

Thermal Behavior of Self-Assembled Monolayers (SAMs)

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I. Introduction

The thermal stability of SAMs is an important consideration because they must be able to withstand the temperatures used in various processing and packaging steps. Alkanethiols adsorbed on Au have been observed to desorb at about 450 K through cleavage of the Au-S bond. The thermal behavior of alkylsiloxane monolayers on oxidized silicon and alkyl monolayers on silicon has not been examined previously.

In the present study we have employed high-resolution electron energy loss spectroscopy (HREELS) to examine the thermal behavior of the two kinds of SAMs. It is found that the alkylsiloxane monolayers are stable in vacuum up to about 740 K independent of chain length. Above that temperature, the monolayers decompose primarily through the cleavage of C-C bonds. HREELS also shows that the alkyl monolayers are stable up to 615 K. Hydrogen is observed on the silicon surface following desorption, likely the result of β -hydride elimination reactions. The desorption temperature is about 100 K lower than that found for alkylsiloxane monolayers on the oxidized silicon.

II. Experimental

Substrates were cut from B-doped Si(100) wafers with resistivity in the range 1-50 Ω cm. The samples were first degreased ultrasonically in chloroform. A chemical oxide was grown by placing the sample in a piranha solution (4:1 mixture of H_2SO_4 : H_2O_2) at 100°C for 10-15 minutes. The sample was rinsed several times in de-ionized water (resistivity = 18 M Ω), then dried using nitrogen. Alkylsiloxane monolayers were formed by placing the oxidized samples in a 2.5 mmol solution of the alkyltrichlorosilane precursor dissolved in 4:1 hexadecane:chloroform for one hour. The samples were then ultrasonically washed in chloroform to remove excess reactants and dried with nitrogen. For the alkyl monolayers, the chemical oxide formed by the piranha solution was etched away by placing the sample in a saturated NH_4F solution (40% in water) for 4 min, followed by a short (1-2 s) water rinse and a 20 s rinse in 2-propanol. To form the alkyl monolayer, the substrate was placed in the alkene at 200 °C with nitrogen bubbling. After 2 hr, the samples were cooled to the room temperature, removed from the alkene, and then rinsed with chloroform. Film quality was checked by water contact angle and ellipsometer.

Samples were introduced into ultrahigh vacuum by means of a load lock system. The chamber contains low energy electron diffraction, Auger electron spectroscopy, HREELS, and a differentially-pumped quadrupole mass spectrometer (QMS) coupled to a temperature controlled for temperature programmed desorption. The thermal behavior of the films was studied by annealing the sample to a given temperature for approximately one minute, during which time the QMS was used to check the composition of the background gas in the range from 1 to 300 amu. After cooling the sample to 120 K, HREEL spectra were obtained in the specular mode using an incident electron energy of 6 eV. HREELS measurements were complemented by contact angle analysis and atomic force microscopy (AFM)

III. Results and Discussion

The HREEL study for the alkylsiloxane monolayers as a function of annealing temperature has been done. The presence of the monolayers is indicated by the C-H stretch centered at 2920 cm^{-1} . The spectra remain unchanged up

to 740 K. Upon annealing to 780 K, the intensities of the C-H modes decrease slightly relative to the Si-O modes, indicating a reduction in the monolayer coverage. Annealing to 815 K results in a further reduction of the C-H intensities and the appearance of two peaks in the C-H stretch at 2920 and 2980 cm^{-1} , along with the appearance of a single peak at 1400 cm^{-1} in the bending region. These peaks are consistent with methyl groups directly bonded to silicon atoms, suggesting that the Si-C bond remains intact even while the chains have begun to desorb; thus, desorption must occur through C-C bond cleavage. After annealing to 850 K the spectrum is dominated by Si-O modes, and a peak appears at about 2300 cm^{-1} which is attributed to the overtone of the Si-O-Si asymmetric stretch [18].

The water contact angle as a function of annealing temperature for OTS-coated Si(100) supports the picture of C-C bond cleavage. Even after HREEL spectra indicate that significant desorption has occurred, the water contact angle remains high. If the monolayers desorbed as entire chains, one would expect that the monolayers would become disordered, and that the underlying oxide would be exposed, both of which would cause a large reduction in the contact angle.

The thermal behavior of the alkyl monolayers is studied by HREELS. The monolayers are stable to about 650 K. With the sample annealed to 650 K, however, several changes take place. The C-H stretching and bending modes decrease in intensity, indicating that the monolayers have begun to desorb. At the same time, the Si-H stretch at 2100 cm^{-1} and the Si-H bend at 620 cm^{-1} appear. Upon annealing to 720 K, the C-H bending modes have completely disappeared and the C-H stretch has further decreased in intensity. It has also broadened, with a shoulder becoming evident at 3050 cm^{-1} . This shoulder is attributable to the C-H stretch of sp^2 bonded carbon. Further annealing to 785 K results in the disappearance of the Si-H stretch, corresponding to the desorption of hydrogen. Upon annealing to 785 K, the spectrum is dominated by a peak at 780 cm^{-1} , which is attributed to SiC vibrational mode, and the Si-O-Si stretch at 1080 cm^{-1} .

The desorption picture which emerged for alkyl monolayers on silicon is the following: Upon heating to 650 K, the monolayers undergo β -hydride elimination, resulting in the formation of hydrogen and an alkene.

IV. Conclusion

The most significant results on the thermal behavior of SAMs derived from RHEELS, contact angle analysis, ellipsometer, and TPD can be summarized as follows.

(i) The alkylsiloxane monolayers are stable in vacuum up to temperatures of about 740 K independent of chain length.

Above 740 K the chains begin to decompose primarily through the cleavage of C-C bonds. The siloxane head groups remain on the surface until about 1100 K.

(ii) The alkyl monolayers are found to be stable up to 615 K. Annealing to 650 K results in intensity reduction of C-H modes and appearance of Si-H modes, suggesting that desorption occurs through β -hydride elimination reactions. The desorption temperature is more than 100 K lower than that of alkylsiloxane monolayers, pointing out the importance of head group bonding in thermal stability of SAMs.