X-ray Reflectivity Study of Mixed Bis-Aminosilane-Vinyl Triacetoxysilane Coatings

Yimin Wang,[1] Jan Ilavsky[2] and Dale W. Schaefer[1,3]

[1]*Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012*
[2]*Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Building 438 E, Sector 33, Argonne, IL 60439*
[3]*Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, NM 87545*

1. INTRODUCTION

Silane surface treatment of metals has emerged in recent years as a promising alternative for chromate pretreatment in metal-finishing industries. Organosilanes are hybrid organic–inorganic chemicals with the general structure $(XO)_3Si(CH_2)_nY$. These hybrids are used as coupling agents for adhesion between organic and inorganic materials. Zhu and van Ooij *et al* [1,2] found that the bis-silanes with the general formula of $(RO)_3Si(CH_2)_3$-R'-$(CH_2)_3Si(OR)_3$ display better corrosion protection than the above monosilane coupling agents. In order to understand the water-barrier properties of the bis-silanes, Pan *et al* [3,4] investigated the water response of solvent-based bis-amino silane, bis-sulfur silane and their mixture by neutron reflectivity.

Despite of the good corrosion performance of above solvent-based silanes, water-based silanes are of more interest because of low VOC emission, ease of preparation, and paint compatibility. A good example of a water-based silane is the mixture of bis-[trimethoxysilpropyl]amine(bis-aminosilane)and vinyl triacetoxysilane (VTAS) reported by Zhu[5]. Bis-amiosilane is hydrophilic, it hydrolyzes rapidly and it gels in water. VTAS, on the other hand, is immiscible in water. Neither neat silane is effective in coating applications. The mixture, however, is miscible with water, does not gel and is effective in anti-corrosion applications. Nevertheless, up to now, the water-

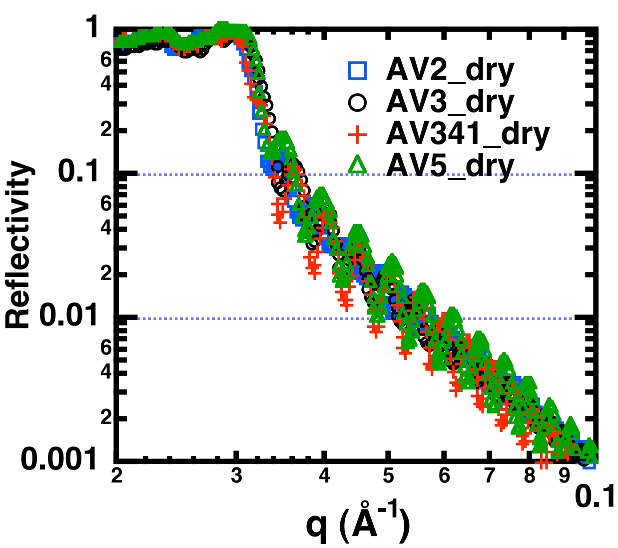


Fig.1(a) Reflectivity of dry films with different A/V ratios.

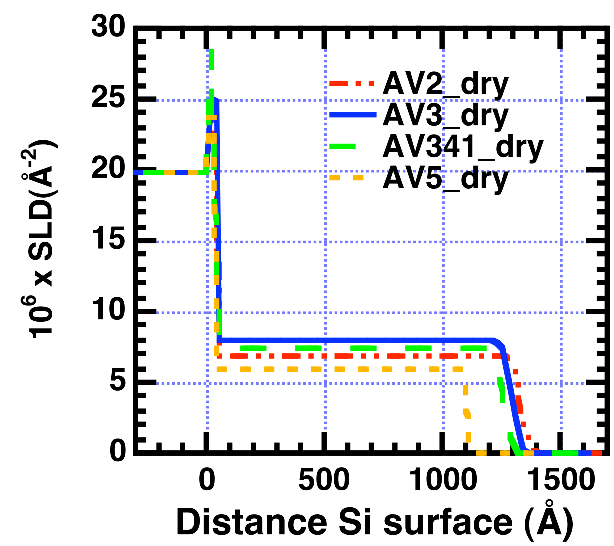


Fig.1(b) SLD from the best fit of reflectivity data in (a) for different A/V ratios.

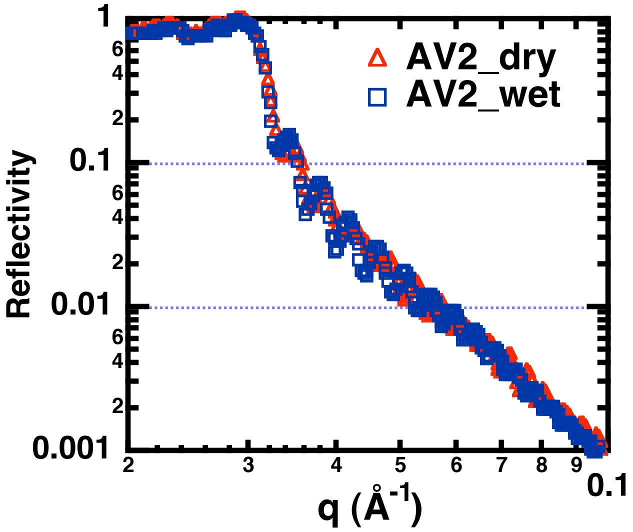


Fig.2(a) The reflectivity of AV2 of dry and wet state.

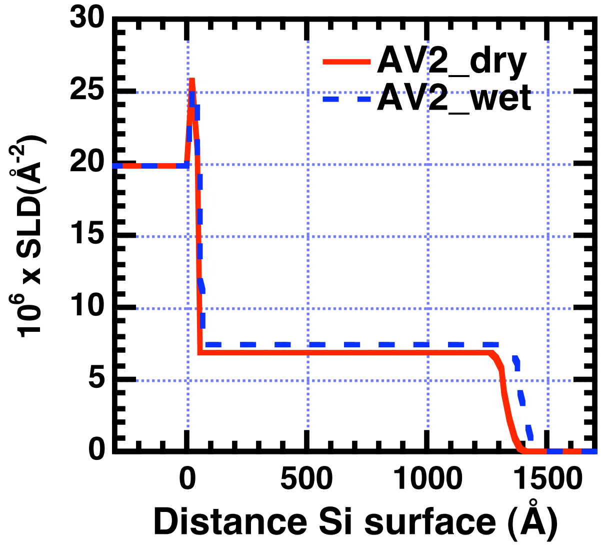


Fig.2(b) The SLD of AV2 of dry and wet state.

response of this system has not been documented. It has been found the ratio between aminosilane and VTAS is critical for anti-corrosion performance of the AV coatings. The difference in performance is presumably related to the water-barrier properties of the AV mixture [6]. In present study, we investigate the influence of A/V ratios in AV mixtures on water-barrier properties and morphology of AV coatings.

2. EXPERIMENTAL

The stoichiometric ratio of between bis-aminosilane and VTAS is A/V = 3, so 4 different ratios (A/V =2, 3, 3.41, 5), which are designated as AV2, AV3, AV341 and AV5 respectively, were chosen for study. The AV341 ratio is selected because it proved to have best performance in anti corrosion tests.

Pure bis-amino silane and VTAS are first mixed and reacted at the above molar ratios. Specifically 5-wt% water solutions of above mixtures were prepared and mixed for 24 hours. Then acetic acid was added to a final concentration of 1.2 wt%. All solutions were then hydrolyzed for 4 hours. The film was deposited using a Larrel single-wafer spin processor (WS-400A-6NPP-Lite, North Wales, PA, USA) on silicon wafers that were pre-cleaned by using "piranha" solution. All above coatings were cured at 180°C for 1 hour.

In order to understand the water barrier properties, the response of the AV films to water vapor was investigated by X-ray reflectivity. The scattering-length density (SLD) and thickness of the film were obtained from the fitting of reflectivity vs. normal component of the momentum transfer (q) using the Parratt formalism. The SLD is determined by the chemical composition and density of a material. The SLD profile in turn determines the reflectivity.

The reflectivity data were taken at the 1-BM beam line at the Advanced Photon Source at Argonne National Laboratory. Vapor conditioned samples were contained in an aluminum can with Kapton® windows. The data are plotted as specular reflectivity vs. q, which is related to the angle of incidence.

3. CALCULATED SCATTERING LENGTH DENSITIES OF PRECURSORS

The SLD of the precursor reactants are summarized in Table 1. Table 2 then shows the calculated SLDs of the various monomer mixtures. The SLD of condensed monomers will not differ greatly from that of the monomer mixtures.

Based on Tables 1 and 2 the X-ray SLD of the AV mixtures is insensitive to chemical composition. Thus the SLD change during film formation likely to be insensitive to different A/V ratios or the presence of water. Nevertheless, if water fills free volume in the films, the SLD is expected to increase.

Table 1. SLD of initial materials and by-products in AV system

Material	Density (g/cm^3)	$10^6 \times$ X-Ray SLD ($Å^{-2}$)
Bis-amino silane ($C_{12}H_{31}O_6Si_2N$)	1.04	9.660
Vinyl triacetoaxysilane ($H_{12}C_8O_6Si$)	1.167	10.340
Water (H_2O)	1.00	9.460
Methanol (CH_4O)	0.791	7.493

Table 2 Calculated SLD of AV monomer mixtures

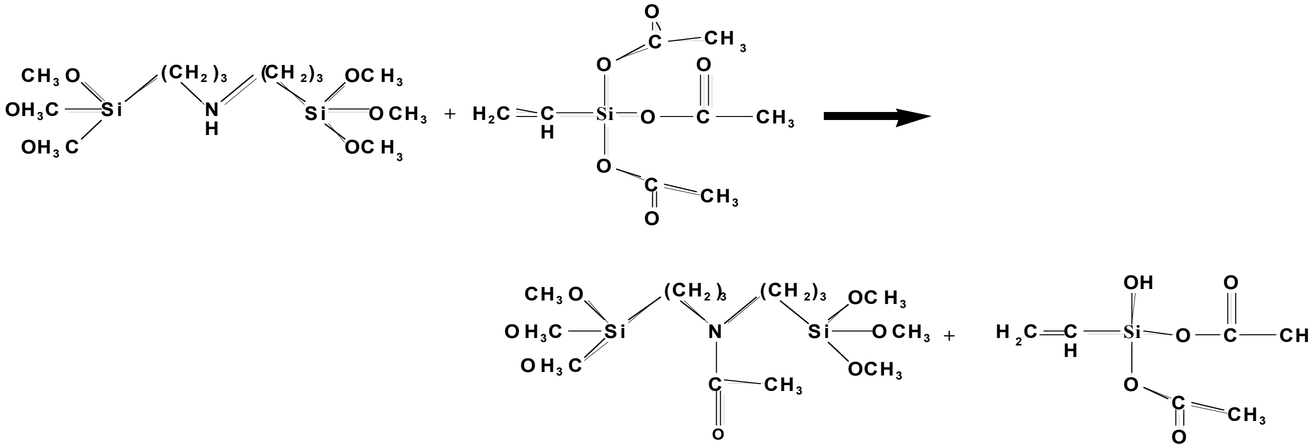
AV mixture	$10^6 \times$ X-Ray SLD ($Å^{-2}$)
AV2	9.82
AV3	9.77
AV341	9.76
AV5	9.73

4. CALCULATED SCATTERING LENGTH DENSITIES OF REACTION PRODUCTS

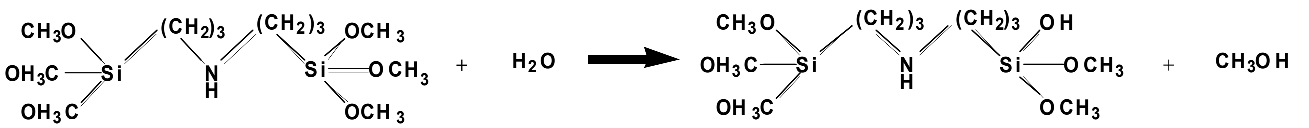
From NMR analysis, the primary reaction in AV system is the reaction between the acetoxy groups of VTAS with the hydrogen on the secondary amino group of bis-amino silane. This reaction is followed by a series of hydrolysis reactions of both bis-amino silane and the reacted bis-amino silane. Finally condensation reactions occur that involve both reacted VTAS and hydrolyzed bis-amino silane. These reactions are summarized below.

The calculated X-ray SLDs of the reaction products above range from 9.30 to 10.4 $\times 10^{-6}$ $Å^{-2}$, which are similar to the SLDs of the initial components from Table 1 and also the AV monomer mixtures from Table 2, which again indicates the SLD is insensitive to the reaction products of the AV system.

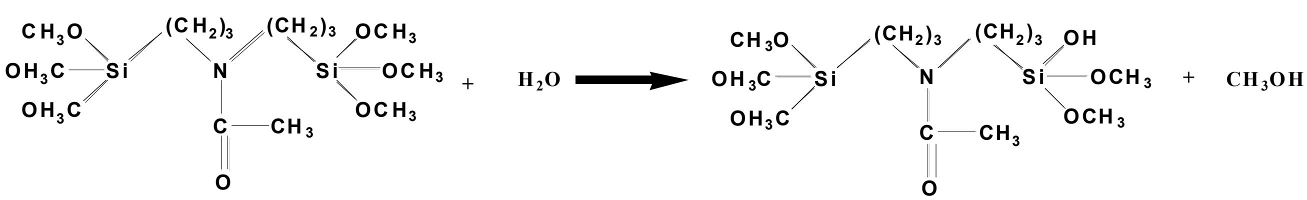
A) Reaction between Bis-amino silane and VTAS



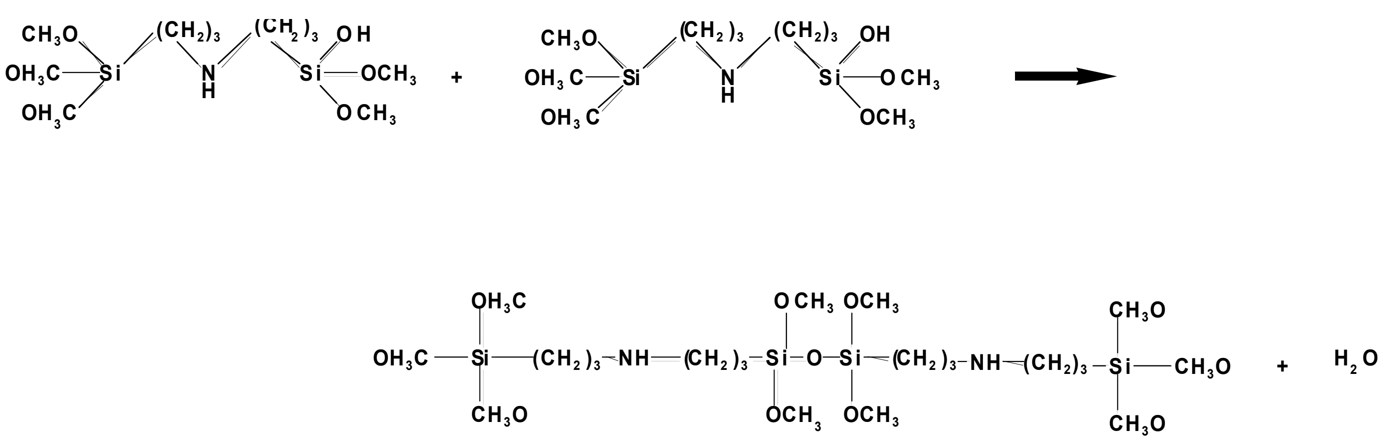
B) Hydrolysis of Bis-amino Silane



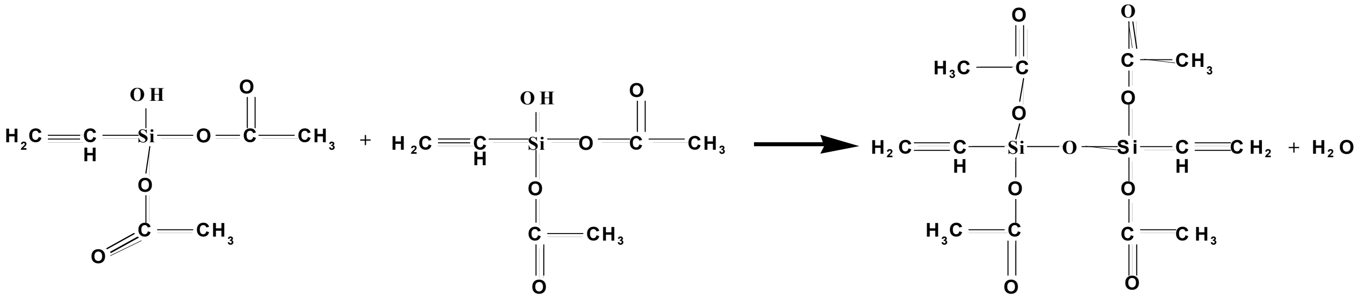
C) Hydrolysis of reacted Bis-amino Silane



D) Condensation of hydrolyzed Bis-amino Silane



5) Condensation of reacted VTAS



4. RESULTS AND DISCUSSION

1) Dry films as a function of A/V ratio

Figure 1 shows the measured reflectivities (a) and the calculated SLD profiles (b) for the AV series. The profiles show the silicon wafer substrate (SLD = 2.0 $\times10^{-5}$ Å^{-2}), whose top surface is designated as zero distance, with a thin native oxide with SLD = 2.5 $\times10^{-5}$ Å^{-2}. The region of interest is the film on top the oxide layer. All the films have a nominal thickness of 1200 Å.

From the best fit SLD profiles in Fig 1 (b) the experimentally determined SLDs range from 6 $\times10^{-6}$ – 8 $\times10^{-6}$ Å^{-2}, which is less than the calculated SLD of both the monomer mixtures and all possible reaction products calculated above (Tables 1 and 2). Since the monomer densities were used in the SLD calculations, these results imply the film densities are below that of the precursors. These films must have considerable free volume. As shown below some of these films show an increase in SLD when imbibed with water, consistent with they hypothesis of high free volume.

It is possible to draw other conclusions from the data in Fig. 1 (a). The AV341 reflectivity curve, for example, shows sharpest fringe pattern indicating the smoothest surface.

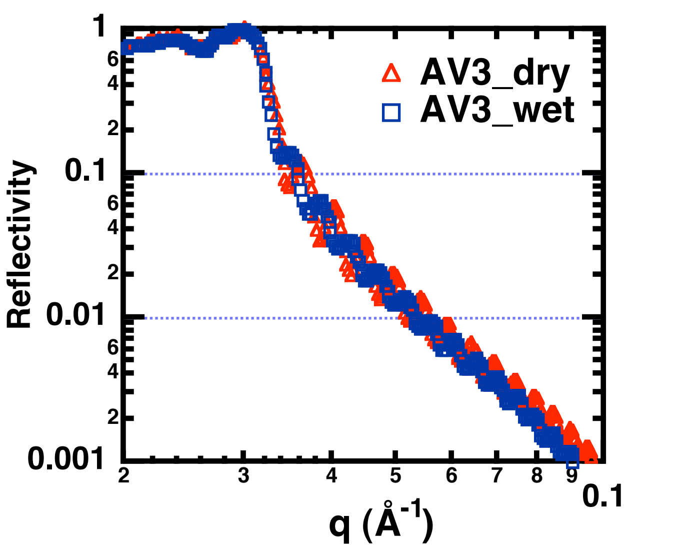


Fig.3(a) The reflectivity of AV3 of dry and wet state

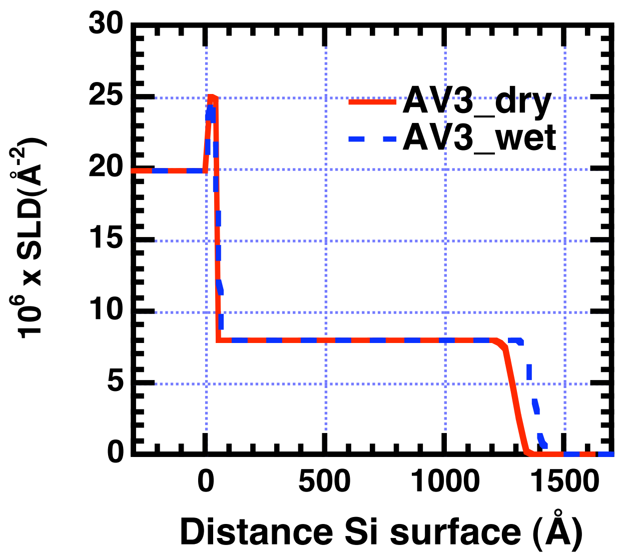


Fig.3(b) The SLD of AV3 of dry and wet state

The largest SLD is observed at A/V = 3 (Fig. 3), which is the stoichiometric ratio. Presumably the stoichiometric coating has the largest physical density and crosslink density leading to the highest SLD. The SLD of the coating decreases both above and below the stoichiometric ratio. AV5 coating has the lowest SLD, possibly because the SLD of the monomer mixture decreases with A/V ratios (Table 2) but also because excess aminosilane will decrease crosslink density to form a more open structure.

2) Water-vapor swollen films

Figs. 2 – 5 compare the reflectivity data and SLD profiles of the as-prepared "dry" state and the vapor-conditioned "wet" state of coatings spun at different A/V ratios. In all cases, the water-conditioned films increase in thickness compared to the dry state. The SLD of all the films is either unchanged or increases in the presence of water vapor. The increase is expected because the SLD of water is larger than that of the dry films. The increase is minimal for the stoichiometric film because it is the densest film.

The SLD of the water-swollen film is that of the components (silane and water) each weighted by volume fraction. Except near stoichiometry (AV3 and AV341) the SLD increases in the wet state indicating the water penetration into the coating. The two samples that are farthest from stoichiometry show an increase in SLD in the swollen state consistent with more water penetration compared to the two samples near stoichiometry.

5. CONCLUSIONS

From the SLD profiles of the coatings deposited at different A/V ratios, it was found that the film deposited at the stoichiometric mole ratio has the highest density due to higher crosslink density and most complete reaction between reactants. The density of the coating decreases in both below and above the stoichiometric ratio.

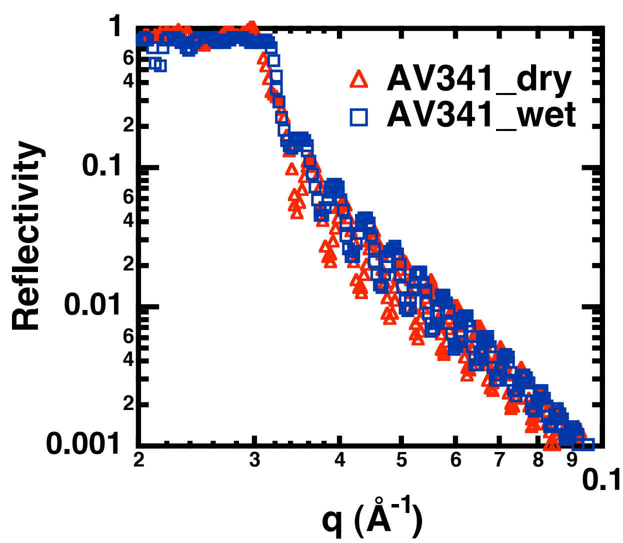


Fig.4(a) The reflectivity of AV341 of dry and wet state

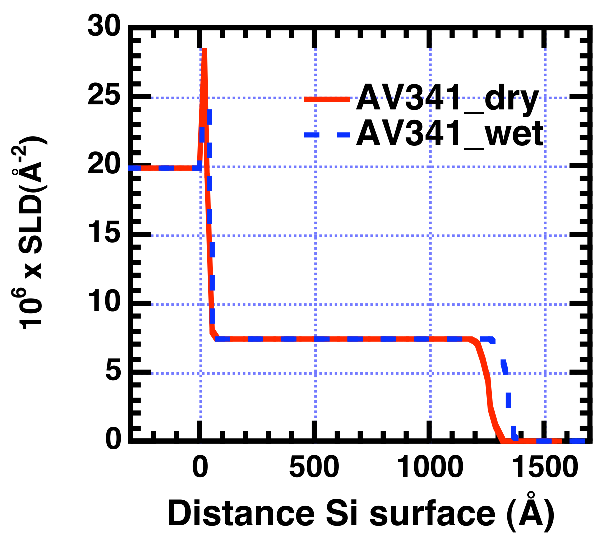


Fig.4(b) The SLD of AV341 of dry and wet state

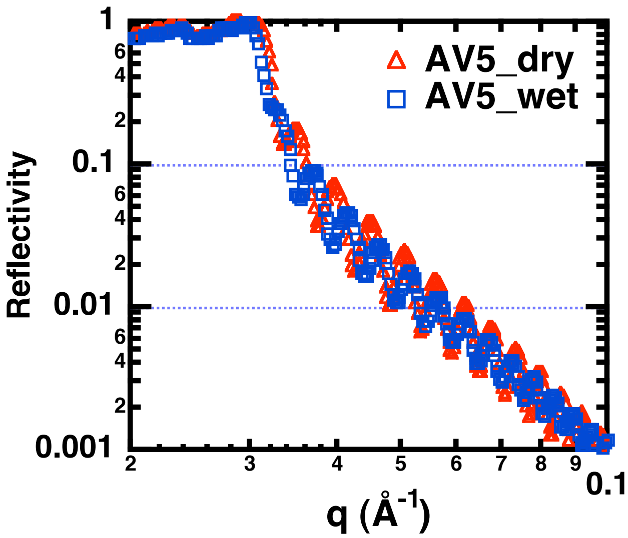


Fig.5(a) The reflectivity of AV5 of dry and wet state.

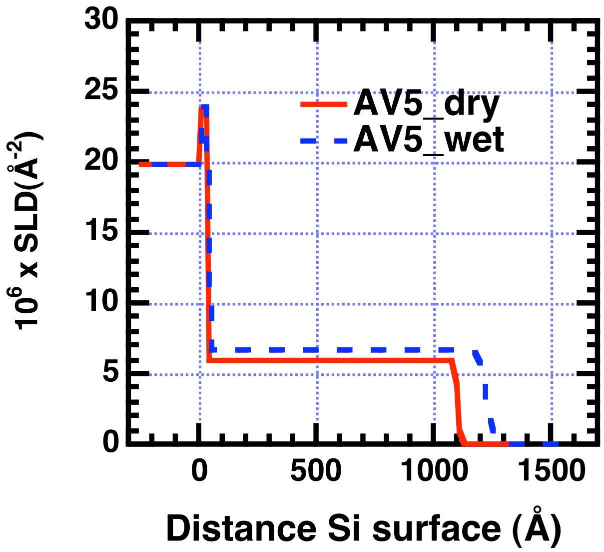


Fig.5(b) The SLD of AV5 of dry and wet state.

The water response also reflects the superior properties of the stoichiometric film. Off-stoichiometry films show more water penetration than films spun near the stoichiometric ratio of A/V = 3. Based on the shape of the XR data, the AV341 sample is the smoothest. This A/V ratio also corresponds to the system that performs best in corrosion tests.

6. ACKNOWLEDGMENT

Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. The facilities of the Manuel Lujan Jr. Neutron Scattering Center are gratefully appreciated. Work at the Lujan Center was supported in part by the Office of Basic Energy Science, U.S. Department of Energy.

7. REFERENCES

[1] Danqing Zhu, Wim J. van Ooij, *Electrochimica Acta* 2004, 49 1113-1125
[2] W. J.van Ooij, Danqing Zhu etc., *Surface Engineering* 2000 16 (5) 386-396
[3] Pan, P.; Yim, H.; Kent, M.; Majewski, J.; Schaefer, D. W. *J. Adhesion Sci. Technol.* 2003, *17*, 2175-2189.
[4] Pan, G.; Yim, H.; Kent, M.; Majewski, J.; Schaefer, D. W. *In Silane and Other Coupling Agents*; VSP: Orlando, FL, 2004; 3, 1-11.
[5] Danqing Zhu, Corrosion protection of metals by silane surface treatment, PhD dissertation, 2002, University of Cincinnati.
[6] Danqing Zhu, Wim J. van Ooij, Progress in organic coatings, 49 (2004)42-53