Man Made and Self Organized Nanostructures

L.F.Chi, T.Drechsler, St.Höppener, S.Rakers, Ch.Röthig, Th.Schwaack, F.Starrberg,H.Fuchs

Westfälische Wilhelms-Universitat
Physikalisches Institut
Wilhelm-Klemm-Str. 10
D-48149 Münster, Germany

(Received: 30 March 1998; accepted: 31 March 1998)

Abstract

Modifications of surfaces on the nanometer scale exhibiting novel electronic and optoelectronic properties may be prepared by selforganizing processes, and local probes such as STM and AFM. Using self-organizing techniques extended structures in one, two and even three dimensions can be made using preformed building blocks made of, for example, supra-molecular structures or metallic nano-clusters. With the local probes zero-dimensional structures can be prepared on predefined surface locations. Here, the preparation of metallic nanowires and new experiments on local surface modifications using STM under ambient conditions and the nanostructuring of surfaces by the adsorption of metallic clusters is reported.

Introduction

The macroscopic physical properties of materials depend in numerous practical applications on the properties of their surface. Therefore, the coating of surfaces with ultrathin organic layers, the smoothing of surfaces with nanometer precision, and the texturing of surfaces are tools to tailor these properties. Specifically, nanostructured surfaces are promising for novel sensoric, electronic and optoelectronic tools and, therefore, induced increased research activities. Depending on the application, surfaces may be modified locally (zero dimensional structures) or in one and two dimensions. One-dimensional structures are interesting for the generation of nanowires as prepared by surface facetting, and adsorption of atoms or molecules at surface steps. Surface tailoring in one or two dimensions using differing chemical moieties leads to chemical differentiation on the nanometer scale which can be applied to prepared three dimensional structures with a laterally well defined chemical composition. Thus, these techniques are of interest for building up novel tailored materials. Below we present some recent results on two-/one- and zero-dimensional nanostructuring.

Two dimensional nanostructures

A suitable technique for surface modification in two dimensions is natural lithography [1] making use of an appropriate nanosized lithographic mask through which materials are deposited onto a flat substrate. This can be easily achieved by applying densely packed monodisperse latex spheres which are commercially available in a wide size range from about 50 nm to several hundred microns. An example is shown in fig. 1. In this case, gold was evaporated onto the latex pattern deposited on a mica surface. After the removal of the organic material metallic dots remain which can subsequently be used as a substrate for reactive organic molecules such as alkane thiols or related materials. This method works well for latex spheres with a diameter down to about 60 - 70 nm. Below this size the empty spaces between the packed spheres will be rapidly obstructed by the deposited material during evaporation and the structures can no longer be produced reliably.

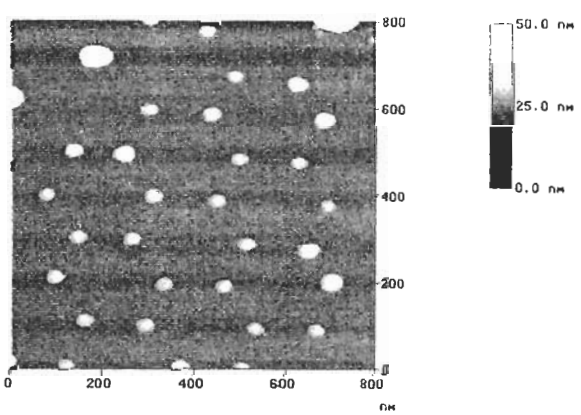

Fig.1 Au-dots produced through a latex mask and subsequent annealing. The dots exhibit a high aspect ratio with a flat top. The dots form rings with a six-fold symmetry representing the structure of the close package of the latex spheres. After evaporation the polymeric latex mesh is removed by an organic solvent [1]. In this picture the latex spheres had a diameter of roughly 200 nm.

For making smaller structure sizes ligand stabilized metal clusters such as Au_{55}, Pt_{309} etc. are appropriate [2]. The organic ligand shell prevents the metallic clusters from merging and simultaneously provides well defined dielectrica between the clusters with a thickness of several nanometers. Thus, these clusters are well suited for single electron tunneling (SET) experiments. Assuming the clusters to represent spherical structures the capacitance of an individual cluster is in the range of 10^{-19}-10^{-18} F. This leads to a total charge energy of $E_c = e^2/2C$ which is considerably larger than the thermal energy $E_{th} = k_B T$ at room temperature. Typically, the Au_{55} clusters exhibit an electrostatic energy of 160-320 meV as compared to the thermal energy of 26 meV at room temperature. Thus, these structures are promising for producing SET like structures which can be operated near or at room temperature. Investigating these systems by using a vertical junction using monolayers of Au_{55} clusters adsorbed on flame annealed gold surfaces the Coulomb blockade as well as the Coulomb staircase could be observed at 100 K(fig.2). The Coulomb blockade effect could also be observed reproducibly at room temperature, however, the Coulomb staircase was only reproducibly obtained at reduced temperatures(100K). As a result, these small systems are well suited to perform SET experiments.

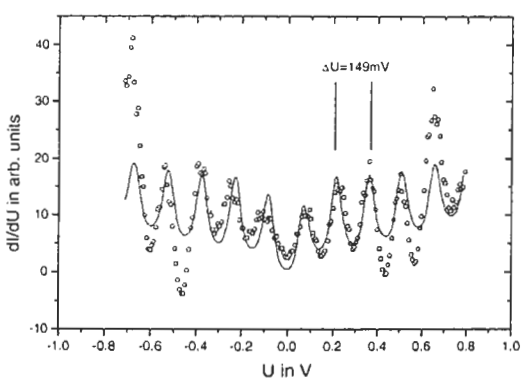

Fig.2 dI/dU characteristic taken with a vertical tunneling junction on Au_{55} clusters (ligand stabilized with monosulphonized Triphenylphosphane) at T = 100 K, averaged from 10 spectra. The Coulomb blockade regime as well as the Coulomb staircase are visible. The analysis provides a capacity of $6.49 \cdot 10^{-19}$ F in good agreement with the theoretical prediction of 3.9 .. $7.8 \cdot 10^{-19}$ F, depending on the dielectric constant of the ligand shell.

One dimensional structures, nanowires

A means for preparing quasi one dimensional metallic nanostructures is making use of swift heavy ion beams impinching on thin dielectric substrates with a thickness of about 10 - 100 nm. For our studies we used mica which can be easily prepared in thin sheets by exposing the samples to swift heavy ion beams of Au^{197}, U^{238} and Cf^{252}. After impact the ion beams produce latent tracks which can be visualized in high resolution AFM as disordered areas with a diameter of about 7 nm. The surrounding areas of the untreated surface exhibit well ordered atomic structures as is typical for a clean mica surface. Applying an etchant such as HF the amorphized region which is considered to represent a state of higher energy is preferentially etched. Depending on the concentration and the etching time straight nanopores can be produced with a well controllable diameter. Larger pores reflect the rhomboedric structure of the substrate (fig. 3). After etching the tracks, the pores can be filled with metals using conventional electrophoresis processes via a continuous preevaporated metallic back electrode on the substrate. Thus, a random array of very thin metallic wires is produced in this way. By using AFM with conductive tips we could check the electrical conductivity of the individual nanowires [3]. These wires can then be used for contacting structures deposited on the surface of the insulating substrate, e.g. transport proteins. In addition, the pores can also be filled with conductive polymers or a mixture of conductive polymers and metals in sequence. This opens a variety of means to tailor these channels.

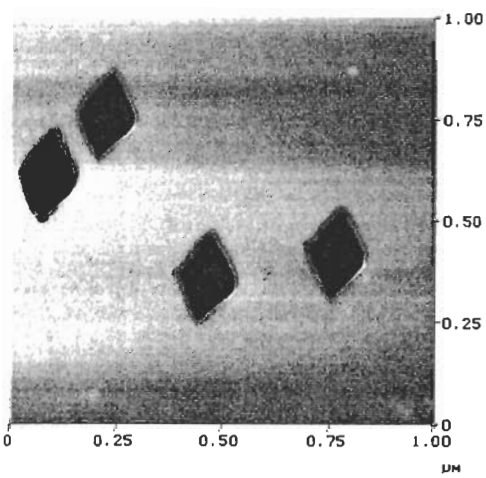

Fig.3 AFM-image of etched nanochannels in mica. The size of the pores is 200 x 100 nm^2. Pore diameters as small as 10 nm can be produced. The pores traverse the whole mica sample, in this example with a thickness of 100 μm, and are open at both ends.

Tip induced nanostructures

While the one- and two-dimensional structures are mainly produced by natural or self organizing processes, local nanostructures can be easily produced by scanned probe techniques such as STM and the AFM. In particular, atomic size and nanometer structures which are stable at room temperature and under ambient atmospheric conditions are of high practical interest.

Layered semiconductors such as WSe_2 and MoS_2 allow us to modify the surface locally by removing individual atoms at room temperature or modifying the electronic state of the material locally by dragging dopant atoms towards the tunneling gap area or by changing locally the surface structure. Mechanical structuring can be done with the STM by tip indentation (plastic deformation) [4] or by applying voltage pulses(fig. 4) [5-9]. Another inte-resting class of materials being suited for ambient condition modification are the blue bronzes, e.g. $Rb_{0.3}MoO_3$. This material is specifically useful to generate nanometer-sized structures by controlled removal of surface material. As shown in fig. 5 such structures can be written reliably on this material with pulse lengths of several hundred nanoseconds only [10]. This is in contrast to materials such as WSe_2 or MoS_2, requiring pulse lengths in the range of several ms to produce atomic size structures. Tunneling spectroscopy investigations revealing the nature of the structures were done under UHV conditions for the layered semiconductors [11].

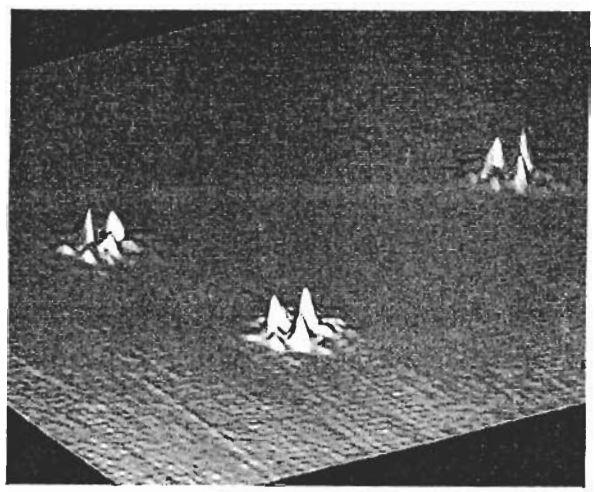

Fig.4 Nanometer structures produced by voltage pulsing on WSe_2. Pulse amplitude: 4.5 V (tip negative), pulse duration: 10 ms. The size of each structure is about 6 nm. There is no material transport from the tip to the surface. The shape of the structures can be explained by an atomic-size defect imaged by a large tip or by a local change in the electronic properties as discussed in [11].

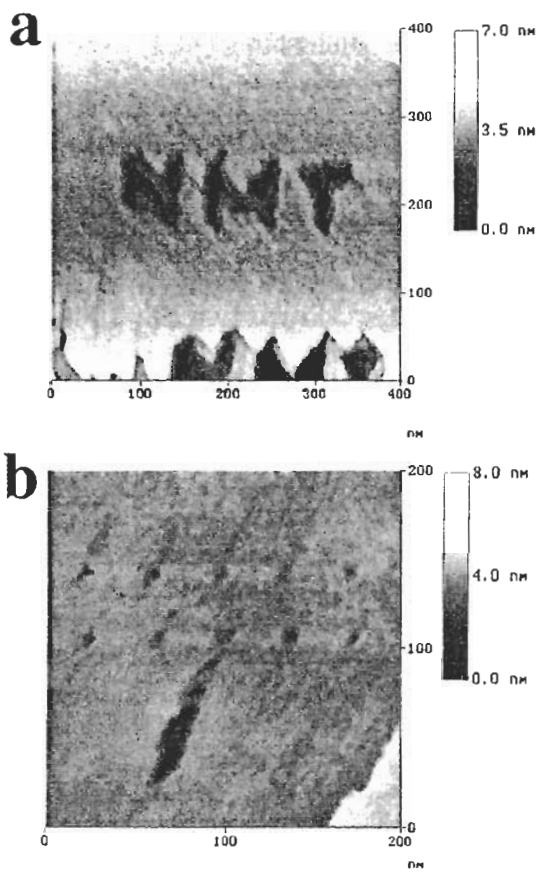

Fig.5 Nanostructures made in $Rb_{0.3}MoO_3$ by voltage pulsing

a) image size: 400 x 400 nm^2, pulse conditions: V_p = 4.4 V; t = 15 msec

Imaging parameters: V_t = -400 mV (sample negative), I_t = 0.5 nA The letters 'NMT' were written on the surface. The rough surface structure is due to the existance of nanoclusters on this surface, i.e. particles between 6 and 30 nm long and 1.5 to 3 nm thick which are removed from the surface. The removal of this particles which are one or two unit cells deep results in holes with flat bottoms as best seen in the letter 'N'.

b) image size: 200 x 200 nm^2, pulse conditions: V_p = 3.5 V; t_p = 750µs. The written structures are the two horizontal lines of five dots each. The structures are fairly round but are not caused by the shape of the tip alone. It is more likely that their shape is due to the removal of nanoclusters from the surface.

References

1. U.Ch. Fischer, H.P. Zingsheim, J. Vac. Sci. Technol. **19**, 1881 (1981)
2. L.F. Chi, M. Hartig, T. Drechsler, Th. Schwaack, Ch. Seidel, H. Fuchs, G. Schmid, Appl. Phys. A, 1998 (in press)
3. S. Höppener, S. Gao, L.F. Chi, H. Fuchs, to be published
4. H. Fuchs, R. Laschinski, Th. Schimmel, Europhys. Lett. **13**, 307-311 (1990)
   L. Eng, H. Fuchs, (Review), Mater. Sci. A **139**, 230-238 (1991)
5. H. Fuchs, Th. Schimmel, Adv. Mater. **3**, 112-113 (1991)
6. Th. Schimmel, H. Fuchs, S.Akari, K. Dransfeld, Appl. Phys. Lett **58**, 1039-1041, 11. March (1991)
7. Th. Schimmel, H. Fuchs and M. Lux-Steiner, Phys. stat. sol. **131**, 47-57 (1992)
8. Th. Schimmel, H. Fuchs, K. Graf, R. Sander, M. Lux-Steiner, Phys. stat. sol. **131**, 89-98 (1992)
9. H. Fuchs, Th. Schimmel, S.Akari, L.M. Eng, M. Anders, Ch. Lux-Steiner, K. Dransfeld, NATO-Series, **Vol. 235**, Workshop 'Manipulations of Atoms in High Fields and Temperatures: Applications', 293-309 (1993)
10. F. Starrberg, T. Schwaack, Ch. Rothig, H. Fuchs, in preparation
11. A. Asenjo, T. Schwaack, P. de Pablo, J. Gomez-Herrero, E.K. Schweizer, C. Pettenkofer, H. Fuchs, A.M. Baro, Surface Science **398**, 231-240 (1998)