INTRODUCTION

Neutron reflectivity is among the few techniques able to probe a buried interface. Through the use of isotopic labeling, complicated interface structures may be determined with a resolution on the order of 5 Å. However, for highly complex thin film and interface structures, it is often necessary to perform complementary experiments to reduce the number of unknown variables, and thus enable an unambiguous interpretation of the neutron reflectivity. To this end, we have combined X-ray and neutron reflectivity to study changes in a metal/polymer interface (molybdenum / polyurethane, hereafter Mo/PU) upon exposure to a humid environment. In particular, we have tracked the adsorption of moisture to the interface and variations in the density of the interphase. This information was obtained as a function of the concentration of a silane coupling agent added to the bulk of the PU. Adhesion of the Mo/PU interface is important to programs in the DOE complex.

To our knowledge, this is the first use of neutron reflectivity to study moisture adsorption at a metal/polymer interface. A recent report by Wu, et al. described the use of neutron reflectivity to study the adsorption of moisture to the interface between a polyimide and the native oxide surface of a silicon wafer. After exposure to a humid environment, they reported an excess of moisture within the first 30 Å from the interface relative to the bulk of the polyimide. The equilibrium excess of moisture at the interface decreased from 17 to 12 % after a silane coupling agent, aminopropyliethoxysilane, was coated onto the surface of the wafer. In that work, the neutron beam passed through the silicon wafer to impinge onto the interface. This was possible due to the very low absorption and scattering of the pure silicon crystal. This geometry does not appear to be possible for a metal polymer interface, and in this work the beam was impinged onto the interface from the PU side. Diffuse scattering was kept at a minimum by using only a very thin (~ 1000 Å) layer of PU. Below we report the first results of this study. Other techniques for studying various aspects of metal polymer interfaces have been described elsewhere in recent reviews.2,3

EXPERIMENTAL

The samples were prepared by first evaporating a thin (~ 1000 Å) layer of molybdenum onto the surface of a polished silicon single crystal. The PU was then spin-
coated onto the surface of the molybdenum from a toluene solution. Three samples were prepared containing 0, 0.63, and 1.93 wt. % 3-glycidoxypropyltrimethoxysilane in the PU. With a solution concentration of 0.02 g/ml and a spinning speed of 700 rpm, thicknesses of ~1000 Å for the cured PU films were obtained. In the uncured state just after the deposition, the thin PU films were extremely fragile, and were destroyed if placed directly into an oven at the cure temperature. To remove the residual toluene and cure the samples at a sufficiently slow rate, the samples were first left covered at ambient temperature for 24 hours, then placed into an oven. The temperature of the oven was ramped from the initial temperature of 40 °C up to 120 °C at a rate of 20 °C/hour. The samples were then left at 120 °C for roughly 16 hours. Approximate thicknesses for the PU and Mo films were obtained using a Dektak profilometer.

The neutron reflectivity was performed on the SPEAR reflectometer at Los Alamos National Laboratory. The X-ray reflectivity was performed on a modified Kratky camera at the Center for Microengineered Ceramics at the University of New Mexico.

**Results and Discussion**

The neutron reflectivity for each sample was measured both in the dry state and after exposure to a saturated D$_2$O atmosphere. Immediately upon exposure to D$_2$O, the reflectivity was measured as a function of time to determine the rate of diffusion of D$_2$O through the ~1000 Å PU film. The reflectivity curves for the three samples varied with time for the first ~30 minutes. The final time-independent curves, along with the curves for the dry samples, are shown in Figure 1.

For each sample, we observe an increase in the reflectivity of the wet samples relative to the dry state. With decreasing concentration of silane, the increase in reflectivity for the wet samples is greater and, in addition, there is a shift in the maxima toward lower $q$ which increases in magnitude. The oscillations in the reflectivity curves are determined mainly by the thickness and roughness of the Mo layer.

To aid in the interpretation of the data in Figure 1, X-ray reflectivity was measured for the 0.0 wt % silane sample in the dry state and also for a sample composed of only the 1000 Å Mo layer on silicon. From these data, it was determined that a thin layer (~26 Å) of lower density (~2/3 that of the bulk Mo) is present at the surface of Mo. This is believed to be an oxide layer which formed after deposition of the Mo film. The roughness of the Mo surface and the roughness of the interface between Mo and silicon were also determined. With this independent information, the main features of the data in Figure 1 can be interpreted unambiguously. The shifts of the maxima relative to the dry state for the 0.0 and 0.63 wt % silane samples indicate that D$_2$O is adsorbing at the Mo/PU interface (and into the oxide layer of the Mo), while no such effect is observed for the sample with 1.93 wt % silane. In addition, a very rough region (~100 Å) of lower scattering length density is obtained between the oxide layer and the bulk PU. Since the presence of D$_2$O can only increase the scattering length density from that of the dry state, we believe this region of lower density is due to portions of the PU pulling away from the interface. It is likely that stresses build up inside the PU layer as it adsorbs D$_2$O, and these stresses lead to thinning of the weak interphase region. This effect is most significant for the sample with no silane.

In conclusion, we have demonstrated that neutron reflectivity, in combination with other techniques, can be used to probe the structure of a metal/polymer interface *in situ*. With decreasing silane concentration, we have observed an increase in the adsorption of D$_2$O to the Mo/PU interface and a thinning out of the interphase region upon exposure to a saturated D$_2$O atmosphere.

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References


Figure 1. Reflectivity for the three samples in the dry state (+) and after exposure to a saturated D₂O atmosphere (+). a). no silane, b) 0.63 wt % silane, and c). 1.93 wt % silane. The solid lines are preliminary least-squares fits to the data using profiles with the characteristics described in the text.

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