an YBa$_2$Cu$_3$O$_y$ layer. Figure 2 presents weak transverse field data (at 100 Oe) at an implantation energy of 8 keV where all muons are stopped within the first YBa$_2$Cu$_3$O$_y$ layer.

For $T_{\text{curie}} = 120$ K $> T > T_c = 65$ K only a moderate depolarization rate is observed, which may arise from the stray fields due to the magnetic domain boundaries of the SrRuO$_3$ layers. Right below $T_c$, however, the depolarization rate exhibits a strong and rather sudden increase. In fact, already at 30 K the depolarization has become so rapid that less than 50 % of the asymmetry remains after the first 10 ns which are not accessible with our present setup. The increase of the depolarization rate below $T_c$ signals a corresponding increase of the magnetic moments within the superconducting YBa$_2$Cu$_3$O$_y$ layer. Certainly it cannot be explained due to the formation of a flux-line-lattice in the SC state. This result agrees very well with the observed increase of the spontaneous magnetization in dc-magnetometry and implies that the magnetic coupling via the YBa$_2$Cu$_3$O$_y$ layer is strongly enhanced in the SC state. Presently we have no definite explanation for the observed effect which seems to contrast general opinion that superconductivity tends to reduce magnetic order.

![Figure 2](image2.png)

**Fig. 2**: Left: Temperature dependence of the magnetization in different external fields. The magnetization shows a dramatic increase below the superconducting transition temperature. Right: Transverse field LE-µSR data obtained after implanting the muons into the YBa$_2$Cu$_3$O$_y$ layer.

12. Snapshots of magnetic flux penetration on a nanosecond timescale

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Flux dynamics in superconductors has been a topic of continuous interest for many years. A variety of flux patterns were observed and thoroughly studied in superconductors with high critical current density 1). Almost the first of these studies revealed a magneto-thermal flux jumps instability of the Bean state. This instability is now well understood and effective methods are developed to obtain the stability margins 2,3). Magneto-optics using a pulsed laser as illumination source allows to carry out studies with a spatial resolution of a few μm and a temporal resolution in the subnanosecond range. With this technique earlier experiments studied the magnetic flux pattern of an dendritic avalanche 4). We greatly improved the temporal and spatial resolution and extended our investigations to study general flux patterns in superconducting films in a perpendicular magnetic field. Depending on the external magnetic field and sample temperature we observe two different regimes how magnetic flux penetrates into a superconductor: in the form of a homogeneous flux gradient, or as ultrafast dendritic flux avalanches with velocities of up to 50 km/s, if initiated by a short laser pulse. In our setup the local rate of change in the magnetic field can exceed 10⁸ T/s.

In our experiments we have used YBa₂Cu₃O₇₋ₓ (YBCO) films with four different thicknesses (100 – 690 nm), grown on a SrTiO₃ substrate by thermal reactive co-evaporation 5). X-ray diffraction and REM measurements showed the c-axis of the films to be perpendicular to the substrate. The superconducting transition temperatures were between Tc₁ = 86 K and Tc₂ = 90 K with critical current densities between jₐ = 2 × 10⁶ A/cm² and jₐ = 4 × 10⁶ A/cm² at T = 77 K.

To visualize the c-component of the magnetic flux distribution a Bi-doped Yttrium Iron Garnet (YIG) film on Gadolinium Gallium Garnet with in-plane anisotropy is used as magneto-optic (MO) layer 6), which is mounted on top of the superconductor 7).

To achieve a high time resolution, a pump-probe technique can be used in combination with a Ti:sapphire pulse laser (τ = 150 fs) as an illumination source. One part of the laser pulse is used to trigger an event, whereas a second part is fed through an optical delay line of up to 150 ns and then used to take a snapshot of the flux distribution. Additionally a conventional lamp can be used to take non time resolved pictures. The YIG film used in our setup allows to obtain a time resolution of about 200 ps 8). This time resolution is sufficient to investigate the flux penetration velocity in superconductors in all situations we found.

Each experiment is done in the following way: First, the YBCO film is zero field cooled below Tc₁. After reaching a stable temperature an external magnetic field Bₐ is perpendicular to the sample surface is applied, and then the laser pulse is triggered.

Due to the field enhancement magnetic flux penetrates into the superconducting film from the edges. The shielding currents prevent the magnetic flux from penetrating into the inner part of the superconductor. The first part of the laser pulse is now used to apply a local magnetic field. This is done by focusing the laser pulse with a cylindrical lens onto the film from the substrate side of the sample. Hereby a line with a width of 50 μm is heated above Tc₂, dividing the quadratic sample knife-like into two rectangular superconducting regions of equal size. Magnetic flux instantaneously (within our experimental time resolution limit) fills the line and the flux density is increased up to a constant value. The time needed to reach this value is smaller than 12.5 ns. At the same time the magnetic flux starts to penetrate perpendicular to the line into the superconducting film. Figure 1 shows the flux profile at 30 K after a time delay of 67.8 ns; additionally the final state is shown.

![Magnetic flux profiles after a time delay of 67.8 ns and of the final state (T = 30 K, Bₐ = 15.2 mT).](image)

We found that homogeneous flux penetration does not develop under every condition, but is restricted to an area in the T/Tc₁ vs. Hₐ/Tc₁ plot as shown in Fig. 2. Dendrites only develop above a certain magnetic field which depends on the temperature. Above a “critical” temperature no dendrites are formed even if one goes to large magnetic fields. This observation is in good agreement with other experiments where instead of the local heating with a laser an external perpendicular magnetic field was swept to nucleate the dendrites 9,10).

The spreading velocity of the dendrites depends on the film thickness but not on the temperature or the external field. The velocity is proportional to the reciprocal film thickness 1/d, i.e. in thin films the velocity of penetration...
is higher.

**Fig. 2:** Shown here is a diagram indicating the two distinct regions of flux dynamics.

Its velocity is on the order of $10^4$ m/s and after a couple of nanoseconds at least one order of magnitude higher than the penetration velocity of the homogeneous flux front and much higher than the speed of sound in the medium (Fig. 3). The dendritic patterns show different details for every new avalanche, however the general phenotype remains the same. The starting points of the avalanches are usually the same, if the external conditions (e.g. the laser focus) are not changed.

**Fig. 3:** Dependence of the penetration velocity on the film thickness.

The double structure of the heated line as seen in Fig. 4 is only observed if dendrites are formed. In the homogeneous regime no decrease of flux in the center of the heated line is found. One explanation of this shape might be that the flux in the middle of the line drains off into the dendritic structure, but no or little flux is flowing from outside into the sample. The overall behavior can be explained qualitatively with slight local variations in the critical current density of the YBCO-film. At places with lower $J_c$ the avalanches are formed. Once the shielding current paths are curved at a location, magnetic flux can penetrate there more easily into the superconductor due to Biot-Savart's law. Moving vortices leave behind a trail of elevated temperature supporting motion of nearby vortices, which in turn contribute to the heating and may lead to large scale avalanches of depinned flux lines. This thermal runaway, where magnetic energy is converted to thermal energy, causes this instability. The damping mechanism is the heat conductance to the substrate. If the external field is too high, permanent damage to the sample may occur, since the sample is heated above the damage threshold. This is of significant importance for applications of HTSC films, e.g. as current limiters.

**Fig. 4:** 3D presentation of magneto-optical images of the flux density distribution after 50 ns and of the final state at 10 K with an applied external field of 30 mT. The size of the images are $2.28 \times 1.52$ mm$^2$ and the maximal magnetic field density is 95 mT.

In conclusion we have studied the dynamics of magnetic flux penetration in superconducting YBCO films on a nanosecond timescale. The magnetic field was applied by heating a narrow line of the sample with a laser pulse while exposing it to an external perpendicular magnetic field, which made it possible to apply an external field on an ultra short time scale. In the homogenous penetration regime the velocity depends on the sample temperature and on the magnetic field. This is in contrast to the dendritic regime where the penetration velocity only depends on the thickness of the sample and not on the temperature or applied field.

We would like to thank E. Il'yashenko for providing the magneto-optic garnet layers.

8. B.-U. Runge et al., to be published
9. T.H. Johanson et al., to be published
13. Interlayer exchange coupling in Fe/Ag/Fe studied by LE-µSR

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Since the first observation of antiferromagnetic coupling of Fe films separated by a Cr spacer by Grünberg et al. the interlayer exchange coupling (IEC) has been subject of intense research over the last few years. The discovery of oscillations in the IEC in a function of spacer-layer thickness by Parkin et al. has led to an increased interest in this field of research. Much experimental effort has been done to measure precisely the strength and period of the IEC in various systems and a remarkable agreement between theoretical results and measurements have been achieved. Nevertheless, the vast majority of the experimental techniques used to study the IEC probe the ferromagnetic layers and very little is known about the induced spin polarization in the non-magnetic layer which mediates the coupling.

Low energy muon spin rotation (LE-µSR) was used to investigate the oscillating spin polarization in the Ag layer of a 4 nmFe / 20 nm Ag / 4 nm Fe trilayer. With this sensitive method the magnetic field distribution in the spacer can be obtained with high precision and compared to theory.

The first approach to describe the IEC is the so-called RKKY model. Originally the RKKY interaction describes the coupling of localized magnetic impurities in a non-magnetic metallic host. The indirect exchange coupling between the magnetic ions is mediated by a spatially oscillating conduction electron spin polarization of the metal. By proper summation, the RKKY interaction can easily be extended to the coupling of two monoatomic magnetic planes embedded in a non-magnetic metal. The coupling can be related to the topology of the Fermi surface of the spacer material. According to this theory the period of the oscillation is determined by critical spanning vectors, qC, nested in the Fermi surface. Each of these spanning vectors lead to a different oscillation which have to be superimposed. The attenuation of the coupling is given by the curvature of the Fermi surface at the end points of qC.

Therefore, in the framework of the RKKY model, an effective coupling of the two magnetic planes through a non-magnetic spacer is described as:

\[ H = -J(d) \cdot \mathbf{M}_1 \cdot \mathbf{M}_2 \]

\[ J(d) \propto \sum p_i \frac{1}{d^{p_i}} \cos(q_c d + \phi) \]

Here, \( \mathbf{M}_i \) is the magnetization of the ferromagnetic layers, \( J \) the coupling constant, \( d \) the distance between the layers with the exponent \( p_i (p_i \leq 2) \). Following this approach, the expected field distribution experienced by the muon can be calculated assuming \( B(x) \sim J(x) \). We have convoluted the spatial field distribution, \( B(x) \), with the muon stopping profile, \( P(x) \), shown together in Fig. 1.

\[ \text{Fig. 1: Muon implantation profile } P(x) \text{ and calculated spatial field distribution } B(x). \]

\( P(x) \) has been calculated with the Monte Carlo Code TRIMSP for muons with an kinetic energy of 3 keV which we used in the experiment. In Fig. 2 the measured LE-µSR data together with the simulated probability function \( P(B) \) is shown. Detailed analysis is in progress but the main features of \( P(B) \) can already be explained by the RKKY model.

\[ \text{Fig. 2: LE-µSR data together with simulation based on the RKKY model.} \]

14. Influence of substrate material and particle shape on the near field distribution of nanoparticles on surfaces

O. Dubbers, H.-J. Münzer, M. Mosbacher, J. Graf, B.-U. Runge and P. Leiderer

The current trend in many branches of industry towards submicron structures requires new methods of surface structuring and has promoted a lot of research in recent years. As the traditional masking approach in optical lithography is limited to a minimal resolvable feature size of about half the wavelength, the Rayleigh diffraction limit, a lot of alternative structuring techniques have been developed.

Some of those methods are based on the application of optical near fields, and one of the first techniques suggested in this direction was the so-called FOLANT (focusing of laser light in the near field of a tip) \textsuperscript{1,2}. Here the tip of a scanning tunneling microscope (STM) is illuminated with a pulsed laser. By this method, structures with lateral dimensions below 30 nm and therefore well below the optical diffraction limit could be produced underneath the tip. It was proposed that the enhancement of the incoming laser field at the tip \textsuperscript{3} is responsible for the structuring. Therefore the setup seemed to be promising both for the study of field enhancement effects at sharp tips, a question of great interest in optics, and for the application to surface structuring.

![Fig. 1: Far field scattered intensity of 810 nm sized polystyrene spheres resting on substrates with different optical constants.](image1)

However, further investigations made clear that the structuring resulted from the thermal expansion of the tip and its subsequent mechanical contact with the surface rather than from field-induced effects \textsuperscript{4-6}. With regard to its application for structuring, the main disadvantage of the illumination of an STM tip is that the process is serial and allows only the production of one single structure per laser pulse.

Therefore, we changed to a technique involving the illumination of micron and submicron sized spherical particles which allows both the study of field enhancement effects and its application for a parallel nanolithography process. The field enhancement underneath the spherical particles results in ablation of the substrate wherever it is exposed to a sufficiently high energy density. Imaging of the ablation pattern leads to a lateral mapping of the field in the vicinity of the particle \textsuperscript{7,8}.

A comparison of those near field distributions after fs laser ablation with numerical simulations enabled a direct validation of the predictions obtained from Mie theory. As the colloidal spheres used in our experiments are commercially available for a broad size, this comparison was possible over a wide range of the so called size parameter \( \pi d/\lambda \), the characteristic parameter of the theory. The main result of these studies is that the calculations reflect the overall field distributions, but there is no quantitative agreement between the experimentally measured and numerically calculated field distributions.

A possible explanation for these findings might be the fact that the Mie theory is only valid for strictly spherical particles in homogeneous media. This ideal geometry, however, is not found in our experiments. Clearly the presence of the substrate should influence the field distribution in the particle/substrate contact area. Additionally, the particles’ shape is not spherical as they are deformed due to the acting van der Waals - forces.

![Fig. 2: Dependence of the far field scattering intensity on the particle shape.](image2)

Therefore, to investigate the influence of the substrate as well as deviations from the ideal case due to particle deformations, we have varied on one hand the substrate material over a broad range of the optical constants, and modified on the other hand systematically the particle shape by annealing. In addition to the near field imaging described above we have measured the scattered intensity in the far field, which is correlated to the near field distribution. For this purpose we collected the scattered light with a darkfield microscope into a spectrometer at an angle of 32° to the incident light.

In Fig.1 the scattered intensity in the far field of 810 nm sized PS particles on different semiconductors and
gold as substrate material are shown. Although for the substrate both the real and imaginary part of the optical constant change a lot, the shape of the observed spectra and the positions of the maxima, which are typical for the Mie theory, only shift by a small fraction in the size parameter. This result is supported by the observations of the near field distributions via local substrate ablation, where also only slight differences in shape of the ablated areas are visible.

Fig. 2 shows the far field intensity for increasing deformation of the particles. The spectra correspond to the particle shape in the box of the same color. As it can be seen on the right side of the image, the annealing leads to an increasing deformation of the particles up to a lenslike geometry, the radius of curvature was very precisely adjustable. Compared to the changes created by different substrate materials the influence of the particle deformation results in much more significant modifications of the scattered spectra. Some extrema totally vanish, others change their height, get much broader and shift by almost one size parameter.

These dramatic changes are also visible in the measured near field distributions. In Fig. 3, the ablation patterns under 320 nm sized PS particles on a silicon substrate are shown for different annealing times and thus increasing deformation. While for small deformations the near field distributions resembles a dipole like double structure as it is typical for small size parameters, this structure vanishes for larger deformations, gets visible again and changes into a spherical shape for large deformations.

The results presented here clearly show the importance of the substrate and the particle geometry for the field distribution at laser-illuminated nanostructures on surfaces. According to our results with respect to this the influence of the structure shape is more important than the optical properties of the substrate.

(2) K. Dickmann and J. Jersch, Laser und Optoelektronik 27 (1995) 76

Fig. 3: Mapping of the near field distribution of particles of different shape on a silicon surface. The ablation sites created by the illumination of the sample with fs laser pulses reflects the intensity distribution.
15. The effect of roughness on the $T_3$ - dewetting of molecular hydrogen

J. Angrik, M. Sohaili, J. Klier and P. Leiderer

Triple-point dewetting of noble gases on solid substrates like Au $^1$ is a well-known phenomenon which always happens below the bulk triple point $T_3$ of the adsorbed gas. One of the first theoretical approaches to the wetting-dewetting of solid substrates by noble atoms and molecules has been done by Gittes and Schick $^2$. In this theory the substrate is considered as an ideal surface (i.e., atomically smooth and so having a well-known lattice parameter) and the thickness of the adsorbed film is related to the substrate-adsorbate interaction strength $R$. However, experiments performed so far show stronger non-wetting, even when the interaction strength is reduced, e.g., by preplating $^3$. For $1.5 \leq R \leq 3$ complete wetting is expected in the solid phase $^2$, in contradiction to the experiment. But all practical substrates have a finite roughness and so one may ask about the role of the roughness profile of the applied substrate on the wetting property. In addition adsorption of impurity layers during the sample preparation and cooling down the cell may change the estimated values of the substrate-adsorbate interaction. Recently, a more realistic calculation has been done by Esztermann et al. $^4$, in which the roughness profile of the substrate is taken into account. The computed results of that investigation predict a significant variation of the film thickness on substrates with different roughness, i.e., the adsorbed film will be thicker on the smoother substrate, and for a certain range of substrate strength ($1.5 \leq R \leq 3$) it will diverge as the roughness goes to zero.

We use an ellipsometry setup, as shown in Fig. 1, to measure the $H_2$ film thickness on the Si substrate. The sample is mounted vertically in a Cu cell with windows for optical access to the sample surface. The whole assembly is placed inside an optical flow cryostat. A laser diode provides a very stable laser beam which passes through a polarizer and compensator before entering the cryostat. After reflection on the sample the beam leaves the cryostat, passes through an analyzer and is detected by a photodiode.

Fig. 2: Shown is the relative $H_2$ film thickness on Si and Au. The data points refer to average values of several cooling and warming runs. The triple point temperature of $H_2$ is 13.95 K. About $T_3$ the film is liquid well below it is solid. The thick wetted film, measured for $T > T_3$, is normalized to 1.

During measurements the optical components remain fixed. Instead of rotating compensator and analyzer (like in ordinary null-ellipsometry) the intensity of the light passing the analyzer is measured. Since the adsorption of hydrogen molecules on the substrate changes the polarization of the reflected beam, the thickness of the adsorbed film can be monitored.

Usually a measuring run is started by doing an adsorption isotherm of $H_2$ at 15 K, well above the triple point temperature. After reaching saturated vapor pressure the temperature is scanned in the range of 13 K to 15 K. Thermodynamic equilibrium is tested by performing different ramping speeds. It turned out that for ramping speeds less than 50 mK/min equilibrium is ensured.

In Fig. 2 the $T_3$ - dewetting of molecular $H_2$ on two different substrates, Si and Au, is shown. Note that the thickness of each film is normalized to its equilibrium film thickness in the complete wetting regime, i.e., at temperatures above 14 K. In Fig. 2 two different regions can be seen: i) for $T > T_3$ (13.95 K) the film thickness is large and
nearly constant for both substrates as expected for complete wetting of the liquid phase; ii) for \( T < T_3 \) triple point dewetting sets in being more pronounced for the relatively rough Au than for the smooth Si substrate. Since the \( H_2 \) van der Waals interaction with Au and Si, respectively, is similar, we interpret this result as a further confirmation that surface roughness contributes to the incomplete wetting of solid films below \( T_3 \).

For the results reported so far there might still be an impurity layer adsorbed on the Si surface. To overcome this problem we will in future measurements use Si substrates which are laser cleaned in-situ. In Fig. 3 it is demonstrated that the Si surface can reversibly be molten and recrystallized, which should result in an impurity-free substrate.

In conclusion, we have investigated and observed the effect of substrate roughness on \( T_3 \)-dewetting. The results are consistent with theoretical estimations \(^4\). In addition, we have used the technique of laser annealing to prepare more ideal surfaces, on which future measurements will be done.

This work was supported by the Deutsche Forschungsgemeinschaft.


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**Fig. 3:** In situ annealing of a Si wafer. The dotted line shows the time dependence of a typical ruby laser pulse. By applying the ns-pulse the reflectivity (solid line) rises to the value of liquid Si which shows that the surface melts (the reflectivity of Si increases by about a factor of 2 upon melting) for about 100 ns in this case.
16. **New insights into steam laser cleaning**

*F. Lang, M. Mosbacher and P. Leiderer*

The removal of particle contamination from surfaces is one of the crucial prerequisites for a further increase in the integration density of ICs and for the progress in nanotechnology. At all stages of the production of ICs, e.g., from the bare Si wafer to the patterned chip, particles even smaller than 100 nm in size can cause a damage to the produced structure and hence be responsible for the failure of the final device.

In the late 1980’s, the experts in the field of cleaning technology predicted that traditional cleaning methods such as ultrasonics and wet techniques would reach their limit of capability. In addition these traditional techniques were and still are harmful to the environment as they consume large quantities of aggressive chemicals and water. Although the traditional methods have been continuously improved, still particle contamination causes considerable production losses, and with further shrinking of line widths there is a definite need to replace traditional methods by new cleaning technologies.

One of these new approaches is called Steam Laser Cleaning (SLC) \(^1\)\(^-\)\(^4\), where a so-called energy transfer medium (ETM), typically a liquid, is applied to the contaminated substrate. A pulsed laser subsequently heats up the substrate, and the ETM is superheated via heat transfer through the substrate/ETM interface. The explosive evaporation of the ETM finally provides the pressure to remove particles adhering to the substrate surface.

More than one decade after the technique of Steam Laser Cleaning has been suggested for particle removal from delicate surfaces for the first time, there is still a lack of understanding of the underlying physical processes and in the determination of the optimum process parameters for efficient cleaning. Early studies during the 1990’s focused on the demonstration of the cleaning effect itself, aiming at a fast implementation of the process as a cleaning method in the semiconductor industry. After the industrial implementation \(^5\) had failed, the research focused on the basic aspects in order to clarify the involved processes, especially laser induced bubble nucleation \(^6\)\,\(^7\). Very recently the extent of superheating of the liquid during the bubble nucleation process could be measured and was found to be in good agreement with theoretical predictions \(^8\). In addition quantitative studies on the SLC process have revealed a universal, i.e. material and size independent, cleaning threshold in laser fluence \(^9\).

However, all these studies have been carried out in bulk liquids (bubble nucleation) or with liquid films of rather undefined thickness (universal threshold). We therefore have developed a setup to apply the ETM in a controlled way on a silicon wafer. Using this setup and varying systematically the ETM properties we have gained new insight into the SLC process.

A frequency doubled Q-switched Nd:YAG laser (FWHM = 8 ns, \(\lambda = 532\) nm) provided the pulses for the heating of the ETM. The setup for the SLC experiments under controlled conditions is shown in Fig. 1.

If the liquid generates a film on the surface, its thickness can be measured with an accuracy in the nm range. In the case of droplet formation comparable conditions can be assured by detecting the characteristic drop of the reflected intensity and the increase in the scattered light. Using this method we were able to carry out SLC measurements under well defined and reproducible conditions for the first time. For the liquids used as an ETM in our experiments we observed a size independent laser fluence threshold for particle removal as it is displayed for water in Fig. 2.

Moreover the precise control of the ETM allows it to study the transition from Dry Laser Cleaning, where no liquid is applied on the surface, to SLC. We found that the

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**Fig. 1:** Experimental setup for SLC with controlled film thickness. By a two-beam-reflectometry method it is possible to determine the film thickness with an accuracy of nanometers. The simultaneous detection of the scattered light by a photomultiplier allows us to draw conclusions on the film roughness as well as on the cleaning efficiency in the SLC process.
removal efficiency jumps up at a certain critical value for the liquid film thickness. In addition redeposition patterns which are characteristic for the film thickness can be observed.

**Fig. 2:** Universal cleaning threshold in SLC when water is used as ETM.

In contrast to other SLC experiments conducted so far, we also examined the cleaned areas with an AFM in order to detect defects with a size of several nm caused by near field enhancement at the contaminants. With regard to possible applications in the semiconductor industry it is essential to avoid these kinds of damages, because they can cause malfunctions just like the particles. Furthermore information about defects underneath the particles is mandatory to elucidate the particle removal mechanism, since substrate ablation may also contribute to the cleaning process.

**Fig. 3:** AFM image of surface damage caused by local field enhancement at the contaminants.

The AFM images revealed two different types of damages. The formation of defects at the particles was observed for certain combinations of the experimental parameters like laser fluence, particle size and the type of ETM used. A typical example of these surface damages is shown in Fig. 3. Additional defects can be caused by drop-focusing, if the liquid does not form a film. These structures are not as high and more widespread as can be seen in Fig. 4.

**Fig. 4:** AFM image of surface damage caused by water droplets that focussed the incoming laser beam in the SLC process.

Concluding our measurements point out, that SLC is a promising cleaning technique permitting the removal of particles with a wide range of sizes at one particular laser fluence. By conducting a thorough inspection of the surface after the SLC process, we determined under which conditions particle removal can be performed without any harm to the substrate. The validity of the universal cleaning threshold, even if defects are created, indicates that explosive liquid evaporation is the predominant cleaning mechanism for all particles used. This assumption is confirmed by evaporation studies under comparable conditions, which show that the universal threshold for the laser fluence is identical to the value for the onset of bubble nucleation in the liquid. Therefore our SLC experiments not only determine process parameters for a possible application but beyond this contribute substantially to unfold the underlying physical effects.

8. P. Leiderer, M. Mosbacher, V. Dobler, A. Schilling, O. Yavas, B.S. Luk’yanchuk and J. Boneberg, in: Laser Cleaning, B. Luk’yanchuk (Ed.) (World Scientific, Singapore, 2002)
17. Characterization of ZrNiSn:Y,Sc, ScM1Sb (M1: Ni, Pd, Pt) and YM2Sb (M2: Ni, Pd, Pt) as new thermoelectric materials

U. Probst, J. Oestreich and E. Bucher

The work in the past year was focused on a material scanning program in the system of the Half-Heusler alloys. Starting point of the research was the compound ZrNiSn and the possibility of changing its physical properties by doping with Y and Sc. In the system (Zr, Y)NiSn the best dimensionless figure of merit of 0.019 at 400 K with a power factor of 1.48×10⁻⁴ WK⁻²m⁻² could be obtained in the compound Zr₀.₉Y₀.₁NiSn. The compound shows a change in both the electrical and the heat conductivity as well as in the Seebeck coefficient after a heat treatment at 1200 K for 500 h to better values. In comparison to this the doping of ZrNiSn with Scandium shows less suitable properties for thermoelectrical application.

The interest was focused especially on the systems YM1Sb (M1X: Ni, Pd, Pt) and YM2Sb (M2: Ni, Pd, Pt), where details of the thermoelectrical properties had not yet been reported in literature.

The synthesis of the materials was performed in an arc furnace from the elements in a stoichiometric mixture. One half of the material was examined as it was, the other half after a heat treatment under different conditions from 900 K to 1200 K for 240 up to 500 hours under inert atmosphere. The material obtained was characterized by x-ray powder diffraction and showed a cubic symmetry with a lattice parameter of 6.280 Å for YNiSb, 6.544 Å for YPdSb and 6.532 Å for YPtSb respectively. The thermoelectrical measurements showed a figure of merit ZT with 0.0039 (300 K) for YNiSb, 0.0124 (360 K) for YPdSb and 0.0706 (300 K) for YPtSb. The three compounds are of p-type, a change to n-type could be obtained by doping YPdSb and YPtSb. Doped YPtSb showed the best features for thermoelectrical application. Upon extrapolation of the dimensionless figure of merit up to 400 K, it reached a value of 0.141.

In the system ScM2Sb with M2: Ni, Pd, Pt the lattice parameter was determined to 6.062 Å for ScNiSb, 6.312 Å for ScPdSb and 6.312 Å for ScPtSb. The dimensionless figure of merit ZT was calculated to 0.024 for ScNiSb, 0.054 for ScPdSb and 0.009 for ScPtSb. In this system, ScPdSb showed the best thermoelectrical properties, upon extrapolation up to 400 K the figure of merit ZT of 0.1 could be reached.

The obtained data for the six compounds are listed in Table 1 (the data marked with * are at 300 K).

Table 1:

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<th>Properties</th>
<th>YNiSb</th>
<th>YPdSb</th>
<th>YPtSb</th>
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<th>ScPdSb</th>
<th>ScPtSb</th>
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18. Electrical properties of Br in GaN

A. Stötzer and M. Deicher
in collaboration with
ISOLDE Collaboration(CERN, Geneva)

The great interest on GaN is mainly based on its applications in optoelectronics and high temperature electronics. Most of the work during the last years have been focused on the optical properties and due to the difficulties in interpreting the gathered data there are only limited reports on the electrical properties of GaN \textsuperscript{1,2}. In spite of the fast development of new growing techniques, GaN is still a highly defective material. Defects are getting distinguishable in electrical measurements like Hall effect if one uses radioactive dopants. The concentration of a defect containing a radioactive atom is changing with the element specific half-life of the decay while the concentrations of all other defects remain unchanged. Therefore, the fraction of activated ions after annealing, the carrier type or the influence on resistivity and mobility can be determined directly from exponential fits to the data.

Although Br can be introduced into GaN during different processing steps, almost nothing is known on its optical and electrical properties. The ionic radius of Br is comparable to the one of N and it possesses a smaller electronegativity. Therefore, if Br resides on a N lattice site, it should act as a double donor in GaN. Earlier photo-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Resistivity $\rho$ (a) and carrier concentration $n$ (b) of $^{77}$Br doped GaN ($10^{13}$ cm\textsuperscript{-2}, 260 keV) plotted as a function of temperature. The solid symbols were recorded 0.5 h after annealing and the open symbols were recorded 50 d after annealing.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Resistivity (a) and carrier concentration (b) of $^{77}$Br doped GaN ($10^{13}$ cm\textsuperscript{-2}, 260 keV) recorded at 300 K as a function of time after annealing.}
\end{figure}

luminescence measurements have identified a transition band related to Br but the recombination mechanism related to this band is still unknown \textsuperscript{3}). To study the electrical properties of Br in GaN, Hall effect measurements on GaN using radioactive $^{77}$Br have been performed.

For the Hall measurements an epitaxial GaN layer of 1.5 µm grown on an AlN/c-sapphire substrate with a size of $5 \times 5$ mm\textsuperscript{2} was used. The nominally undoped layer was n-type with a free carrier concentration of $5 \times 10^{16}$ cm\textsuperscript{-3} prior to the annealing. The sample was doped by ion implantation with the radioactive isotope $^{77}$Br at the on-line mass separator facility ISOLDE at CERN. The isotope $^{77}$Br transmutes with a half-life of 57 h to stable $^{77}$Se. The implantation energy was 260 keV and an implantation dose of $1 \times 10^{13}$ cm\textsuperscript{-2} was used. To reduce the implantation induced damage the sample was annealed 600 s in an evacuated quartz ampoule together with a piece of elemental Si at 1573 K \textsuperscript{4}). During annealing a SiN\textsubscript{x} layer develops at the GaN surface which prevents the epitaxial layer from decomposition usually observed at such high annealing temperatures. After annealing the SiN\textsubscript{x} layer
was removed by etching in a solution of 2 HF : 5 HNO₃ : 2 C₂H₄O₂. The electrical characterization was performed by van der Pauw Hall measurements using alloyed (473 K, 60 s) indium contacts at the corners of the sample. Fig. 1 shows the resistivity $\rho$ (a) and the net carrier-concentration $n = (N_D - N_A)$ (b) of the $^{77}$Br-doped sample recorded 0.5 h (solid symbols) and 50 d (open symbols) after implantation and annealing as a function of temperature. One can clearly observe, that during the 50 d the carrier-concentration $n$ increases (Fig. 1b) and the resistance $\rho$ decreases (Fig. 1a). GaN is a highly n-type material and the observed behavior can only be explained if Se acts as a single donor and Br forms no double donor – at least no shallow one. The recoil energy transferred to $^{77}$Se due to the electron capture decay of $^{77}$Br is only 13 eV, far to small to induce a change of the lattice site during the decay. It can not be excluded that Br forms donor states located deep in the band gap which are ionized only to a small fraction at the temperatures used for this experiment.

In Fig. 2 the resistivity (a) and carrier-concentration (b) recorded at 300 K for different times after the doping are shown. The solid lines correspond to exponential least square fits described in detail in ref. 5. The observed changes are small – only about 8% of the $^{77}$Se atoms are electrically active - but they agree very good with the expected changes due to the half-life of $^{77}$Br and have to be caused by the decay of $^{77}$Br.

(3) A. Stötzler, R. Weissenborn, M. Deicher and the ISOLDE Collaboration, Annual Report Solid State and Cluster Physics 1998, Universität Konstanz, p. 43
19. Annealing of Br-implanted GaN

A. Stötzler and M. Deicher
in collaboration with
ISOLDE Collaboration (CERN, Geneva)

Using the radioactive isotope $^{77}$Br, the optical $^1$) and electrical $^2$) properties of the possible double donor in GaN have been studied. At least at room temperature and below, no ionized donor states of Br have been observed, but about 8% of $^{77}$Se atoms created by the $^{77}$Br decay act as single donors as expected for Se residing on N sites in the GaN lattice. $^{77}$Br has been introduced in GaN by ion implantation and the implantation induced lattice defects have been removed by thermal annealing.

The daughter isotope $^{77}$Se decays via $\gamma$-radiation to its ground state and it exists an isomeric state with a half-life of 9 ns which is suitable for perturbed $\gamma\gamma$ angular correlation measurements (PAC). Via nuclear quadrupole interaction, PAC is extremely sensitive to defects present in the immediate neighborhood of the PAC probe atom. Due to the wurtzide structure of GaN, even $^{77}$Br residing on substitutional lattice sites with a defect free surrounding observe a non-zero electric field gradient.

The PAC spectrum shows that after annealing at 1573 K, the majority of the $^{77}$Br reside on unique lattice sites, probably the N sites. The observed distribution of electric field gradients clearly shows that different kinds of lattice defects are still present in the neighborhood of the dopants. These defects can hamper the electrical activation of the dopants. This is consistent with a small observed fraction (8%) of electrically active $^{77}$Se donors.

For the PAC measurements an epitaxial GaN layer of 1.5 $\mu$m grown on an AlN/c-sapphire substrate with a size of 5 $\times$ 5 mm$^2$ was used. The nominally undoped layer was n-type with a free carrier concentration of $5 \times 10^{16}$ cm$^{-3}$ prior to the annealing. The sample was doped by ion implantation with the radioactive isotope $^{77}$Br at the on-line mass separator facility ISOLDE at CERN. The isotope $^{77}$Br transmutes with a half-life of 57 h to stable $^{77}$Se. The implantation energy was 260 keV and an implantation dose of $1 \times 10^{13}$ cm$^{-2}$ was used. To reduce the implantation induced damage the sample was annealed 600 s in an evacuated quartz ampoule together with a piece of elementary Si at 1573 K $^3$). During annealing a SiN$_x$ layer develops at the GaN surface which prevents the epitaxial layer from decomposition usually observed at such high annealing temperatures. The PAC measurements have been performed at room temperature using a standard 4-detector PAC setup. The c-axis of the GaN crystal has been oriented perpendicular to the detector plane.

Fig. 1 shows a PAC spectrum (left) along with its Fourier transform (right) recorded after annealing at 1573 K. The PAC spectrum shows that about 60% of the $^{77}$Br/$^{77}$Se atoms are exposed to a distribution of electric field gradients characterized by a mean value $\nu_Q = 62$ MHz. The observed damping corresponds to a broad distribution of electric field gradients of $\Delta \nu_Q = 250(25)$ MHz. This result shows that after annealing at 1573 K the majority of the $^{77}$Br reside on unique lattice sites, probably the N sites. The observed distribution of electric field gradients clearly shows that different kinds of lattice defects are still present in the neighborhood of the dopants. These defects can hamper the electrical activation of the dopants. This is consistent with a small observed fraction (8%) of electrically active $^{77}$Se donors.

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Fig. 1: PAC spectrum (left) along with its Fourier transform (right) of GaN doped with $^{77}$Br by ion implantation ($10^{13}$ cm$^{-2}$, energy 260 keV) and annealed at 1573 K.
20. Absorberlayers for CuGaSe$_2$ solar cells

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in collaboration with
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In the recent past several efforts have been made at the LS Bucher to develop a suitable process for the preparation of CuGaSe$_2$ thin film solar cells. The main focus was on the application of a fast RTP-annealing of stacked elemental layers. In spite of obtaining single phase material (as measured by XRD) for stoichiometric and gallium rich compositions, the resulting films showed some undesirable features. These were mainly small grain sizes and an inhomogeneous elemental distribution across the film thickness. The layer sequence of the precursors turned out to have only a minor influence on the properties of the reacted films. In 2001 the major goal of the work was to determine processing conditions to improve the properties of CuGaSe$_2$ films, as observed for RTP-annealed stacked elemental layers.

It was shown that the crystallinity of the CuGaSe$_2$ films can be significantly enhanced when applying annealing temperatures above 600 °C. This is connected to a homogenization of the elemental distribution over the film thickness, and a clearly visible shift of the lattice constants. It was concluded that the gallium incorporation into the CuGaSe$_2$ structure is dependent on the processing temperature. For typical annealing temperatures below 600 °C the actual CuGaSe$_2$ crystallites, irrespective of the integral composition of the films, have compositions close to stoichiometry. The “excess gallium” accumulates in regions close to the substrate.

Although the investigations showed that an annealing at 700 °C or even at 800 °C leads to significant improvements, the implementation of the results, with regard to absorber preparation, is problematic. First a suitable substrate/back-contact combination has to be found. Additionally, after annealing at 700 °C and above, severe crack formation could be detected.

Lower processing temperatures can not be compensated by a prolonged annealing. This was demonstrated by the comparison with processes with an increased annealing time of one hour. One of the processes was again carried out at atmospheric pressure in Ar/Se-ambient, the other in evacuated quartz glass ampoules with additional selenium. In both processes a flatter temperature ramp of fifteen minutes instead of ten seconds was applied. For all temperatures these “slower” processes produced films of clearly inferior crystallinity. Also undesired copper selenides could be detected over the whole temperature range, besides XRD signals of crystalline selenium between 100 °C and 300 °C. The selenium-crystallization is connected to the formation of small droplets of this element. After annealing at 300 °C the excess selenium vanishes, but it is obvious that such an inhomogeneous distribution has to be avoided during all phases of the processing. This is thus one argument to pass through the temperature range below 300 °C as fast as possible.

The major reason for the worse crystallinity, in the case of the processes with flatter temperature ramp, is connected to the elemental gallium. It was shown that the elements copper and gallium have the tendency to separate instead of intermixing when exposed to temperatures of about 300 °C. This effect is probably enhanced due to a wetting of the substrate by the liquid gallium. It is important to mention that this separation effect occurs at temperatures below the range in which a significant chalcopyrite formation takes place. With increasing ramp time the metals also have an increased retention period in this temperature range. The separation is therefore more complete and is hindering a mixing of the elements. This can be suppressed by a steep temperature ramp, but not totally avoided, as the results of the RTP-processed samples indicate.

Despite the described unfavorable properties of RTP-annealed stacked elemental layers, the RTP-process seems to be the best approach. Slight improvements could be expected by applying an increased annealing temperature. This however would first require to find a suitable substrate back-contact combination. Even if such a combination would exist, a possible increase of the annealing temperature would be limited due to crack-formation within the absorber structure. Therefore it is doubtful if significant improvements can be made when using stacked elemental layers, mainly because of the elemental gallium. This however does not exclude that significantly better results can be obtained when replacing the elemental gallium for example by Ga$_2$Se$_3$ layers. The observed temperature dependency of gallium incorporation and crystallinity could also motivate the application of increased temperatures during processes with continuous grain growth, for example co-evaporation.
21. Novel crystalline silicon solar cells


The research in the group of Novel Devices focuses on new innovative device designs. Currently, new crystalline silicon solar cells are investigated with interesting properties like bifacial light collection, high voltages and rear contact solar cells.

1. Back contact solar cells

Back contact solar cells are devices in which contacts of both polarities are located on the rear surface unlike the n⁺p⁺ design of conventional solar cells. These solar cells have considerable advantages like the potential for higher conversion efficiencies, easier module assembly as well as homogenous optical appearance.

Different device designs for back contact solar cells have been investigated in the last years, amongst them the Emitter Wrap Through (EWT) solar cell 1,2). A schematic illustration of the EWT solar cell design is given in Fig. 1. The current collected in the front side emitter is conducted through small laser drilled vias to the emitter contact on the rear therefore avoiding any metallization on the front surface. The rear side of the solar cell consists of an interdigitated contact pattern of p- and n-type regions (see Fig. 1). These contact regions have to be electrically isolated, which is one of the main tasks in the manufacturing process and which was intensively investigated. The techniques for junction definition can be divided into three main groups: removal of the doped n⁺-layer after diffusion (e.g. by abrasive methods), prevention of n⁺-diffusion on certain areas on the rear (diffusion barrier) and the direct formation of rectifying p/n-junctions (e.g. by P-Al co-diffusion). The main difference between the techniques is the state of the p/n-junction on the rear after cell processing. If abrasive methods are used, the p/n-junction is in a highly damaged part with a high surface recombination velocity. This enhances the saturation current density of the second diode J_{02}. Since the EWT solar cell has a large length of open p/n-junctions at the surface, abrasive methods are not well suited for EWT solar cells. The focal point of our investigations on junction definition for EWT cells were on the other two techniques: diffusion barriers as well as P-Al co-diffusion.

Diffusion barriers have been investigated for two techniques of solar cell metallization: screen printing and electroless plating. For screen printed EWT solar cells a screen printable diffusion barrier was locally deposited and fired. In the processing of Buried Contact BC-EWT solar cells, LPCVD-SiNx was deposited on the rear. This dielectric was opened locally for the p- and n-contacts by laser ablation in parallel with the hole drilling. In both cases the p/n-junctions are passivated by a dielectric layer. A completely different approach is the formation of rectifying p/n-junctions by the simultaneous diffusion of P and Al in one thermal cycle. The transition between the p and n-doped regions has rectifying properties when certain process parameters are applied 3,4).

Fig 1: Schematic illustration of an Emitter Wrap Through (EWT) solar cell with screen printed metallisation.

EWT solar cells have been processed with the three different techniques for junction definition 1-4). The results of the IV-measurements are summarized in Tab. 1. Each individual process leads to very high J_{sc}, moderate V_{oc} and good efficiencies. The efficiencies of 16.1% (SP) and 16.6% (BC) are the highest efficiencies reported for EWT solar cells using industrial processing techniques without photolithography. The high J_{sc} can be attributed to zero grid shading losses and a second carrier collecting junction on the rear surface. A slightly reduced V_{oc} is a consequence of the second carrier collecting junction if materials with a small ratio of diffusion length to cell thickness are used. The moderate FF has different reasons. For screen printed solar cells a rather high series resistance R_s currently prevents a higher FF. The buried contact technology indicates that a low R_s can be obtained if a good cell metallization is realized. Currently the FF is limited by a rather high J_{02}. At this stage, the cause of the increase in J_{02} is not fully understood, but it is expected that an incompletely removed laser damage has contributed significantly 2).
The high shunt resistances $R_{sh}$ (normally in the range of several thousand $\Omega \text{cm}^2$) of the EWT solar cells applying co-diffusion shows that junction definition can also be accomplished without the deposition of diffusion barriers using this rather simple technique.

2. Highly efficient mechanically V-textured silicon solar cells applying a novel shallow angle contacting scheme

Mechanical surface texturization leads to a reduction in cell reflectance, an improvement in light trapping and an increase in carrier collection probability. Additionally, the mechanical structuring method opens numerous possibilities of novel cell concepts like LOPE, MECOR (Mechanically CORrugated) cells, LAMELLA cells and POWER (Polycrystalline Wafer Engineering Result) cells. Hereby, the MECOR and POWER solar cell concepts rely on mechanical texturing of both surfaces. The fabrication of single sided textured cells allows the separation of effects related to the front and those originating from the rear side texture. Therefore single sided textured cells, in which either the front or the rear side was structured, have been processed and characterized.

The mechanical V-groove surface texturization was carried out applying a conventional dicing machine equipped with a bevelled saw blade ($35^\circ$ or $60^\circ$ tip angle). Two main structures have been examined leading to two different types of front side metallization. One approach leaves plateaus for the metal grid fingers and the other forms higher V-groove tips for the shallow angle finger evaporation (SAFE) in conjunction with shallow angle photolithography (SAP).

![Fig. 2: Schematic representation of the SAP-technique (left) and a SEM-picture of a successful SAP (right).](Image)

The difficulty of any photolithography on textured surfaces is the complete coverage with photoresist of the wafer surface especially at the edges and ridges. Therefore a novel photolithographical processing sequence was established taking into account the demand of a fully coverage (see Fig. 2). The key result of the optimization is that the light exposure and development duration have to be very carefully matched with the special drying sequences of the particular multi layer photoresist system which in turn depends on the chosen kind of surface texture.

Different single sided textured solar cells have been processed as indicated in Tab. 2. The efficiency of 19.8% of the front textured cell with SAP&SAFE metallization indicates the high potential of these techniques. Once the fill factor is well above 80% the efficiency will reach 20.5%. Unfortunately the fill factor is quite low due to local shunt resistances caused by contacting the base with the emitter contact. Despite of that the open circuit voltage $V_{OC}$ is almost as high as for the flat reference cell. Hence there is no disadvantage due to mechanical texturization with respect to $V_{OC}$ at this level of efficiencies. But the saturation current $J_{02}$ of the second diode is by a factor of ten higher compared to the flat reference. A factor of two could be explained by the enlarged front surface area, i.e. by a doubled emitter area. Furthermore, the handling of mechanically textured cells with sharp tips could also result in shunt effects. This is currently under investigation.

**Table 2: Illuminated IV-parameters of different types of single sided mechanically textured solar cells and a flat reference cell (all cells: floatzone silicon, cell area $4 \text{ cm}^2$, $0.5 \Omega \text{cm}$).**

<table>
<thead>
<tr>
<th>Cell type</th>
<th>$V_{OC}$ [mV]</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>FF  [%]</th>
<th>Efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front texture/</td>
<td>675</td>
<td>37.7</td>
<td>77.7</td>
<td>19.8</td>
</tr>
<tr>
<td>SAP&amp;SAFE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rear texture/</td>
<td>667</td>
<td>32.7</td>
<td>80.2</td>
<td>17.5</td>
</tr>
<tr>
<td>local SAP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flat reference</td>
<td>677</td>
<td>32.2</td>
<td>81.2</td>
<td>17.8</td>
</tr>
</tbody>
</table>

The front side textured cell with plateaus for the finger grid features a lower short circuit current. This is due to a higher reflectance caused by the flat plateaus (12-14%) and the shallower V-grooves compared to the SAP&SAFE cell. The rear side textured cell with flat front surface shows a significant loss in $V_{OC}$. The main reason is an enhanced rear surface recombination. Computer simulations with DESSIS ISE show that a rear surface velocity lower than 100 cm/s is necessary to maintain the same $V_{OC}$ as for the flat reference cell.

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22. New crystalline silicon materials

G. Hahn, P. Geiger, D. Sonntag, P. Fath and E. Bucher

1. Improvements of carrier lifetimes in ribbon silicon by gettering and hydrogenation steps

The research in the group of New Crystalline Silicon Materials is focused on the properties of alternative photovoltaic materials to standard ingot cast silicon wafers and the development of adapted solar cell processes for these materials. Wafers cut from ingots (mono- or multicrystalline) are currently the dominant semiconductor source for the photovoltaic market. New cost effective ribbon silicon wafer technologies came up in the past decade as an alternative. These ribbons normally contain more crystal defects, but material properties can be improved in the solar cell process by gettering and hydrogenation steps. One of the main characteristics of the solar cell wafer is the lifetime of minority charge carriers which was investigated in EFG (Edge-defined Film-fed Growth) silicon, as one cost effective ribbon candidate.

![Defect etching and P-Diffusion](image1)

**Fig. 1:** Minority carrier lifetimes in EFG silicon after different processing steps (same scaling).

Lifetimes have been mapped after different processing steps using the microwave photoconductance decay (μ-PCD) technique (Fig. 1). The as grown material shows bulk lifetimes $\tau_{\text{bulk}}$ in the range of 1 μs after a defect etching step which can be slightly improved by a gettering step using the P-diffusion. A big boost in lifetime can be seen after the incorporation of atomic hydrogen with the microwave induced remote hydrogen plasma (MIRHP) passivation method. Lifetimes of up to 300 μs can be achieved in selected areas of the wafer. The enhancement reached by the H-passivation is stable after illumination of 10 hours (1 sun) proving that this method is well suited for the use in solar cell processes where stable performance has to be accomplished. Nevertheless, strong inhomogeneities are still present in the material even after hydrogenation. The areas showing lower lifetimes after gettering and hydrogenation are responsible for the limitation of solar cell performance after completion of the manufacturing process. Therefore, a detailed analysis of the material is very important in order to determine the specific impurities and/or defects present in these areas. This analysis is currently under way in cooperation with other project partners.

Furthermore, from Fig. 1 it can be concluded that different kinds of defects are present. Areas with similar lifetimes in the as grown sample after etching (marked with red, green and white) can result in totally different material quality after gettering and hydrogenation. This means that the lifetime measurement of the as grown sample alone is not sufficient in order to determine the underlying defects.

![Histograms of bulk lifetimes](image2)

**Fig. 2:** Histograms of the bulk lifetimes shown in Fig. 1 after different processing steps. Visible are slight improvements after P-diffusion (P-gettering effect) and a large increase after hydrogenation which is stable under illumination.

In Fig. 2 the histograms of the lifetimes shown in Fig. 1 again demonstrate the effectiveness of the gettering and hydrogenation steps.

2. Recombination and scattering of minority charge carriers in ribbon silicon material

The mobility of minority charge carriers in cost effective multicrystalline silicon material is not easy to detect, but can give important information about scattering
mechanisms present in this material. Additionally, a comparison between scattering and recombination behaviour can give a closer insight in the physics at work.

For this study we have chosen RGS (Ribbon Growth on Substrate) silicon, a ribbon silicon material which is still in the R&D phase. A processed solar cell was analysed with LBIC (light beam induced current) which results in a mapped distribution of the diffusion length of the minority charge carriers $L_{\text{diff}}$ (Fig. 3 top). Afterwards the metallic contacts have been removed and the lifetimes $\tau_{\text{bulk}}$ have been measured using the $\mu$-PCD technique (Fig. 3 middle). These two maps have been used to calculate the diffusion constant of minority carriers $D_n$ in p-type material (Fig. 3 bottom) according to

$$L_{\text{diff}} = \sqrt{D_n \tau_{\text{bulk}}}$$

![Fig. 3: Determination of the minority carrier diffusion constant $D_n$ (bottom) in ribbon silicon by combining LBIC data of a processed solar cell (top) with lifetime data from $\mu$-PCD measurement (middle).](image)

The mean value of $D_n$ is reduced to 10 cm$^2$/s in this material due to the presence of scattering centres as compared to 27 cm$^2$/s expected for monocrystalline silicon of the same resistivity. As can be seen from the white marked regions, normally a higher $L_{\text{diff}}$ is combined with higher values of $\tau_{\text{bulk}}$. Nevertheless, in some areas an apparently higher $L_{\text{diff}}$ corresponds to a low $\tau_{\text{bulk}}$ (black areas). This is a hint for the presence of non-planar emitter structures in this material, forming a 3-dimensional extension of the current collecting emitter into the silicon bulk.

By this mechanism, carriers created deep in the bulk can be collected despite of a low lifetime and low diffusion length, which is measured incorrectly in the case of a non-planar emitter structure. $D_n$ values exceeding 27 cm$^2$/s can therefore not be trusted and are attributed to regions of non-planar emitter structures whose existence is well known in this material.

![Fig. 4: Recombination (top) and scattering (bottom) behaviour in RGS silicon obtained from the data shown in Fig. 3.](image)

In order to investigate, whether areas of increased recombination are combined with areas of increased scattering and vice versa, the data given in Fig. 3 have been used for an additional analysis shown in Fig. 4. For some areas a correlation between recombination and scattering is visible (areas 1,4), whereas for other regions no direct correlation could be demonstrated (areas 2,3). It can be seen that increased recombination is not necessarily combined with increased scattering, although this holds true for some structures within the sample.


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23. Thin film silicon solar cells on upgraded metallurgical silicon substrates prepared by liquid phase epitaxy

K. Peter, R. Kopecek, J. Hötzel, P. Fath and E. Bucher

Thin layers of about 30 µm thickness were grown on upgraded metallurgical (UMG) silicon substrates by liquid phase epitaxy (LPE) from an indium solvent. Instead of adding electronic grade silicon to the solution, a melt back step was carried out before each growth process to supply silicon to the melt from the UMG-Si wafers. We present a LPE technology which is capable to be directly scaled up to a few hundred layers per run. Solar cells have been fabricated by an industrial low cost process (η > 10%).

1. Introduction

While R&D is ongoing to develop a Solar Grade silicon feedstock, recent results show that existing metallurgical grade silicon (MG-Si) can be modified without the need for complex high cost chlorosilane chemistry to purify the product. Such UMG-Si material gives a reasonable efficiency solar cell provided a thin film of silicon is used on the substrate cast from the UMG material. The UMG-Si was fabricated at Elkem in a pilot scale (300 kg each batch) from metallurgical grade silicon based on both pyro- and hydrometallurgy refining processes. Large ingots of about 140 kg of UMG-Si were produced by directional solidification at Eurosolare. Most of the impurities except boron were accumulated on the surface by this casting process.

The standard sliding boat approach 1) contains several disadvantages such as problems of solvent removal, limited wafer size capability and the necessity of changing the solvent after each epitaxial growth sequence. Therefore in prior investigations we reported on the development of a horizontal dipping apparatus presented in 2) for fast subsequent layer growth using an “infinite” solvent. In this work the LPE apparatus was expanded for the growth of 6 layers per run in a batch type system. A batch of 16 substrates is currently under construction.

Solar cells have been fabricated by an industrial low cost process. Both emitter and contact formation were carried out by screen printing. PECVD SiN was used as an antireflection and passivation layer as well as a hydrogen source for bulk passivation. Typical efficiencies of η = 8.3 - 9.0% were achieved with this process. Recent results predict higher efficiencies of η = 10.5 - 10.8%. Thereby the short circuit current was limited due to the small layer thickness of 30 µm. Thicker layers or application of effective light trapping should increase the efficiency in further work.

2. UMG Si development and crystallization

Metallurgical grade silicon melts were refined to remove in particular the harmful SiC particles and some metallic impurities 3). The refined melt was then alloyed with Ca to make it leachable and solidified. The cast ingots were crushed into lumpy silicon of about 30 mm size. On solidifying the melt, pure silicon crystals appeared in a separate phase and the complex impurity phase accumulated on the grain boundaries of these crystals. Leaching was carried out with suitable leach liquors in a dedicated chemical plant. The leached out silicon was than sieved and classified. The product is upgraded granular UMG-Si with main size fraction of 0.2 – 2 mm.

Large cast ingots were fabricated by Eurosolare in a furnace specially adapted for the use of UMG-Si 4). The wafering of the blocks were carried out in a wire sawing machine with conventional performance as for EG-Si based ingots.

3. LPE deposition

Thin layers of 30 µm thickness were grown on the UMG-Si substrates by LPE from indium solution, starting at temperatures around 990 °C and cooling down to 890 °C. The optimum carrier concentration of the thin solar cell absorber of 5×10^{16} cm^{-3} was obtained with 0.1 wt% Ga content in the melt 5). Instead of adding electronic grade silicon as a source to the solution, a melt back step was carried out before each growth process to supply silicon to the melt from the UMG-Si wafers. It is expected, that the upgrading of the indium by zone melting needs less energy and effort than the purification of metallurgical silicon to electronic grade Si. Up to three substrates are dipped horizontally into the indium solvent with an equidistant spacing of 3 mm as shown in Fig. 1. In the majority of cases LPE deposition took place on both the upper and the lower side of the substrates. The surfaces of the
epi-layers were very smooth causing the In solvent draining off the wafer after epitaxial growth. The grown layers did not show any interruption even at the grain boundaries (see the real picture of LPE layer in Fig. 1 after SECCO etching) and showed a similar overall thickness of about 30 µm sufficient for photovoltaic applications. In order to avoid an unintentional growth on both sides of the UMG-Si substrate, one side was coated by a thermal oxide in some cases prior to LPE growth.

4. Solar cell processing

Solar cells have been fabricated based on emitter diffusion by screen printing and firing of a phosphorous dopant paste. The cells were finished by industrial processes like PECVD SiN deposition and screen printed contacts, leading to $\eta = 9\%$.

Recently, after implementation of the batch process (Fig. 1), improved epi-layers and solar cells have been achieved, resulting in an efficiency of up to $\eta = 7.2\%$ without antireflection coating ($I_{SC} = 16.2$ mA/cm$^2$, $V_{OC} = 584$ mV, $FF = 76\%$, $A = 3$ cm$^2$). The high reflectance of the cells predicts an efficiency of $\eta = 10.5-10.8\%$, which exceeds the highest value reported on this material up to now $^4$ ($\eta = 10.0\%$).

The values of $V_{OC} = 584$ mV and $FF = 76\%$ without surface passivation confirm the high quality of the epitaxial layers on UMG-Si substrates. In addition light trapping would drastically increase the current of the 30 µm thick solar cells. All solar cell parameters have been measured under standard conditions (100 mW/cm$^2$, AM1.5, 25 °C).

5. Conclusion

It is demonstrated that metallurgical silicon is an important candidate to replace the shortcoming EG-Si feedstock for the production of thin film solar cells. The UMG-Si feedstock is developed at pilot scale and can be produced in large quantity. LPE was used to provide a thin silicon layer onto the UMG-Si wafer in a batch type system. The solar cell parameters demonstrate the high quality of the LPE layers on the UMG-Si substrate.

In principle a horizontal batch apparatus can be scaled up to 300 wafers (125×125 mm$^2$), which are dipped into a solvent filling up a crucible of 1m height. As much as 10 such vertical systems could be placed next to each other into a furnace of 2 m width. A circle time of 6 hours per run would result in about 8 layers per minute or more than 6 MW per year respectively. The costs for the LPE deposition are thus calculated to be about 0.10 Euro per wafer (including the up-grading of solvent) and the energy consumed would be 20 Wh per wafer which corresponds to an energy payback time of 2-3 days.

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References:

24. **Simultaneous determination of “shape” and “color” of clusters**

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For a given number of atoms in a small nanoparticle or cluster various different geometric arrangements of the atoms are possible (isomers). E.g., for the famous cluster $\text{C}_{60}$ not only the stable fullerene (“soccer” ball) has been found in experiments, but also several different ring-like and graphite-like isomers have been identified $^1$. Many more isomers might exist if the proper methods for generation are applied. Each of these isomers have the same number of atoms, but different shape and different properties. $\text{C}_{60}$ in its fullerene structure is a semiconductor, but the properties of the other isomers of $\text{C}_{60}$ are generally unknown. The reason is, that the properties are usually determined by spectroscopic methods (vibrational spectroscopy, photoelectron spectroscopy), which are applied to mass-separated ion beams. Until yet it was not possible to select certain isomers at the same mass and, accordingly, the vibrational or electronic spectra correspond to a superposition of signals from various isomers. Previously, this difficulty has been partially overcome by generating the most stable isomer only by optimizing the source conditions $^2$. As a consequence, there is almost no information about the properties of all other, less stable isomers. But such information might be important. E.g., diamond is just a less stable (metastable) “isomer” of bulk graphite.

The shape of a cluster isomer can be determined by ion mobility spectroscopy (IMS) $^{1,3}$. The ions are dragged by an electric field through an inert gas (He) and their maximum velocity depends on their shape. Compact cluster ions are faster than more open structures. If a bunch of ions is injected into the gas cell, different isomers arrive at different times at the exit of the gas cell. However, with IMS the isomers are separated and detected, but there is no information about properties. Here, we combine IMS with photoelectron spectroscopy (PES) $^4$ to gain structural information and information about properties for different isomers.

The experimental set up is displayed in Fig. 1. Negatively charged cluster ions are generated in a pulsed arc cluster ion source and injected into a gas cell filled with helium. A weak electric field pulls the anions through the cell and after passing the cell the anions enter the acceleration region of a time-of-flight mass spectrometer (TOF). At the exit of the gas cell an electrostatic gate allows only anions to enter the mass-spectrometer, which have spend a certain time in the gas cell corresponding to a certain mobility. E.g., for small carbon clusters a short time corre-

![Fig. 1: Schematic diagram of the new IMS/TOF/PES instrument.](image-url)
sp onds to the more compact ring-shaped clusters, while the carbon chains need a longer time passing the gas cell.

The anions are accelerated in the time-of-flight mass-spectrometer and pass through the interaction region of an electron spectrometer. In the spectrometer, a mass-selected bunch is irradiated by a UV-laser pulse and the kinetic energy of the detached electrons is measured by the time-of-flight method. Without the gas cell, this method is a standard method of photoelectron spectroscopy of mass-selected anions, which has been used in Konstanz for several years now. Insertion of the gas cell allowing for isomer separation reduces the ion intensity by about two orders of magnitude. This is the reason, that no isomer-separated spectra have been obtained from any cluster with any experiment until today. We solved the intensity problem by optimizing the source intensity, the efficiency of the electron spectrometer and the transmission of the gas cell.

In Fig. 2 first isomer-resolved photoelectron spectra of carbon cluster anions with $n = 9$ and 11 atoms are shown. In this three-dimensional picture various photoelectron spectra are shown for different ion mobilities (IMS drift times) and two sorts of spectra can be identified for $C_{11}^-$: the one of the ring isomer (short drift time, peak at short electron time-of-flight) and the one of the chain isomer (long drift time, peak at long electron time-of-flight). For $C_9^-$, only the chain isomer is observed, because the ring isomer is unstable for small carbon clusters with $n < 10$.

In the future, a new improved experimental set up will be constructed, which allows for the spectroscopy of rare and exotic isomers with low relative abundance. With this improved set up, a new dimension of nanostructure research will be opened: beside the dimension of size now the new dimension “shape” appears and many new species might be discovered with each having new and unexpected properties. Examples of strange and interesting structures to begin with are the “tadpole” and the smallest possible fullerene $C_{20}$.

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(1) G. von Helden et al., Science 259 (1993) 1300
(5) S. Burkart et al., Chem. Phys. Lett. 301 (1999) 546
(7) H. Prinzbach et al., Nature 407 (2001) 60
25. Highest electron affinity as a predictor of cluster anion structure

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Small cluster (typically comprising several to several tens of atoms) offer a bridge between molecular and solid state physics. This bridge is made possible because with increasing cluster size, all cluster properties (e.g., structural, mechanical, thermal, electronic, and optical) evolve from molecular values to bulk values in non-trivial ways, often revealing new and surprising results.

A fundamental difficulty of cluster studies is that experimental accessible quantities are often highly sensitive to cluster structure. However, there is no known general experimental method for determining cluster structures and indeed such structures are known experimentally only for a handful of special cases. Therefore, theoretical analyses of experimental results usually begin by determining cluster structures. Subsequent agreement between theory and experiment on other cluster properties is then typically invoked as evidence in support on the computed structure.

Theoretical computations of cluster structures almost invariably assume that experimental conditions allow for thermodynamical equilibrium, so that the cluster probed are very close to their ground state 1. Based on this paradigm, sophisticated ground state searching algorithms, using various forms of molecular dynamics and genetic algorithms have emerged. Very often one finds many isomers that are very close in total energy, but differ significantly in structural and other properties. The fundamental assumption of thermo-dynamical equilibrium means, that in experiments the most stable ground state isomer is observed and that is at the heart of the above mentioned approaches and is usually taken for granted. However, its verification is by no means obvious, and little has been done to explore substitute theoretical algorithms for isomer search and identification in the absence of equilibrium.

We pursued these questions by investigating negatively charged bare and deuterated silicon clusters, produced in a plasma environment- an important system for both basic research and technological applications. By combining photoelectron spectroscopy (PES) and ab initio density functional theory calculations, we show that cluster formation in this system is kinetically, rather than thermodynamically limited. We further show that the kinetic limitation results in a highest electron affinity rule replacing the lowest total energy rule as the guideline to isomer selection.

We have compared experimental and theoretical PES curves for negatively charged Si$_m$D$_n$ clusters (4 < m < 10, 0 < n < 2, D denoting deuterium), produced using a pulsed arc cluster ion source. A selection of PES curves is given in Fig. 1. In this figure, each measured spectrum is compared with the theoretical PES curve found to be in best agreement with experiment.

For each cluster type, the structure of the isomer yielding the shown theoretical data is given as an insert. Below we refer to these isomers as experimentally observed. The agreement between theory and experiment is excellent and this strongly suggests that our identification of the observed structures is valid.

![Experimental PES data (bottom curves), compared with theoretical PES data (top curves) taken from the isomers yielding best agreement with experiment. Isomer structures are given as inserts.](image)

Fig. 2 compares, for several cluster types, the PES data of the experimentally observed isomer and the PES data for the isomer of lowest energy for which the computed PES curve disagrees with the experimental one. The latter is referred to as the experimentally not observed isomer below. Fig. 2 also compares the structure, total energy and vertical electron affinity of those isomers. Intriguingly, the experimental observation of a given isomer does not seem to have any correlation with minimum energy considerations. For example, the observed Si$_6^-$ isomer is lower in total energy than the first unobserved one by 0.2 eV. In many cases, however, the observed isomer...
is higher in total energy than some unobserved ones, e.g., by 0.3 eV for Si₈⁺ and 0.7 eV for Si₁₀⁺.

Fig. 2: Comparison of experimental PES data (bottom curves) and theoretical PES data for the isomer yielding the best agreement with experiment (center curves) and for the isomer of lowest total energy for which the computed PES curve disagrees with the experimental one (top curves). Structures, total energy differences and electron affinities are given as insets. The upper right corner shows a schematic configuration-coordinate diagram for the charged and neutral states that defines the vertical detachment energy (VDE) and the vertical electron affinity (VEA).

If one rejects computational artefacts as the explanation of these results, one must conclude that the observed isomers are often metastable, i.e., their ground state configuration corresponds to a local minimum which is not the ground state. This indicates that thermodynamic equilibrium was not obtained experimentally. If not the minimum energy is the criterion for which isomer is observed experimentally, can one formulate an alternative predictive criterion for metastable isomer observation? We believe that the key to such an criterion is the negative charge of the clusters. We assume that the clusters are initially formed as neutrals, with low energy isomers formed as essentially equal probabilities due to the extremely high effective temperature during their formation. The clusters subsequently attract an electron from the plasma. The most probable process is for the electron to bind to the cluster with the highest vertical electron affinity (VEA). In addition, high VEA isomers are favoured by charge transfer reactions between anionic and neutral clusters. In these reactions, electron hopping from an isomer with a lower EA to one with a higher EA is energetically favourable and can occur spontaneously. As a result, the most abundant negatively charged species will be not the most stable isomers, but the metastable ones with a high electron affinity. The highest vertical electron affinity would then replace the lowest total energy as the pertinent criterion for isomer selection.

For 18 of the 20 cluster types studied here, the observed isomer was indeed consistent with the highest vertical electron affinity rule. The two exceptions can be discussed and rationalized in a more elaborate paper.

In conclusion, our findings point to a need for a stringent examination of the traditional assumption of thermodynamically limited cluster formation and for appropriate modification in the interpretation when the thermodynamic limit is not realized experimentally. In the case of negatively charged clusters generated with a pulsed arc cluster source, the traditional lowest total energy rule can be replaced by a highest electron affinity rule.

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26. The structure of large metallocarbohedrene clusters

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Metallocarbohedrene clusters ("metcars") have attracted considerable attention since their discovery by Castleman and coworkers \(^1\). They found the M\(_{13}C\(_{12}\) (M = Ti, Zr, V, Hf, Nb) cluster to be a prominent "supermagic" cluster similar to C\(_{60}\) and proposed a structure for this cluster in which both metal and carbon atoms are present in the wall of a symmetric cage with 12 five-membered rings. Even more interesting is the proposed growth pattern of larger metcars. Bulk TiC and ZrC have a cubic structure and small clusters of these materials might form microcristals. Accordingly, the appearance of magic numbers corresponding to the 3x3x3, 4x4x4 and 5x5x5 nanocubes (M\(_{13}C\(_{14}\), M\(_{18}C\(_{29}\), M\(_{22}C\(_{35}\), respectively) can be expected. Experimentally, Wei et al. observed the magic numbers M\(_{13}C\(_{21}\), M\(_{18}C\(_{29}\) and M\(_{22}C\(_{35}\). These clusters exhibit an excess of carbon atoms and their stability has been explained by the assumption of a "multi-cage" structure completely different from the bulk cubic structure. Fascinating new bulk materials might be built of such multi-cage clusters.

To gain additional information about the geometric structure of larger metcars we have generated very large clusters using an additional annealing process. The clusters are produced in a pulsed arc cluster ion source (PACIS) and annealed in a subsequent discharge, which presumably results in a relaxation of the clusters into their ground state geometry. We measured time-of-flight mass spectra of ions directly produced by the PACIS. Fig. 1a displays a section of a mass spectrum of Ti\(_n^+\) cluster cations using pure He as carrier gas.

The mass resolution of the time-of-flight spectrometer is \(m/\Delta m = 400\) and the widths of the peaks assigned to certain clusters correspond to the isotope distribution of Ti. Due to residual carbon in the source the Ti\(_n^+\) clusters have a higher intensity than the bare Ti\(_n^+\) clusters. In Fig. 1b a small amount of CH\(_4\) is added to the carrier gas. Several mixed clusters consisting of Ti, C and H atoms can be observed with the maximum intensity for Ti\(_n^+\)C\(_1H_m^+\) (m = 0-3) clusters. At a higher relative concentration of CH\(_4\) (Fig. 1c) the mass spectrum displays a structureless continuum of peaks. Fig. 1d displays the mass spectrum obtained under similar conditions as in Fig. 1c, but with the annealing discharge switched on. The spectrum alters dramatically. Now, the peak assigned to Ti\(_8^+\)C\(_{12}^+\) is prominent, in agreement with mass spectra of metal-carbon cluster cations obtained with a laser vaporization source \(^1\).

Fig. 2a displays a mass spectrum of Ti\(_n^+\)C\(_m^-\) cluster anions produced with optimum conditions for the generation of small metcars. The mass spectrum is different from the one of the positively charged clusters and two groups of intense features around Ti\(_7^+\)C\(_{13}^-\) (marked A) and Ti\(_{13}^+\)C\(_{22}^-\) (marked B) can be observed. We confirmed the assignments of the peaks by recording corresponding photoelectron spectra. The peak assigned to Ti\(_8^+\)C\(_{12}^-\) is a local maximum, but in contrast to the spectrum of the cations it is not a prominent peak and even smaller than the one assigned to Ti\(_7^+\)C\(_{13}^-\). This surprisingly low abundance of Ti\(_8^+\)C\(_{12}^-\) might not be related to its stability, but may be related to its low electron affinity.

![Fig. 1](image)

Fig. 1: (a) Section of a time-of-flight mass spectrum of Ti\(_n^+\) clusters with bare He as a carrier gas. The high intensity of Ti\(_n^+\)C\(_m^+\) clusters is due to residual carbon in the source; (b) Same as (a), but obtained with a small amount of CH\(_4\) in the He carrier gas. The main peaks are assigned to Ti\(_n^+\)C\(_1H_m^+\) clusters with m = 1-4; (c) Same as (a), but obtained with a medium concentration of CH\(_4\) in the He carrier gas; (d) Same as (c), but with the annealing discharge switched on.

Keeping the adjustments of the mass spectrometer constant, the source in Fig. 2b is tuned to produce larger clusters of anions. Compared to Fig. 2a the group of peaks around Ti\(_7^+\)C\(_{13}^-\) (A) vanishes, but the main peak B observed in Fig. 2a assigned to Ti\(_8^+\)C\(_{12}^-\) can still be observed with reduced intensity. The small feature at slightly larger mass assigned to Ti\(_{14}^-\)C\(_{24}^-\) is still visible, too, and from this similarity we conclude that the two features marked B in Figs. 2a and 2b have the same origin and that the corresponding Ti\(_{13}^+\)C\(_{22}^-\) clusters probably have identical structures.

In Fig. 2b with peak B a new progression of maxima (marked B-H) starts which we tentatively assign to geometric shell closings. As obvious from Fig.2b, the relative
distances between the maxima increase. This is in disagreement with the assignment to geometrical shell closings, if a "multi-cage" growth pattern is assumed. There, a shell closing happens with each closing of a new cage and since the cages are of equal size (Ti₆C₁₂ units), the distances between neighbouring shell closings should not increase.

The increasing mass difference between successive shell closings which can be observed experimentally coincides approximately with cubic fcc shell closings (indicated by arrows in Fig. 2b). Peak B correspond to the 3x3x3 cube, feature E to the 4x4x4 cube and the last resolved maximum to the 5x5x5 cube. The other maxima roughly correspond to closings of subshells (like feature G: 4x5x5). This assignment is supported by the observation that features assigned to symmetric cubic shells are relatively sharp compared to the maxima assigned to subshells, which have a step-like broad shape. The maxima are shifted to slightly larger values compared to the expected positions of the cubic shell closings. We assume that these cubic structures have additional atoms bound at the corners of the cubes. Such a structure has been proposed for the Ti₁₃C₂₂⁺ cluster.

The Ti₁₃C₂₂ cluster is the smallest species belonging to this series and is assigned to the 3x3x3 nanocube with 8 additional carbon atoms stabilizing the corners of the cube. Both, the 4x4x4 and 5x5x5 cubes show a similar shift to slightly larger mass indicating a similar uptake of excess carbon atoms. Therefore, the excess of carbon atoms, which gave rise to the idea of a multi-cage growth pattern of metcars, can alternatively be explained by the tendency of surface carbon atoms to form dimers by the adsorption of additional carbon atoms. Our observation contradicts the "multi-cage" and the "quantum wire" growth models.

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(1) B.C. Guo et al., Science 255 (1992) 1411
(2) S. Wei et al., Science 265 (1992) 818
27. Chemisorption on small clusters: can vertical detachment energy measurements provide chemical information? H on Au as a case study

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Determining the structure of small atomic clusters uniquely is an almost impossible task for experiments alone. Nevertheless a number of sophisticated physical measurements have been used on size-selected clusters to this end. For example, mobility measurements can determine their global shape as proved for aggregates of diverse elements 1), and useful information on their geometry can be provided by photoabsorption and photodetachment spectra, when combined with reliable calculations 2). A related task, at least as ambitious, is that of using the same physical probes to understand cluster chemisorption, namely to identify size effects and especially the most probably chemisorption sites a metal cluster offers to hydrogen, oxygen, or carbon monoxide. Photoelectron detachment has recently been extended to anionic metal clusters with chemisorbed CO and hydrogen 3,4). However, the power and limitations of this technique to fingerprint reactive sites, also when combined with calculations, are unclear and need to be accessed. This is the purpose of our investigation. The work we present here should clarify some of the general- and so far overlooked – problems one encounters when trying to apply such experimental data to the realm of cluster chemistry.

We have chosen an interesting and well-defined system as a case study: hydrogen adsorption on gold clusters. Because of their relevance in newly fabricated, gold based nanostructured materials, the physical and chemical properties of gold cluster have recently attracted a lot of attention. Anionic clusters (in this case Auₙ⁻) are often probed by photoionizing them and locating in the spectrum the lowest energy peak that corresponds to the binding energy of the ejected electron in the structure of the anion. This is commonly defined as the vertical detachment energy (VDE) and is the quantity targeted by calculations. It is generally compared to values computed for a few isomers, and assumed to identify the ground-state structure of the anion 2). This quite general assumption is what we are considering here critically in the case of chemisorptive systems. The specific questions we address are: Can we use VDE values to identify where hydrogen preferentially sits? Do they probe the lowest energy structures?

Gold clusters were generated in a pulsed arc cluster ion source operated with a He carrier gas with a strong admixture of hydrogen (10 - 50%). The target material (Au) is eroded and cooled down by interaction with the carrier gas. A mixture of Auₙ clusters and atomic hydrogen, in neutral and charged states, enters the extender and cools down to about room temperature. Neutral Auₙ cluster and hydrogen anions are expected to form with higher probability, and give rise to the hydrogenated AuₙH⁻ anionic clusters. Photoelectron spectra of mass-selected anions are collected in a “magnetic bottle”-type electron spectrometer.

Fig. 1 shows the photodetachment spectra measured for the AuₙH⁻ clusters with n = 2 - 6. That of AuH⁻ extends to lower energy, and the VDE is located at 0.9 eV.

Fig. 2a illustrates several calculated geometrical isomers of the AuₙH⁻ clusters, ordered according to their thermodynamic stability ∆E. Here, we focus on the comparison of calculated and experimental VDEs. As shown in Fig. 2b, VDEs do not correlate with ∆E, and depending on the specific size, they may or may not change from isomer to isomer. Fig. 2c illustrates the theory values of the VDEs versus experiment. Each curve refers to a different choice of the anionic cluster isomer: the ground state, and the one(s) with gold atoms in a structure similar (apart from relaxation) to that of the bare cluster, in either the neutral or the anionic state. The standard interpretation of the measured VDE (which we call the thermodynamical one) associates it to the energy necessary to detach an electron from the anion in its ground state. The values obtained in this way agree well with experiment for n = 1,2,3, and 6, whereas for n = 4 and 5 they are 1eV higher.
In contrast, if we assign the measured VDEs to those isomers that are structurally related to the neutral bare Au\textsubscript{n} clusters, we find that the agreement is excellent for all clusters considered (see Fig. 2c). We call this interpretation “parent-related”. The excellent agreement suggests, that the clusters do not assume thermal equilibriums, but “freeze” in a geometry, which is related to their growth path. In our apparatus, neutral aggregates form with a higher probability than charged ones, and H is more likely to be present in the anionic than in the neutral form. This suggest that when a H\(^+\) hits a neutral Au\textsubscript{n} cluster (and this is the most probable chemisorption event), it binds strongly, and the newly formed cluster may have a low probability to transform to the ground state. Our results corroborate this picture: (i) The binding energies of these states are high (4 – 5 eV). The channel Au\textsubscript{n} + H is indeed the one gaining far more energy from the formation of Au\textsubscript{n}H than Au\textsubscript{n}\textsuperscript{-} + H and Au\textsubscript{n}H\textsuperscript{+} + Au, namely by more than 1 eV for all n. (ii) The energy barriers for the transformation to the ground state are 1500 K or more. In Fig. 2c we also report the results for another “parent-related” interpretation, with Au\textsubscript{n}\textsuperscript{-} as parents. They become relevant when atomic rather than anionic H is chemisorbed. Clearly, this formation path is not relevant.

According to this comparison of calculated isomers and the experimental results, the most probable route of formation is the chemisorption of anionic H\(^-\) to neutral Au\textsubscript{n} clusters. It also reveals, that VDEs are not good probes for the energetically favorable chemisorption sites. What one can retain form our experience is that, in general, for adsorbed systems caution must be exercised in ascribing VDEs to ground state structures and in considering them as a test of structure optimizations, as is commonly (and more successful) done for bare clusters. Although VDEs cannot be used as fingerprints of preferential chemisorption sites, photodetachment spectra, especially if vibrationally resolved, may still provide interesting information on cluster chemisorption when aided by reliable modeling and simulations.

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(1) G. von Helden et al., Science 259 (1993) 1300
28. A new form of bulk silicon consisting of “magic” clusters?

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Since the discovery of the “supermagic” cluster C_{60} \footnote{1} the possibility of the synthesis of new materials consisting of highly stable clusters fascinates many researchers. In case of C_{60} and similar fullerenes like C_{70} and La@C_{82} such materials exist and, e.g., fullerite - the bulk material formed by weakly interacting C_{60} “soccer balls” - represents a new form of carbon besides diamond and graphite \footnote{2}. This discovery triggered a revolution of research in carbon based materials. The question arises, whether “magic” clusters of other elements like Si or Al might be suitable as building blocks of new cluster materials. In experimental studies of free clusters in the gas phase many other very stable clusters have been found like C_{32} \footnote{3} or Si_{4} \footnote{4,5}. In addition, there are also theoretical predictions of possible building blocks of new materials like e.g. Al_{13}H \footnote{6,7} and Si_{43} \footnote{8}.

Here we present combined experimental and theoretical results \footnote{9} on the interaction between neighboring “magic” clusters. As a first example, magic Si_{4} clusters are selected. Experimentally, the clusters are mass-selected and soft landed on an inert van-der-Waals surface \footnote{10}. They are probably highly mobile on this surface at room temperature and will immediately form large islands of bulk Si if there wouldn’t be a barrier against fusion. The samples are studied using XPS and, in contrast to an earlier study of Si_{40} on amorphous carbon \footnote{12}, the spectra contradict the formation of large islands supporting the existence of a barrier. Theoretically, the interaction potential between two approaching Si_{4} clusters is calculated for two geometries and for both channels a barrier against fusion is found which is large compared to room temperature. Accordingly, a new bulk of pure Si consisting of Si_{4} clusters should exist. And even more general, if this is true for some magic silicon clusters it might also be true for many other clusters found to be stable in the gas phase.

Results of our \footnote{9} DFT-computations \footnote{13-15} for the Si_{4}-clusters are shown in Fig. 1, displaying the calculated potential energy of two interacting Si_{4} clusters as a function of distance. The corresponding geometries are shown in the inserts. Neutral Si_{4} in its electronic ground state is a planar rhombus and there are several geometries possible for two tetramers approaching each other. We assume the Si_{4} clusters lie flat on the surface and, therefore, we restricted our calculations to planar geometry of two Si_{4} approaching each other with the two obtuse (a) or sharp (b) corners encountering. For the geometry displayed in Fig. 1a the potential energy increases monotonously with decreasing distance corresponding to a repulsive interaction. The two clusters do not fuse. If the two Si_{4} approach with the sharp corners ahead a bond is formed (Fig. 1b). A minimum with a binding energy of 1.3 eV is calculated corresponding to the formation of a Si_{8} cluster. The geometry corresponding to this minimum does not correspond to the equilibrium geometry of a Si_{8} \footnote{15,17} cluster (in fact it is 2.7 eV higher in energy) and represents a metastable isomer.

The large differences between the two geometries displayed in Fig 1a and b might be explained by the different coordination of the Si atoms which are involved. In Fig. 1a there are Si atoms which already have three bonds formed within the clusters, while in Fig. 1b the “reacting” Si atoms have a lower coordination. Accordingly, for the latter case a bond is formed. We consider these two reaction channels as the most favorable ones. Other channels were attempted but during the approach clusters had the tendency to rearrange to a configuration similar to the one in Fig. 1b. Important in Fig. 1b is the small increase of the potential energy at a distance of 3.1 Å. This barrier is 0.3 eV high and, therefore, it might not be overcome at kinetic energies corresponding to room temperature. Accordingly, for both reaction channels the calculation predict a repulsive interaction at lower temperatures.

![Fig. 1: Calculated potential energy curves for two neutral interacting Si_{4} clusters. Two different reaction channels have been calculated: the two tetramers approaching each other with the flat (a) and sharp (b) corners ahead. Case (a) is repulsive, while in case (b) a bond is formed. In (b) an energy barrier is observed at a distance of 3.1 Å and a height of 0.3 eV.](image-url)

These theoretical findings support the results of an experimental study of Si_{4} clusters deposited on HOPG at room temperature. The experimental set up has been described in detail elsewhere \footnote{10}. We assume that the interaction of these clusters with the substrate is weak and no change of the geometric and electronic structure of the Si_{4} is to be expected. In addition, most likely the clusters lie flat on the surface, are highly mobile at room temperature and approach each other in geometries similar to the ones calculated above. The samples are studied using XPS and only the peak corresponding to the 2p core level of Si is examined in detail (Fig. 2, left column). The area of this feature corresponds to the amount of Si deposited on the HOPG. For clean bulk Si an almost symmetric peak centered at a binding energy of 99.4 eV is observed (Fig. 2c, left column). For the deposition of Si atom ions on HOPG (Fig. 2b, left column) a similar peak is observed with a
shoulder corresponding to an unresolved feature at 101 eV binding energy. For Si$_4$ clusters deposited on HOPG (Fig. 2a, left column) a shift of the main peak of 0.5 eV towards higher binding energy and a slightly more intense shoulder corresponding to a broad peak around 102 eV is observed.

The small features at binding energies around 101 – 102 eV are assigned to Si atoms bound to carbon atoms. The chemical shift depends on the coordination number (e.g., Si$_2$-C, Si-C or Si-C$_2$). Some atoms and clusters migrate to monoatomic steps and defects on the HOPG surface and form a covalent bond with carbon atoms. The main peak corresponds to Si atoms bound to Si atoms. The observed shift of 0.5 eV between the deposited clusters and the deposited atoms is essential. We explain this shift by a lower average coordination number of the Si atoms in clusters. Similar shifts have been observed in XPS spectra of various mass-selected deposited clusters. In these experiments the clusters are not mobile on the surface, or, if the clusters can diffuse, the shift vanishes with time due to the formation of large bulk-like islands. These findings indicate that deposited Si$_4$ clusters do not form larger islands but remain as individual clusters on the surface.

![Fig. 2: Left: XPS spectra of the Si 2p peak recorded for (a) Si$_4$ clusters deposited at 5 eV onto HOPG (2% coverage), (b) positively charged Si atoms deposited at 5 eV onto HOPG (2% coverage) and (c) for a Si bulk reference sample. Fits of the experimental data are also displayed in the figure. Right: XPS spectra of the Si 2p feature recorded for (a) Si$_4$ clusters deposited at 5 eV onto amorphous carbon (4% coverage), (b) positively charged Si atoms deposited at 5 eV onto amorphous carbon (3% coverage) and (c) for a Si bulk reference sample.](image)

To support our findings we repeated the above experiments with a different sample: amorphous carbon. This surface consists of very small graphitic sheets with no ordering and the number of dangling carbon bonds is extremely high. This surface is more reactive than HOPG and might bind adsorbates easily. We generated this surface by sputtering HOPG with Ar ions at a kinetic energy of 1 keV. For this surface, we find a sticking coefficient of 50% for the Si$_4$ cluster ions in fair agreement with earlier studies. Fig. 2 (right column) displays the corresponding XPS data in comparison with the Si 2p bulk feature. As expected, for the deposition of Si atom ions (Fig. 2b, right column) at low coverages of up to 4% ML almost no pure Si-Si bonds but only Si atoms bound to carbon are found. No Si islands are formed but the Si atoms are trapped at surface defects.

In contrast, the XPS feature corresponding to the soft landed Si$_4$ cluster ions (Fig. 2a, right column) does not exhibit a difference to the case of the HOPG surface (Fig. 2a, left column). The tetramers do not react with defect sites of the amorphous carbon and do not coalesce as to be expected for “magic” clusters. Again, these findings support our hypothesis, that Si$_4$ clusters are suitable as building blocks for a cluster material.
29. Experimental setup for electronic transport measurements through individual clusters

J. Grebing, M. Grass, M. Mathes, G. Ganteför and E. Scheer

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. From investigations of the simplest imaginable circuit – a single atom between two metallic electrodes – it is known that changing the precise atomic arrangement and bonding strength of the central atom to its neighbors alters the transport properties crucially. Unfortunately, with the usual experimental techniques for fabricating single-atom contacts, i.e. modified scanning tunneling microscopy (STM) techniques or mechanically controllable breakjunctions (MCB, see report by Kunej et al.) no direct information is available about the atomic ordering in the contact region 1).

From the theoretical side, a quantum chemical model has been put forward that successfully describes the differences in the transport properties of single-atom contacts made of different elements 2).

However, when increasing the size of the contact, e.g. by replacing the single atom by a few atoms or a molecule, too many atomic arrangements are possible and thus too many parameters have to be taken into account in the calculations to allow the successful calculation of the transport properties.

We therefore wish to measure the transport properties of a system that is slightly more complex than a single-atom contact but with known atomic structure, e.g. a cluster of the size of a few atoms.

In a similar experiment by Bezryadin et al. 3) the transport through ligand-stabilized Pd clusters of diameter $\approx 17$ nm contacted between two Pt electrodes at constant distance has been studied (Fig. 1). It turned out that with this method only very highly resistive tunneling contacts to the electrodes were possible giving rise to charging effects but not to metallic transport behavior.

In order to avoid this difficulty, small mass selected clusters should be used that are stable in ultrahigh vacuum conditions without ligands. We choose a system consisting of “magic” Si$_4$ clusters, which will be contacted by adjustable electrodes fabricated by the MCB technique.

In a recent experiment it has been shown that Si$_4$ clusters - when deposited onto highly oriented pyrolitic graphite (HOPG) - do not coagulate to larger particles. They are therefore discussed as building blocks of a possible bulk material with unusual properties, similar to crystals of the fullerene C$_{60}$ 4). In previous deposition experiments on gold substrates, strong interactions between the clusters and substrate have been detected hindering the formation of a cluster solid.

The cluster ions are generated using a pulsed arc cluster ion source (PACIS) 5). Subsequently they are mass selected with a 45° sector magnet, decelerated down to a kinetic energy of 5 eV, and soft-landed on the substrate.

![Fig. 1: Left: Micrograph of Pt electrodes separated by a 14 nm gap after trapping a single $\approx 17$ nm Pd particle. Right: Current-voltage curves of a similar junction measured at room temperature and at 4.2 K (symbols). The solid lines are fittings to a Coulomb blockade theory taking into account voltage dependent tunnel barriers (for details see (3)).](image)

![Fig. 2: Principle of cluster deposition by “soft-landing” on a substrate, prepatterned with MCB electrodes.](image)

For the present experiment the substrate will be a bronze or stainless steel wafer with a polyimide insulating layer, prepatterned with breakjunction electrodes. The electrodes will be broken to form a narrow-gap (a few Å) tunnel contact in the UHV chamber in order to avoid contamination while monitoring the tunnel resistance. An electrostatic trapping 3) procedure will be used to pull individual clusters into the gap: During the cluster deposition a voltage in the order of a few volt will be applied between the electrode pair, giving rise to a highly enhanced inhomogeneous electric field in the gap region. A shunt resistance in series with the electrodes limits the current and guarantees that as soon as a cluster closes the gap, the voltage across the cluster-junction is short-circuited. By a feed back loop, the cluster deposition will be stopped (see Fig. 2).

The coupling of the electrodes to the cluster can then be
adjusted by controlling the bending of the MCB substrate. The measurement of current-voltage characteristics allows the characterization of the electronic structure of the cluster.  

As a first step a particular sample holder has been constructed that consists of the following components and fulfills the following requirements (see Figs. 3 and 4):  

- Soft landing of the clusters by applying a deceleration voltage on the substrate (electrical insulation of the sample).  
- Exact positioning of the substrate in the center of the cluster beam (beam diameter ≈ 5 mm) and perpendicular to the beam direction.  
- MCB mechanism that allows the bending of the substrate for forming and controlling the tunnel gap with an accuracy of a few picometer.  
- In situ transport measurements (current-voltage characteristics) for junctions in the order of kiloohms to gigaohms.  
- Transfer system, removable from cluster beam and vacuum chamber for sample exchange without breaking the vacuum.  
- Fitting into the existing cluster-deposition setup without disturbing beam geometry and diagnostic equipment.  
- UHV compatible.

Fig. 3: Sample holder used for transport measurements through individual clusters. The sample holder is mounted on a UHV compatible transfer mechanism equipped with a turbomolecular pump, a gate valve and a PC controlled dc-motor for adjusting the MCB electrodes (not shown). The angle between driving rod and deposition plane was necessary because of the location and the size of the accessible free port of the vacuum chamber.

Fig. 4: Photographs of different details of the sample holder. The movable stage, the plug for electrical wiring, and the insulating supports are made of Vespel® and stainless steel.

First experiments will be carried out using Al electrodes. The electrodes are covered with a native oxide layer since they are exposed to ambient conditions before mounting onto the sample holder. This oxide layer is expected to provide only weak interaction with the clusters, similar to the behavior of HOPG. Only the tips of the electrodes offer metallic surfaces to the clusters since the nanobridge is broken under UHV conditions.

(3) A. Bezryadin et al., Appl. Phys. Lett. 71 (1997) 1273  
30. Cluster experiments using a free electron laser


In experiments on clusters and nanostructures with sizes below 10 nm it turned out to be essential to have perfect mass-separation. Each additional atom changes the structures and the properties drastically. E.g., the structure of the well-known C\textsubscript{60} is a hollow sphere (“soccer ball”) with electronic properties similar to a semiconductor. In contrast, the structures of C\textsubscript{59} and C\textsubscript{61} are unknown and their properties are probably similar to the ones of a metal\textsuperscript{1}. Such structural changes are also induced by reactions of bare clusters with adsorbates like hydrogen atoms or CO molecules. E.g., structures and properties of Au\textsubscript{n} and Si\textsubscript{n} clusters are dramatically altered by the addition of just one hydrogen atom\textsuperscript{2,3}.

Accordingly, perfect mass-separation is essential for experiments on clusters and almost all successful cluster experiments have been done on mass-selected cluster ion beams\textsuperscript{4}. However, the disadvantage of these techniques is the very low intensity of such beams and many techniques of structural analysis, which are commonly used in the study of bulk materials, surfaces and molecules, cannot be applied to cluster ions. Such techniques are, e.g., XPS (X-ray photoelectron spectroscopy), EXAFS (extended x-ray absorption fine structure) and NEXAFS (near edge absorption fine structure) which operate with synchrotron radiation in the regime between $h\nu = 50 - 2000$ eV. For spectroscopy on ion beams high intensities of the used radiation is necessary, which so far can only be provided by lasers. However, laser generate radiation up to a photon energy of about $h\nu = 10$ eV and, therefore, XPS, EXAFS and NEXAFS cannot be applied to mass-selected clusters ion beams yet.

Most recently, however, it is possible to generate high intensity radiation using free electron lasers (FEL). Such a free electron laser is under construction at the TESLA Test Facility at DESY in Hamburg\textsuperscript{5}. In its final stage, it will provide wavelengths down to 6 nm ($h\nu = 200$ eV) in the vacuum ultraviolet (VUV-FEL) and soft-X-ray regime and will deliver sub-picosecond radiation pulses with gigawatt peak powers. Right now, first experiments using this new techniques are carried out around 100 nm ($h\nu = 10 - 20$ eV).

The laser radiation provided by the VUV-FEL in Hamburg can be used for many different experiments and one application, which is planned for the near future, is the spectroscopy of mass-selected cluster ions. The BMBF (Bundesministerium für Bildung und Forschung) supports a collaboration of six research groups from various German universities for conducting such an experiment. A newly designed apparatus consisting of a cluster ion source, a mass-spectrometer and an analyzer chamber will be finished at the end of 2002. The apparatus is designed to allow for various different experiments on cluster ions. As cluster source either a laser vaporization source, a pulsed arc cluster ion source or a magnetron sputter source can be used. For mass-separation, a high-resolution sector magnet is available or, if necessary, the cluster ions can be separated using the time-of-flight method. For spectroscopy, different detectors can be mounted in the analyzer chamber like an ion time-of-flight mass spectrometer, an electron time-of-flight spectrometer or a hemispherical electron energy analyzer.

At the beginning photoelectron spectroscopy of deep valence and shallow core levels is planned. The high photon energy already available in the present stage of the FEL (15 – 30 eV) will allow to conduct many exciting experiments for the first time. From the wealth of possible studies a few ones are selected, which can be done with relatively low photon energies and on clusters, which can be generated in relatively large amounts. The proposed experiments can be classified into two groups:

(i) XPS: photoelectron spectroscopy on shallow core levels. For the first time this experiment will allow a direct insight into atomic coordination of free clusters. In a first step we will focus on bare clusters of selected elements (W, Pb, Sn, Ge, …), which have core levels at relatively low binding energies and, accordingly, XPS can be done using relatively low photon energy. For bare clusters, the core level binding energy depends on the coordination number of the atoms in the cluster and, therefore, on the geometry. The core level binding energy should be different for “bulk” and “surface” atoms. Accordingly, it should be possible, to distinguish between “inner” and “outer” atoms in the cluster. One interesting question is the limiting cluster size for the appearance of “inner” atoms, because very small clusters have no “inner” atoms.

Although Pb, Sn and Ge are in the same group of the periodic table, the bulk materials have different structures: Pd has a metallic, high coordinated structure, while Ge is a semiconductor with the low coordinated diamond structure. The geometrical structure of the corresponding clusters is generally not known and in the case of Sn, which is “in between” Pb and Ge, there might be a size-dependent structural transition, which can be revealed using XPS.

Core f-orbitals of transition metals, like W (4f\textsubscript{7/2} = 31 eV, 4f\textsubscript{5/2} = 34 eV), will be energetically accessible by the photon energy of the FEL. Due to the high cross section, sharpness and relatively large energy splitting between the f\textsubscript{7/2} and f\textsubscript{5/2} components the spin orbit coupling, core level shift and peak shape can be probed as a function of cluster size. Generally due to their high intensity, the inner shell f-orbitals of W serve as important ESCA lines in surface spectroscopy. Also, W clusters are relatively easy to be
prepared without oxygen-contamination.

In a next step we want to apply the new XPS technique to reacted species like Ge clusters passivated with hydrogen. Similar to Si (which needs much higher photon energy and therefore is not considered for the first experiments) hydrogen passivation of the dangling bonds of Ge clusters should have dramatic influence on the geometry (adsorption site, adsorbate induced reconstruction, increase of the band gap). The XPS spectra will give direct insight into the changes at the surface and will reveal adsorbate sites.

(ii) UPS: photoelectron spectroscopy on valence states (ultraviolet photoelectron spectroscopy=UPS). Although there already are many photoelectron spectra on gas-phase mass-selected clusters, the valence orbitals at high binding energies cannot be fully mapped with conventional lasers. But these orbitals determine, e.g., the magnetic and catalytic properties. The properties of standard magnetic materials like Ni depend on the interaction of the 3d electrons, which, on the other hand, are responsible for the geometrical structures. For clusters, however, almost nothing is known about the relationship between geometry and magnetism. E.g., the surprisingly low total magnetic moment of Ni13 is probably related to its geometric structure, but this is just an assumption. Such effects could efficiently be studied by valence band spectroscopy of the 3d orbitals. For systematic measurements experiments require photon energies above 10eV. A second goal of valence band photoelectron spectroscopy is CO chemisorption on transition metal clusters. In sharp contrast to bulk metal surfaces almost nothing is known about adsorption sites and the nature of the chemisorption bond in clusters. This can be studied by the spectroscopy of the CO orbitals involved in the chemisorption bond (3σ, 1π, 4σ - orbitals of CO). These orbitals have binding energies between 10-15eV and can be studied with the FEL. Furthermore, the binding energies of aromatic ligands, like arenes (＞10 eV), are of particular interest as they form many transition metal-organic compounds, e.g. ferrocene-derivates, which are of principal interest for catalytic reactions. The difference between p-p and p-d interactions can be made by comparison of adsorption onto transition metals (e.g. Pt) and main group metals like, e.g., Pb.

As a first step we want to start with studies on the structure of mass-selected clusters and nanoparticles by making use of the high photon flux of the FEL. In the future we would like to take also advantage of the time structure of the FEL. Using the same experimental set up, mass-selected clusters can be photoexcited with a conventional femtosecond laser pulse triggering a fast electronic or chemical process. The dynamics of this process can be studied by recording XPS spectra as function of the delay times between the ultra short laser and FEL pulses. Such sequences of XPS spectra would be movies of the structural dynamics of excited clusters. With this technique, e.g., the real-time desorption of CO molecules from transition metal clusters could be demonstrated. The reorganization of the electronic and geometric structure on a femtosecond time scale is another issue of key importance.

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(1) S.H. Yang et al., Chem. Phys. Lett. 139 (1987) 233
(2) D. Fischer et al., Chem. Phys. Lett. 361 (2002) 389
(3) L. Kronik et al., Nat. Mat. (2002), in print
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31. Phase transitions and quantum effects in pore condensates

J. Hoffmann and P. Nielaba

Materials properties of systems condensed into pores of nanometer length scales (i.e., Vycor, Gelsil) are different from those of bulk systems. Important reasons for these effects are the geometrical finite size effects (the atomistic material structure cannot be neglected), the interaction of the material with the surrounding “glass”-matrix and the large interface contributions relative to the volume. Typical nano-pore materials are Vycor and Gelsil. Phase transitions of pore condensates in nanopores have been investigated by experimental methods recently.\(^1\),\(^2\). Besides spinodal decomposition, phase transition temperature reductions have been studied for cylindrical nano-pores with small diameters.

With computer simulations (CRAY-T3E) we have analyzed many interesting properties of “Ar”- and “Ne”-pore condensates recently (modeled as Lennard-Jones systems with particle diameter \(\sigma\) and interaction energy \(\epsilon\), in our computations we use particle masses \(m^*=m\sigma^2\varepsilon/\hbar^2 = 100\) and \(m^*=1000\) for simplicity well approximating the particle masses of Ne and Ar (\(m^*=112\) and \(m^*=1160\)). These systems have, like the “bulk”-systems, an liquid phase transition at low temperatures, the precise shape of the phase diagram is strongly influenced by the system geometry (pore radius).

It turns out that with increasing attractive wall interaction the critical density increases, the adsorbate density increases strongly, and the condensate density increases weakly. A meniscus is formed with increasing curvature, the configurations become less stable and the critical temperature decreases. The critical temperature is reduced with decreasing pore diameter. Beginning from the wall, a formation of layered shell structures is found which may favor or disfavor the occupancy of sites at the pore axis due to packing effects.

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\(k_B T/\epsilon\)

\[\Psi_6\]

**Fig. 1:** Configurations of a classical LJ-condensate (\(N = 1500\)) in a cylindrical pore of radius \(R = 4\sigma\), and length \(L = 60\sigma\) at \(T^* = 0.6, 0.46, 0.2\) (from left to right). The potential parameters for the wall-particle interactions are: \(\sigma^{WP} = 1.094\sigma\), \(\epsilon^{WP} = 1.509\epsilon\).\(^5\)

**Fig. 2:** Bond orientational order parameter for the outer layer versus temperature of a classical LJ-condensate in a cylindrical pore of radius \(R = 4\sigma\). Parameters as in Fig. 1.

The triple point temperature is influenced by the geometrical finite size effects (pore radius) as well as by the wall-particle interaction. At sufficiently strong wall-particle interaction (\(\epsilon^{WP} = 1.509\epsilon\), \(\sigma^{WP} = 1.094\sigma\)) we find a two step fluid-solid phase transition. In Fig. 1 we show typical configurations for a pore with radius \(R = 4\sigma\) at three temperatures. At \(T^* = 0.6\) the system is fluid, at \(T^* = 0.46\) the central condensate region is frozen and the adsorbate region is fluid, and at \(T^* = 0.2\) the adsorbate is frozen as well. At \(T^* = 0.575\) a solidification of the condensate phase is found by a jump in the energy. The condensate freezes in one piece from the cylinder wall to the axis. The remaining fluid adsorbate phase solidifies only at \(T^* = 0.375\). The bond orientational order parameter \(\Psi_6\) of the outer layer is presented in Fig. 2. Indeed the two step “freezing” scenario is supported by these data as well. In Fig. 2 hysteresis effects are analyzed as well. Only a little effect on the values of \(\Psi_6\) is found on heating or cooling the system.
A different scenario was found for even stronger interactions between the wall and the particles: The system freezes at the cylinder wall due to the strong binding energy to the wall. Between the layer at the cylinder wall and the next layer only a very small particle exchange is found. The region close to the cylinder axis however is still fluid and freezes only at lower temperatures. The different behavior of layer-wise freezing in systems with strong wall-particle interaction and the block-wise freezing for small particle-pore-interactions can be understood as follows: particles in the second layer can be treated as particles in a pore with Radius \( R_{\text{eff}} = R - \sigma \) with a potential consisting of the particle-wall potential and the particle-particle potential to the particles in the first layer. Latter is in the order of \( 3\epsilon \) since there are 3 nearest neighbors in the first layer. The effective outer potential for the second layer is in the same order as the outer potential for particles in the first layer for systems with small wall-particle interactions. For even stronger wall particle potentials the effective outer potential for the inner layers differs from the potential of the outer layer. Such two stage freezing phenomena were observed in experiments of melting and freezing of Ar in Vycor pores recently 5).

decided by the symmetry properties of its nearest neighbors. In case of the FCC-structure the neighborhood of a particle has point symmetry in contrast to the case of the HCP-structure. Figure 3 shows the different regions with local FCC and HCP structure of a simulation in the NpT-ensemble at \( p = 0 \) and \( k_B T/\epsilon = 0.15 \).

At low temperatures quantum effects become important which have been ignored in most of the existing theoretical studies of pore condensates. By path integral Monte Carlo simulations 6–9) the effect of the quantum mechanics on the potential energy as a function of the temperature has been quantified. 3,4) In contrast to classical simulations we obtain by PIMC simulations for Ar- and Ne-condensates an horizontal temperature dependency of the energy resulting in a decrease of the specific heat to zero at small temperatures in agreement with the third law of thermodynamics. The resulting phase diagram for Ar- and Ne-condensates and a comparison with classical computations shows important quantum effects 4). In the Ne-system (containing the lighter particles) a significant reduction (by about 5-10%) of the critical temperature is found due to quantum delocalizations as well as a strong reduction of the solid density and a crystal structure modification in comparison with the classical case.

\[ \text{Fig. 3: Solid condensate (3000 LJ-particles) in a cylindrical pore of radius } R = 10\sigma \text{ at } T^* = 0.15 \text{ and } p = 0 \text{ (NpT-ensemble). Interaction potential parameters for the wall particle interaction: } \sigma_{WP} = 1\sigma, \epsilon_{WP}, n^W = 0.5\sigma^2. \]

Black particles: local HCP-symmetry, white particles: local FCC-symmetry, gray particles not having either symmetry.

For small pore radii and not too small wall-particle interactions we observe a layering structure of the condensate. For a bulk system instead one would expect a crystalline FCC or HCP structure. In agreement with this for large pore diameters and not too strong wall-particle interactions indeed no layering structure is found. In this case structures are formed with local FCC- or HCP-order. The membership of a particle to the lattice structures is

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32. Melting of hard disks in two dimensions

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One of the first continuous systems to be studied by computer simulations 1) is the system of hard disks of diameter \( \sigma =1 \) interacting with the two body potential,

\[
V(r) = \begin{cases} 
   \infty & r \leq \sigma \\
   0 & r > \sigma 
\end{cases}
\]

(1)

Despite its simplicity, this system was shown to undergo a phase transition from solid to liquid as the density \( \rho \) was decreased. The nature of this phase transition, however, is still being debated. Early simulations 1) always found strong first order transitions. As computational power increased the observed strength of the first order transition progressively decreased! Using sophisticated techniques Lee and Strandburg 2) and Zollweg and Chester 3) found evidence for, at best, a weak first order transition. A first order transition has also been predicted by theoretical approaches based on density functional theory 4). On the other hand, recent simulations of hard disks 5) find evidence for a Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) transition 6) from liquid to a hexatic phase, with orientational but no translational order, at \( \rho = 0.899 \). Nothing could be ascertained, however, about the expected hexatic to the crystalline solid transition at higher densities because the computations became prohibitively expensive. The solid to hexatic melting transition was estimated to occur at a density \( \rho_x \geq 9.1 \). A priori, it is difficult to assess why various simulations give contradicting results concerning the order of the transition. In Ref. [7] we took an approach, complementary to Jaster’s, and investigated the melting transition of the solid phase. We showed that the hard disk solid is unstable to perturbations which attempt to produce free dislocations leading to a solid \( \rightarrow \) hexatic transition in accordance with KTHNY theory 6) and recent experiments in colloidal systems 8). Though this has been attempted in the past 9,10), numerical difficulties, especially with regard to equilibration of defect degrees of freedom, makes this task highly challenging.

The elastic Hamiltonian for hard disks is given by

\[
F = -P \epsilon_y + B / 2 \epsilon + (\mu + P) (\epsilon_x / 2 + 2 \epsilon_y),
\]

(2)

where \( B \) is the bulk modulus. The quantity \( \mu = \mu + P \) is the “effective” shear modulus (the slope of the shear stress vs shear strain curve) and \( P \) is the pressure. The Lagrangian elastic strains are defined as

\[
\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial R_j} + \frac{\partial u_j}{\partial R_i} - \frac{\partial u_i}{\partial R_j} - \frac{\partial u_j}{\partial R_i} \right)
\]

(3)

where the indices \( i,j \) go over \( x \) and \( y \) and finally, \( \epsilon_x = \epsilon_{xx} + \epsilon_{xy} \) and \( \epsilon_y = \epsilon_{yx} - \epsilon_{yy} \). The displacement vector \( \mathbf{u} \) is the deviation of an atom from the nearest perfect lattice point \( \mathbf{R} \).

The KTHNY-theory 6) is presented usually for a 2-d triangular solid under zero external stress. It is shown that the dimensionless Young’s modulus of a two-dimensional solid, \( K = (8 / \sqrt{3}) (\mu / \sigma) / (1 + \mu / (\lambda + \mu)) \), where \( \mu \) and \( \lambda \) are the Lamé constants, depends on the fugacity of dislocation pairs, \( y = \text{exp}( -E_T / K) \), where \( E_T \) is the core energy of the dislocation, and the “coarse-graining” length scale \( l \). This dependence is expressed in the form of the following coupled recursion relations for the renormalization of \( K \) and \( y \):

\[
\begin{align*}
\frac{\partial K^{-1}}{\partial l} &= 3 \pi y^2 e^{-\frac{K}{8 \pi}} \left[ I_0 \left( \frac{K}{8 \pi} \right) - \frac{1}{4} I_1 \left( \frac{K}{8 \pi} \right) \right], \\
\frac{\partial y}{\partial l} &= (2 - \frac{K}{8 \pi}) y + 2 \pi y^3 e^{\frac{K}{16 \pi}} I_0 \left( \frac{K}{8 \pi} \right)
\end{align*}
\]

where \( I_0 \) and \( I_1 \) are Bessel functions. The thermodynamic value is recovered by taking the limit \( l \rightarrow \infty \).

**Fig. 1:** Schematic flows of the coupling constant \( K \) and the defect fugacity \( y \) under the action of the KTHNY recursion relations. The dashed line is the separatrix whose intersection with the line of initial state (solid line connecting filled circles, \( y(0) = 0 \), \( K(0) = 0 \)) determines the transition point \( T_c \).

We see in Fig. 1 that the trajectories in \( y-K \) plane can be classified into two classes, namely those for which \( y \rightarrow 0 \) as \( l \rightarrow \infty \) (ordered phase) and those \( y \rightarrow \infty \) as \( l \rightarrow \infty \) (disordered phase). These two classes of flows are separated by lines called the separatrix. The transition temperature \( T_c \) (or \( \rho_x \)) is given by the intersection of the separatrix with the line of initial conditions \( K(0) \) and \( y = \text{exp}( -E_T / K) \) where \( E_T \sim c K / 16 \pi \). The disordered phase is a phase where free dislocations proliferate. Proliferation of dislocations however does not produce a liquid, rather a liquid crystalline phase called a “hexatic” with quasi-long ranged (QLR) orientational order but short ranged positional order. A second K-T transition destroys QLR orientational
order and takes the hexatic to the liquid phase by the proliferation of "disclinations" (scalar charges). Apart from $T_c$ there are several universal predictions from KTHNY-theory, for example, the order parameter correlation length and susceptibility has essential singularities $\left( e^{-\tilde{t}}, \tilde{t} \equiv T / T_c - 1 \right)$ near $T_c$. All these predictions can, in principle, be checked in simulations $(^5)$. One way to circumvent the problem of large finite size effects and slow relaxation due to diverging correlation lengths is to simulate a system which is constrained to remain defect (dislocation) free and, as it turns out, without a phase transition. Surprisingly, using this data it is possible to predict the expected equilibrium behavior of the unconstrained system. The simulation $(^7)$ is always started from a perfect triangular lattice which fits into our box - the size of the box determining the density. Once a regular MC move is about to be accepted, we perform a local DeLaunay triangulation involving the moved disk and its nearest and next nearest neighbors. We compare the connectivity of this Delaunay triangulation with that of the reference lattice (a copy of the initial state) around the same particle. If any old bond is broken and a new bond formed (Fig. 2) we reject the move since one can show that this is equivalent to a dislocation-antisdislocation pair separated by one lattice constant involving dislocations of the smallest Burger's vector.

![Fig. 2: Typical move which attempts to change the coordination number and therefore the local connectivity around the central particle. Such moves were rejected in our simulation.](image)

Microscopic strains $\epsilon_{ij}(\mathbf{R})$ can be calculated now for every reference lattice point $\mathbf{R}$. Next, we coarse grain (average) the microscopic strains within a sub-box of size $L_x \times L_y = L_x^2 \int d^3 r \epsilon_{ij}(\mathbf{r})$ and calculate the ($L_y$ dependent) quantities $(^1)$,

$$
S_{++}^\rho = <\epsilon_{xx} \epsilon_{xx}>, \quad S_{--}^\rho = <\epsilon_{yy} \epsilon_{yy}>, \quad S_{\|\perp}^\rho = 4 <\epsilon_{xy} \epsilon_{xy}>.
$$

The elastic constants in the thermodynamic limit are obtained from, the set: $B = 1 / 2 S_{++}^\rho$ and $\mu_{eff} = 1 / 2 S_{--}^\rho = 1 / 2 S_{\|\perp}^\rho$. We obtain highly accurate values of the unrenormalized coupling constant $K$ and the defect fugacity $\gamma$ which can be used as inputs to the KTHNY recursion relations. Numerical solution of these recursion relations then yields the renormalized coupling $K_R$ and hence the density and pressure of the solid to hexpatic melting transition.

We can draw a few very precise conclusions from our results. Firstly, a solid without dislocations is stable against fluctuations of the amplitude of the solid order parameter and against long wavelength phonons. So any melting transition mediated by phonon or amplitude fluctuation is ruled out in our system. Secondly, the core energy $E_c > 2.7$ at the transition so KTHNY perturbation theory is valid though numerical values of nonuniversal quantities may depend on the order of the perturbation analysis. Thirdly, solution of the recursion relations shows that a KTHNY transition at $P_c = 9.39$ preempts the first order transition at $P_{c1} = 9.2$. Since these transitions, as well as the hexpatic-liquid KTHNY transition lies so close to each other, the effect of, as yet unknown, higher order corrections to the recursion relations may need to be examined in the future. Due to this caveat, our conclusion that a hexpatic phase exists over some region of density exceeding $\rho = .899$ still must be taken as preliminary. Also, in actual simulations, cross over effects near the bicritical point, where two critical lines corresponding to the liquid-hexpatic and hexpatic-solid transitions meet a first order liquid-solid line (see for e.g. Ref. $(^12)$ for a corresponding lattice model where such a situation is discussed) may complicate the analysis of the data, which may, in part, explain the confusion which persists in the literature on this subject.

33. Time-dependent density functional theory for lattice systems

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Density functional theory (DFT) represents a powerful tool for studies of phase transitions in classical systems 1). On one hand, DFT is ideally suited for a microscopic description of first-order phase transitions, and has found numerous applications to condensation or freezing phenomena and the respective influence of surfaces, reduced dimensionalties or confinement. On the other hand, the DFT can be combined with microscopic dynamics to provide generalized mean-field kinetic equations for non-equilibrium processes like phase ordering processes and spinodal decomposition. Generalized Allen-Cahn and Cahn-Hilliard equations have been derived recently from this “time-dependent density functional theory” (TDDFT) within the lattice gas approach 2) allowing in particular a description of such processes in binary metallic alloys, intercalation compounds, submonolayer films adsorbed on solid surfaces etc. A review article on mean-field kinetic equations and their applications is in preparation.

Current work is focused on quantitative tests of TDFT. Well suited tests cases are onedimensional lattice models, where the equilibrium free energy functional is exactly known. As shown previously, (see also the Annual Report 2000) the equilibrium distribution function in 1-d lattice models based on short-range interactions satisfies a generalized Markov property, which allows the explicit derivation of the free energy and local density correlators as functionals of the density 3,4). Using these results, the TDFT-scheme was applied to hopping diffusion of interacting particles on a linear chain. In comparison with Monte Carlo simulations, quantitative agreement was found for the temporal evolution of density profiles and density correlations 5).

Further steps were taken by applying the TDFT-scheme to spin relaxation in a Glauber chain 5). First, we derived kinetic equations in the form of generalized Allen-Cahn equations (“model-A” in the language of critical dynamics), where the thermodynamic driving force is determined by the exact free energy functional of the static theory. Spin density profiles evolving from an initially sharp wall between an up-spin and down-spin domain are shown in Fig. 1a. Again the agreement with Monte Carlo simulation is excellent. By contrast, ordinary mean-field theory even qualitatively fails to reproduce the correct spin-density profiles, see Fig. 1b, because it ignores the stabilizing influence of spin correlations.

An extension of these studies to 1-d kinetic Potts models is in progress. A first step consists in a comparison of DFT results for the static spin distribution of inhomogeneous Potts-chains with the transfer matrix method. In addition we currently investigate diffusion of particles with an internal spin degree of freedom as an exemplification of coupled conserved and non conserved dynamics.

Fig. 1 (a) Evolution of spin density profiles in a Glauber-chain with $\beta I = 2$ and $\beta h = -0.1$, where $I$ and $h$ are the exchange interaction and the external magnetic field, respectively. Full lines: TDFT, data points: MC simulation; (b) Same as (a) from ordinary kinetic mean-field theory.

(1) For a review, see H. Löwen, Phys. Rep. 251 (1994) 237
34. Ordering kinetics in a fcc A₂B binary alloy model: Monte Carlo studies

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Several face-centered cubic binary metallic alloys, like Cu₃Au, Cu₃Pd, Mg₃In, Co₃Pt, etc. exhibit long range order with a L1₂-structure. A well-studied system is Cu₃Au which undergoes a first-order bulk transition at a temperature T₀ = 663 K. In the bulk, Au-atoms preferentially occupy one of the four simple cubic sublattices of the underlying fcc-lattice. The ground state therefore is 4-fold degenerate. The antiphase domain structure is anisotropic as a result of the existence of two types of antiphase boundaries separating the 4 types of energetically equivalent equilibrium domains: low-energy (type-I) and high-energy (type-II) walls.

Surface-induced ordering kinetics in such metallic alloys have been investigated within Monte Carlo simulations using an atom-vacancy exchange mechanism [1] (see the Annual Report 2000). The results of these simulations revealed a strong dependence of the kinetics of the surface segregation front on the final temperature Tₖ to lie significantly above the ordering spinodal, Tₖ > Tₛₚ (quench into the metastable regime) or below, Tₖ < Tₛₚ (quench into the unstable regime). Below Tₛₚ a growth of the surface segregation proportional t¹/₄ was found.

These results motivated us to perform more detailed Monte Carlo simulations for bulk systems within this model. Again we observed two clearly distinct ordering scenarios whether the final ordering temperature Tₖ falls above or below the ordering spinodal Tₛₚ. For shallow quenches (Tₖ > Tₛₚ) we identify an incubation time τᵢₙc which characterizes the onset of ordering through the formation of overcritical ordered nuclei. The used atom-vacancy exchange algorithm together with experimental information on tracer diffusion in Cu₃Au alloys allows us to estimate the physical time scale connected with τᵢₙc in that material, see Fig. 1.

Deep quenches, Tₖ < Tₛₚ, result in spinodal ordering. Coarsening processes at long times proceed substantially slower than predicted by the Lifshitz-Allen-Cahn t¹/₂ law, see Fig. 2. Structure factors related to the geometry of the two types of domain walls are found to be consistent with Porod’s law in one and two dimensions, see Fig. 3.

Fig. 1: Incubation times τᵢₙc versus reduced temperature Tᵢ. The inset shows the same data (full symbols) after conversion to the physical time scale, together with incubation times measured [2] in Cu₃Au (open symbols).

Fig. 2: First moments k|| (t), proportional to the reciprocal average distance between high energy type-II walls, show growth proportional to t¹ with n ≈ ½, for t ≫ τᵢₙc.

Fig. 3: Scaled structure factors k||S||(k,t) (a) and k⊥S (k,t) (b) calculated for Tᵢ = 0.5465 T₀ < Tₛₚ: the slopes of the dashed straight lines represent a decay according to Porod’s law in one (a) and two dimensions (b).

35. Nucleation on top of islands in epitaxial growth

S. Heinrichs and P. Maass

Whether thin films in epitaxy become rough or grow smoothly layer by layer depends on the onset of second layer nucleation on top of islands in the first layer: If the rate of this nucleation is large, it is likely that mounds are formed before layer completion, while small second layer nucleation rates favor layer by layer growth. The nucleation on top of an island occurs once atoms form a nucleus that is stable on all experimentally relevant time scales. The size of such a stable nucleus must exceed the critical size \( i \). This size is one for many metals and typically larger than one for semiconductors. A crucial parameter for the nucleation rate is the energy barrier an adatom has to overcome when leaving the island over the step edge.

In order to extract the step edge barrier from experiments focusing on second layer nucleation, we developed a theory that can quantitatively describe the nucleation process also in the presence of adatom interactions \(^1\). The interactions considered are the presence of unstable sub-critical clusters and ring barriers between pairs of adatoms. The physical origin of these ring barriers lies in a distortion of the electronic structure in the atomic layer below the adatom. The theory is based on our recently developed rate equation approach \(^2\), which describes the time evolution of the nucleation process by the probabilities for an island to be in a certain state that is determined by the number of adatoms on top of the island and the way these adatoms are decomposed into clusters. The fundamental processes considered are the deposition rate onto the island, the loss rate for adatoms leaving the island by surmounting the step edge barrier, the attachment rates for single atoms to intermediate clusters and the dissociation rates of unstable clusters. In the presence of ring barriers the approach of two atoms is hindered by a circular barrier around each atom, and additional rates for formation and breakup of pairs of adatoms bound via the ring barrier enter the problem. The time evolution of the probabilities can be determined analytically only in the simplest cases, but a numerical solution turns out to be very efficient. The approach also gives detailed insight into the dominant microscopic pathways that are followed to form a stable nucleus on top of the island.

To apply our theory we consider the determination of step edge barriers in second layer nucleation experiments where one measures the probability that a stable cluster has nucleated on top of a growing island. In systems with a ring barrier, second layer nucleation will be aggravated and nucleation sets in later. A repulsive ring barrier therefore has an effect similar to a reduced step edge barrier, and thus yields an apparent measurement value \( \Delta E_v^{(0)} \) smaller than the "true" \( \Delta E_v \).

On the other hand, metastable dimers facilitate the formation of a stable nucleus, leading to values \( \Delta E_v^{(0)} \) larger than \( \Delta E_v \). Figure 1 shows the relative measurement errors when neglecting interactions as a function of the interaction strength, demonstrating the importance of including interaction effects in the evaluation of experimental data.

Second layer nucleation experiments for Ag/Pt(111) were performed by Bromann et al. \(^3\) with an analysis based on a "mean-field theory" \(^4\). However, a scaling analysis shows that this theory is not applicable for systems with critical nuclei \( i \leq 2 \) because these systems are dominated by fluctuations. \(^5\) With the rate equation theory the value for \( \Delta E_v \) is revised from the original value of 30 meV to 68 meV. For the Ag/Pt(111) system density functional calculations \(^6\) predict significant ring barriers for adatoms moving on one monolayer Ag. When including the ring barriers in the analysis, we obtain \( \Delta E_v = 52 \text{meV} \) \(^1\).

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36. Constant dielectric loss response in disordered systems

T. Höhr, P. Pendzing, C. Kircher, W. Dieterich and P. Maass

Disordered solids containing charged, mobile defects generally show pronounced dispersion in their dynamic conductivity or, equivalently, a “non-Debye” dielectric relaxation. Ion-conducting glasses or defective crystals have been studied under this aspect, with the aim to gain microscopic information and control on the ion migration in their specific atomic environments. For measuring frequencies in the Megahertz regime a power-law-type dispersion \( \sigma_{ac}(\omega) \sim \omega^n \) with \( n < 1 \) is “universally” observed in many different materials. More recent studies have detected a behavior \( \sigma_{ac}(\omega) \sim \omega \) at higher frequencies /low temperatures as a “second universality”, which is equivalent to a nearly constant dielectric loss (NCL), described by a frequency-independent imaginary part of the dielectric susceptibility \( \chi''(\omega) \). Similar behavior is known also for dielectric relaxation in certain anorganic and organic glass-forming melts. The physical origin of NCL spectra should be sought in non-activated defect displacements with amplitudes smaller than interatomic distances. Convincing model studies, however, are still lacking.

In this project (see also the Annual Report 2000) we elaborate on the idea that long-range interactions among dipolar centers can give rise to long-time tails in dielectric relaxation, consistent with NCL-type spectra. Evidence for the relevance of this mechanism emerged from dynamic Monte Carlo simulations of a “dipolar lattice gas”. This model consists of a spatially random assembly of dipolar centers, where charged particles (ions) perform reorientational steps next to their associated immobile counterion. Contrary to any description in terms of a superposition of Debye-contributions to the spectra, the present version of the dipolar lattice gas emphasizes the importance of dipole-dipole interactions.

Extensive Monte Carlo simulations were performed to obtain the dielectric loss spectrum

\[
\chi''(\omega) = \omega \beta \text{Re} \int_0^\infty dt \langle \vec{P}(t) \cdot \vec{P}(0) \rangle e^{i\omega t}
\]

with \( \vec{P} \) the total polarization and \( \beta = 1/k_B T \). Calculated spectra are shown in Fig. 1 for several temperatures, normalized by the typical interaction strength \( V_{dip} \) between centers. The decay of the “self-part” of the correlation function \( \langle \vec{P}(t) \cdot \vec{P}(0) \rangle \) can be decomposed into a short-time contribution, which corresponds to relaxation of a particular dipole in a static energy landscape and a long-time contribution due to temporal renewals in the minimum energy configuration seen by an individual dipole. The latter process turns out to be responsible for the slow decay at long times, in contrast to the Debye-like behavior of the initial decay.

An analytic argument that random dipolar interactions will quite generally lead to slow relaxation of the polarization, proceeds as follows. A selected dipolar defect will interact most strongly with its closest neighbor. One may then estimate its relaxation time from the strength of the dipolar interaction \( V_{dip}(r) \) if that neighbor is at distance \( r \), in competition with \( k_B T/V_{dip} \). Introducing the probability density for closest neighbor distances \( r \), one can perform a disorder average to obtain a correlation function that decays logarithmically in time.

Further notable features of this model are a significant enhancement of the overall NCL-response \( \chi''(\omega) \) relative to the “self-part” \( \chi_{self}(\omega) \), the appearance of different concentration dependent scenarios in approaching a constant loss under decreasing temperature and a robustness of the results against changes in the character of positional disorder.

\[\text{Fig. 1: Dielectric loss spectrum } \chi''(\omega) \text{ of a dipolar lattice gas with } c = 1/64 \text{ at different reduced temperatures } \theta = k_B T/V_{dip} \text{ showing the gradual transition between Debye and NCL-behavior. Continuous line represents the self-part of the susceptibility at } \theta = 0.8.\]

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III. Publications and Talks

1. Publications

**Group of Prof. E. Bucher**

V. Alberts, M. Klenk and E. Bucher:
*Phase Separation and Compositional Changes in Two-Stage Processed Chalcopyrite Thin Films*
Thin Solid Films 387 (2001) 44

A. Boueke, R. Kühn, P. Fath, G. Willeke and E. Bucher:
*LATEST RESULTS ON SEMITRANSPARENT POWER SILICON SOLAR CELLS*

P. Geiger, G. Hahn, P. Fath and E. Bucher:
*Comparing Improved State-of-the-Art to Former EFG-Ribbons with Respect to Solar Cell Processing and Hydrogen Passivation*

M. Klenk, V. Alberts, O. Schenker, and E. Bucher:
*Control of Two-Step Growth Processes of Chalcopyrite Thin Films by X-Ray Fluorescence Spectroscopy*

M. Klenk, O. Schenker, V. Alberts and E. Bucher:
*Properties of Flash Evaporated Chalcopyrite Absorber Films and Solar Cells*

A. Kress, O. Breitenstein, S. Glunz, P. Fath, G. Willeke and E. Bucher:
*Investigations on Low-Cost Back-Contact Silicon Solar Cells*

S. Scheibenstock, S. Keller, P. Fath, G. Willeke and E. Bucher:
*Progress in Monolithic Series Connection of Wafer-Based Crystalline Silicon Solar Cells by the Novel “HighVo” (High Voltage) Cell Concept*

*Stable and Metastable Vortex and the First-Order Transition Across the Peak-Effect Region in Weakly Pinned 2H-NbSe₂*

B. Wölfing, C. Kloc, J. Teubner and E. Bucher:
*High Performance Thermoelectric Tl₅Bi₂Te₆ with an Extremely Low Thermal Conductivity*

**Group of PD M. Deicher**

K. Bharuth-Ram, A. Burchard, M. Deicher, H. Hofsäss, H. Quintel, M. Restle and C. Ronning:
*Implantation sites of heavy ions in diamond*

M. Dietrich, J. Bartels, M. Deicher, K. Freitag, V. Samokhvalov and S. Unterricker:
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*The Strange Diffusivity of Ag Atoms in CdTe*
Physica B 308/310 (2001) 963

**Group of Prof. W. Dieterich**

O. Dühr, W. Dieterich and A. Nitzan:
*Charge Transport in Polymer Ion Conductors: A Monte Carlo Study*
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O. Dürr, H.L. Frisch and W. Dieterich:  
*Melt viscosities of lattice polymers using a Kramers potential treatment*  

M. Kessler, W. Dieterich and A. Majhofer:  
*Monte Carlo simulation of subsurface ordering kinetics in an fcc-alloy model*  

F. Eurich and P. Maass:  
*Soft ellipsoid model for Gaussian polymer chains*  

S. Heinrichs and P. Maass:  
*Comment on “Determination of Interlayer Diffusion Parameters for Ag/Ag(111)”*  

R. Kenzler, F. Eurich, P. Maass, B. Rinn, J. Schropp, E. Bohl and W. Dieterich:  
*Phase Separation in Confined Geometries: Solving the Cahn-Hilliard Equation with Generic Boundary Conditions*  

P. Maass and B. Rinn:  
*Equilibrium and Non-Equilibrium Dynamics in Random Energy Landscapes*  
(Special issue on the occasion of the 75th birthday of Professor M. Pollak)  

B. Rinn and P. Maass:  
*Comment on “Radial fluctuations induced stabilization of the ordered state in two-dimensional classical clusters”*  

B. Rinn, P. Maass and J. P. Bouchaud:  
*Hopping in the Glass Configuration Space: Subaging and Generalized Scaling Laws*  

**Group of Prof. G. Ganteför**

M. Astruc Hoffmann, G. Wrigge, B. v. Issendorff, J. Müller, G. Ganteför and H. Haberland:  
*Ultraviolet Photoelectron Spectroscopy of Si₄ to Si₁₀₀*  

B.K. Rao, P. Jena, S. Burkart, G. Ganteför and G. Seifert:  
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*Laser Cleaning of Polymer Surfaces*  
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*Optical field enhancement effects in laser-assisted particle removal*  

H.-J. Münzer, M. Mosbacher, M. Bertsch, J. Zimmermann, P. Leiderer and J. Boneberg:  
*Local field enhancement effects for nanostructuring of surfaces*  

**Group of Prof. P. Nielaba**

K. Binder, S. Sengupta and P. Nielaba:  
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J. Hoffmann and P. Nielaba:  
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**Group of Prof. G. Schatz**

M. Albrecht, A. Maier, F. Treubel, M. Maret, R. Poinsot and G. Schatz:  
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Antiferromagnetic ordering in superconducting YBa$_2$Cu$_3$O$_{6.5}$  

**Group of Prof. E. Scheer**

R. Häussler, E. Scheer, H. B. Weber and H. v. Löhneysen:  
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Generalized conductance sum rule in atomic break junctions  
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2. Conference Contributions

Group of Prof. E. Bucher

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Strasbourg / France, 5. – 8.6.2001

P. Geiger, G. Hahn, P. Fath and E. Bucher:
Comparing improved state-of-the-art to for EFG Si-ribbons with respect to solar cell processing and hydrogen passivation

D. Sontag, G. Hahn, P. Fath, and E. Bucher:
Two dimensional resolution of minority carrier diffusion constants in different silicon materials

G. Hahn, D. Sontag and C. Haessler:
Current collecting channels in RGS silicon solar cells – are they useful?

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Jeju / Korea, 11. - 15.6.2001

P. Fath:
Industrial Manufacturing of Semitransparent Crystalline Silicon POWER Solar Cells

G. Hahn, P. Geiger, D. Sontag, P. Fath and E. Bucher:
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Influence of an ammonia activation prior to the PECVD-SiN deposition on the solar cell performance

O. Klettke, D. Karg, G. Pensl, M. Schulz, G. Hahn and T. Lauinger:
Formation of the chromium-boron complex in solar-grade multicrystalline silicon

W. Neu, A. Kress, W. Jooss, P. Fath and E. Bucher:
Low cost multicrystalline back contact silicon solar cells with screen printed metallization

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A. Castaldini, D. Cavalcoli, A. Cavallini, M. Rossi, T. Pernau and M. Spiegel:
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High speed and high accuracy IQE and \( L_{\text{eff}} \)-mapping – a tool for advanced quality control in the PV industry

J.P. Rakotoniaina, O. Breitenstein, M. Langenkamp, M. Werner and G. Hahn:  
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B. Terheiden, B. Fischer, P. Fath and E. Bucher:  
Highly efficient mechanically V-textured silicon solar cells applying a novel shallow angle contacting scheme

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Seattle / USA, 12. - 16.11.2001

Perpendicular magnetic anisotropy in nanostructured CoPt\(_3\) (111) films

Group of PD M. Deicher

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Puri / India, 12. - 17.2.2001

M. Deicher:  
Radioactive ion beams: Applications to semiconductor and surface physics

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Hamburg / Germany, 26. - 30.3.2001

M. Dietrich, J Bartels, K. Freitag, M. Deicher, V. Samokhvalov und S. Unterricker:  
Beeinflussung des elektrischen Feldgradienten in \( \text{BaTiO}_3 \) durch ein äußeres elektrisches Feld
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Hämeenlinna / Finland, 2. - 7.7.2001

M. Deicher:
Applications of Radioactive Ion beams to Solid State Physics

21st Int. Conference on Defects in Semiconductors (ICDS-21)
Giessen / Germany, 16. – 20.7.2001

H. Wolf, M. Deicher, V. Ostheimer, A. Rodriguez-Schachtrup, N.A. Stolwijk and Th. Wichert:
The strange diffusivity of Ag atoms in CdTe

Sommerschule “Ionenstrahlen und Nukleare Sonden”
Bad Blankenburg / Germany, 23. - 28.9.2001

M. Deicher:
Identifizierung von Defekten in Halbleitern durch Radio-Tracer-Methoden

Arbeitstreffen “Forschung mit nuklearen Sonden und Ionenstrahlen”
Freiberg / Germany, 3. - 5.10.2001

A. Stötzler, M. Dietrich und M. Deicher:
Was sind die Eigenschaften von Ga-Antisite-Defekten (Ga\textsubscript{N}) in GaN?

Group of Prof. W. Dieterich

8\textsuperscript{th} Int. Workshop on Disordered Systems
Andalo, Trento / Italy, 5. - 8.3.2001

P. Maass:
Glassy Dynamics in the Configuration Space: Aging, Subaging and Multiple Scaling Regimes

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Hamburg / Germany, 26. - 30.3.2001

S. Heinrichs und P. Maass:
Bestimmung von Schwoebel-Barrieren mit Nukleationstheorien

M. Kessler, A. Majhofer and W. Dieterich:
Dynamische Monte-Carlo-Simulationen zu oberflächeninduzierten Ordnungsphänomenen in Cu\textsubscript{3}Au-Legierungen

F. Scheffler und P. Maass:
Feldfluktuationen in ungeordneten Systemen magnetischer Nanocluster

Int. Workshop on Frontiers in the Physics of Complex Systems
Minerva Center, Bar-Ilan University /Israel 25. - 28.3.2001

W. Dieterich, T. Höhr and P. Maass:
Collective dynamics in a random dipolar system and the constant loss response in glasses

O. Dürr, T. Volz, W. Dieterich and A. Nitzan:
Diffusion in a Polymer Network - A Dynamic Percolation approach

ECAMP VII - The 7th European Conference on Atomic and Molecular Physics
Berlin / Germany, 2. - 6.4.2001

F. Eurich and P. Maass:
Gaussian ellipsoid model for polymer chains
Polymer Electrolyte Symposium 2001
Noordwikkerhout / The Netherlands, 14. - 16.5.2001

O. Dürr, W. Dieterich and A. Nitzan:
Diffusion in polymer electrolytes and the dynamic percolation model

O. Dürr, T. Volz, W. Dieterich and A. Nitzan:
Diffusion in a Polymer Network: A Dynamic Percolation Approach

4th Int. Discussion Meeting on Relaxation in Complex Systems
Heraklion / Greece, 18. - 26.6.2001

W. Dieterich:
Relaxation in random dipolar systems and the constant loss response in glasses

P. Maass:
Hopping Dynamics of Ions in Glasses: Dispersive Transport and Changes in Stoichiometry

P. Maass:
Aging Dynamics in the Configuration Space: General Scaling Forms and Multiple Scaling Regimes

SIMU 2001 - Bridging the Time-Scale Gap
Konstanz / Germany, 10. -13.9.2001

F. Eurich and P. Maass:
Gaussian ellipsoid model for polymer chains in bulk and film geometry

F. Eurich and P. Maass:
Gaussian ellipsoid model for polymer chains

M. Kessler, A. Majhofer and W. Dieterich:
Monte Carlo simulation of subsurface ordering kinetics in an fcc-alloy

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Altenberg / Germany, 20.8. - 2.9.2001

S. Heinrichs and P. Maass:
Second Layer Nucleation in Thin Film Epitaxy

Neue Wege in der Medizin
Glarus / Switzerland, 20. - 22.9.2001

A. Heinen:
Experimente, Ergebnisse und Gedanken zu einem neuen ultraschnellen Informations- und Regelsystem - Modell für den menschlichen Körper

79th Int. Bunsen Disc. Meeting: Ionic Motion in Materials with Disordered Structures
Münster / Germany, 10. - 12.10.2001

W. Dieterich:
Dynamics of disordered dipolar systems

Int. Conf. on Horizons in Complex Systems

P. Maass:
Anomalous Relaxations in Disordered Dipolar Systems

F. Scheffler and P. Maass:
Spin Precession in Disordered Systems
Group of Prof. G. Ganteför

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Jerusalem / Israel, 18.2. - 20.2.2001

G. Ganteför:
*Ultrafast electronic processes in size-selected clusters*

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M. Grass, D. Stolcic, G. Ganteför, T. Schlenker, J. Zimmermann, J. Boneberg and P. Leiderer:
*A new cluster material of silicon?*

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Berlin / Germany, 28.6. - 29.6.2001

G. Ganteför:
*Deposition von massen-selektierten Silizium- und Aluminiumclustern auf inerten Substraten*

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William College, Williamstown MA / USA, 8.7. - 13.7.2001

G. Ganteför:
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Group of Prof. P. Leiderer

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Group of Prof. P. Nielaba

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Group of Prof. E. Scheer

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3. Lectures

Group of Prof. E. Bucher

P. Fath: Foliensilizium: Neue Materialien für die Photovoltaik?
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P. Fath: Solar cell research at the University of Konstanz
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Group of Prof. W. Dieterich

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**Group of Prof. G. Schatz**

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4. Theses

Group of Prof. E. Bucher

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**Group of Prof. P. Nielaba**

M. Frick:  *Phasenumwandlungen in Quantenfluiden unter Berücksichtigung der Quantenstatistik*
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**Group of Prof. G. Schatz**

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5.6. – 28.7. 2001  
19.10. – 1.11.2001  
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<td>17.6 – 14.7.2001</td>
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<tr>
<td>Prof. Dr. A. Nitzan</td>
<td>Tel Aviv / Israel</td>
<td>30.6. – 6.7.2001</td>
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<tr>
<td>Prof. Dr. M. Telo da Gama</td>
<td>University of Lisbon / Portugal</td>
<td>10.9. - 13.9.2001</td>
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