Hydrothermal Degradation of Bis-Silane Films

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1. INTRODUCTION

Functionalized silanes are widely used as protective coatings and interface coupling agents.[1] Certain bis-silanes, for example, are effective anti-corrosion agents. In virtually every application, the longevity of the film is a key performance parameter. In an attempt to quantify film robustness we use neutron reflectivity (NR) to study the hydrothermal response of bis-silane films.

The hydrothermal response of bis[3-(triethoxysilyl) propyl]tetrasulfide (bis-sulfur) and bis-trimethoxysilylpropyl]amine (bis-amino) as well as mixtures of these silanes is of particular interest. Mixed silane is reported to enhance greatly the corrosion resistance compared to the two individual silanes.[2, 3] Here we study the two neat silanes and a mixed silane at a sulfur/amino weight ratio of 3/1

2. DEGRADATION MECHANISM

Hydrolysis of siloxane (Si-O-Si) network bonds or Me-O-Si bonds is believed to be the primary degradation mechanism when organosilane films are exposed to the environment.[4] Assuming a first-order reaction in each species, the rate of hydrolysis increases exponentially with temperature. Elevated temperature also raises the solubility of oligomers generated from hydrolysis, which accelerates the desorption rate.[4] Therefore, when silane films are exposed to the environment, especially under long exposure at high humidity and/or elevated temperature, degradation of silane films can occur rapidly leading to film failure.[5]

3. FACTORS CONTROLLING FILM DEGRADATION

The nature of the bridging group, the film thickness and the curing temperature are believed to control the water barrier properties of silane films.[6] Since degradation is linked to hydrolysis, these factors should also play important roles in hydrothermal stability of bis-silane films.

I. Bridging group

Bridging group (amine or polysulfur in our case) is the key factor determining the intrinsic properties of silane films. For bis-amino silane hydrolysis is relatively fast because the secondary amine-bridging group is hydrophilic and the local concentration of water within the film is relatively high. Also, the amine group can act as a catalyst accelerating the hydrolysis of siloxane

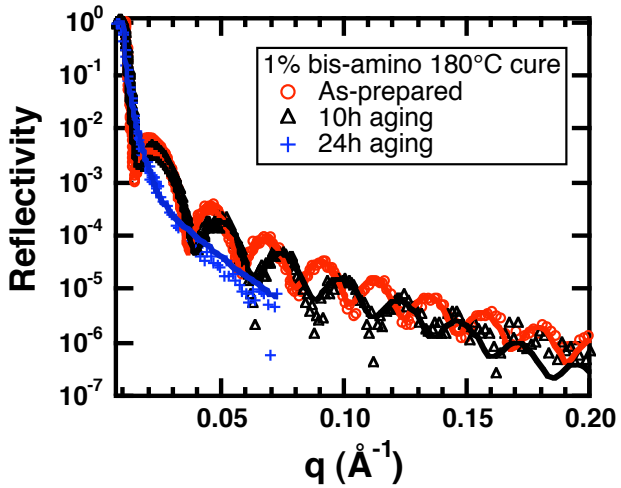

Fig. 1a: Neutron reflectivity data from 1% bis-amino silane films cured at 180°C as-prepared, after 10 and 24 hours exposure to 80°C liquid water. The curves through the data correspond to best fits using model SLD profiles in Fig. 1b.

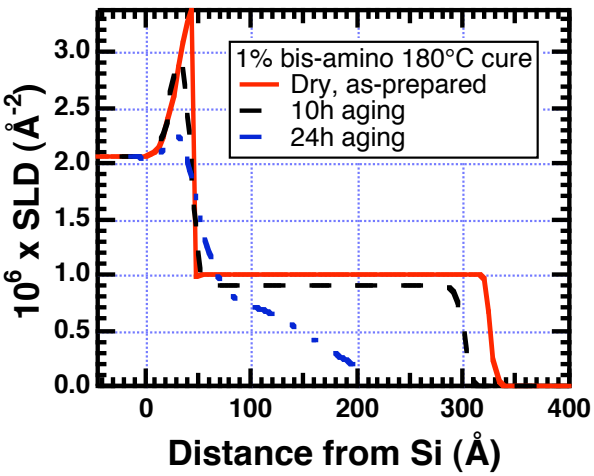

Fig. 1b: Best-fit scattering length density profiles corresponding to the curves through the data in Fig. 1a.

bonds. Bis-sulfur silane, on the other hand, has a hydrophobic bridging group. The lower concentration of water within the film results in a slower rate of hydrolysis.[2] The bridging group affects the top-surface morphology and the degree of condensation of film as well.[6]

II. Thickness of the film

Film thickness also plays an important role in water barrier properties. Generally, it takes more time to degrade a thicker film.[6] As we find below, however, the thickness dependence of degradation can be quite complicated. As we show below, bis-sulfur shows qualitatively different behavior in thick and thin film realizations.

III. Curing temperature

Film cure temperature and curing time can affect the crosslink density, as the curing time and temperature may be insufficient to achieve full cure. Elevated curing temperature or extended curing time leads to more complete cure and thus the maximum crosslink density.[6] Higher crosslink density, in turn, should lead to more stable films.

4. STRATEGY

A series of the silane films were made by varying silane type, film thicknesses and curing temperatures. Neutron reflection (NR) was performed on the SPEAR neutron reflectometer at Los Alamos National Laboratory. By fitting the measured reflectivity vs. angle-of-incidence data using the Parratt algorithm, the change of scattering length density (SLD) profile normal to the surface can be used to track the progress of hydrothermal degradation and thereby establish the key factors controlling film stability. Assuming that the SLD of the degraded film contains two components (silane and Si-OH) each weighted by its volume fraction in the redried film (equation 1) the extent of hydrolysis can be calculated.[6] In Equation (1) "silane" refers to the film SLD measured in the dry state and "Si-OH" refers to the partially hydrolyzed silane remaining in the water-

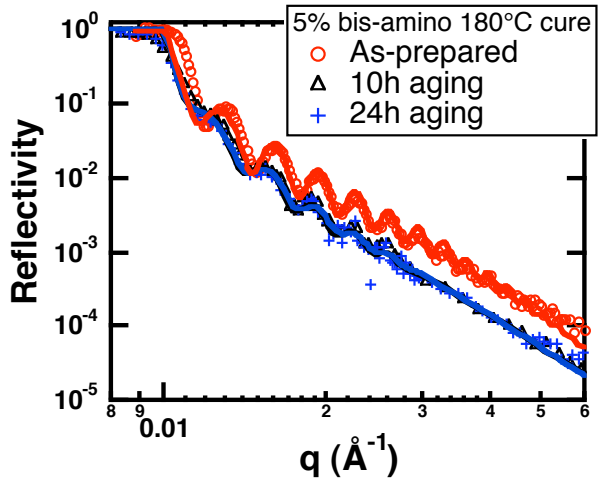

Fig. 2a: Neutron reflectivity data from 5% bis-amino silane films cured at 180 °C as-prepared and after 10 and 24 hours exposure to 80°C liquid water. The curves through the data correspond to best fits using model SLD profiles in Fig. 2b.

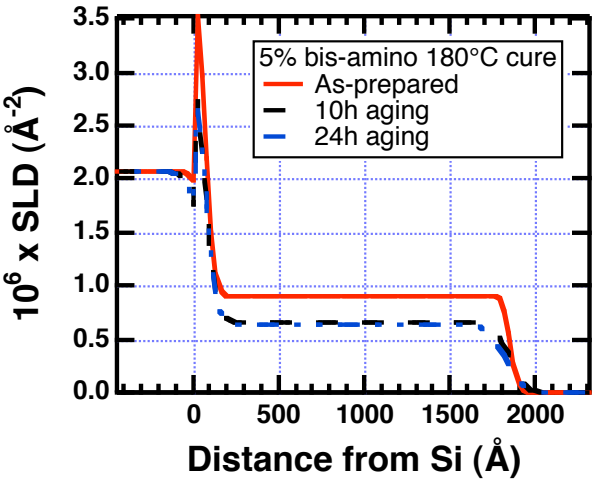

Fig. 2b: Best-fit scattering length density profiles corresponding to the curves through the data in Fig. 2a.

conditioned film.

$$SLD = \varphi_{Si-OH} SLD_{Si-OH} + \varphi_{silane} SLD_{silane} \quad (1)$$

5. EXPERIMENTAL PROCEDURES

The silicon wafers were cleaned by using "piranha" solution. The film was deposited using a Larrel single-wafer spin processor (WS-400A-6NPP-Lite, North Wales, PA, USA), and was cured in an oven at 80°C or 180°C for 1 hour. All the samples were measured as-prepared and also after 10 and 24 hours exposure to liquid H_2O at 80°C followed by redrying. The water-conditioned films were studied in the redried state.

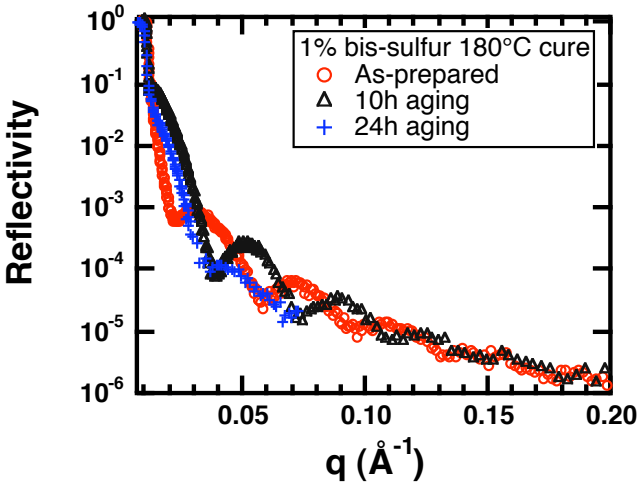

Fig. 3: Neutron reflectivity data from 1% bis-sulfur silane films cured at 180 °C as-prepared and after 10 and 24 hours exposure to 80 °C liquid water. The film thickness is about 200 Å.

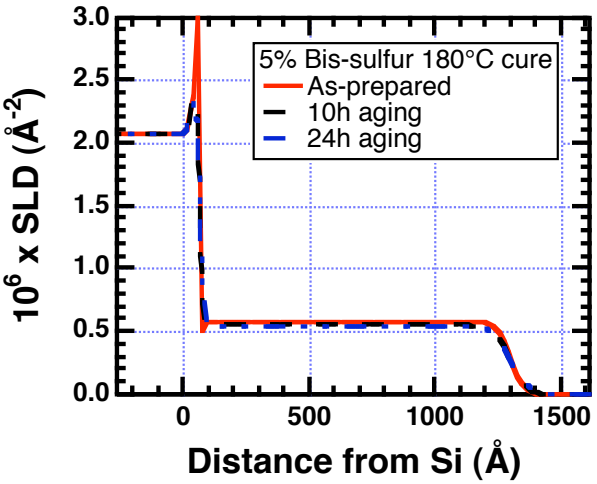

Fig. 4: SLD Profile for 5% bis-sulfur silane films cured at 180 °C as-prepared and after 10 and 24 hours exposure to 80 °C liquid water.

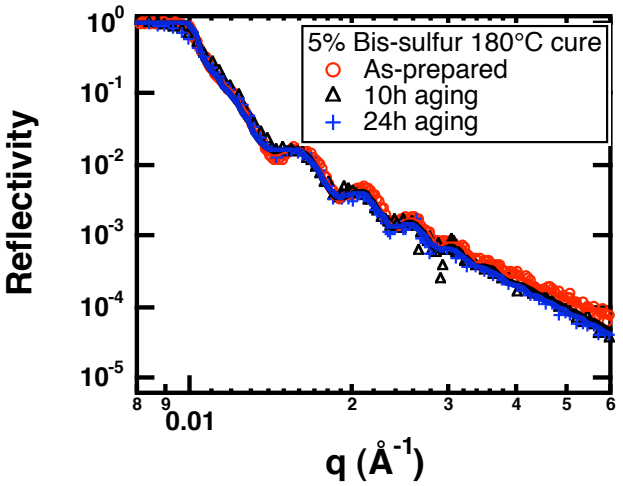

Fig. 5a: Neutron reflectivity data from 5% bis-sulfur silane films cured at 180 °C as-prepared and after 10 and 24 hours exposure to 80°C liquid water. The curves through the data correspond to best fits using model SLD profiles in Fig. 5b.

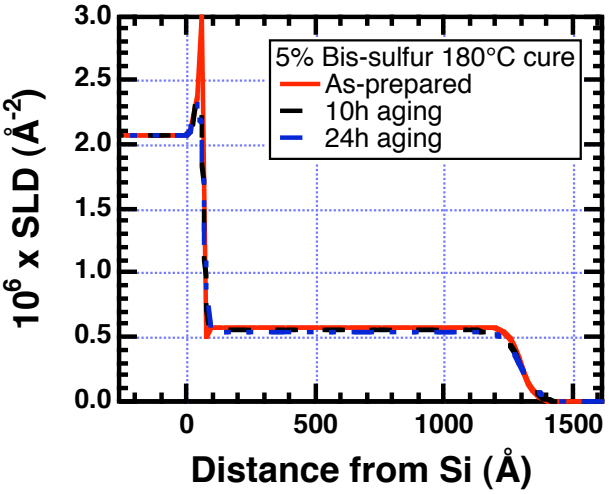

Fig. 5b: Best-fit scattering length density profiles corresponding to the curves through the data in Fig. 5a.

6. RESULTS AND CONCLUSIONS

I. Figs. 1 and 2 show the measured neutron reflectivity and the resulting SLD profiles for bis-amino films subject to liquid water (H_2O) conditioning at 80 °C for times up to 24 hours. These films were spun from 1% or 5% solution and cured at 180 °C. Bis-amino films show fast degradation no matter how thick the films are.

II. Figs. 3 and 4 compare the reflectivity curves for bis-sulfur films spun from 1% and 5% solutions and cured at 180 °C. These data show that thickness becomes the key factor when the thickness is below 200 Å. The thinner films, spun from 1% solutions, restructure radically during exposure leading to major shifts in the reflectivity curves (Fig 3). The thicker films, spun from 5%

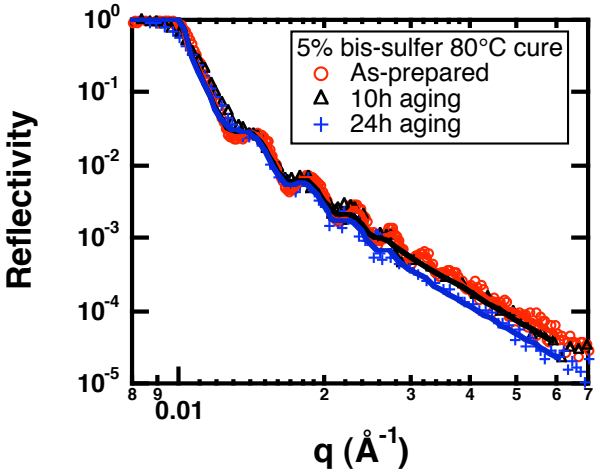

Fig. 6a: Neutron reflectivity data from 80°C curing 5% bis-sulfur silane films as-prepared, after 10 and 24 hours exposure to 80°C liquid water. The curves through the data correspond to best fits using model SLD profiles in Fig. 6b.

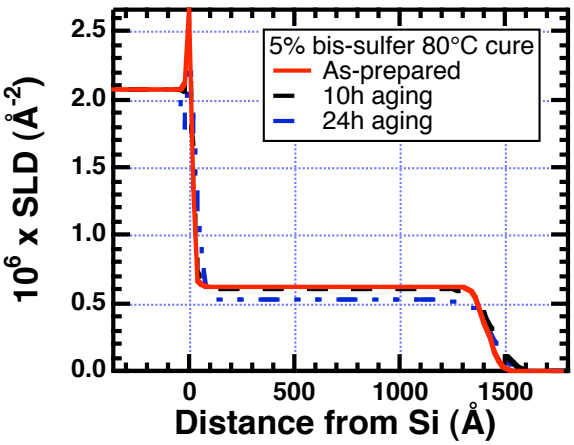

Fig. 6b: Best-fit scattering length density profiles corresponding to the curves through the data in Fig. 6a.

solutions, on the other hand, change very little for aging times up to 24 hours (Fig.4). SLD profiles for the 1% system in Fig. 3 are not shown because we are unable to find a reasonable layered model that fits the NR data.

III. Elevated curing temperature (180˚C vs. 80˚C) gives improved hydrothermal stability to bis-sulfur films. The NR data and SLD profiles in Fig. 5 for a 180 ˚C cure shows less change than in Fig. 6 for a 80˚C cure.

IV. For mixed amino-sulfur films degradation is enhanced compared to neat bis-sulfur films. Fig. 7 shows the reflectivity and SLD profile for mixed films containing bis-sulfur and bis-amino in a 3/1 ratio. Although mixed films show improved corrosion protection compared to either neat bis-amino or neat bis-sulfur, the presence of bis-amino leads to a susceptibility to hydrothermal degradation.

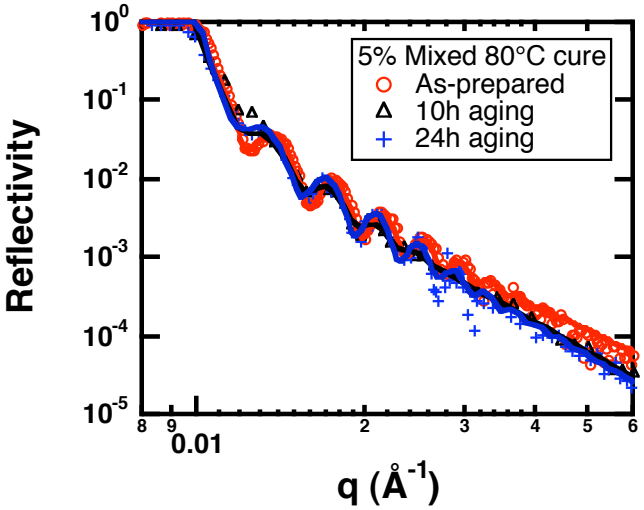

Fig. 7a: Neutron reflectivity data from 5% mixed silane films cured at 80 °C as-prepared and after 10 and 24 hours exposure to 80°C liquid water. The curves through the data correspond to best fits using model SLD profiles in Fig. 7b.

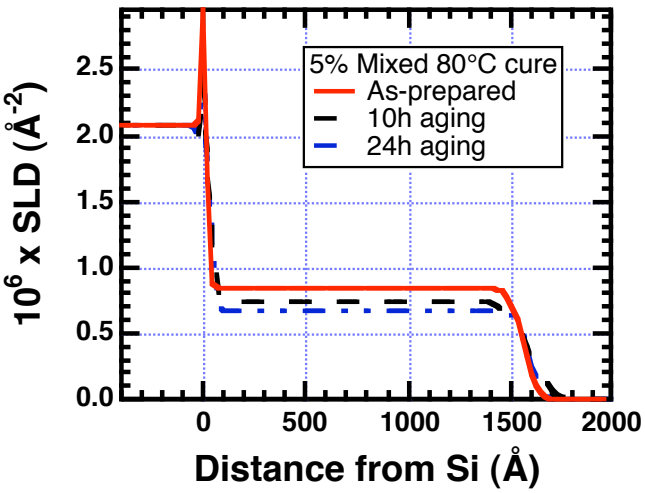

Fig. 7b: Best-fit scattering length density profiles corresponding to the curves through the data in Fig. 7a.

7. ACKNOWLEDGMENT

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