

DSM Science & Technology Awards 2005

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Summary of Thorsten Balgar's research

The starting point of Thorsten Balgar's research is the self-assembly of molecules such as octadecyltrichlorosilane (OTS) on silicon. From a number of studies it is known that these molecules form a monolayer by self-assembly. For this purpose silicon samples are dipped into a solution of these molecules in toluene. The silicon samples have been oxidized before in Piranha solution. In solution the molecules hydrolyze and form with the residual water contents silanols. On the surface these agglomerate by grafting and cross linking. Depending on the water contents in the toluene solvent, the monolayer is formed in several minutes. Atomic Force Microscopy (AFM) studies carried out by Thorsten Balgar show that the organic monolayer has a height of approx. 2.4 nm, which corresponds well to the length of the molecules in all-trans configuration. Hence, it is safe to assume that the molecules are standing normal to the surface or are inclined by an angle not larger than 30°.

AFM images taken by Thorsten Balgar on samples at various stages of the monolayer formation show that compact islands are formed during the growth, which have a fractal shape. Such shapes can be corroborated by a mechanism in which the molecules first adsorb in a

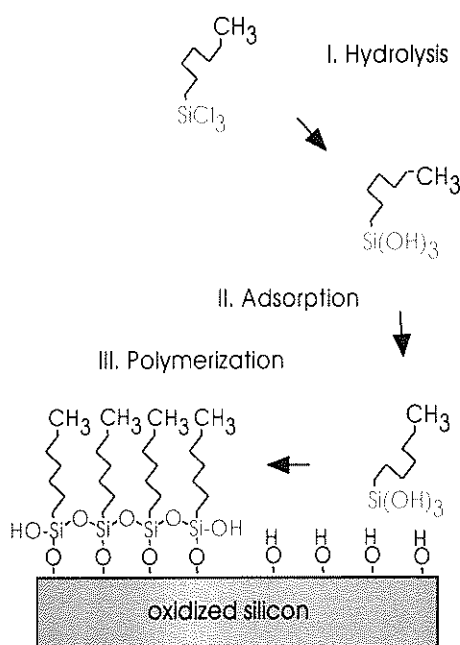


Fig. 1: Schematic of the organic monolayer self-assembly of octadecyltrichlorosilane (OTS) on oxidized silicon.

mobile physisorbed state on the silicon substrate. Upon diffusing on the surface a molecule may hit the boundary of an existing island. Here, it can attach itself with a certain probability. Once this step happened the molecule becomes immobile. The latter leads to the fractal shapes of the island.

These studies of the growth kinetics lead to a first publication by Thorsten Balgar (Surf. Sci. 532/5, 963 (2003)). With this study a controversy in the literature could be resolved. Different growth kinetics had been reported by ex-situ and in-situ studies. The work by Balgar established that the differing findings are due to removal of the mobile molecular phase from the sample in the case of ex-situ studies.

These ideas have been taken up in later work forming the Diploma thesis of Rafael Bautista (Langmuir 19, 6590 (2003)) where it was shown that the island formation kinetics and their respective shapes can quantitatively be described by a kinetic Monte Carlo model.

Thorsten Balgar went on to prepare laterally structured self-assembled monolayers. Structured monolayers have so far been obtained by transfer imprinting methods or by local destruction of a previously homogenous monolayer. Both methods have some disadvantageous aspects. Transfer imprinting typically leads only to very weakly bound adlayers, which are chemically unstable and can be easily wiped off. Selective destruction by photo- or e-beam lithography is likely to leave a layer of debris, e.g. carbon behind.

Hence, the goal of Thorsten Balgar was to develop a constructive method. I.e. the substrate should be prepatterned whereafter the monolayer should only form on these prepared areas. An appealing approach for this goal is laser direct writing. In prior work, Müllenborn (Appl.

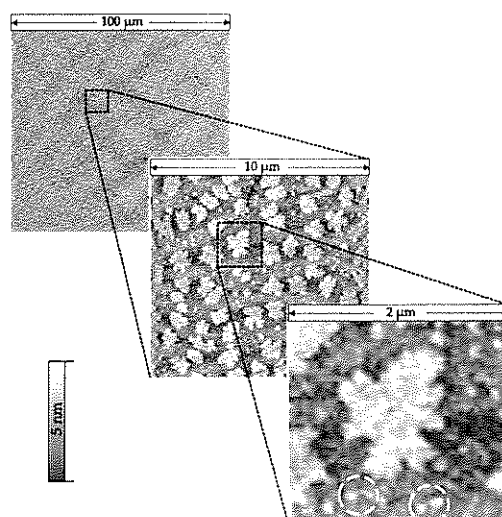


Fig. 2: Islands formed during the growth of a OTS monolayer as made visible by atomic force microscopy. Between the islands of fractal shape are smaller yet mobile agglomerates observed.

Phys. Lett. 69, 3013 (1996)) had shown that a focused Ar-ion-laser beam can be used to locally oxidize a hydrogen terminated silicon surface with submicron resolution.

Structures are achieved in laser direct writing by moving the sample relative to the focus of the laser beam. Writing speeds of several millimeter per second are achievable.

Thorsten Balgar has developed three methods to achieve a structured OTS-monolayer (Fig. 3):

- prepatterning of a hydrogen terminated silicon surface
- patterning of an oxidized silicon surface
- removal of the adsorbed monolayer by laser pyrolysis

The first method starts from a hydrogen terminated silicon surface which can easily be prepared by wet chemical methods. The hydrogen termination serves as chemical passivation. Hydrogen terminated silicon is inert in air for periods of several hours. In the focus of the laser beam the hydrogen termination is removed and a thin oxide layer results. The areas which were not hit by the laser are still hydrogen passivated. Hence, the OTS monolayer should only form on the areas marked by the laser. However, the experiments carried out by Thorsten Balgar show that this is not immediately true. Apparently, the density of hydroxyl groups on the laser prepared oxide is not large enough to support formation of the OTS monolayer. This shortcoming can be overcome by a treatment of the sample in boiling water for 1 minute. This treatment increases the hydroxyl group density on the laser marked areas. Dipping such a sample in the OTS solution yields selective formation of the organic monolayer on the laser written areas. Fig. 3 (top images) shows an AFM image of such a sample, where the lines written by the laser are only partially covered by the OTS monolayer. The formation of the latter has been intentionally interrupted since the observation of the characteristic islands associated with the monolayer formation serve as unambiguous indication of the ongoing growth. The areas between the lines are still sufficiently passivated by the hydrogen termination and remain uncovered by OTS.

Thorsten Balgar has been able to write laser lines on which later OTS is assembled with a width of 120 nm. It is reasonable to assume that further optimization of the experimental set-up and procedures would allow to achieve a minimal structure width below 100 nm. The results were achieved using a laser set-up with a diameter of the laser focus of 2.8 μm . This finding indicates that the laser writing process is highly nonlinear such that only the core of the laser beam induces formation of the surface oxide. This finding is consistent with an observed sharp threshold in laser power density for the writing process. Only at rather low lateral writing speeds do the lines become wider. The observed line width is rather constant at writing speeds between 5 and 25 mm/s. It can be foreseen that a writing speed of 200 mm/s is feasible.

The observation that the hydroxyl density of the laser written areas is not sufficient to support formation of an OTS monolayer is the starting point for an alternative approach. Starting with a surface oxidized silicon sample, lines are written by the focused laser. The laser interaction

results in a reduction of the surface hydroxyl coverage in the areas exposed to the laser beam. Consequently, the OTS monolayer is not formed on the areas which interacted with the laser, but on the non-modified areas. The net result is a structured monolayer which may be regarded as the negative of the structure obtained by the first method (Fig. 3 middle).

The third method starts from a sample which has been covered by an OTS monolayer. Laser writing removed the OTS layer where the laser radiation interacts with the sample (Fig. 3 bot-

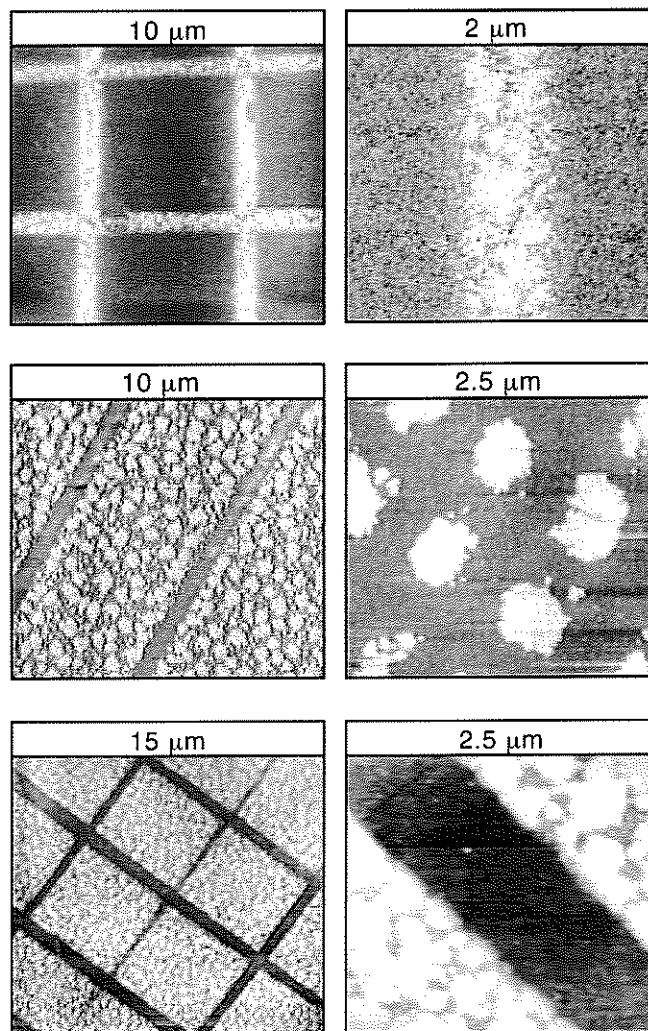


Fig. 3: AFM images of sample structured by laser direct writing. The top two images are taken from a sample where the hydrogen termination has been removed by laser direct writing resulting in a thin oxide stripe. The middle two images are obtained from a sample where the surface oxide layer has been locally reduced in hydroxyl coverage by laser direct writing. The bottom two images show a sample where an OTS monolayer has been locally removed by laser pyrolysis. The OTS coverage is in all cases intentionally incomplete in order to be able to image islands as indicator of monolayer growth

tom). The topological height difference between the OTS covered areas and the written lines is similar to the length of the OTS molecules. Hence only a small fraction of the material remains as debris.

In summary, Thorsten Balgar has demonstrated that structured organic monolayers on silicon can be prepared by laserwriting in several ways. It is worth noting, that the characteristic line width of approx. 200nm is obtained in all three methods. The procedures work in ambient air and there is no need for ultra high vacuum techniques.

It can be envisioned that these methods can be extended to OTS like molecules which carry a functionalized head group. Alternatively, the assembled structures can be functionalized by further wet chemistry. Subsequently, new structures can be marked by laser writing, on which in the next step again an organic monolayer is assembled from molecules with a different functionality. The result would be a chip with areas of different chemical functionality which have size dimension of several hundred nanometers.

It are these options which make the results obtained in the work by Thorsten Balgar remarkable.