



STM and HREELS investigation of gas phase silanization on hydroxylated Si(100)

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ABSTRACT

The gas phase anhydrous reaction of glycidoxypropyldimethylethoxysilane (GPDMEs) with a model hydroxylated surface has been investigated using high-resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). Water dissociation on the clean reconstructed (2×1) -Si(100) surface was used to create an atomically flat surface with ~ 0.5 ML of hydroxyl groups. Exposure of this surface to GPDMEs at room temperature under vacuum was found to lead to formation of covalent Si–O–Si bonds although high exposures (6×10^8 L) were required for saturation. STM images at the early stages of reaction indicate that the reaction occurs randomly on the surface with no apparent clustering. The STM images together with semi-empirical (AM1) calculations provide evidence for hydrogen bonding interactions between the oxygen atoms in the molecule and surface hydroxyl groups at low coverage.

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1. Introduction

Silane coupling agents have the ability to form a durable bond between organic and inorganic materials, and thus have been used extensively for modifying the surface physical and chemical properties of oxide surfaces. Silanization usually takes place via reaction of hydrolyzable substituents (alkoxy or chloro groups) with surface hydroxyl groups resulting in formation of a covalent linkage. There are two basic paths for the silanization reaction. The simplest path is via a direct elimination reaction between the reactive alkoxy or chloro groups with surface hydroxyls. The more common reaction path involves the participation of water. In this two step process, the silane groups first hydrolyze to form silanols followed by a condensation reaction with the surface hydroxyl groups resulting in formation of a covalent bond. The latter reaction pathway is considerably more facile than the anhydrous route. However, the condensation reaction can also lead to cross-linking between silanes and polymer growth, complicating the surface structure [1,2].

Earlier studies of silanization focused on the silanization of silica in aqueous solution, aimed at understanding and optimizing the adhesive properties of silanes [3–5]. Due to the competition between reactions with surface hydroxyl groups and intermolecular coupling reactions leading to polymerization, the film quality was found to be very sensitive to deposition conditions resulting in limited reproducibility. In order to improve reproducibility of the film quality, silanization under non-aqueous solution was widely studied [6–8]. The quality of the thin film was improved by controlling the quantity of the trace water in the

solution as well as on the substrates [6]. Substrates used in these studies were typically silica powders or native SiO₂ on silicon wafer. Under well-controlled conditions, silanization in anhydrous solution occurs via direct reaction with surface hydroxyl groups, but is usually relatively slower than the two step hydrolyzation–condensation pathway. An alternative method to control the water content is to carry out the reaction in the vapor phase. In this case the main source of water is from the substrate, which can be easily controlled or eliminated by annealing to appropriate temperature in vacuum. Comparison of monolayer films produced by vapor and solution phase processes have indicated that improved film quality can be achieved via the former approach [9–14].

To better understand the silanization reactions and the morphology of the resulting films, a well-defined model hydroxylated surface is desired. Water has been observed to dissociate on a clean reconstructed (2×1) -Si(100) surface to form covalent Si–OH and Si–H bonds, resulting in a surface with ~ 0.5 ML of surface hydroxyl groups [15–22]. The flatness of this surface and the absence of an insulating oxide layer enable the use of scanning tunneling microscopy (STM) to observe the atomic scale morphology of the surface after silanization. In our UHV system, the model surface can be exposed to organosilanes at the load lock chamber and transferred back to the UHV system without exposure to the air. As a result the entire investigations were carried out in the vacuum environment, eliminating uncertainties and contamination associated with removing the samples to air.

In this paper, we employ the model hydroxylated Si(100) surface to investigate the silanization reaction of 3-glycidoxypropyldimethylethoxysilane (GPDMEs) using STM and high-resolution electron energy loss spectroscopy (HREELS). HREELS is used to identify the attached species after the exposure of GPDMEs to the surface. Compared to similar surface vibrational spectroscopies, such as FTIR, HREELS is much more sensitive at the low frequencies suitable for studying the Si–O–Si bond

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formation. The choice of GPDMS was motivated by the extensive use of epoxy silanes to immobilize probe molecules (oligonucleotides or proteins) for biosensor applications [23–25]. Compared with the more commonly used epoxysilane, (3-glycidioxypropyl)trimethoxysilane (GPTMS), GPDMS has a higher vapor pressure. The presence of a single alkoxy group ensures that cross-linking and polymerization reactions are fully prevented.

2. Experimental

The studies were carried out entirely in a UHV chamber equipped with both STM and HREELS. An LK3000 spectrometer (LK Technologies, Bloomington, IN) was employed for the HREELS measurements. Spectra were acquired in the specular geometry (60° with respect to the surface normal) at an incident beam-energy of 6 eV and the spectrometer resolution of 6 meV (56 cm^{-1}). The STM used for the experiments was a UHV1 from Omicron. STM images were rendered into grey scale and flattened using in-house software developed by Doug Moffatt of SIMS-NRC.

Samples were cut from Si(100) wafers (Virginia Semiconductor, n-type 1–10 $\Omega \text{ cm}$) and cleaned by rinsing with ethanol, prior to transfer into the UHV chamber. The sample was degassed at $\sim 580^\circ \text{C}$ overnight followed by cooling to room temperature and flashing to 1100°C to obtain a clean (2×1) Si(100) surface. This surface was then exposed to 100 L H_2O at room temperature to obtain the hydroxylated Si(100) surface. The surface quality was monitored by HREELS and STM, as shown in Figs. 1 and 2 in the next section. The 100 L exposure used here is well in excess of the 10 L H_2O reported to be sufficient to saturate the surface [15] in order to attempt to minimize the density of residual dangling bonds.

GPDMS (Aldrich, >97%) was placed into a glass vessel, connected to the gas manifold of the UHV system and purified by several freeze-pump-thaw cycles. Prior to each exposure, the solution was purified using a single freeze-pump-thaw cycle. Due to the high exposure pressures (up to 10 mTorr) required in the current studies, reactions were carried out in the turbo pumped loadlock of the UHV system (base pressure $\sim 1 \times 10^{-7}$ Torr). Higher exposure pressures were monitored using a convectron gauge while pressures below 0.1 mTorr were measured using a cold cathode gauge. Due to a concern with the cold cathode gauge stimulating reactions or contaminating the sample, the gauge was turned off during the actual reactions. The pressure of

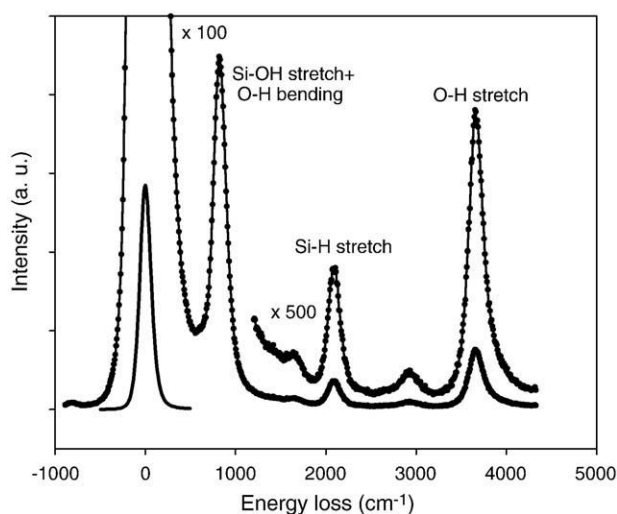


Fig. 1. HREEL spectrum of hydroxylated surface prepared by exposure of 100 L H_2O on the clean Si(100) surface.

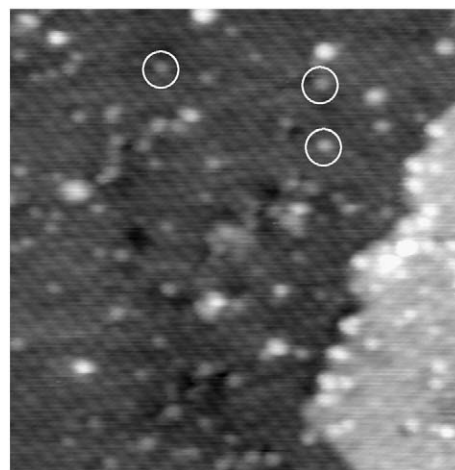


Fig. 2. Constant current STM image (-2.5 V , 30 pA , $25 \times 25 \text{ nm}^2$) of the hydroxylated Si(100) surface. Examples of residual dangling bond features are indicated by white circles.

GPDMS was estimated by measuring the pressure at the same valve position used for the exposures.

3. Results and discussion

The model hydroxylated Si(100) surface formed via dissociation of water was characterized by HREELS and STM. Fig. 1 shows the HREEL spectrum of the surface obtained after exposing the clean Si(100) surface to 100 L H_2O . The elastic peak is considerably broader (FWHM of 140 cm^{-1}) than the spectrometer resolution, which can be attributed to the excitation of the free carrier plasmon mode arising from the substrate dopants. The spectrum is dominated by a strong peak at 820 cm^{-1} , which can be attributed to the stretch mode of Si–OH [15]. The O–H bending vibration also falls into this range and cannot be distinguished from the Si–OH stretch mode. Exchange of the O–H groups with O–D resulted in the appearance of two loss modes in this region of the spectrum (not shown) at 650 and 810 cm^{-1} , which are assigned to O–D bending and the Si–OD stretching modes respectively. The loss peak around 3670 cm^{-1} is from the O–H stretch, while the peak around 2090 cm^{-1} is from the Si–H stretch. The weak peak at around 1665 cm^{-1} is from the overtone of the Si–OH stretching mode. In addition to these peaks which are expected from the dissociation of water to form Si–OH and Si–H groups a weak peak at $\sim 2940 \text{ cm}^{-1}$ can be assigned to the C–H stretch arising from a small degree of hydrocarbon contamination introduced during sample flashing and water dosing.

A typical STM image of the hydroxylated Si(100) surface is shown in Fig. 2. The dimer rows of the (2×1) Si(100) are clearly seen, indicating that the dimer structure is maintained after water exposure, consistent with previous studies [18,26,27]. A number of small ($1\text{--}2 \text{ \AA}$) protrusions are observed, most of which are asymmetrically positioned with respect to the dimer row. These protrusions can be assigned to isolated dangling bonds arising from the presence of both inter and intradimer dissociation pathways. From this image the dangling bond density is observed to be $\sim 2.4\%$ ML in agreement with previous work [27]. In addition to the dangling bond features a considerably smaller density of larger ($3\text{--}4 \text{ \AA}$) protrusions are observed and are likely due to contamination arising in the cleaning or water dosing steps.

Fig. 3 shows the evolution of the spectra upon exposing the hydroxylated surface to GPDMS at various pressures and times followed by annealing at $\sim 200^\circ \text{C}$ for 5 min. The annealing is used to remove physisorbed silanes and is also used for the STM measurements

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