

Morphology and Water Barrier Properties of Silane Films: The Effect of Process Parameters

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Organosilanes are candidates to replace chromates as metal surface pretreatments to inhibit corrosion. Current research shows that silane films are strictly water barriers and show no electrochemical corrosion inhibition.^{1,2} To improve the corrosion performance of silane film, therefore, the foremost objective is to improve water resistance. An understanding the interaction of silane with water is required to achieve this goal. Here, we use neutron reflectivity (NR) to elucidate the morphology of silane films, and the response of these films to water conditioning.

The silanes studied include bis[3-(triethoxysilyl)propyl]tetrasulfide (bis-sulfur) and bis-trimethoxysilylpropylamine (bis-amino) as well as mixed films. Performance tests^{3,4} show that hydrophilic bis-amino silane does not offer good corrosion protection on either aluminum alloy or hot-dip galvanized steel (HDG). Hydrophobic bis-sulfur silane, on the other hand, performs well on aluminum alloy, but failed on steel due to the insufficient wetting on Zn oxide. Bis-sulfur/bis-amino mixture at the ratio of 3/1 greatly enhanced the corrosion resistance compared to the two individual silanes.

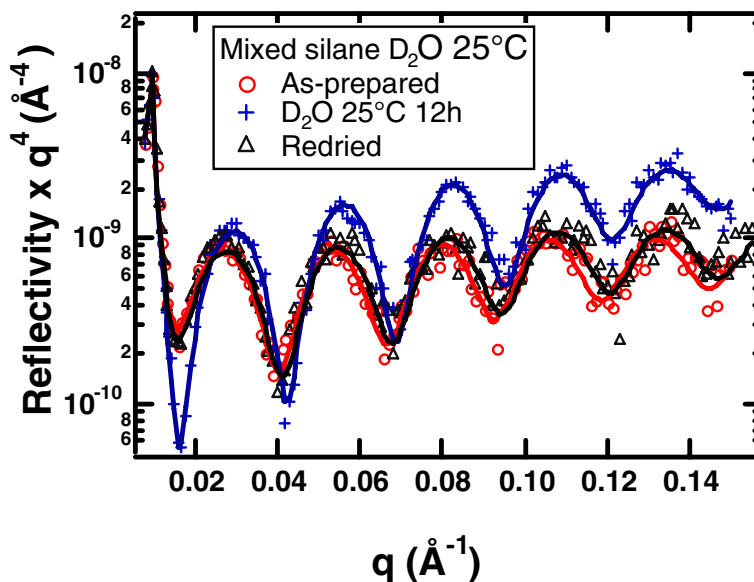
Initial studies were performed on films spin-coated on silicon wafer substrates and cured at 80°C. This study focused on the effect of the bridging group on the structure, morphology and water barrier properties of the films as well as the mechanism underlying these performance results. Subsequent work addresses the same systems deposited on aluminum substrates with higher concentration and cured at 180°C. Our goal is to clarify the relationship between processing parameters, silane film morphology and water-barrier properties while developing a database for optimizing the performance in anti-corrosion applications.

The NR yields structure information on the length scales from 10Å to 2000 Å. NR can easily examine interfaces that are buried well within a sample. In NR, contrast between different chemical species arises from variations in the scattering length density (SLD), which

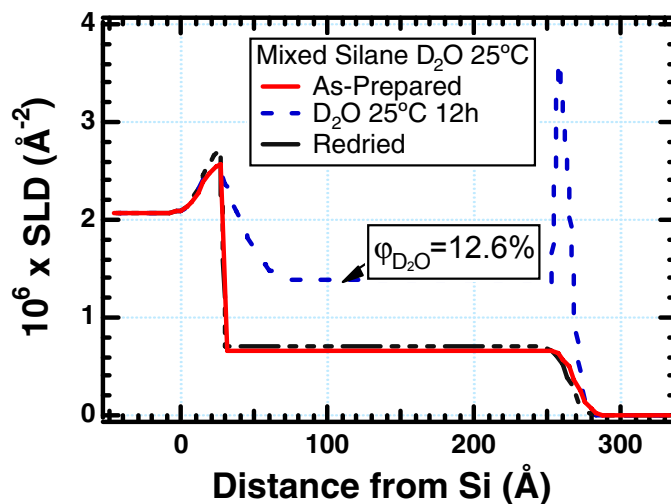
is characteristic of each material. In particular, strong neutron reflectivity contrast between the silane film and the swelling solvent can be obtained using deuterium-rich solvents such as heavy water (D_2O).

A 1% silane solution was prepared by adding the silane to a mixture of DI water and ethanol. The ratio of silane/DI water/ethanol was (1/9/90) (w/w/w). During the second stage of study, 5% solution was made in similar way with the ration of silane/DI water/ethanol 5/5/90. Acetic acid was used to adjust the pH to 7.8 for bis-amino silane and 3.9 for bis-sulfur silane. The mixture solution was made by mixing the individual silane solution at a bis-sulfur/bis-amino ratio of 3/1. During the second stage of study, 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 are then applied to Al surface using the same spin-coating technique. NR data were obtained for the films as-prepared, after exposure of the film to saturated D_2O vapors at both room temperature and 80°C, and again after re-drying. The test in the re-dried state determines if there is chemical degradation of the film.^{5,6}

The intensity of the reflected neutrons is measured as a function of angle. The SLD profile was then obtained by inversion of the reflectivity data using the recursive Parratt fitting procedure. Figure 1a showed the reflectivity data for mixed silane film on silicon oxide as-prepared, swollen to equilibrium in D_2O vapor at room temperature, and then re-dried. The SLD profiles corresponding to the fits in Figure 1a are shown in Figure 1b.



(a)



(b)

Figure 1 (a): Neutron reflectivity data from mixed silane film as-prepared (\circ), after exposure to D_2O vapor at room temperature for 12 h ($+$) and after re-drying (Δ). The curves through the data correspond to best fits using model SLD profiles in (b). (b) Best-fit SLD profiles corresponding to the curves through the data in (a). The calculated volume fraction of D_2O in the swollen film is 12.6%. (NR was performed on the SPEAR at LANL)

SLD profiles showed that water barrier ability of mixed silane is roughly that of both components weighted by their volume fraction. At room temperature, the volume fraction of water is 41% in bis-amino silane film, 7.8% in bis-sulfur silane and 12.6% in the mixed silane. Bridging group is the key factor that controls the morphology and water-barrier properties of silane films. After re-drying following room-temperature conditioning, the reflectivity curves of bis-amino, bis-sulfur as well as the mixed film all return to the as-prepared profile indicating no chemical reaction occurred at room temperature. With $80^\circ C$ water-vapor conditioning, however, the reflectivity of the redried film remains elevated relative to the as-prepared film due to formation of Si-O-Si- and Si-OD in bis-sulfur silane and the exchange of the amine proton with a deuteron in bis-amino silane. After $80^\circ C$ vapor conditioning, the thicknesses of the bis-sulfur film and mixed silane film decrease, which is consistent with the condensation of ethoxysilyl groups to Si-O-Si. Based on the enhanced shrinkage that occurs following water-vapor conditioning of the mixed film, condensation is accelerated in the mixed silane. Regarding to the precursor solution, bis-amino silane may act as a catalyst in the hydrolysis of bis-sulfur silane leading to more silanols groups in the solution, which in turn improves the wettability of the solution. Therefore, accelerating the hydrolysis of residual unhydrolysed group of hydrophobic silane is the key to improving wettability and anti-corrosion performance.

The substrate does not play the key role for the water barrier properties of silanes. The films deposited on Al substrate and silicon wafer have similar bulk properties and top surface morphology. We conclude that a 200-Å silane film is thick enough that the substrate does not affect the top surface or the bulk structure.

Higher curing temperature leads to denser film for bis-sulfur and mixed silane film, whereas the temperature effect on bis-amino silane film is negligible. This result confirms that bis-amino silane is highly hydrolyzed and condensed at a curing temperature of 80°C. Further increasing in cure temperature does not affect the bulk structure of the film. Based on contact angle, however, higher curing temperature does modify the surface structure, leading to the minimization of the influence of the bridging group.

Film thickness is an important variable that controls water-barrier performance: Bis-sulfur silane provides an adequate barrier to water penetration only for films cured at high temperature whose thickness exceeds 1200 Å. Figure 2 showed the vapor conditioning result of 5% bis-sulfur silane film cured at 180°C. The significant observation is that the reflectivity curve is almost the same as the as-prepared film. There is almost no absorption of water. Therefore, for bis-sulfur silane films, both larger thickness and higher cure temperature are critical for effective water-barrier properties. By contrast, bis-amino films show no performance improvement with increased thickness and curing temperature.

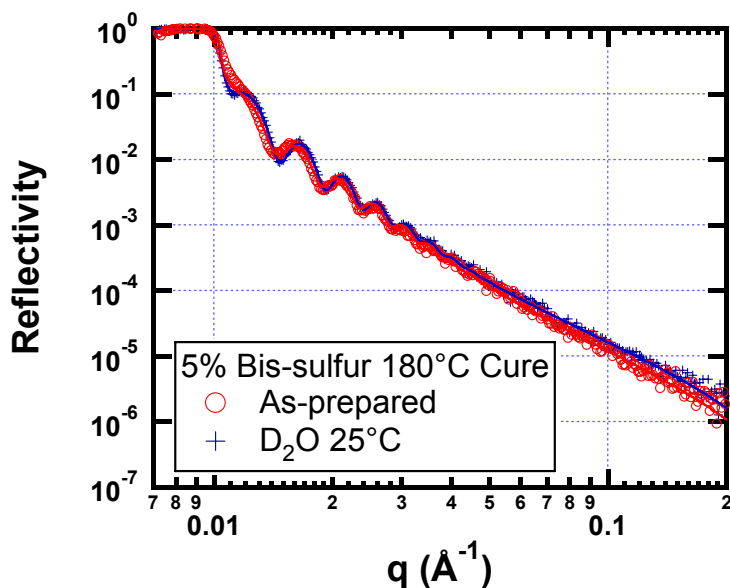


Figure 2: Neutron reflectivity data from 5% bis-sulfur silane film cured at 180°C as-prepared (○), after exposure to D₂O vapor at room temperature.

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References:

- (1) Van Ooij, W. J.; Child, T. *Chemtech* **1998**, 28, 26.
- (2) Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum Press: New York, 1991.
- (3) Van Ooij, W. J.; Zhu, D. *Corrosion* **2001**, 57, 413.
- (4) Zhu, D.; Van Ooij, W. J. *J. Adhesion Sci. Technol.* **2002**, 16, 1235.
- (5) Yim, H.; Kent, M. S.; Hall, J. S. *J. Phys. Chem. B* **2002**, 106, 2474.
- (6) Kent, M. S.; Smith, G. S.; Baker, S. M.; Nyitray, A.; Browning, J.; Moore, G.; Hua, D. W. *Journal of Materials Science* **1996**, 31, 927.