Bernhard Kaiser
Bert Stegemann

Nanoscience with Atomic Precision

At length scales of several nanometers material properties differ completely from the well-known bulk behavior, i.e. effects due to the reduced size of the system become dominant. Nanotechnology will make use of the emerging new chemical and physical properties of these nanomaterials. The research in the group focuses on how these properties depend on the size of the system in order to design new materials with well-defined functionality.

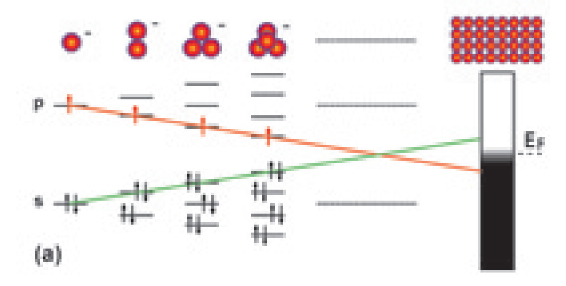


Fig. 1
(a) Schematic diagram for the development of the electronic level structure in mercury clusters from the atom (left) to the bulk (right). (b) Photoelectron spectra of negatively charged mercury clusters with increasing number of atoms n from top to bottom (taken from ref. 3).

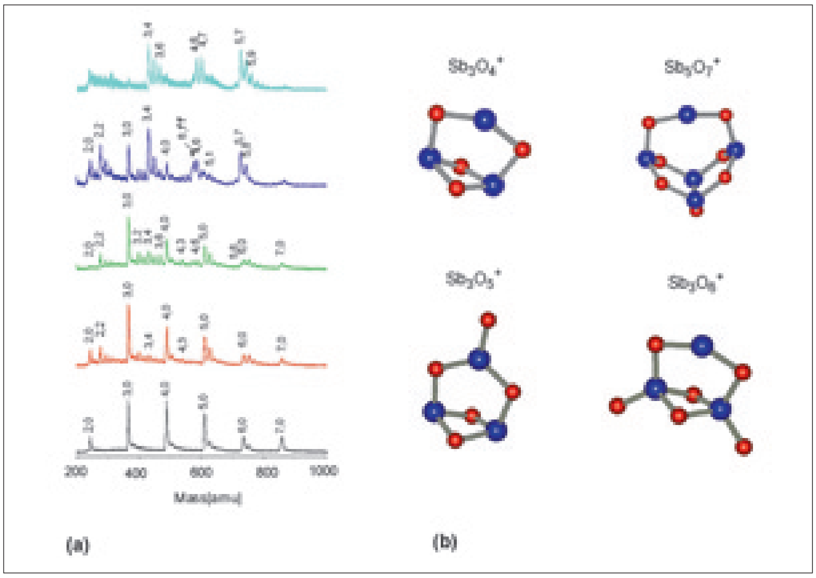
At the dawn of the new century nanotechnology has become one of the most frequently used terms in the scientific as well as in the public literature. A nanometer is one millionth of a millimeter, roughly the length of three to four atoms aligned in a row. Transistor switches on a silicon wafer have already reached sizes below one hundred nanometers. Small platinum particles of about this size are responsible for the catalytic reaction of carbon monoxide in our car exhaust systems. Particles smaller than about ten nanometers possess new physical and chemical properties, since quantum size effects become dominant. How these properties vary with particle size is widely unknown. A detailed understanding of the size dependence has a direct influence on the design of new materials with a well-defined functionality, since the electronic and geometric structures are directly linked to the electric, magnetic, thermal, optical, and chemical properties *(from form to function)*.

To address these fundamental questions we either synthesize clusters (agglomeration of atoms or molecules containing between two and several thousands of atoms) in the gas phase with atomic precision, investigate their size-dependent properties, and use them deliberately to form well-defined nanostructures on surfaces, or we employ self-assembly techniques to control the formation of supramolecular structures from suitable inorganic or organic precursor molecules.

The structure and the properties of the clusters can already be analyzed in the molecular beam by mass spectrometry, photoelectron spectroscopy, and surface-induced dissociation. Deposited clusters and nanostructures are investigated by temperature variable scanning probe microscopy and -spectroscopy (STM), electron microscopy (SEM) and photoelectron spectroscopy. Further information about chemical reactivity is obtained by thermodesorption mass spectrometry. Especially the combination of gas and condensed phase methods allows us to achieve a complete understanding of the size-dependent cluster and nanoparticle properties.

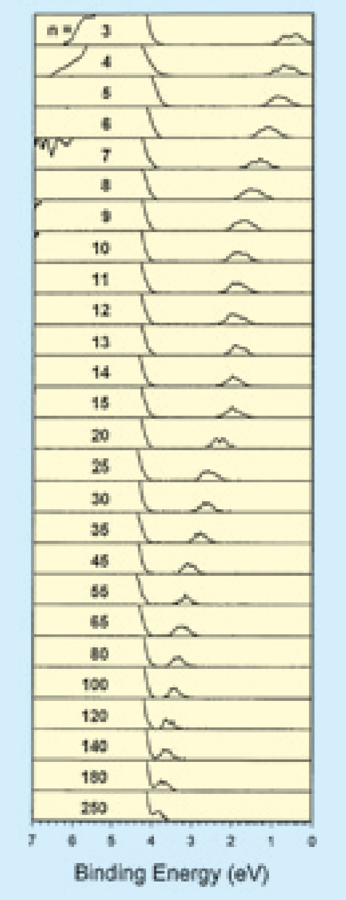
Many of the used experimental setups are unique. They have been especially designed and setup in our group according to the special requirements in order to answer the above stated demanding scientific questions.

Fig. 2
(a) Mass spectra of antimony oxide clusters at increasing oxygen partial pressure from bottom to top. The numbers above the peaks x,y denote the corresponding cluster Sb_xO_y. (b) Structures calculated for different size clusters (blue: antimony, red: oxygen).



Nanotechnologie

Im Größenbereich von einigen Nanometern unterscheiden sich die Materialeigenschaften deutlich von den bekannten Eigenschaften makroskopischer Systeme, d.h., es treten neue Effekte aufgrund der reduzierten Systemgröße zutage. Die Nanotechnologie will die neuen chemischen und physikalischen Eigenschaften dieser Nanomaterialien nutzen. Zentrales Thema der Forschung in der Arbeitsgruppe ist es, ein vertieftes Verständnis darüber zu erzielen, wie die neuen Eigenschaften von der Größe des Systems abhängen. Mit diesem Wissen ist es dann möglich, gezielt neue Materialien mit einer genau definierten Funktionalität zu synthetisieren.



How many atoms make a metal? [1]

A metal is easily recognized by its very good thermal and electric conductivity and by its high reflectivity. These properties are almost entirely due to its electronic band structure. One of the fundamental questions in nanoscience is: How does the electronic band structure of a metal evolve as a function of particle size, i.e. starting from a single atom and adding other atoms one by one? Such an investigation is presented in Fig. 1 for the case of mercury clusters. [2, 3] Fig. 1 (a) shows the electronic configuration of negatively charged mercury clusters as a function of size. In order to become metallic in the bulk the s- and p-states have to overlap. Photoelectron spectroscopy probes the development of the electronic structure as is shown in Fig. 1 (b): The signal at low binding energy is due to the single electron located in the lowest unoccupied molecular orbital (LUMO) of the cluster whereas the signals at higher binding energy are due to the electrons from the highest occupied molecular orbitals (HOMO). The observed HOMO – LUMO band gap closes for clusters consisting of more than 200 atoms, i.e. below this size mercury clusters are definitely non-metallic.

Magic numbers

Magic numbers have been and are still a very important subject for the investigation of cluster properties. Fig. 2 (a) shows typical mass spectra of antimony oxide clusters in a molecular beam. [4] At low oxygen partial pressure only the pure antimony clusters are observed. With increasing oxygen partial pressure almost any possible combination of antimony and oxygen is observed in the mass spectrum. At the highest investigated oxygen partial pressure only a few intense mass peaks survive. These mass peaks are assigned to clusters of exceptional stability, the so-called magic numbers. In combination with high-level computational methods it is possible to assign well-defined structures to the magic number clusters (see Fig. 2 (b)), even if different isomers might exist. [5, 6]

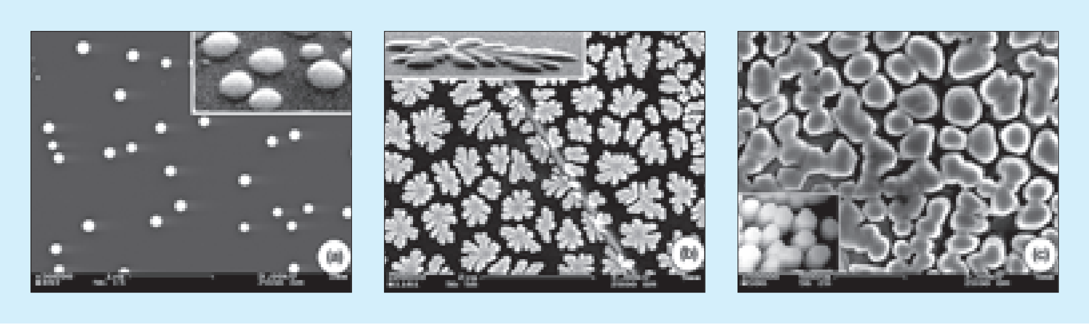
Crystal growth

Sb_4-clusters deposited onto the graphite (0001) surface (HOPG) at room temperature form nearly spherical islands through diffusion and coalescence at a low total coverage (Fig. 3 (a)). [7] At higher coverage a transition from the spherical to a tip-splitting morphology is observed (Fig. 3 (b)). This change is due to a size-dependent amorphous to crystalline phase transition, which leads to a large energy release and to a kinetically controlled reorientation of atoms inside the particle. The dynamic restrictions lead to the observed growth morphologies, which are widely observed in natural systems ranging from the formation of snowflakes to bacterial growth. A detailed understanding of the atomic processes involved in these morphology transformations will therefore be of importance for all scientific disciplines. Additional deposition of antimony clusters leads finally to the thermodynamic stable structures of the facetted single crystals of bulk antimony (Fig. 3 (c)).

Storage of chemical energy

The deposition of Sb_4-clusters onto the Au(111)-surface leads to the formation of small two-dimensional islands (Fig. 4 (a)). [8] At higher coverage the internal structures of the islands can be atomically resolved

Fig. 3
SEM-pictures taken after deposition of Sb_4 onto HOPG at room temperature (RT) for three different coverages (a) 4 monolayers (ML), (b) 40 ML and (c) 200 ML. The insets show magnifications of selected areas taken for tilted surfaces to illustrate the 3D-character.



(Fig. 4 (b)). The comparison of the measured atomic distances in different crystal directions (Fig. 4 (c) and (d)) with the known bulk structure of aurostibite (from diffraction experiments, Fig. 4 (e) and (f)) shows a very good agreement. From this we can conclude that the deposition of Sb_4 onto Au(111) leads to the spontaneous formation of alloy islands. Since this process is exothermic, it might be used for a nanoscale power plant to deliver the energy necessary to drive nanoengines. [9]

New element modifications

Fig. 5 shows the structures, which are formed after the deposition of Sb_4-clusters onto MoS_2(0001) at a substrate temperature of 90 K. [10] Discrete islands grow in a three-dimensional mode, i.e. like the formation of a pyramid (Fig. 5 (a) and (b)). From the cross section of one of the islands it is clearly seen that each additional layer adds about 0,5 nanometer in height (Fig. 5 (c)). At higher coverage the island structure can be atomically resolved (Fig. 6 (a)). [11,12] Since it is not possible with a STM to resolve single atoms inside the Sb_4-cluster the structure shown in Fig. 6 (b) has been derived to explain our measurements. Each spot in the STM-picture therefore corresponds to exactly one Sb_4-cluster. This is the first time that an elemental modification consisting just of tetrahedra, which is known for the lighter homologues arsenic and phosphorous, has been observed for antimony. Therefore it seems to be feasible to stabilize new elemental modifications on the nanometer scale using clusters as the precursor material.

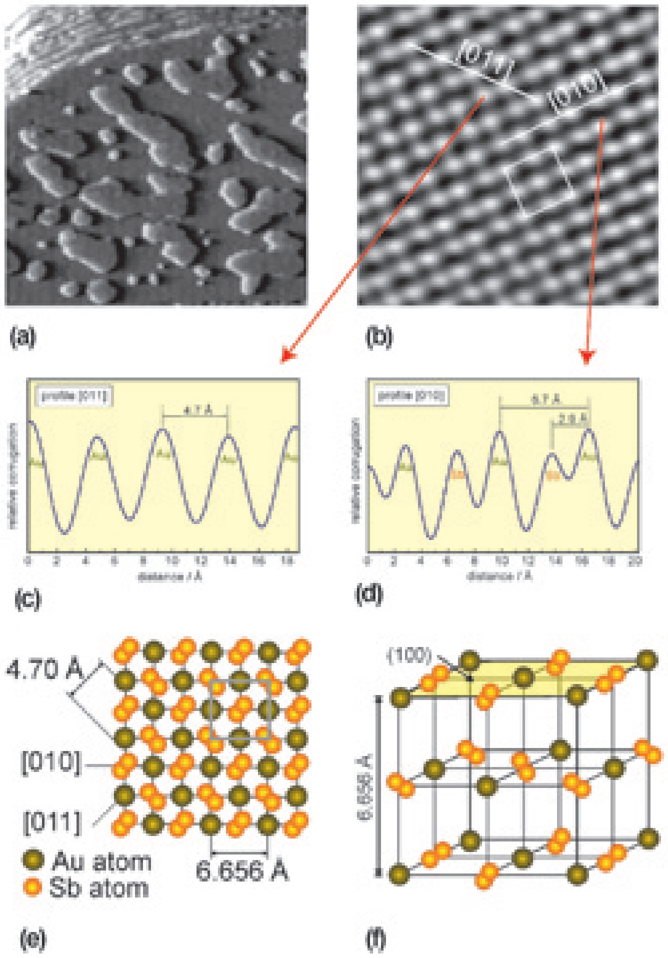
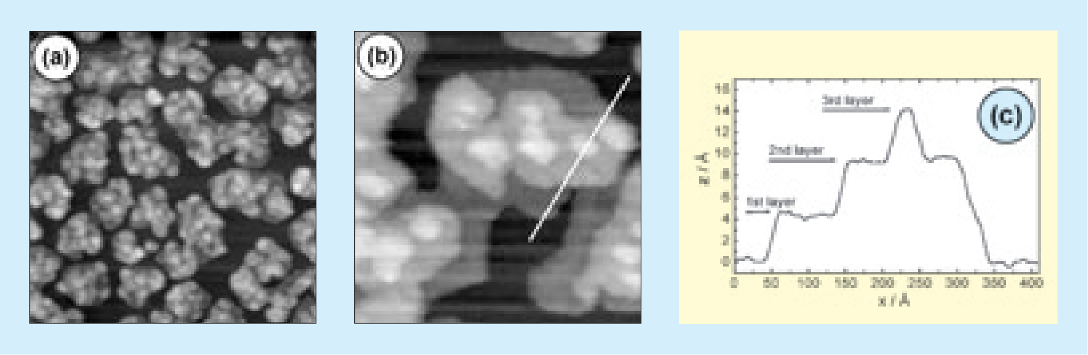


Fig. 4
STM-pictures of (a) 0.2 ML Sb_4 on Au(111) at RT (image size 150 x 150 nm^2), and (b) 1 ML Sb_4 on Au(111) at RT (image size 3.95 x 3,95 nm^2). c) and (d) Profiles along the lines shown in (b). (e) Top view of the $AuSb_2$-surface: the grey square corresponds to the white square in (b). (f) 3D-picture of the $AuSb_2$ bulk structure.

Outlook

The here-depicted aspects can just give a short glimpse of the exciting phenomena observed and feasible in

Fig. 5
STM-pictures of 1.3 ML Sb_4 on MoS_2 (0001) at 90 K:
(a) 248 x 248 nm^2, (b) 62 x 62 nm^2. (c) Profile along the white line drawn in (b).



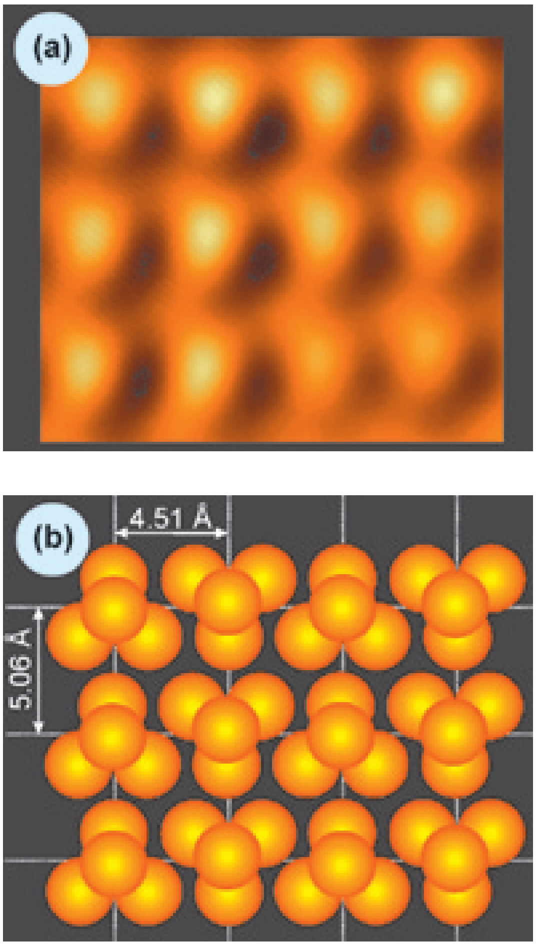
the area of nanosciences. There are still much more, which are yet to be discovered, and which might lead to a new industrial revolution similar to the technical and scientific progress made in the last century by microelectronics.

Acknowledgements
We especially thank the following people for their fruitful cooperation and support: T.M. Bernhardt, J. Opitz-Coutureau, H. Kaukel, K. Rademann. Financial funding was given by the Deutsche Forschungsgemeinschaft and by the Humboldt-Forschungsfonds.

References

[1] *P.P. Edwards / C.N.R. Rao,* The Metallic and Nonmetallic States of Matter, Taylor & Francis, London (1985).

Fig. 6
(a) STM-picture of 2 ML Sb_4 on MoS_2 (0001) at 90 K (1,8 x 1,8 nm^2). (b) Schematic picture of the arrangement of Sb_4-clusters on the surface to explain the observed structure in (a).



[2] *B. Kaiser / K. Rademann,* Photoelectron Spectroscopy of Neutral Mercury Clusters Hg_x ($x \leq 109$) in a Molecular Beam, Phys. Rev. Lett. 69, 3204 (1992).
[3] *R. Busani / M. Folkers / O. Cheshnovsky,* Direct Observation of Band-Gap Closure in Mercury Clusters, Phys. Rev. Lett. 81, (1998).
[4] *B. Kaiser / T.M. Bernhardt / M. Kinne / K. Rademann,* Formation of antimony oxide clusters in a molecular beam, Int. J. Mass Spectrom. 177, L5 (1998).
[5] *B. Kaiser / T.M. Bernhardt / M. Kinne / K. Rademann / A. Heidenreich,* Formation, Stability and Structures of Antimony Oxide Cluster Ions, J. Chem. Phys. 110, 1437 (1999).
[6] *J. Opitz-Coutureau / A. Fielicke / B. Kaiser / K. Rademann,* Antimony and Bismuth Oxide Cluster Ions, Phys. Chem. Chem. Phys. 3, 3034 (2001).
[7] *B. Kaiser / B. Stegemann / H. Kaukel / K. Rademann,* Instabilities and pattern formation during the self-organized growth of nanoparticles on graphite, Surface Science 496, L18 (2002).
[8] *B. Stegemann / T.M. Bernhardt / B. Kaiser / K. Rademann,* STM investigation of surface alloy formation and thin film growth by Sb_4 deposition on Au (111), Surf. Sci. 511, 153 (2002).
[9] *F. Besenbacher / J. K. Norskov,* How to power a nanomotor, Science 290, 1520 (2000).
[10] *B. Stegemann / B. Kaiser / K. Rademann,* Subsequent layer growth of supported nanoparticles by deposition of Sb_4 clusters onto MoS_2(0001), New Journal of Physics 4, 89.1 (2002).
[11] *T.M. Bernhardt / B. Stegemann / B. Kaiser / K. Rademann,* Kristalline Strukturen aus Sb_4-Molekülen in dünnen Antimonfilmen, Angewandte Chemie 115, 209 (2003).
[12] *B. Stegemann,* Wechselwirkungen monodisperser Antimon-Cluster mit Oberflächen: Diffusion, Wachstum und Strukturbildung im Nanometerbereich, Dissertation, Institut für Chemie, Humboldt-Universität, Berlin, 2003.

Internet:

www.chemie.hu-berlin.de/bernd/index.html

PD Dr. Bernhard Kaiser
Born 1959. Studies of Chemistry in Marburg and Bristol, England. PhD 1989. Postdoctoral stays at the University of Hawaii, USA and in Marburg. Since 1994 at the Department of Chemistry, Humboldt-Universität. Habilitation 1999. He was awarded an Erskine Visiting Fellowship at the University of Canterbury, New Zealand in 2001.

Dr. Bert Stegemann
Born 1968. 1993–94 Fulbright Scholar, Studies of Optical Sciences at theUniversity of Arizona, Tucson; 1997 Diploma in Physics, Humboldt Universität, 2003 PhD in Physical and Theoretical Chemistry.

Contact
Humboldt-Universität
zu Berlin
Faculty of Mathematics
and Natural Sciences I
Department of Chemistry
Brook-Taylor-Str. 2
D–12489 Berlin-Adlershof
Phone:+49-30-2093–5561
Fax: +49-30-2093–5586
E-Mail: bernhard.kaiser@
chemie.hu-berlin.de