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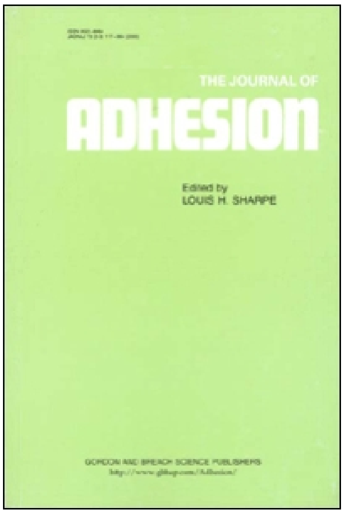

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X-ray Photoelectron Study of Chemical Interactions at Ti/Polymer Interfaces

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X-ray Photoelectron Study of Chemical Interactions at Ti/Polymer Interfaces*

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We have used X-ray photoelectron spectroscopy to study the chemical interactions at the interface formed during in situ deposition of Ti atoms on epoxy, triazine, and polystyrene surfaces. We find that for deposition on thick polymer films (1–2 mm) the primary component at the interface is TiO_2 with small amounts of titanium nitride and titanium carbide. The source of the oxygen in the TiO_2 is water or molecular oxygen dissolved in the polymer films. We also find that the Ti/triazine interface is more stable to heat treatment than the Ti/epoxy interface. This result is attributed to the higher glass transition temperature of triazine. For thin triazine films (~100Å) we observe that titanium carbide is the dominant product, with smaller amounts of oxide and nitride. Aging in air causes the carbide and nitride to convert to the more thermodynamically-stable oxide. Titanium carbide is also the primary initial species at the Ti/polystyrene interface.

KEY WORDS XPS; interfacial interactions; titanium/triazine interface; titanium/epoxy interface; titanium/polystyrene interface; interface stability; interfacial aging; chemistry at interfaces; microelectronics.

INTRODUCTION

Understanding and improving adhesion at metal/polymer interfaces is essential to advancement in the microelectronics industry. The stability and long term reliability of a metal-polymer interface is a key objective in the design and manufacture of devices. The fundamental understanding of the chemical and physical phenomena that occur at such interfaces, during and after their formation, is a prerequisite to controlling the adhesion problems associated with them.

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Distinction should be made between coating of metal surfaces with polymer films, where the metal surface is oxidized due to atmospheric exposure (and often contains adsorbed contaminants, notably hydrocarbons), and metallization of polymer surfaces, where metal atoms are deposited on the surface of the polymer under high vacuum. In both cases a variety of pre- and post-formation treatments (such as exposure to plasmas, ion bombardment, and thermal annealing) can drastically alter the performance of the interface. In this work, deposition of Ti atoms on polymer surfaces is considered.

The most studied interfaces are those of polyimide with different metals. Ho and co-workers[1-6] studied the interface of PMDA – ODA with Cu, Al, Ni, and Cr. They found that the morphology and strength of the interface depended upon the specific metal/polyimide chemistry. In particular, Cu and Ni, which react weakly with polyimide, tend to diffuse some distance into the polymer before agglomeration into metallic islands. Al, a much more reactive metal, reacts and intermixes with polyimide. In this case the intermixed region extends approximately 50Å. X-ray photoelectron spectroscopy was used to show that the Al reacted with the polymer in the intermixed region. Cr intermixes very little with the polyimide, apparently because the initially-deposited Cr forms strong chemical bonds with the polyimide and inhibits subsequent interdiffusion. Furman and coworkers[7] have studied the adhesion of Cr to rf-treated polyimide surfaces and observed significant adhesion degradation upon thermal exposure, attributed to the presence of absorbed water. Ohuchi and Freilich[8] reported results on Ti/PMDA – ODA systems, and observed two regimes. At low Ti coverage the metal atoms react with the carbonyl groups, while at higher coverages titanium carbide formation is observed.

In a recent study, Opila and co-workers[9] have used X-ray absorption spectroscopy to study the adsorption of Ti on epoxy and triazine. They concluded that Ti adsorption is greatly affected by oxygen in the polymer film, presumably oxygen that is either present in the polymer during metal deposition (as part of its chemical structure) or quickly diffuses into the polymer (as absorbed water for example). The purpose of the present study is to understand better the chemical and physical phenomena, such as chemical reactions and diffusion, respectively, that occur during in situ deposition of Ti atoms onto polymer surfaces. X-ray photoelectron spectroscopy is used as the analytical tool for this purpose, due to its surface sensitivity. The polymer surfaces (epoxy, triazine, and polystyrene) are examined at different Ti coverages. The effect of sample annealing after the deposition is also explored.

EXPERIMENTAL SECTION

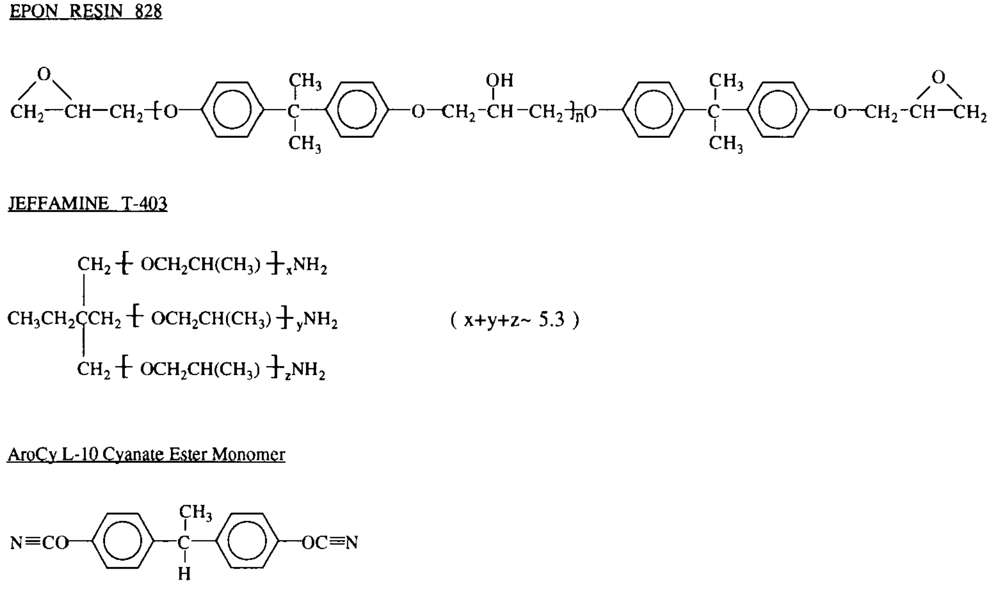
Instrumentation

Most of the experiments were performed in the Scienta 300 XPS system at Lehigh University. Al Kα X-rays were excited using 1.5–7 kW power incident on a rotating Al anode and monochromatized. The experiments were performed at a pass energy of 150 eV for the thick samples (which required charge neutralization) and 75 eV for the thin samples, and an energy step of 0.05 eV (under these conditions the FWHM of the $Ag3d_{5/2}$ peak is 0.53 eV). Base pressure in the analysis chamber was typically

1×10^{-9} Torr during the analysis. A Physical Electronics 5600 XPS system equipped with a monochromator was also used to examine the air-aged samples. The monochromatic Al Kα X-rays were used at a power of 400 W. The experiments were performed at a pass energy of 29.35 eV, and an energy step of 0.125 eV (under these conditions the FWHM of the $Ag3d_{5/2}$ peak is 0.72 eV). Base pressure during data acquisition varied from 1×10^{-9} Torr to 2×10^{-10} Torr for thick and thin polymer films, respectively. Some discoloration was observed in the epoxy samples but no detectable change in the spectra was seen in the time scale of the experiments (most acquisition times were less than 60 min).

Polymer Substrate Preparation

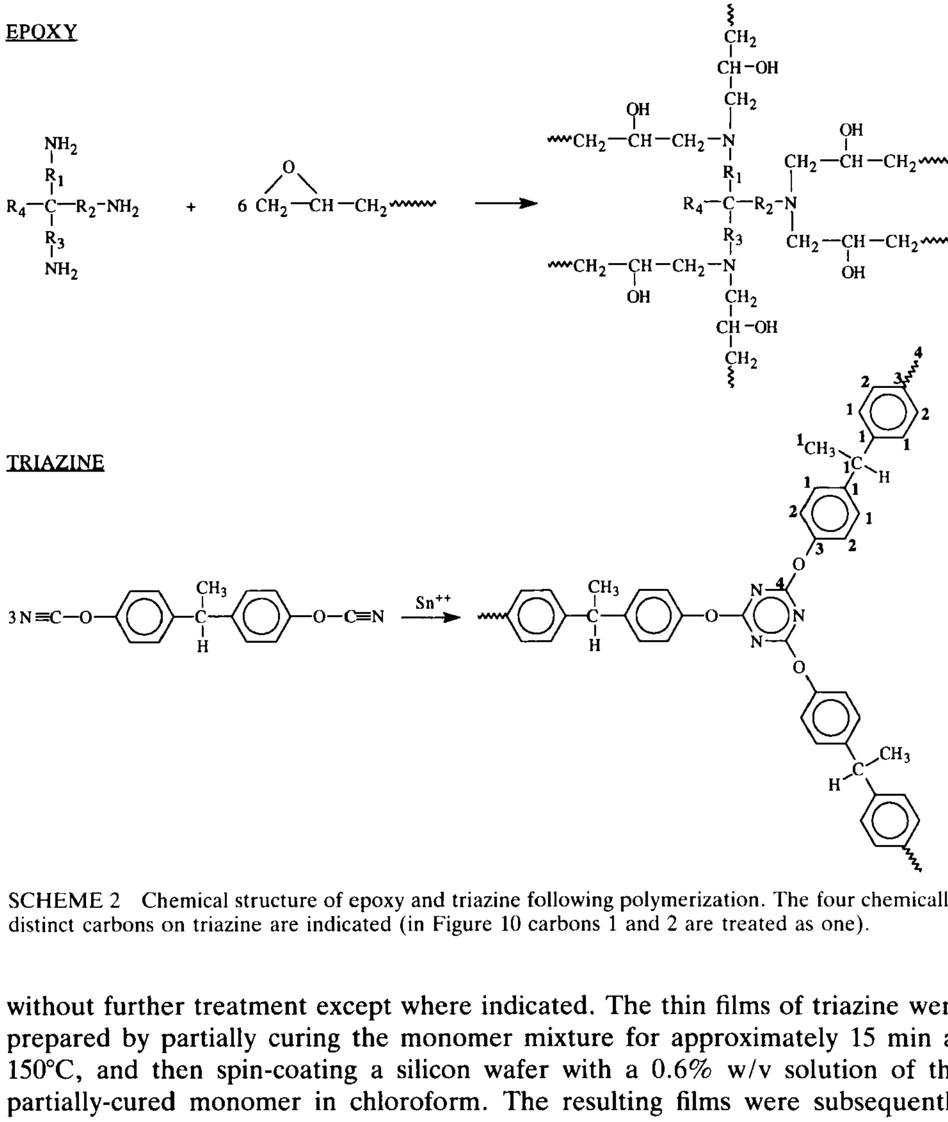
The polymer substrates were prepared as either macroscopic specimens 1–2 mm thick or 100Å films on silicon wafers. The thick specimens were prepared by curing films of the low molecular weight monomers (approximately 1–2 mm) in aluminum dishes. The epoxy was prepared by curing a mixture of 100 g of EPON Resin 828 (Shell Chemical Company) with 36 g of Jeffamine T-403 at 60°C for 2.2 hr under nitrogen. The triazine polymer was 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 hr under nitrogen. The structures of the chemicals are shown in Scheme 1 and the polymerization reactions in Scheme 2. The cured polymer surfaces were used



Dibutyl Tin Dilaurate

$(CH_3(CH_2)_{10}COO)_2Sn\ ((CH_2)_3CH_3)_2$

SCHEME 1 Chemical structure of EPON Resin 828, T-403 Jeffamine, AroCy L-10 Cyanate Ester Monomer and Dibutyl Tin Dilaurate.



SCHEME 2 Chemical structure of epoxy and triazine following polymerization. The four chemically-distinct carbons on triazine are indicated (in Figure 10 carbons 1 and 2 are treated as one).

without further treatment except where indicated. The thin films of triazine were prepared by partially curing the monomer mixture for approximately 15 min at 150°C, and then spin-coating a silicon wafer with a 0.6% w/v solution of the partially-cured monomer in chloroform. The resulting films were subsequently cured at 150°C for 3 hr under nitrogen. The polystyrene samples were prepared by spin-casting a dilute solution of the polymer onto a silicon wafer to a dry thickness of 200Å.

Ti Deposition

Ti metal depositions were performed in a high vacuum preparation chamber isolated from the analysis chamber by a gate valve. Ti (99.9% purity from Alfa Metals) was evaporated from a carbon crucible that was heated resistively to 1450°C. The top of the crucible was approximately 15 cm below the sample surface during deposition. Base pressure in the preparation chamber was approximately 3×10^{-9} Torr with the crucible heated but the shutter closed. The pressure increased to approximately

5×10^{-8} Torr during deposition due to radiant heating of the polymer and outgassing (there was no increase in pressure during deposition of Ti on clean copper and gold surfaces and on thin polymer films). The actual temperature of the polymer during deposition is not known.

Rate Calibration

The rate of deposition was monitored with a quartz crystal oscillator and found to be 1.7×10^{13} atoms/cm^2-sec. The quartz crystal monitor was placed approximately 5 cm above the sample, so it may slightly underestimate the deposition rate. One sample, epoxy with a Ti deposition of 4 minutes, was examined with Rutherford Backscattering Spectroscopy and had a Ti coverage of 4.9×10^{15} atoms/cm^2 corresponding to a deposition of 2×10^{13} atoms/cm^2-sec. Thus, a Ti deposition of 1 min at these conditions yields a coverage of 1.2×10^{15} atoms/cm^2, which, assuming uniform layer and bulk density, translates to a rate of 2Å/min.

RESULTS AND DISCUSSION

Thick Epoxy Films

The C1s and O1s core level XPS spectra of the epoxy surface prior to titanium deposition are shown on Figure 1a. Both spectra suggest the presence of two chemically-distinct oxygen functionalities in the polymer. The high-binding-energy peak in the O1s spectrum and the intermediate peak in the C1s spectrum correspond to the aliphatic carbon-oxygen bonds of the polymer. The other two peaks correspond to a carbonyl functionality that originates from an unknown bulk or surface impurity. Figures 1b–f show the C1s, O1s, and Ti2p core level XPS spectra of epoxy for different Ti film thicknesses indicated in the caption. The C1s spectra suggest that the C—O and C=O functionalities are depleted during Ti deposition while the aromatic strcture remains largely unaffected (the $\pi - \pi^*$ peak in the C1s spectrum is still present after a 20Å deposition). A relatively small peak at low binding energy that corresponds to titanium carbide is also observed at the highest coverage. The Ti2p core level spectra suggest that, up to a thickness of 6Å, the titanium is primarily in the form of TiO_2 (Figure 1d–e).[10] After a 12Å Ti deposition (Figure 1f), the low binding energy peak corresponding to Ti metal and intermediate peaks corresponding to suboxides, nitrides, and carbides are also observed. Accordingly, in the O1s spectrum (Figure 1b–c) an inorganic component peak appears at low binding energy and grows as more titanium is deposited on the polymer surface. In Figure 2 the integrated areas of the O1s, N1s, and Ti2p peaks normalized with the C1s area are plotted as a function of Ti film thickness. We observe that the Ti2p signal grows non-linearly with time, suggesting that Ti atoms diffuse into the polymer during deposition. The diffusion is accelerated by radiant heating of the polymer during deposition, and the fact that the glass transition temperature of epoxy is relatively low (80°C). The N1s signal is barely detectable after 6 min (12Å Ti) suggesting that nitrogen is desorbed during deposition. The O1s signal, on the other hand, grows at a similar rate to the Ti2p signal. This signifies the importance of

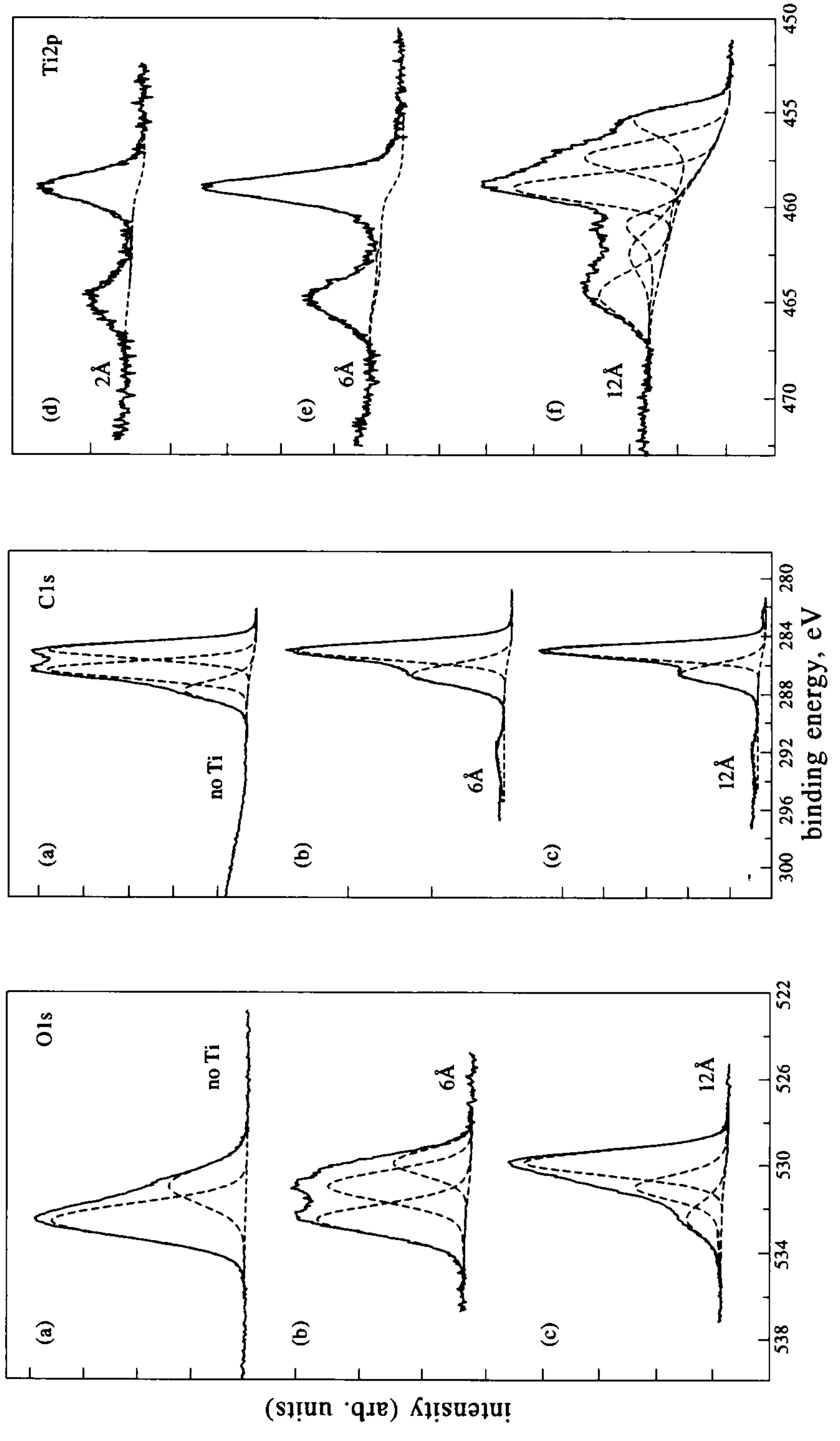


FIGURE 1 O1s, C1s, and Ti2p core level XPS spectra of titanium deposited on thick epoxy specimens. The Ti film thicknesses are indicated on the spectra. Photoelectron takeoff angle: 90°.

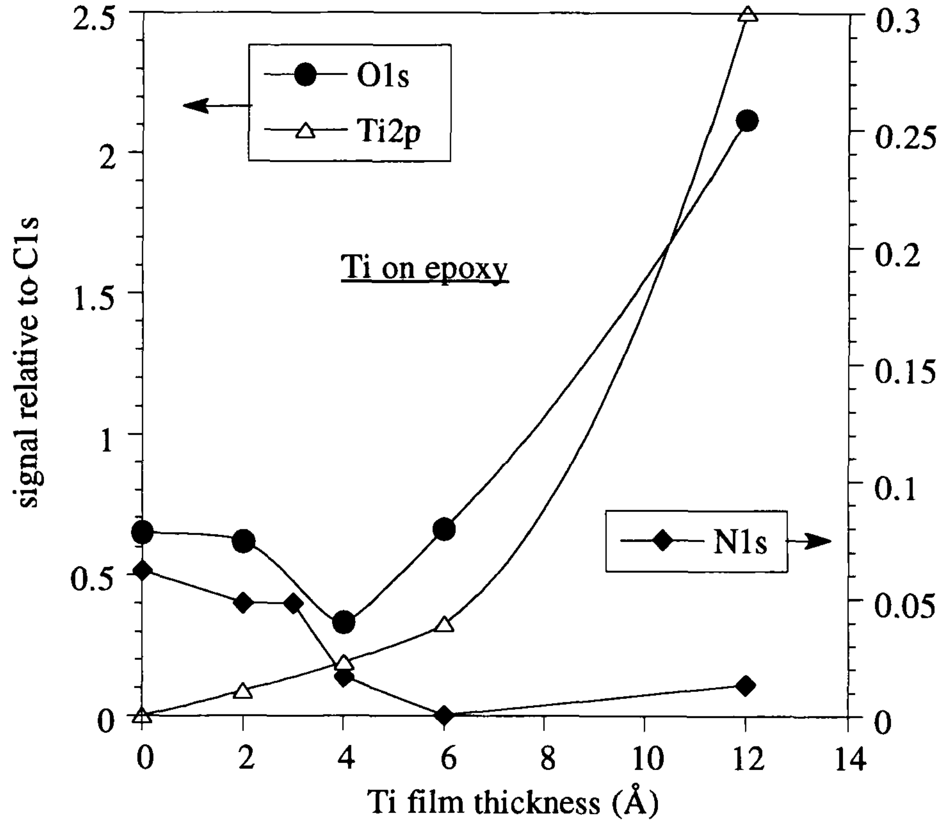


FIGURE 2 O1s, N1s, and Ti2p signal as a function of Ti thickness on thick epoxy specimens. The signals were normalized to the same C1s signal. Photoelectron takeoff angle: 90°.

oxygen in the formation of the interfacial products and suggests that oxygen from sources other than the polymer itself, such as dissolved water or oxygen from the background, contributes to the formation of the oxide. To check the latter, we deposited Ti on clean copper and gold surfaces under the same conditions and we saw only metallic titanium in the XPS spectrum (a small amount of oxygen was seen in the survey spectra for long deposition times but no detectable TiO_2 was observed). Therefore, the main source of oxygen is the polymer itself.

In order to explore further the effect of heating on the physical characteristics of the interface, we deposited 12Å of Ti on an epoxy surface and then heated the sample for 1 hr at 200°C in vacuum. The results are shown in Figure 3. The Ti2p signal decreased significantly after heating while the small metallic component at low binding energy disappeared. In the O1s spectrum the inorganic component peak (TiO_2) at low binding energy decreased relative to that of the polymer (C—O), which became dominant again. These observations are in agreement with the earlier assertion that, when the polymer is radiantly heated during deposition, Ti atoms diffuse into the polymer, resulting in a non-linear curve for Ti2p signal *vs.* deposition time.

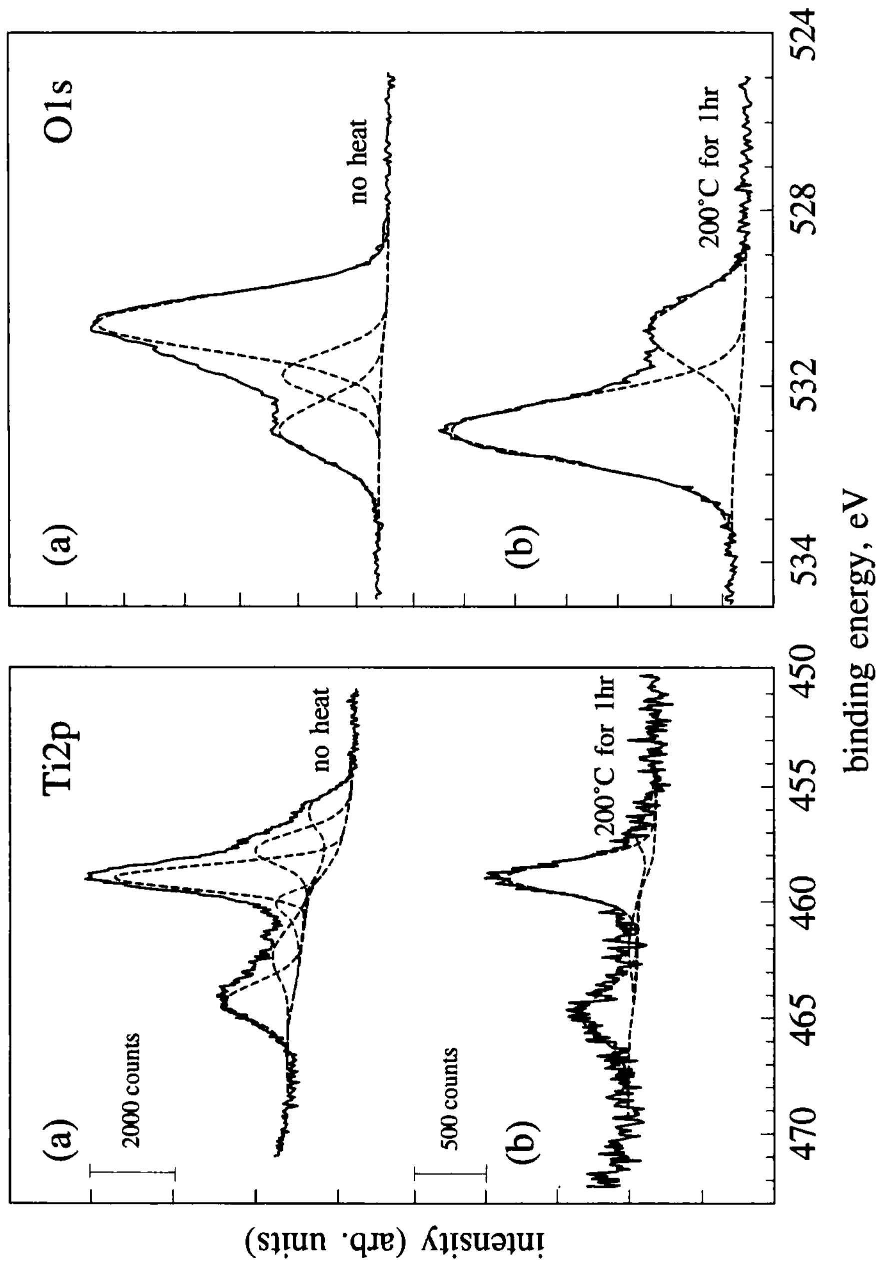


FIGURE 3 Effect of heating at 200°C for 1 hr on the Ti2p and O1s core level spectra of an epoxy surface with 12Å Ti. Photoelectron takeoff angle: 90°.

Thick Triazine Films

The results from Ti deposition on triazine are similar to that of epoxy in some ways. As Figure 4 shows, initially TiO_2 is the dominant species at the interface with Ti metal becoming more important with time. The N1s spectra indicate the presence of titanium nitride at the interface (not seen for epoxy), and the O1s spectra show the inorganic component peak coming from TiO_2. As Figure 5 shows, the O1s signal reaches a plateau suggesting that the contribution from absorbed water is smaller than with the epoxy. The N1s signal remains relatively unchanged. Another difference with epoxy is that upon heating at 200°C for 1 hr, no significant change occurs in the spectra. This result is expected, since the glass transition temperature of triazine is ~180°C (compared with ~80°C for epoxy), and it is thus thermally more stable.

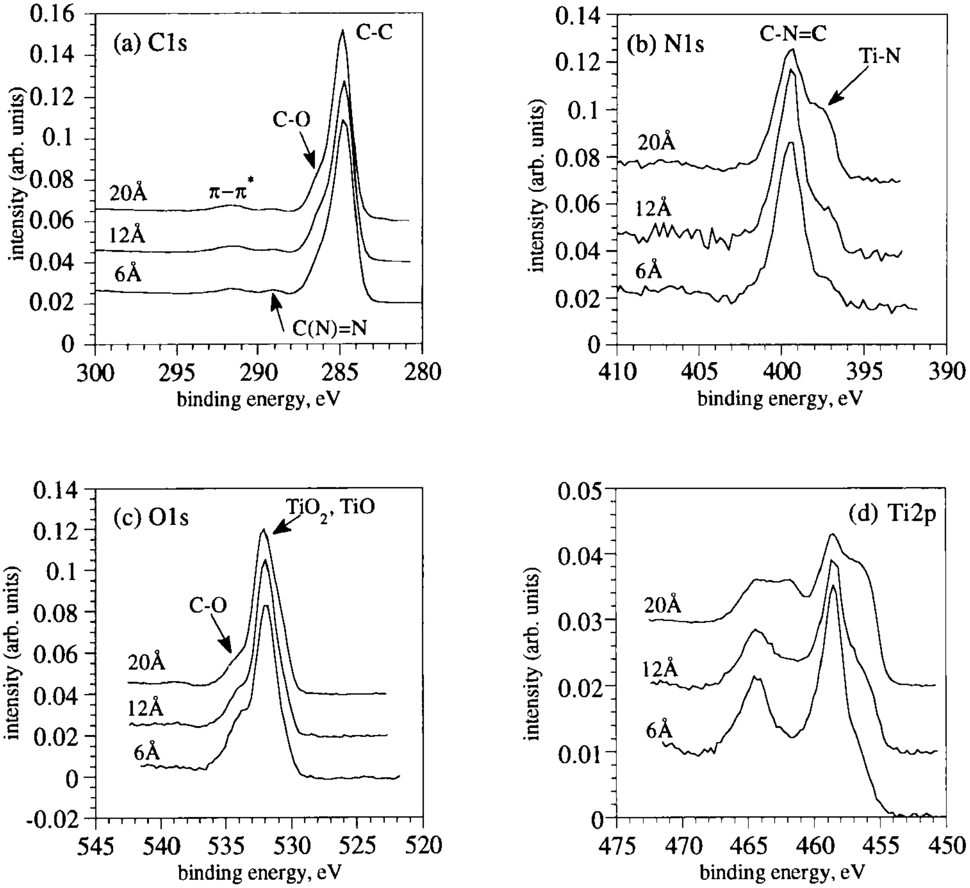


FIGURE 4 Evolution of the (a) C1s, (b) N1s, (c) O1s, and (d) Ti2p core level spectra for Ti deposition on thick triazine specimens. Each spectrum is normalized to an integrated intensity equal to one. Photoelectron takeoff angle: 90°.

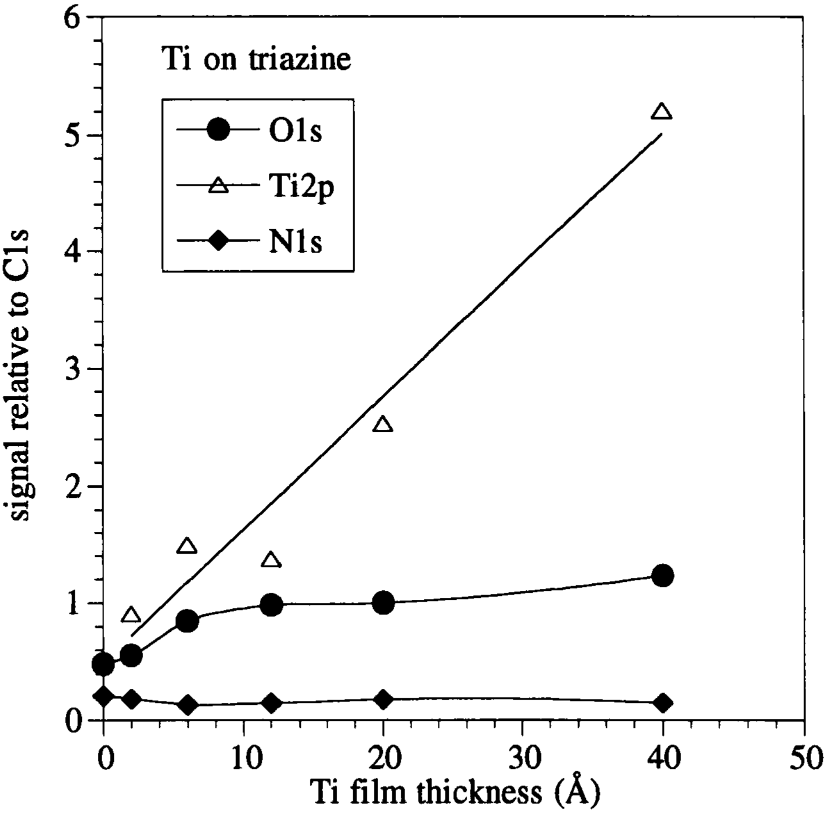


FIGURE 5 Ols, Nls, and Ti2p signal as a function of Ti deposition on thick triazine specimens. The signals were normalized to the same Cls signal. Photoelectron takeoff angle: 90°.

Thin Triazine Films

The main observation made in the previous sections is that, when Ti atoms are deposited on epoxy and triazine surfaces, TiO_2 is the dominant species at the interface due to water absorbed in the thick polymer specimens (to a much lesser extent in triazine). In order to increase the polymer surface-to-volume ratio, we prepared very thin triazine films of the order of 100Å by spin-coating a silicon wafer with partially-cured polymer and then curing the film to completion. Thin films have the additional advantage of not requiring charge neutralization during spectral acquisition.

The results from the thin film experiments are shown in Figures 6–9. Figure 6 shows the Cls core level spectra of triazine with 0, 2, 4, 8, 16, and 32Å of Ti for 90° and 10° photoelectron takeoff angle. The data are normalized so that the integral of the Cls curve is equal to one. The low binding energy peak that grows with time corresponds to titanium carbide and was only seen in very small amounts in the thick polymer films. The carbide peak is even more dominant at the surface-sensitive 10° takeoff angle where both the $\pi - \pi^*$ transition peak and the triazine ring peak

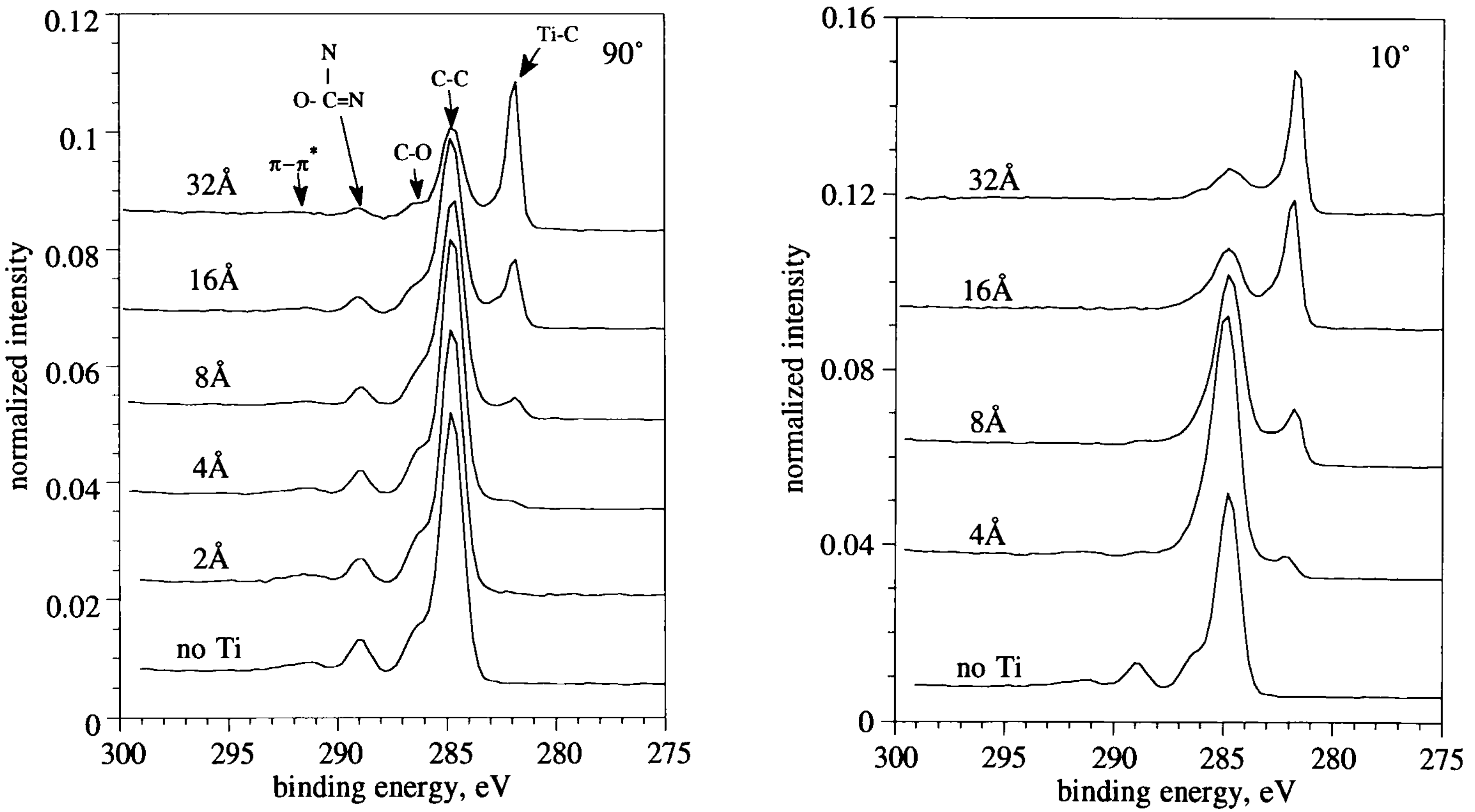


FIGURE 6 Evolution of the C1s core level spectra for Ti deposition on thin triazine films, at 90° (left) and 10° photoelectron takeoff angle. Each spectrum is normalized to an integrated intensity of one.

virtually disappear. This suggests that the triazine and aromatic rings are sites of reaction between the Ti atoms and the polymer. This is in contrast to the epoxy for which the aromatic structure remains intact after a 20Å Ti film is deposited.

It should be noted here that some of the samples were reexamined with XPS after a two-month exposure in the laboratory environment and they showed a significant reduction in TiC content. (Figures 7a–b for C1s). This is consistent with the fact that titanium carbide is thermodynamically less favorable than the titanium dioxide. In the case of thick polymer films, where plenty of oxygen and water are dissolved in the polymer, TiO_2 is the dominant product, although TiC may still be the intermediate product. For thin polymer films, TiC dominates at high vacuum but, upon exposure to atmospheric conditions, it converts to the more stable dioxide.

The N1s, O1s, and Ti2p core level spectra for thin triazine films are shown in Figure 8. These were normalized to an integrated intensity of one. The N1s spectra show the growing presence of a titanium nitride peak at low binding energy, similar to the thick film behavior. Note that this is in contrast to epoxy where nitrogen desorption was observed. In the O1s region the inorganic component peak at low binding energy is still the most dominant one. The Ti2p spectra show that carbides, oxides, and nitrides are the main components at the interface for short deposition times but at longer deposition times the Ti metal peaks overshadow everything else.

The O1s, N1s, and Ti2p signals normalized by the C1s signal are shown in Figure 9. The qualitative behavior is similar to Figure 5 for thick triazine films. The Ti2p signal increases linearly with time, consistent with a sharp, chemically-bonded interface (as opposed to a diffuse, possibly physically-interlocked interface). The O1s signal increases more slowly while the N1s signal remains relatively unchanged. The curve fitting results of the C1s, O1s, and N1s peaks are plotted in Figure 10. Consistent with previous observations, they show an increase in TiC, TiN, TiO, and TiO_2

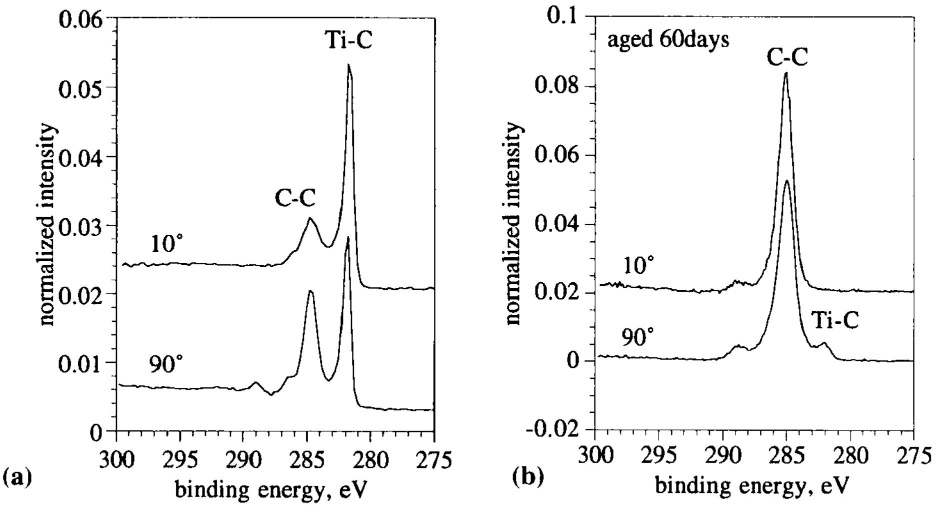


FIGURE 7 C1s core level spectra of 32Å of Ti on thin triazine films: (a) as deposited, and (b) after 60-day aging in air. The photoelectron takeoff angle is indicated on the figure.

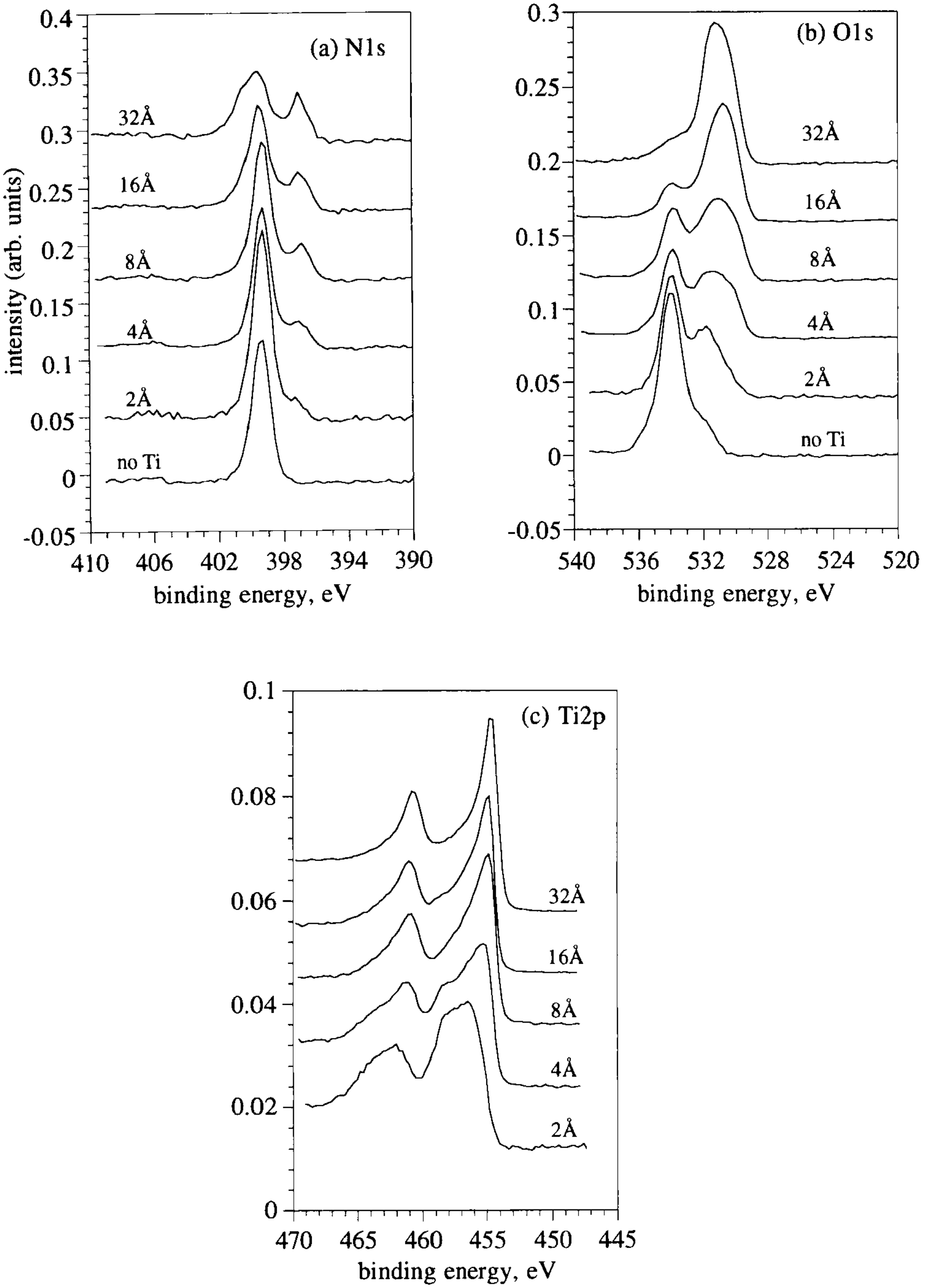


FIGURE 8 Evolution of the (a) N1s, (b) O1s, and (c) Ti2p core level spectra for Ti deposition on thin triazine films. Each spectrum is normalized to an integrated intensity of one. Photoelectron takeoff angle: 90°.

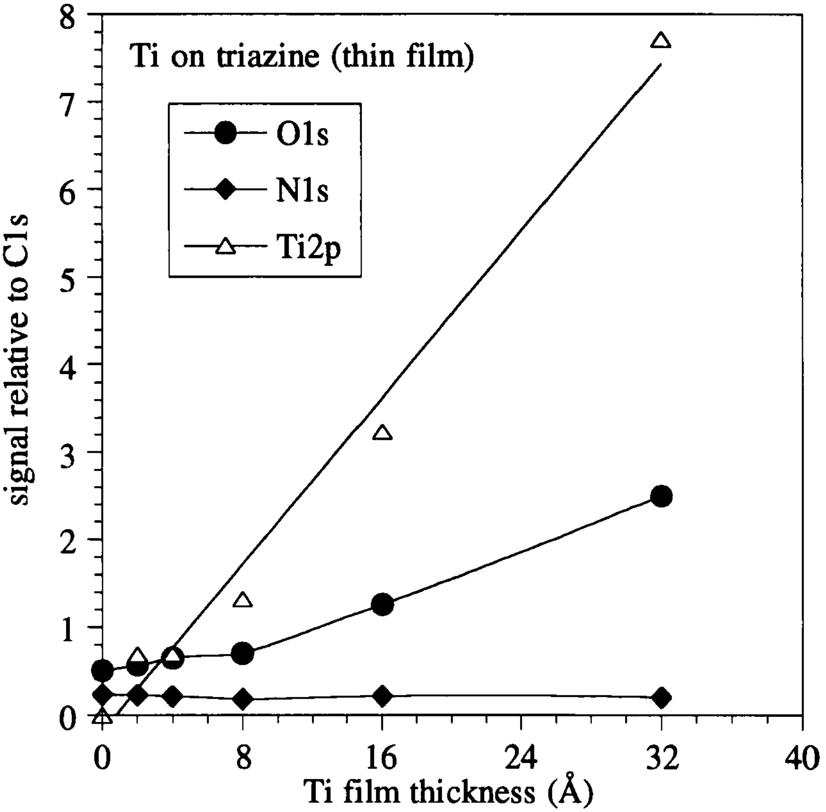


FIGURE 9 O1s, N1s, and Ti2p signal as a function of Ti thickness on thin triazine films. The signals were normalized to the same C1s signal. Photoelectron takeoff angle: 90°.

functionalities at the expense of C—O—C, C=N—C, and O—C(N)=N functionalities associated with the triazine ring.

Thin Polystyrene Films

Polystyrene, in contrast to both epoxy and triazine, does not have oxygen or nitrogen in its structure, but has an aromatic component that showed reactivity with Ti atoms deposited on thin polystyrene films. Any observed oxygen in the film would be physically rather than chemically bonded to the polymer. Polystyrene films, 200Å thick, were prepared by spin-coating from solution. The XPS survey showed a relatively small oxygen peak, indicating the presence of dissolved oxygen in the film. As Figure 11 shows, titanium carbide is the main product during Ti deposition, with small amounts of TiO_2. Note that the $\pi-\pi^*$ peak disappears at the surface-sensitive grazing photoelectron takeoff angle, indicating that the aromatic component is attacked by the Ti atoms. Ti metal is still the dominant feature in the Ti2p core level spectra. However, at grazing angle the oxide-to-metal ratio increases, indi-

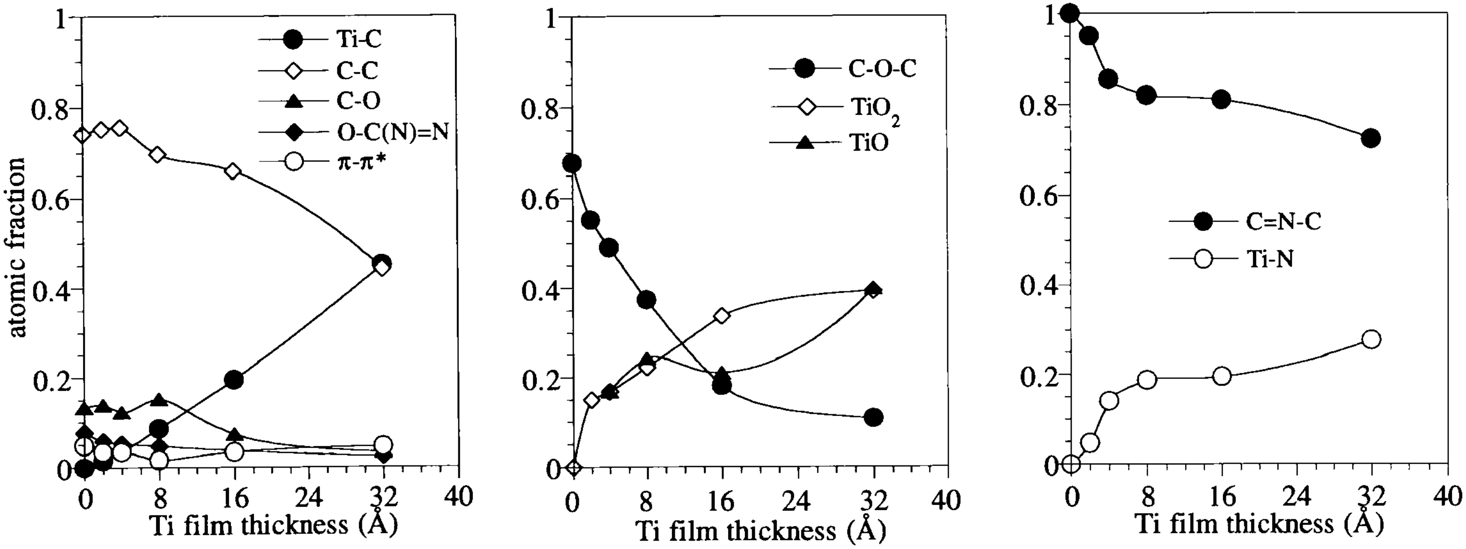


FIGURE 10 Curve fitting results for the spectra of Figures 6 and 8. Evolution of the different chemical states of carbon, oxygen, and nitrogen with Ti deposition time. Photoelectron takeoff angle: 90°.

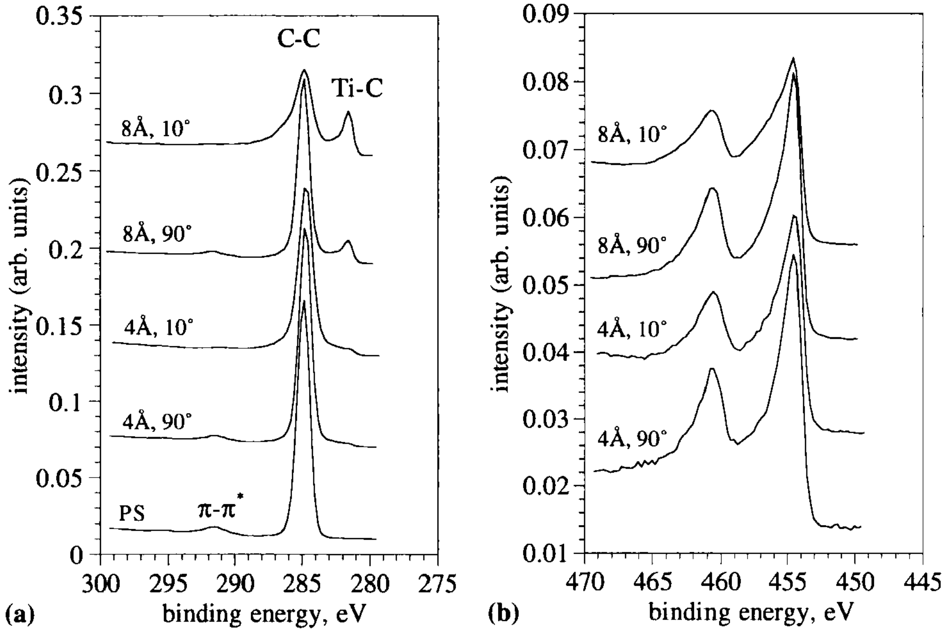


FIGURE 11 Evolution of the (a) C1s and (b) Ti2p core level spectra for Ti deposition on thin polystyrene films. Each spectrum is normalized to an integrated intensity of one. Photoelectron takeoff angle: 90°.

cating that at least some of the oxide is on the top surface, probably due to background oxygen. This effect has been observed for thin triazine films as well.

CONCLUSIONS

X-ray photoelectron spectroscopy was used to study the chemical interactions at the interface formed when Ti atoms are deposited in situ on epoxy, triazine, and polystyrene surfaces. Thick polymer films, having appreciable amounts of dissolved oxygen, formed TiO_2 at the interface, with very small amounts of carbide and nitride. Thin triazine and polystyrene films, having a much larger surface-to-volume ratio, have much less dissolved oxygen and form mainly TiC at the interface. The Ti reaction sites are the aromatic and triazine rings for triazine and the aromatic rings for polystyrene. However, upon exposure to the laboratory environment, TiC converts to the thermodynamically favorable TiO_2.

These observations have important implications for the stability and long term reliability of such interfaces. Ti is very reactive and appears to react approximately statistically with the various functional groups of a polymer surface to form the various carbides, nitrides, oxides, and suboxides. In the presence of water or molecular oxygen, which is already absorbed in the film or subsequently diffuses into the film, these titanium compounds are oxidized to TiO_2. Heating accelerates this process. Similarly, heating the sample to temperatures greater than the T_g of the polymer accelerates diffusion of the TiO_2 into the bulk of the polymer. Mechanical and aging studies are required to determine if a thin reacted layer consisting of Ti carbides, nitrides, and oxides exhibits better adhesion than a diffuse TiO_2 layer.

Acknowledgments

F. X. Ventrice of AT&T Bell Laboratories prepared the thick epoxy and triazine samples.

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