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LETTER TO THE EDITOR

Surface Functionalization of Silicon Oxide at Room Temperature and Atmospheric Pressure

A novel method to derivatize silicon surfaces with 3-mercaptopropylsilane molecules has been developed and optimized. This method is based on an argon flow that increases the evaporation rate of the silane molecules by lowering the partial pressure of the silane molecules in gas phase above the liquid silane, at room temperature. X-ray photoelectron spectroscopy studies of the surfaces showed a dense monolayer coverage as well as hydrolysis of the silane methoxy groups. Atomic force microscopy was used to investigate the roughness of the surfaces after each step of the derivatization process. Since the final surface has a measured surface roughness of 0.19 nm, this method will be especially useful for further synthetic routes and advanced single molecule detection studies of interactions on surfaces as well as improvement of existing conventional techniques for surface derivatization and analysis. © 2002 Elsevier Science (USA)

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During the past two decades, many efforts have been directed to achieving surface chemical derivatization. The most widely used surfaces are gold and silicon, as well as silicon-related materials such as glass. The chemistry on gold surfaces is mostly based on thiol compounds or alkanethiol self-assembled monolayers (SAMs) (1–4). The chemistry on silicon surfaces is more diverse. Passivated silicon is mostly derivatized using alkenes at high temperatures (5–8), while a more common way to functionalize silicon surfaces is silanization of the native silicon oxide layer. So far, many different methods have been developed in order to obtain stable, flat, and highly functionalized silicon surfaces. Liquid phase preparations (9–12) are extensively used but result in unstable and nonuniform layers. Gas phase preparations have been shown to produce better quality surfaces. Indeed, heating of the silane reagent (13) or vacuum distillation (10, 11) appear necessary since their low vapor pressure at room temperature only allows a very low amount of molecules to adsorb to a silicon oxide surface. Nevertheless, the use of high temperature during the deposition of silane molecules onto surfaces results in a high variation of silane amounts and quality of the silane layer and the vacuum distillation process requires several hours. On the other hand, the silanization process consists of two steps, hydrolysis of alkoxy groups followed by condensation of surface silanols with silane molecule silanols. Previous studies (14, 15) strongly support the fact that, in an anhydrous environment, these two steps occur when the silane molecules come in contact with the water layer adsorbed on the silicon oxide surface (Fig.1). Methoxy groups from silane molecules could also react directly with an accessible and acidic surface silanol (14). The presence of multilayers of water is likely to be responsible for the nonuniformity of the silane layer since the silane monomers polymerize before reaching the silicon oxide surface.

The new method described in this paper meets room temperature, atmospheric pressure, and anhydrous condition requirements. The derivatization is performed in a reactor filled with dry argon to achieve an anhydrous and particle-free environment. The partial pressure of silane molecules, 3-mercaptopropyltrimethoxysilane (3-MPTMS) in vapor phase at room temperature is lowered by the argon flow directed near and above the surface of the liquid phase silane. The evaporated silane molecules are removed and directed upwards toward the outlet. Thus, an increased number of molecules come in contact with the silicon oxide surface placed in the reactor tube. Consecutive X-ray photoelectron spectroscopy for chemical analysis (ESCA) showed a full monolayer coverage. Different reagent exposure times have been tested, showing that the amount of silane on the surface increases with increasing time up to a reaction time of 30 min. Longer reaction times result in the same number of silanes on the surface. No curing step (heating in anhydrous atmosphere) is found to be necessary after exposure of the surfaces to the reagent. Surface roughness after reaction was as low as 0.30 nm, as studied by atomic force microscopy (AFM). Sonication was applied after reaction, resulting in a decrease of surface roughness to 0.19 nm. The surfaces still display the same amount of silanes after sonication, which indicates reorganization of the molecules on the surface, as well as after 24 h in water, thus proving to be very hydrolytically stable. This new method permits the production of nearly atomically flat, high-quality silane layers with a very high reproducibility (average sulfur XPS peak area 2.65 ± 0.52) at room temperature using a short reaction time, rendering them very suitable for further synthesis involving single biomolecule analysis.

P-doped ⟨100⟩ single crystal silicon surfaces (Silchem, Germany) were cleaned using a Piranha solution, $H_2SO_4 \cdot H_2O_2$ 30% (v/v) 2 : 1, and rinsed with ultrapure water (18 MΩ, low organic content). The wet surfaces were transferred to a 50-ml, upside-down-mounted, polypropylene reaction tube (TPP, Switzerland) and dried by holding them in the tube in front of a dry argon flow for 5 min until no more water is visible on the surface (Fig. 2). The surfaces were then moved up through an opening in a polypropylene grid placed 3 cm above the tube opening, as depicted in Fig. 2, and placed on top of the grid, without having been in contact with ambient atmosphere. The argon flow, which is entering the tube through a pipette tip with a 2-mm diameter, was then set to approximately 1 L/min. The tube was closed with a lid containing 10 or 20 μl of 3-MPTMS reagent (ABCR, Karlsruhe, Germany). Three different silane exposure times were tested; 60, 30, and 15 min, the latter two followed respectively by 30 and 45 min in the argon flow after the removal of the silane, in order to have the same total time of incubation in the argon flow. The whole process is performed at room temperature (21°C).

ESCA spectra at 10° and 90° takeoff angle (TOA) were acquired in a Scienta-300 instrument (Scienta, Uppsala, Sweden) using monochromized Al $K\alpha$ x-ray radiation with an energy of 1487 eV and a pass energy of 300 eV, immediately after the surfaces were removed from the reaction tube. AFM imaging was then performed with a PicoSPM using MacMode (Molecular Imaging Inc., Phoenix, AZ) using magnetically coated silicon-based tips (Silicon-MTD Ltd., Moscow, Russia), as well as a Nanoscope III (Digital Instruments, Santa Barbara, CA) using Pointprobe tips (Nanosensors GmbH, Norderfriedrichskoog, Germany).

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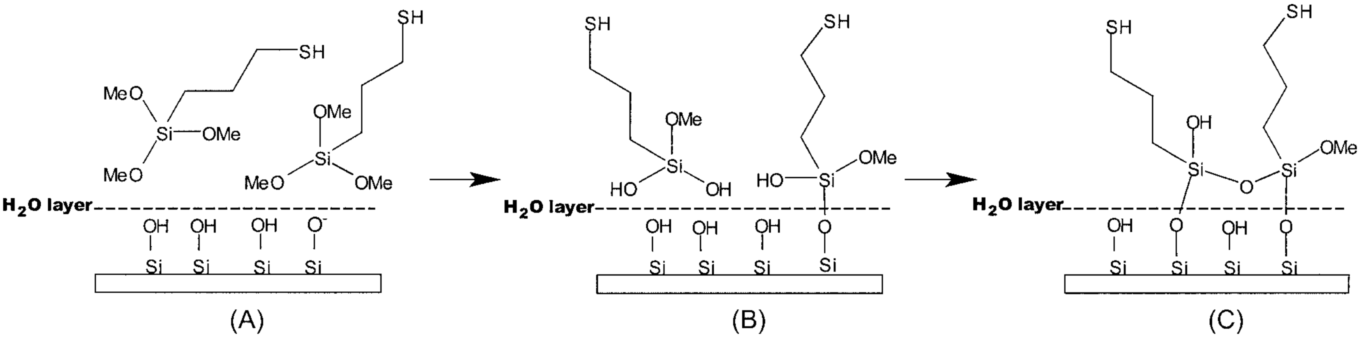

FIG. 1. Schematic of the silanization reaction using 3-MPTMS. The silane molecules reach the silicon oxide surface (A) and react directly with deprotonated hydroxyls or are hydrolyzed to silanols by water from the hydration layer (B). These silanols subsequently condense either with surface silanols to result in covalent bonds between the silanes and the surface, or with other silanes to create a siloxane network (C).

After ESCA and AFM analysis the surfaces were sonicated, first for 10 min in 99.5% ethanol followed by 10 min in ultrapure water, to remove loosely bound molecules, and dried in an argon flow. After sonication, ESCA as well as AFM analysis were repeated as before sonication. Average RMS values with their standard deviation were calculated using the Nanoscope III software over areas of $1 \times 1\ \mu m^2$ as well as $500 \times 500\ nm^2$, on at least three different sites on the same sample. The curing step was performed by placing the derivatized surface in a glass beaker closed and filled with dried argon, on a heating plate.

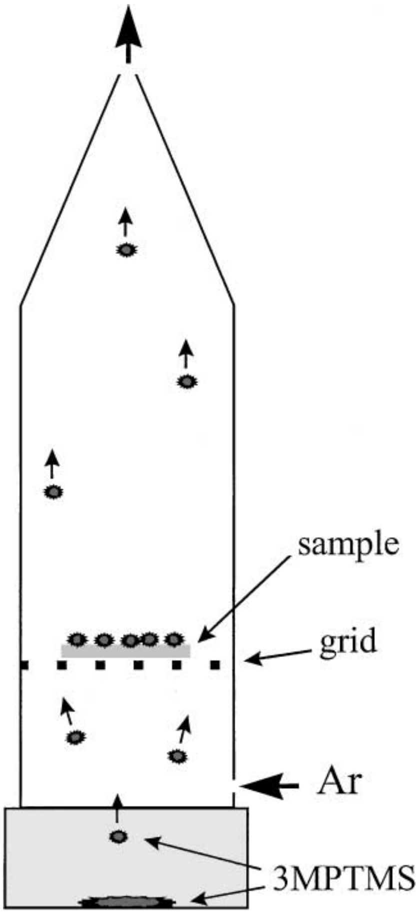

FIG. 2. Schematic drawing of the reaction chamber. The sample, still wet after cleaning, is dried inside a 50-ml polypropylene reactor tube while being held in front of the inlet of the argon flow. Once dried, the sample is moved up through a grid and placed on the grid. The liquid reagent is placed in the lid of the tube. For details, see text.

Sulfur and carbon in a 1 : 3.3 ratio were detected at 10° TOA on the surfaces (Figs. 3A and B), indicating deposition of the silane molecules on the surface and hydrolysis of at least two methoxy groups out of three, since no oxidized carbon peak was observed in the spectra. This observation indicates that the hydrolysis reactions described in Fig. 1 do occur. The presence of the silane molecules on the surface shows that the argon flow not only helps to keep the environment anhydrous, but also enhances silane evaporation and directs the silane molecules towards the silicon surface, since at room temperature and atmospheric pressure without argon flow, little to no sulfur is detected unless the reaction time exceeds two hours. The amount of sulfur on the surfaces reaches a saturation level after 30 min of exposure to the 3-MPTMS reagent, since 30 and 60 min exposure give the same XPS peak area of sulfur in the ESCA spectra (Fig. 3B inset). The use of 10 or 20 μl of 3-MPTMS does not modify the results; already using 10 μl there is an abundance of reagent in the reaction tube. In addition, a good reproducibility was achieved with this silanization method. The average sulfur XPS peak area over five runs at 90° TOA was calculated to be 2.65 ± 0.52.

Since the 10° TOA is more surface-sensitive than the 90° TOA, a comparison of ESCA spectra taken at those angles can be used to qualitatively elucidate the orientation of molecules on the surface. The C : S ratio measured at 90° TOA was 4.43, the C : S ratio at 10° TOA was 3.28, indicating a relatively larger increase in intensity for sulfur than for carbon, going from 90° TOA to 10° TOA. This suggests that generally the sulfur atoms are facing away from the surface and the silane group is attached to the surface. We have compared the sulfur signal from a dense self-assembled octadecanethiol monolayer on a gold surface obtained by M. Wirde *et al.* using the same ESCA instrument (16) to the sulfur signal of the 3-MPTMS layer on silicon oxide obtained with our method at a TOA of 90°. The gold surfaces have been reacted for at least 24 h in an ethanol solution containing 1 mM of the reagent and formed a complete dense monolayer. After correction for the background differences and the attenuation of the signal by the C_{18} chains on the gold surface, it was found that the alkylthiol monolayer had only 2.3% more sulfur than the silicon oxide surface reacted with our new method. This shows that the 3-MPTMS layer is a densely packed monolayer.

Sonication did not reduce the number of sulfurs on the surfaces, as indicated by identical ESCA integrated intensity values for the sulfur signal before and after sonication at both 90° and 10° TOA. The contact angle was measured to be 69° before and after sonication. We imaged our surfaces using AFM in order to calculate the RMS roughness using the Nanoscope III software. Qualitative roughness measurements with AFM depend strongly on the specific type of tip used. However, by using the same tip for all surfaces, we obtained a quantitative difference in roughness before and after sonication. The RMS roughness went down from 0.31 ± 0.04 nm to 0.22 ± 0.01 nm over a $1 \times 1\ \mu m^2$ area after sonication, and from 0.30 ± 0.01 nm to 0.19 ± 0.01 nm over $500 \times 500\ nm^2$ areas (Fig. 3C+D). Wet chemistry gives surfaces with high surface roughness, that the authors describe as 1- to 3-nm-high domains (12) in the

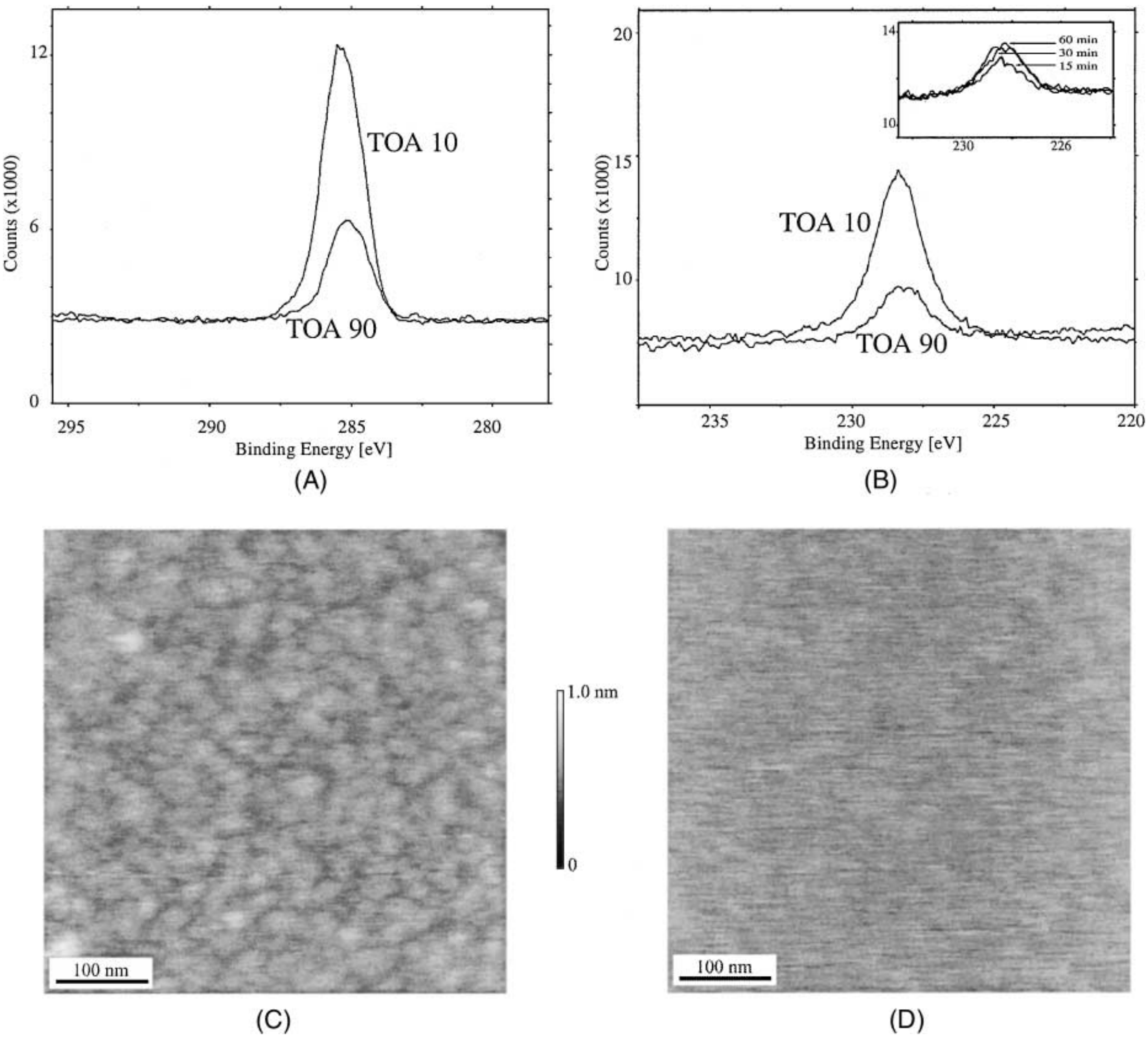

FIG. 3. (A) C1*s* and (B) S2*s* ESCA spectra acquired at 10° and 90° take-off angle (TOA) relative to the surface. The C : S ratios of 4.43 for 90 TOA and 3.28 for 10 TOA indicate the proper orientation of 3-MPTMS with the sulfur facing away from the surface. Inset: S2s spectra acquired after derivatization using increasing reaction times, showing increasing amounts of sulfur up to 30 min and saturation (as derived from the peak area) after 30 min. Macmode AFM images of a derivatized surface (C) before and (D) after sonication. The surface roughness is calculated to be 0.30 nm before and 0.19 nm after sonication. This indicates a reorganization of the 3-MPTMS molecules on the surface during sonication, resulting in a nearly atomically flat surface.

best case. The surfaces obtained with heat evaporation indeed have a low RMS value, 0.1 nm calculated over a $1 \times 1\ \mu\text{m}^2$ area (13). Nevertheless, the integrated intensity of the sulfur peak shows a 2.4 times lower value at TOA 90° than on surfaces made using this new method. The decrease in the RMS despite the constant amount of sulfur and contact angle indicates a rearrangement of the molecules on the surface without desorption. According to Stevens (17), a siloxane bond between two silane groups of adjacent 3-MPTMS molecules is shorter than the distance defined by the Van der Waals radius of the two carbon chains of those molecules. Even in the case of a hydrogen bond between two 3-MPTMS silanol groups, this distance is still shorter. This would imply that two adjacent 3-MPTMS molecules which are bound to each other by their silanol groups, covalently or not, will have the top of their carbon chains pointing away from each other, inducing a slight tilt of the molecules and leading to 3-MPTMS domains with a convex shape, that can be related to the features observed on the surfaces (Fig. 3C). The loss of 0.1 nm in surface roughness is certainly significant when the surface is going to be used for single molecule studies. But compared to, on one hand, the length of the molecule, about 0.8 nm, and on the other hand, the domains observed on the surface (Fig. 3C), about 30 nm in diameter, it represents a very small change due to a minor rearrangement within the overall monolayer structure. This slight change is detectable by a method as topography-sensitive as AFM, but neither using the contact angle method nor by ESCA.

Furthermore, the 3-MPTMS layer obtained with this method was stable after 24 h in ultrapure water, as was the layer cured at 130°C for 12 h. A crucial point of layer stability is polymerization of the silane molecules to form a network on the silicon oxide surface as well as bonding of a few silanes to the silicon oxide. These are very slow reactions at room temperature, usually enhanced by high temperatures, ranging from 120°C to 200°C (18). Nevertheless, the curing step did not add to the stability of the layer, but resulted in identical ESCA spectra as obtained before curing, indicating that the silanization process is almost complete. In addition to lowering the vapor pressure of the 3-MPTMS reagent at the bottom of the reactor tube, the argon flow could possibly lower the partial pressure of the products of the reaction as well. Removing the products of the hydrolysis and condensation steps away from the surface means that the reaction will be driven toward the formation of those products, enhancing the rate of the silanization process. It is also possible that the argon flow reduces the thickness of the surface hydration layer, making the surface silanols more accessible for direct reaction with the silane molecules (Fig. 1).

Consequently, this monolayer is more likely to be held together mostly by covalent siloxane bonds, although a few noncovalent hydrogen bonds could still be present, both between the silanols of the 3-MPTMS molecules and between the 3-MPTMS silanols and the hydroxyls of the silicon oxide surface. The explanation for the minor rearrangment responsible for the lower RMS value after sonication would be that the hydrogen bonds between the 3-MPTMS silanol groups are broken during the sonication and consequently, these molecules are free to rearrange in preferred configurations. This would only occur for a minority of 3-MPTMS molecules, resulting in the small change observed in surface roughness.

These results illustrate the advantages of using an inert gas flow to achieve the silicon oxide derivatization: (i) the argon flow increases the silane evaporation rate, making the surface derivatization possible at room temperature, (ii) it allows the reaction to proceed in anhydrous and contamination-free conditions, and (iii) it might have a rate-enhancing effect on the silanization process. Therefore, the method described presents several improvements over existing methods of silanization, the most important ones being its good reproducibility and performance under ambient conditions at room temperature. Using this method, nearly atomically flat thiol monolayers on silicon oxide surfaces are obtained within 30 min of reaction time. Those surfaces are ideal for further synthesis using reactions with, in the case of a sulfur outermost atom, thiolated single molecules.

We have developed a method for the fast silanization of silicon oxide surfaces at room temperature under ambient conditions. Derivatized surfaces were analyzed using ESCA, indicating a dense monolayer, and proved to be extremely flat, as measured by AFM, rendering this method very suitable for the production of substrates for single molecule studies employing techniques such as AFM. The silane molecules were found to be correctly oriented with the sulfur atoms facing away from the surface, making it very feasible to use the sulfur end atoms for reaction with thiolated single molecules. Similarly, other end atoms could be employed for different target groups.

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