1 of 1

X-RAY ABSORPTION STUDIES
OF Ti/POLYMER AND Cr/POLYMER INTERFACES

R. L. OPILA*, K. KONSTADINIDIS*, A. O. IBIDUNNI**, A. J. DAVENPORT*** AND H. S. ISAACS***
*AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974
**AT&T Bell Laboratories, 1600 Osgood Street, North Andover, MA 01845
***Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973

ABSTRACT

The interface formed between metals, Ti and Cr, and polymers, epoxy and triazine, have been studied, non-destructively, using x-ray absorption spectroscopy. The metals were sputtered onto the polymer surfaces. Titanium reacts extensively, up to Ti thicknesses of 100 Å while Cr remains primarily metallic. In situ heating at 200°C increases the extent of reaction for both metals. Heating has a greater effect on metal/epoxy interfaces than metal/triazine. Titanium and Cr were ion implanted into the polymer in order to determine the interactions of isolated metal atoms with the polymer. Titanium and Cr appear to form oxides as the final reaction product, and the Ti is tetrahedrally coordinated.

INTRODUCTION

Interfaces between metals and polymers are important in the microelectronics, aerospace, and automotive industries. The chemical interactions between the metal and polymer determine the adhesion and, thus, the long term reliability of the interface. The chemistry at the interface develops after the initial formation of the interface, yet few non-destructive techniques exist to examine the chemistry at interfaces.

The objective of this work is to understand the interactions between metal atoms and polymers at interfaces, after the interface has been formed. We chose x-ray absorption spectroscopy because of the sensitivity of the absorption edge to the chemical state of the metal atom. In addition, the x-rays can penetrate through a considerable thickness of material to reach the interface. This technique requires that the spectra of standard model compounds be acquired for comparison.

We report results on interfaces formed between two metals, Ti and Cr, and two polymers, triazine and epoxy. The samples are prepared by sputter deposition of metal atoms on polymer surfaces. The effects of sputtering the polymer surface prior to deposition, and heating the sample after deposition were also examined.

EXPERIMENTAL

Polymer Preparation. The samples for ion implantation were prepared by curing films (1 to 2 mm thick) of the low molecular weight monomers. The samples used as substrates for metal deposition were prepared by spin coating on alumina substrates and curing. The epoxy samples were prepared by curing a mixture

Mat. Res. Soc. Symp. Proc. Vol. 304: 1993 Materials Research Society

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

of 100 g of EPON Resin 828 (Shell Chemical Company) with 36 g of Jeffamine T-403 at 60°C for 2.2 h under nitrogen. The triazine samples were prepared by curing 100 g of AroCy L-10 cyanate ester monomer (Rhone-Poulenc) with 0.06 g of dibutyl tin dilaurate at 150°C for 3 h under nitrogen. The cured polymer surfaces were used without further treatment.

Metal Deposition and Ion Implantation. Metal films of up to 300 Å were sputter deposited on the polymer surface followed by 1000 Å of Pd, without breaking vacuum. The Pd acted as a protective layer to prevent oxidation at the outer Ti surface. Three doses of Ti or Cr ions were implanted into the epoxy or triazine: 1×10^{16} , 3×10^{16} , and 1×10^{17} atoms/cm².

Instrumentation. The x-ray absorption experiments were performed at beamline X-19A at the National Synchrotron Light Source at Brookhaven National Laboratory. The energy scale was calibrated using thin Ti and Cr foils. The spectra of a series of standard compounds (high purity powders finely dispersed on polyimide tape) were taken in transmission. These included the oxides, nitrides, carbides, and hydrides of Ti and Cr. A typical spectrum spanned the range 200 eV above and below the K edge (4766 eV for Ti and 5989 eV for Cr). The background was subtracted using a least squares fit to the background at energies lower than the absorption edge. For *in situ* heating a mica-insulated thermofoil heater (Minco Products, Inc.), clamped between a heat sink and a backing plate, was used. The target temperature was reached in less than 5 min.

RESULTS AND DISCUSSION

Figures 1 and 2 show the x-ray absorption spectra for the Ti and Cr standards. In general, the energy of the absorption edge moves to higher energy as the formal valence of the metal increases. Also the intensities of the features in the near edge region decrease. The sharp pre-edge feature in the spectrum of CrO₃ is an exception to these tendencies, and will be discussed below. The spectra of 100 Å and 250 Å of Ti (beneath 1000 Å of Pd) on epoxy are shown in Fig. 3. The sharp edge feature, indicative of Ti metal, is only present for the 250 Å film, indicating that at least 100 Å of Ti have reacted with the epoxy. The 250 Å film is substantially different than pure metallic Ti, demonstrating that large amounts of Ti have reacted. In contrast to Ti, Cr does not show any evidence of extensive reaction for 300 Å films. Figure 4 compares a 300 Å Cr film on epoxy and a thin Cr foil.

Figure 1 X-ray absorption spectra of Ti standards.

Figure 2 X-ray absorption spectra of Cr standards.

Figure 3. X-ray absorption spectra of Ti sputter-deposited on epoxy: 250 Å (dotted line), and 100 Å (dotted-dashed line). Ti metal (solid line).

Figure 4. X-ray absorption spectra of Cr metal (dotted line), and 300 Å Cr film sputter deposited on triazine (solid line). Inset: expanded edge region.

The effect of heating is shown in Figs. 5 and 6 for Ti and Cr-deposited samples. The metallic edge feature present in the spectrum of 250 Å Ti on epoxy decreases as the sample is heated at 200°C for up to 2 h. A similar effect was observed for the 300 Å Cr film on epoxy as shown in Fig. 6 for different heating times. For the case of Cr/epoxy, much less reaction occurs. Heating had less effect on metal/triazine interfaces than on metal/epoxy interfaces.

Figure 5. X-ray absorption spectra of 250 Å Ti sputter deposited on epoxy: no heat (solid line), 30 min at 200°C (dashed line), and 2 h at 200°C (dotted line).

Figure 6. X-ray absorption spectra of 300 Å Cr on triazine: no heat (solid line), heat at 200°C for 2 h (dotted line), heat at 200°C for 2.5 h (dashed-dotted line). Inset: expanded edge region.

Previous work studying the development of Ti/polymer interfaces using x-ray photoelectron spectroscopy corroborates these results [1]. Ti has been shown to diffuse more into epoxy films than triazine or polyimide films upon heating, due to the lower T_g of epoxy. Similar work suggests that Cr forms more stable and thinner interfaces with polymers than many other metals. Ho and co-workers compared the adhesion of Cu, Al, Ni, and Cr evaporated onto pyromellitic dianhydride-oxydianiline (PMDA-ODA), a polyimide, and found that the degree of reaction varied substantially [2-7]. For example, Cu and Ni, which react weakly with polyimide, tend to diffuse approximately 100 Å into the polymer before agglomeration into metallic islands. Al, a much more reactive metal, reacts and intermixes with the polyimide. In this case, the intermixed region was found to extend approximately 50 Å into the polymer. Based on XPS data, Al reacted with the polymer in the intermixed region. Chromium had the strongest adhesion and intermixed very little with polyimide. Apparently the initially deposited Cr forms strong chemical bonds with the polymer, inhibiting subsequent interdiffusion.

The effect of ion bombardment (backspattering) before metal deposition has been previously investigated [9]. Backspattering of the polymer causes substantially less metallic Ti to remain in the film. Subsequent heating consumes even more metal. Backspattering has at least two effects: roughening increases the surface area, and surface damage creates unstable chemical species on the polymer surface. Both effects cause more metal to be consumed upon deposition than on a smooth, non-ion bombarded surface.

Ion implanted samples were prepared to determine how individual metal atoms might interact with the polymer substrates. The ion doses were chosen to minimize polymer damage and metal atom interactions, yet provide sufficient atom density for reasonable signal-to-noise. The overall shape of the spectra for all three doses (1×10^{16} , 3×10^{16} , and 1×10^{17} atoms/cm²) in both polymers were very similar. The spectrum of Ti ion-implanted into triazine at a dose of 3×10^{16} atoms/cm² is shown in Fig. 7. The spectrum is quite different from any of the standards. The sharp pre-edge feature occurs at higher energies (by 2 to 3 eV) than the metallic edge feature seen for Ti metal. This pre-edge feature has been seen in the K absorption edge of Cr in Na₂CrO₄ [10], V in CrVO₄ [11], TiO substitutionally doped into SiO glass [12], and Fe³⁺ in silicate glass [10]. In all four cases reported, the probed atom is in a tetrahedral symmetry. The presence of a pre-edge has been attributed to a dipole allowed transition from the 1s to an antibonding T_2 level of primarily 3d character. The transition is allowed due to mixing of the ligand 2p and metal 3d orbitals [10,13]. For these reasons CrO₃ has a pre-edge feature as shown in Fig. 2.

The chemistry of Ti implanted into the polymer is not obvious from its spectrum. However, previous XPS experiments, in which reactions at the surface of these polymers were studied, show that Ti forms various carbides, nitrides, and sub-oxides upon arriving at the polymer surface. In fact, Ti products and polymer degradation is nearly statistical, *i.e.*, Ti reacts indiscriminately with all functional groups studied. If H₂O or O₂ are present in the polymer, these nitride, carbide, and sub-oxide products are quickly oxidized to TiO₂. Since these thick polymer samples are difficult to outgas completely,

it is likely that any Ti-compounds formed immediately after implantation are fully oxidized. Thus, the implanted Ti has probably formed a tetrahedrally coordinated compound with oxygen as the nearest neighbor. Considerable support for this hypothesis could be obtained if extended x-ray absorption fine structure (EXAFS) measurements were carried out.

Figure 7. X-ray absorption spectrum of 3×10^{16} Ti atoms/cm² ion-implanted into triazine polymer.

Figure 8. X-ray absorption spectrum of 3×10^{16} Cr atoms/cm² ion-implanted into triazine (full line) and the Cr_2O_3 standard (dotted line).

All Cr-implanted samples had spectra similar to the Cr_2O_3 standard as shown in Fig. 8 for 3×10^{16} atoms/cm² in triazine. Heating the specimen for up to 2 h at 200°C did not change any of the spectral features. It is likely that Cr forms carbide-type products upon implantation, as has been seen on polyimide surfaces. However, as oxygen-containing species diffuse near these carbide products, oxidation ensues. Since the Cr species are readily oxidized, further heating to 200°C is expected to have little effect. As for the Ti case, EXAFS would permit this model to be verified.

CONCLUSIONS

X-ray absorption spectroscopy can be used to study the chemistry of metal/polymer interfaces non-destructively. At least 100 Å of Ti deposited on epoxy and triazine surfaces reacts with the polymer. Further reaction ensues upon heating. Chromium films deposited on polymer substrates appear to be much more less reactive, even upon heating. It is likely that the reaction products are oxides, as shown by ion implantation experiments. Sputtering the polymer surface prior to metal deposition appears to result in the consumption of more metal.

ACKNOWLEDGMENTS

The authors gratefully acknowledge A. E. White and K. T. Short for preparing the ion implants and M. A. Marcus for helpful discussions.

This work was performed in part under the auspices of the U. S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Science under Contract No. DE-AC02-76CH00016. Experiments were carried out NSLS Beamline X-19A.

REFERENCES

1. K. Konstadinidis, R. L. Opila, A. C. Miller, J. A. Taylor, J. Adhesion, In press.
2. P. S. Ho, P. O. Hahn, J. W. Bartha, G. W. Rubloff, F. K. Legoues, and B. D. Silverman, J. Vac. Sci. Technol. A3, 739 (1985).
3. R. Haight, R. C. White, B. D. Silverman, and P. S. Ho, J. Vac. Sci. Technol. A6, 2188 (1988).
4. J. W. Bartha, P. O. Hahn, F. Legoues, and P. S. Ho, J. Vac. Sci. Technol. A3, 1390 (1985).
5. P. O. Hahn, G. W. Rubloff, and P. S. Ho, J. Vac. Sci. Technol. A2, 756 (1984).
6. P. O. Hahn, G. W. Rubloff, J. W. Bartha, F. Legoues, R. Tromp, P. S. Ho, Mat. Res. Soc. Symp. Proc., 40, Materials Research Society, p. 251 (1985).
7. R. M. Tromp, F. Legoues, and P. S. Ho, J. Vac. Sci. Technol. A3, 782 (1985).
8. B. D. Silverman, P. N. Sanda, and P. S. Ho, J. Polym. Sci., 23, 2857 (1985).
9. R. L. Opila, R. L. Masaitis, A. O. Ibiidunni, A. J. Davenport, H. S. Isaacs, and J. A. Taylor, submitted to J. Electrochem. Soc.
10. A. Bianconi, E. Fritsch, G. Calas, and J. Petiau, Phys. Rev. B32, 4292 (1985).
11. J. Wong, F. W. Lytle, R. P. Messmer, and D. H. Maylotte, Phys. Rev., B30, 5596 (1984).
12. R. B. Greigor, F. W. Lytle, D. R. Sandstrom, J. Wong, and P. Schulz, J. Non-Cryst. Solids, 55, 27 (1983).
13. F. W. Kutzler, C. R. Natoli, D. K. Misemer, S. Doniach, and K. O. Hodgson, J. Chem. Phys., 73, 3274 (1980).

**DATE
FILMED**

12 / 29 / 93

END