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Self-assembled monolayers on silicon oxide

Christian Belgardt, Harald Graaf*, Thomas Baumgärtel, and Christian von Borczyskowski

Center for Nanostructured Materials and Analytics, Institute of Physics, Chemnitz University of Technology, Reichenhainer Str. 70, 09107 Chemnitz, Germany

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* Corresponding author: e-mail harald.graaf@physik.tu-chemnitz.de, Phone: +49 371 531 34807, Fax: +49 371 531 834807

We evaluated the wet-chemical formation of octa-decyltrichlorosilane (OTS) self-assembled monolayers on silicon substrates with a silicon oxide layer. Our investigations were focussed on the influence of the reaction time on the surface energy. The surface energy was thereby calculated by measuring the static contact angle of two probe liquids on the surface. We found that only high reaction times of several hundred minutes yield a high quality monolayer with a minimal surface energy. A clear increase of the dispersive part of the surface energy for short reaction times is found. This can be explained by a high ratio of gauche-conformation within the alkyl chains accompanied by a rather slow rearrangement of the chains inside the monolayer to form a densely packed all-trans conformation.

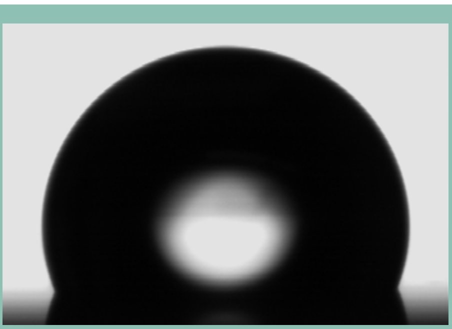

Image of a water droplet on an OTS self-assembled monolayer-terminated silicon oxide surface. The contact angle is about 111° indicating a high quality of the OTS monolayer.

1 Introduction Self-assembled monolayers are well known in the scientific world and widely used to influence the chemical and physical properties of various surfaces. Most monolayers are formed by a chemical reaction of a terminal head group with the surface of a solid. For the widely-used silicon oxide, a treatment by silane molecules is the favoured way to produce chemically and physically stable monolayers. By using ω-substituted alkyl silanes it is possible to achieve different functionalities at the outer surface of the self-assembled monolayer (SAM). Such SAMs have been reported from alkylsilanes with terminal functional groups as halogen [1-5], cyanide [2], mercapto [6], pyridyl [6], phenyl [7] or vinyl [8–14]. Monolayers with a very low surface free energy can be obtained by partially fluorinated alkylsilanes [1, 15–17].

Silane monolayers are also of general interest in the field of organic electronics. Here such monolayers have been used for a control of the charge carrier density in organic field effect transistors (OFET) [18]. Those monolayers increase the performance of an OFET drastically, where long alkyl chains, as they are obtained by octadecyltrichlorosilane (OTS), showed the highest effect [19]. This favourable change can be understood as a combination of different effects. First of all, the silane groups react with hydroxyl groups at the silicon oxide surface (so called silanol groups) and therefore prevent a capturing of electrons by these silanols under formation of hydrogen and negatively charged terminal oxygen at the surface [19]. This capturing mechanism is not vanishing completely because it is known that not all silanol groups on the surface are eliminated by reaction with the silane [20]. Furthermore the formed alkyl monolayer acts as a barrier for the charge carriers (here a tunnel barrier) to reach the still existing traps at the silicon oxide surface. This effect is especially large for OTS as the monolayer consists of 18 carbon atoms [9]. Finally an alkyl monolayer affects also the morphology of the formed organic film. For pentacene it has been reported, that the grains formed by vacuum deposition are smaller on OTS treated silicon oxide but showed an improved contact between individual grains [21], and a decrease in the leakage current trough the gate oxide [22]. Overall an increase of the field effect mobility of about a factor of 5 to 10 and an increase in the On/Off ratio of a factor of 2 to 10 has been found [21]. In local potentiometry measurements it has been shown, that the treatment of the gate oxide with OTS led to a more symmetric electric field within the channel of the OFET [23].

The formation of such OTS and other silane monolayers can be achieved by different methods. One typical preparation procedure is the chemical vapour deposition (CVD) [24]. A high quality monolayer was reached after a deposition time of around 1 hour. Interestingly the film thickness is still increasing after one hour from around 1.6 nm to around 2 nm after 3 hours indicating, that the formation of a densely packed SAM needs at least 3 hours by the CVD method [24].

A more favoured way of SAM formation in the scientific community is the silanisation from solution. This method of formation by immersion of the oxide substrate into a millimolar solution of OTS was reported e.g. by Sagiv [25]. The silanisation reaction is discussed by a multi-step process, where first a physisorbtion takes place followed by a hydrolysis of the chlorosilane groups with water molecules forming a thin water layer on top of the silicon oxide. Finally a covalent grafting and an in-plane reticulation lead to the strongly bonded SAM [26]. The growth mechanism in solution was studied by atomic force microscopy, where a formation of islands of OTS was found which tends to grow and form a closed monolayer within about 120 seconds. Up to a medium coverage of 0.75 monolayers a linear growth followed by a slow saturation were discussed as a clear hint for a Langmuir adsorption kinetic [27]. Theoretical calculations indicate that the growth of SAM on hydroxylated substrates can be qualitatively modelled by considering adsorption, diffusion, grafting and cross linking of pre-ordered alkylsilanol clusters [28].

The quality of the formed self-assembled monolayers, especially made by OTS, was previously investigated by different methods. Beside optical and electrochemical characterizations [29] as well as friction force investigations [30] especially water contact angle measurements are a common method to characterize the monolayer by obtaining the surface energy [31]. It should be noted, that the water contact angle for OTS monolayers differs significantly in the literature, where values between 98° and 114° are reported [30–32]. As the main reason for the irreproducibility of film preparations between different labs is the existence of a critical temperature T_C, being about 28 ± 5°C for OTS which is in the same regime as the typical lab temperatures [32]. Goldmann et al. showed that only for temperatures below 28 °C an ordered monolayer can be obtained. A total surface coverage of 100% (consisting mainly of an unordered liquid extended (LE) phase and partially an ordered liquid condensed (LC) phase) was reached after ~10 minutes at 25 °C [33]. Next to the temperature, also the alkyl chain length has a strong impact on the formation kinetics of covalently bound alkyl SAM [34]. The longer the used molecules, the more time is necessary to reach a highly ordered monolayer but on the other hand the stability of SAM consisting of long chain molecules is likely to be higher than for such made of shorter ones.

We will report here on the influence on long reaction times of OTS on the hydrophobicity and the surface energy of the self assembled monolayer. The characterization of the SAM was done by static contact angle measurements. By using different liquids the surface energies of the samples with its polar and dispersive components was determined.

2 Experimental

In order to form high quality monolayers it is very important to ensure a high level of cleanliness to keep the error by contamination as low as possible. All samples were cut from the same wafer (n-Si[100], resistivity of around 15 Ωcm with 70 nm silicon oxide grown in a dry oxidation process at 1000 °C), are freshly cleaned and prepared exactly by the same procedure as follows. At the beginning of the preparation all the working appliance were cleaned by Hellmanex II solution (Hellma GmbH & Co. KG, Germany). The silicon was cleaned with acetone (Merck KGaA, 99.9%), ethanol (Merck KGaA, 99.9%), and Millipore (ultrapure deionized water with a resistivity of 18.2 MΩ / cm) in the ultra sonic bath for 5 minutes in this order. Finally it was dried with nitrogen. After this procedure, the samples were cleaned with 'piranha' acid solution (2 parts of hydrogen peroxide (Merck KGaA, 30%) and 3 parts of sulphuric acid (Merck KGaA, 96%)) at 65 °C in an ultrasonic bath. After this cleaning the samples have been washed with Millipore and dried with nitrogen again before the samples were immersed into the silane solution at room temperature, which was always at a constant value of around 20 °C to ensure that we are below the critical temperature T_C. The relative humidity was always at a value of about 30%.

For the silanisaton a 0.5 mM OTS (ABCR GmbH & Co. KG, contains <3% Isomers) solution in toluene (Merck KGaA, 99.9%) was used. A small droplet of water was added to the solution because a certain amount of water seems to be necessary for the formation of high quality monolayers [26].

After a certain reaction time, which was varied between 1 minutes and 8 hours, the samples were removed from the silane solution. The final treatment of the silicon consisted of three ultrasonicated baths in toluene, acetone and ethanol for approximately 4 minutes in each case, with Millipore flushing between the baths and at the end. After removing of the remaining moisture by nitrogen, the samples were ready for measuring the surface.

With contact angle measurements, an indirect determination of the surface energy and therefore an assessment of the surface is possible. For these measurements we used an OCA-20 contact angle meter (Data Physics, Germany) and

its software with the sessile drop method. This means that a small amount of a test liquid was placed on the sample surface and the profile of the liquid droplet was captured with a CCD camera. The contact angle was evaluated by the provided software. To determine the surface energy contact angles of two different test liquids have to be obtained. As test liquids we used water (Millipore) and diiodomethane. All contact angle measurements have been carried out at room temperature and under air atmosphere.
The surface topography was observed using an atomic force microscope (Level AFM, Anfatec GmbH, Germany) and standard silicon cantilevers (Tap 300, Budget Sensors, Bulgaria). The SAM thickness was checked by spectroscopic ellipsometry (VASE-ellipsometer, J.A. Woollam Co. Inc.).

3 Results and discussion Figure 1 presents the obtained contact angles for water and the non-polar diiodomethane. The silanol density was increased by the treatment with piranha acid, which led to a contact angle of about 40° for both water and diiodomethane. With increasing reaction time the contact angles increase rapidly and form stable values of about 108° for water and 70° for diiodomethane. The water contact angle is close to the 111° which are typically reported for OTS layers in literature [30]. Interestingly these highest values are only reached after around 450 minutes. From AFM topography measurements it is known that a closed monolayer is reached after a few minutes [27]. We found no islands for the samples at any deposition time which indicates, that the SAM is closed. Since there should be a significant height difference between LE phase and LC phase of about 1 nm [33], it can also be concluded that the sample surface consist of only one phase on a lateral scale of the AFM tip radius (~10 nm) or above. Also the total roughness does not change for these samples. The absolute roughness (rms ≈ 0.30 nm) is nearly identical to that of the pure silicon oxide surface (rms ≈ 0.31 nm), which shows that there are no surface irregularities which can be detected by a standard silicon tip. The topography is mainly determined by the silicon oxide surface. The low roughness of the silicon oxide is likely necessary to reach high quality OTS monolayers with a nearly all-trans configured alkyl chains with an almost perpendicular orientation [35]. Former investigations showed clearly that the quality of the SAM decreases with an increasing surface roughness leading to an increasing fraction of gauche conformation in the alkyl chains [36].

The average film thickness was obtained to be no more than (2.2 ± 0.2) nm for growth times smaller than 500 minutes. This indicates clearly that only one monolayer of OTS molecules is formed. Since the length of a single stretched OTS molecule is approximately 2.4 nm [37], a nearly upright standing alkyl-chain with all-trans conformation (LC phase) can be assumed as it is predicted in [38]. For growth times higher than 500 minutes the situation changes: the roughness of the sample increases to more than 1 nm. Also the film thickness increases which we attribute to a beginning out of plane polymerization and thus to the formation of a three dimensional siloxane network. This also leads to larger variation in the water contact angles which vary between 100° and 110°. Therefore the following evaluation is only done for film growth times less than 500 minutes.

From the two different contact angles we calculated the surface energy of the samples with its polar and dispersive contributions by using the model developed by Owens, Wendt, Rabel and Kaelble (OWRK) [39] (Fig. 2).

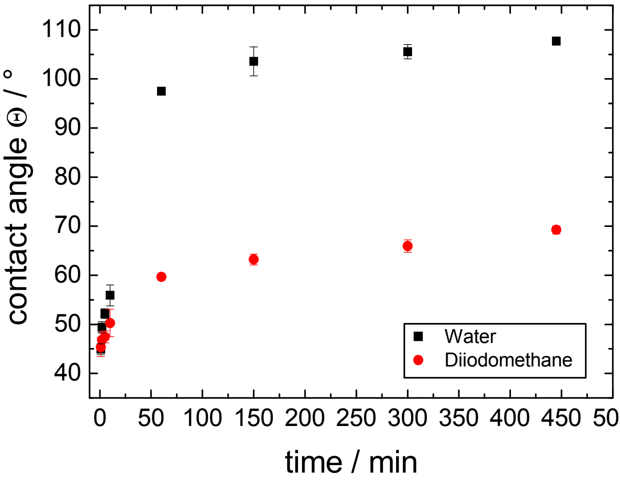

Figure 1 Contact angles of water (■) and diiodomethane (•) on OTS covered thin silicon oxide films (oxide thickness 70 nm) over reaction time.

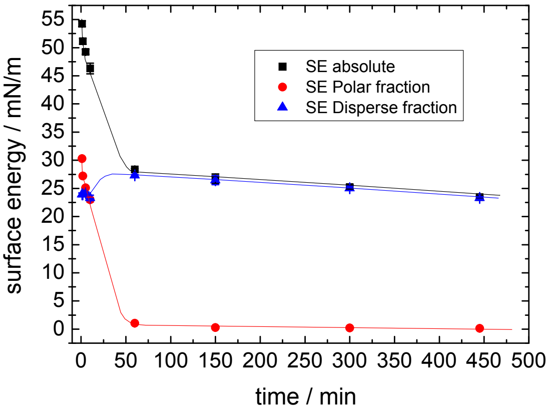

Figure 2 Change of the surface energy (■) and its polar (•) and non-polar (▲) component with reaction time. The error bars are as small as the indicated data points. The lines are only guides for the eyes.

As expected the surface energy decreases with the formation of the alkyl SAM. The surface tension of the pure OTS monolayer after 450 minutes reaches 24.5 mN/m which is slightly higher than the around 21 mN/m reported before. [26] The decrease of the surface energy of about a factor of 2 compared to the pure silicon oxide surface is mainly due to a nearly vanishing of its polar component which has a value of around 30 mN/m for the hydrophilic pure silicon oxide surface. This is due to the reaction of the strongly polar silanol groups with the silane molecules and the formation of the monolayer of alkyl chains at the surface of the silicon oxide.

For the non-polar component of the surface energy a slight increase within the first 60 minutes can be calculated from the contact angles, which point to an increase of e.g. van der Waals interactions. Such a change could be due to an increase of the surface roughness and therefore an increase in the interface area between the liquid and the solid. As our topography investigation showed no significant change on a resolution scale of 10 nm such a rather macroscopic influence can be neglected. We attribute this finding therefore to a lower ordering of the alkyl chains within the self assembled monolayer for shorter reaction times. This can be understood regarding the expected growth mechanism with the formation of small islands. When the Islands grow together a grain boundary is formed, where the molecules tend to arrange in a gauche conformation. Such gauche conformations of the n-alkyl chain are typical for less ordered OTS monolayers, which can be also detected by high resolution infrared spectroscopy [1]. As the grain boundaries are very small and the alkyl chains are flexible and tend to fill the gap between the islands, the boundaries are not visible by atomic force microscopy. On the other hand the less ordered alkyl chains can slightly increase the microscopic surface (within a few Å) which causes an increase in the dispersive interaction of the surface with the liquid. The all-trans conformation which shows the smallest surface energy at the highest water contact angle can only be reached after a rearrangement of the alkyl chains due to further chemisorbtion of additional OTS molecules. This process is rather slow, as the quite dense packed monolayer hinders the free OTS molecules to reach the still existing silanol groups on the silicon oxide surface. The process could maybe accelerated by increasing the reaction temperature. Interestingly, we reached minimum dispersive surface tension only after 450 minutes which is in contradiction to Goldmann et al. which stated that a pure LC phase containing all-trans conformation is reached after 90 to 100 minutes [33]. It should be noted that their investigations have been carried out for silicon covered by a thin silicon oxide layer (1.8 nm thickness), while our samples were covered by a 70 nm thermally grown oxide film as it is typically used for gate insulator in organic field effect transistors. The differences in oxide height and preparation method may have an influence on the distribution and evolution of the different phases.

4 Conclusions

We have demonstrated that a high quality SAM by OTS molecules with a high water contact angle of around 108° and a small surface energy of about 24.5 mN/m can only be reached after at least 440 minutes reaction time. For shorter times a closed film can be obtained where the quality is much lower leading to an increase in the dispersive interaction. This is attributed to a high fraction of gauche conformation within the alkyl-chains caused by e.g. grain boundaries between the islands. The following rearrangement and further chemisorbtion is hindered due to the quite dense packed SAM reached after the first formed islands grew together. To obtain reproducible results in organic electronics using such self-assembled monolayers formed by OTS we recommend therefore to draw the attention also on the reaction time of the silane molecules with the gate oxide.

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