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Morphology and water-barrier properties of silane films on aluminum and silicon

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Abstract

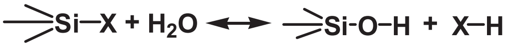
The goal of this study is to understand the effect of the substrate on the morphology and water-barrier properties of bis-silane films. Silane films are deposited on both Si and Al. Neutron reflectivity is used to assess the effect of hydrothermal conditioning on the films. Aluminum on silicon (no silane) was characterized first to facilitate understanding of the more complicated silane on Al-coated Si. A 200-Å Al layer with 55-Å oxide covers the surface of the silicon wafer. The reflectivity data show that water penetrates into the oxide layer. Silane films deposited on either Al or Si substrates have similar bulk and top-surface morphology. Studies of silanes on Si wafers, therefore, can be generalized to include Al. The substrate–silane interface, however, does depend on both the substrate and the silane. Because pH of the bis-sulfur silane solution is outside of the stability range for Al_2O_3, dissolution of the thin oxide film occurs during solution deposition. A water-depletion area is formed at the interface region due to this reaction.

Keywords: Silane film; Neutron reflectivity; Water-barrier; Interface

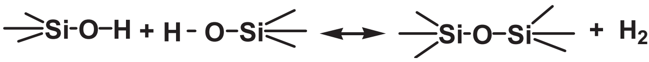
1. Introduction

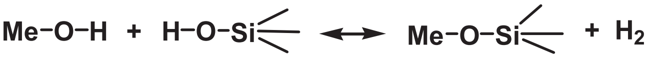
Organosilanes as corrosion inhibitors have been extensively studied during recent years [1–6]. Of particular interest are bifunctional organosilanes with the general structure $X_3Si(CH_2)_nY_m(CH_2)_nSiX_3$, where X is methoxy or ethoxy (capable of hydrolysis) and Y is an organofunctional group such as an amine group or a chain of sulfur atoms [7–10]. The idea of using silanes as corrosion inhibitors, for example, is based on the hydrolysis and condensation reaction of silane to form oxane bonds between the silane and metal substrate as proposed by Plueddemann [11]:

In solution, the silanes hydrolyze to generate active silanols



When applied to the metal surface, silanol groups can react with each other to form Si–O–Si bond and can also react with the metal hydroxide groups (Me–OH) to form oxane bonds.





A highly crosslinked film is formed during this process. Electrochemical data are consistent with the conclusion that the film functions as a physical water barrier [2,3]. To improve the hydrothermal stability, therefore, the foremost objective is to improve the water resistance. Understanding of water–silane interaction is essential for optimizing the properties of the silane films.

Using neutron reflectivity (NR) we have completed a comprehensive study on the morphology of silanes films deposited on silicon wafers, and the response of these films to water conditioning [12,13]. The systems we studied are bis-[triethoxysilylpropyl]-tetrasulfide (bis-sulfur) and bis-[trimethoxysilylpropyl]amine (bis-amino) as well as mixtures of

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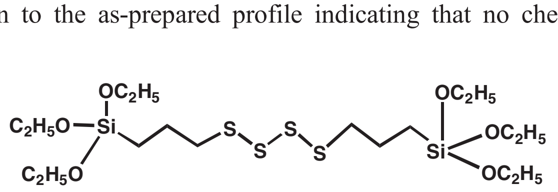
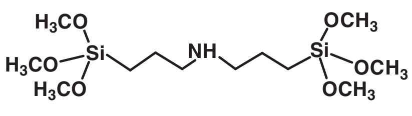
these silanes. These two silanes show contrasting behavior traceable to the bridging group. The chemical structures are shown in Fig. 1. Bis-sulfur silane, with an average of four sulfur atoms in the bridge, is more hydrophobic but hydrolyzes slowly. Bis-amino silane, on the other hand, is more hydrophilic due to the secondary amine in the bridge and hydrolyzes somewhat faster [8]. The bare anti-corrosion performance (without top coating) of bis-amino, however, is not as good as that of the bis-sulfur silane. Interestingly, a bis-sulfur/bis-amino (3/1) mixture shows greatly enhanced corrosion resistance compared to the two individual silanes, and provides protection for many metals [10]. When deposited on Si, we were unable to identify any distinguishing morphological feature of the mixed film compared to the neat films that could account for the superior performance of the mixed film. On aluminum, however, we do find unusual etching behavior in bis-sulfur that is not found for the mixed film.

NR yields structural information normal to the film surface on length scales from ~10 to ~2000 Å [14]. Contrast between different chemical species arises from variations in the scattering length density (SLD). The SLD represents the scattering power of a substance. The SLD is calculable from the chemical formula and mass density. The structure of the film normal to the surface therefore can be obtained based on the SLD profiles, which are extracted from the reflectivity data using standard inversion techniques. Since deuterium has a much higher scattering length than hydrogen, deuterated water (D_2O) is used to challenge the films. The films were tested as-prepared, after exposure of the film to saturated D_2O vapor at both room temperature and 80 °C, and again after re-drying. The reflectivity of the as-prepared and re-dried films is measured with desiccant inside the sample holder. For the swelling measurement the desiccant is removed and several drops of D_2O are introduced. All NR measurements are performed at room temperature, including those samples preconditioned at 80 °C.

On Si substrates, SLD profiles show that the water-barrier ability of the mixture is roughly that of both components weighted by their volume fraction. After re-drying, the SLD curves of bis-amino, bis-sulfur as well as mixed silane film all return to the as-prepared profile indicating that no chemical reaction occurs at room temperature. At 80 °C, however, some alteration occurs since some deuterium remains in the film. Both bis-amino and mixed silane films show a peak in SLD profile near the air side. One important feature revealed in the SLD profile is a 10-Å hydrophilic layer at the oxide–silane interface in all three films. This layer might due to unreacted –OH groups on the silicon wafer surface forming a hydrophilic layer that attracts water through hydrogen bonding.



(a) Bis[3-(triethoxysilyl)propyl]tetrasulfide (Bis-sulfur silane)



(b) Bis-[trimethoxysilylpropyl]amine (Bis-amino silane)

Fig. 1. Molecular structure of (a) bis-sulfur silane; (b) bis-amino silane.

Studies have shown that metal oxides strongly affect the molecular structure as well as other properties of silane films [15,16]. Metal oxide surfaces may differ due to isoelectric point, solubility of the metal hydroxide in water as well as the density and acidity of hydroxyl groups [11]. Therefore, we expected that the amount of unreacted –OH depends on the substrate. Al alloy substrates might have different density of unreacted –OH that could influence the deposited silane film.

Neutron reflectivity on Al substrates was carried out to study the effect of substrate on the water-barrier properties. Because a thick silicon wafer is required to achieve the smoothness required for NR, an Al layer was e-beam evaporated on a silicon wafer. The Al film thickness is around 200 Å and roughness is about 10 Å. Silane films were then applied to the Al surface using the same spin-coating technique. NR data were obtained on virgin films and on the same films following the hydrothermal conditioning.

2. Experimental method

2.1. Materials

Bis[3-(triethoxysilyl)propyl]tetrasulfide (bis-sulfur) $(H_5C_2O)_3Si\text{-}(CH_2)_3\text{-}S_4\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$ and bis-[trimethoxysilylpropyl]amine (bis-amino silane) $(H_3CO)_3Si\text{-}(CH_2)_3\text{-}NH\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$ were provided by OSi Specialties (Tarrytown, NY). The molecular structures are shown in Fig. 1. The silanes were used without further purification. The silicon wafers used as substrates were polished 2-in. diameter single crystals (111) wafers obtained from Wafer World, Inc. (West Palm Beach, FL, USA). D_2O (99.9 at.%) was obtained from Aldrich and used as received.

2.2. Procedure

The wafers were cleaned by immersion in a freshly prepared "piranha" solutions (conc. H_2SO_4/H_2O_2 30%=7:3 v/v) at room temperature for at least 30 min. After immersion, the substrates were rinsed repeatedly with de-ionized (DI) water.

The Al layer was deposited on the silicon wafer by e-beam evaporation. A cathode is heated by driving 25 A through it. The resulting electrons are accelerated toward the target (Al) by a 12-kV dc power supply. The beam is bent by electromagnets to center the beam in the target. The power is increased until the metal's evaporation temperature is reached. The thickness is monitored by a crystal mass monitor.

A 1 wt.% bis-sulfur silane solution was prepared by adding the silane into a mixture of DI water and ethanol. The ratio of