Reactions at the polyimide–metal interface

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Ultra-high-vacuum spectroscopic techniques are utilized to investigate the mechanism of the interfacial reactions of copper and titanium with polyimides. Ultra-violet photoemission spectroscopy of *in situ* deposited Cu on polyimides suggests that covalent interaction between the metal and the polymer is absent. Model studies confirm this finding. Alternatively, deposition of Ti onto polyimides shows the presence of strong covalent interaction between the imide moiety of the polymer backbone and the metal. Solution model studies support a mechanism for the Ti–polyimide reaction involving initial Ti–O bond formation followed by Ti–C bonding at higher coverages of material.

(Keywords: polyimide; interface; titanium; copper; X-ray photoelectron spectroscopy; ultra-violet photoelectron spectroscopy)

INTRODUCTION

Recent developments in microelectronics have underscored the importance of metal–polymer interactions and adhesion. While adhesive forces can often be altered through mechanical means, covalent interactions are critical in metal–polymer interfacial phenomena. In an effort to characterize these covalent properties of dissimilar interfacial media, we have studied the chemistry of the titanium and copper interface with polyimides.

The interaction of various metals with polyimide surfaces has been reported previously[1–6]. Chou[1,2] has studied interfacial reactions of metallized polyimide using X-ray photoemission spectroscopy (XPS) and has found that there are changes in the carbonyl region of the carbon (1s) band upon evaporation of Cr and Ni overlayers onto cleaned polymer surfaces, while the addition of Ag and Cu lead to no apparent changes. Hahn *et al.*[3] have added ultra-violet photoemission spectroscopy (UPS) to the study of the same problem and have found that, in addition to changes in the carbonyl region of the XPS spectrum, the addition of monolayers of reactive metal vapours to polyimide surfaces effects changes in the nitrogen and oxygen lone pairs appearing in the UPS spectrum. Sanda *et al.* have suggested that there is observable interaction between Cu and the ether moiety of polyimides through the use of model systems[7]. While these studies represent significant advancements in the understanding of the metal–polyimide interactions, they are largely phenomenological in their scope. It is the purpose of this paper to present our initial work on the interaction of Ti and Cu with polyimides in order to understand the chemical mechanism of the interfacial process. This goal is achieved through a unique blend of surface science and organic chemistry.

EXPERIMENTAL

Samples of poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-ODA) were prepared by chemical conversion of the corresponding polyamic acid. In this process, 5.7% polyamic acid in dimethylacetamide (DMAc) was spin-coated at 2000 rpm under dust-free conditions onto a polished aluminium peg. After coating, the peg was placed at 90°C for 10 min, after which it was immersed for a period of 2 h in a solution of 1:1 pyridine/acetic anhydride. Profilometry reveals the resulting polyimide film to be approximately 1000 Å thick. Samples of poly(*p*-phenylene diamine pyromellitimide) (PMDA-PD) and poly(4,4′-thiodiphenylene pyromellitimide) (PMDA-SDA) were prepared in a similar manner.

Photoelectron spectroscopy experiments were performed in a dual-chamber ultra-high-vacuum (u.h.v.) system. Briefly, the analysis chamber is equipped with XPS, UPS, Auger electron spectroscopy (AES) and mass analysis. Metal deposition sources, sample heater and sample introduction systems are located in the preparation chamber, connected to the analysis chamber via a u.h.v. isolation valve; the sample is transferred between chambers with a linear motion feedthrough.

XPS and UPS were obtained using a double-pass cylindrical mirror analyser with non-monochromatic Mg Kα (1253.6 eV) radiation and He II (40.8 eV) resonance radiation, respectively. Copper was sublimed OFHC from a copper sample heater with a power-regulated tungsten dispenser cathode. Deposition of titanium was carried out using high-purity Ti–Mo alloy which was Joule-heated to obtain a sublimed Ti vapour. Extreme care was taken to prevent metal vapour–residual gas reaction during the course of the reaction, particularly in the case of Ti deposition.

Polyimide samples were heated to 400°C in the u.h.v. chamber to drive off water vapour, as monitored by mass spectroscopy. Metal deposition was carried out *in situ* at room temperature, and surface coverage was calibrated by monitoring both XPS and AES peak intensities of the metal as a function of deposition time. Deposition was found to follow Stranski–Krastanov kinetics with initial monolayer formation, followed by island deposition.

The solution studies herein described utilize the imide model shown below (**I**).

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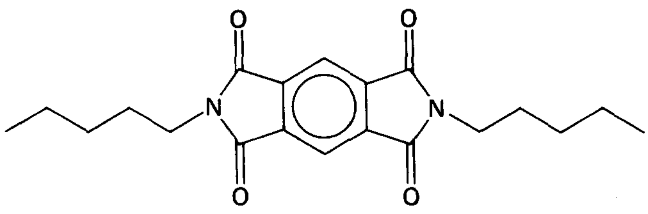
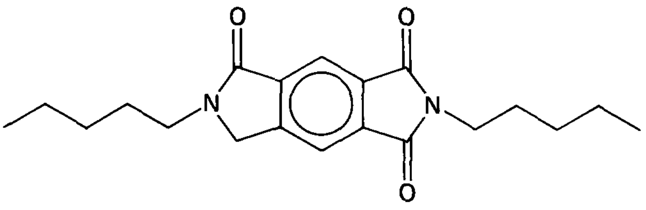


I

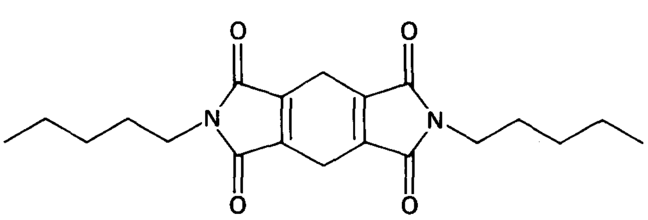
This species presents the advantage of high solubility in inert solvents such as dimethoxyethane (DME). The compound is synthesized by condensation of pyromellitic dianhydride with amylamine at 120°C in dry DMAc, followed by recrystallization from DMAc. Reaction of I with Ti^0 is achieved in a manner similar to that published by McMurray[8]. In a heterogeneous reaction, 0.29 g (1.86 mmol) $TiCl_3$ is dissolved in 10 ml dry DME under Ar. To the rapidly stirring solution is added 0.45 mg clean Li wire. The mixture is refluxed under Ar for 1 h and then cooled to room temperature. **I** (0.15 g, 0.46 mmol) is dissolved in 2 ml dry DME and slowly added to the rapidly stirring mixture. After addition is complete, the reaction mixture is stirred for 2 h at room temperature, followed by reflux for 24 h. After cooling, the reaction mixture is filtered through Florisil and the filter cake rinsed with DME. Starting material is recovered by slow removal of DME. Remaining solvent is removed under vacuum, leaving a brown sludge. The major component of this mixture is identified as the reduced diimide shown below (**II**).



II

Mass spectral analysis of the compound revealed a molecular ion peak at *m*/*e* 342 and major fragmentation peaks at *m*/*e* 285 and 228, corresponding to loss of C_4H_9 from each of the *n*-alkyl chains. N.m.r. data are obtained and found to be consistent with the compound **II** shown above: ^{1}H n.m.r. ($CDCl_3$ (δ 8.25 (s, 1H), 7.90 (s, 1H), 4.52 (s, 2H), 3.71 (dt, 2H), 3.65 (dt, 2H), 1.70–0.85 (tm, 18H).

Alternatively, the reaction of **I** with another Ti^0 model, bis(toluene)titanium, in tetrahydrofuran (THF) at room temperature resulted in the formation of the same reduced imide as shown above (**II**). Additionally, two other products were identified by g.c.–m.s. as the species shown below (**III** and **IV**).



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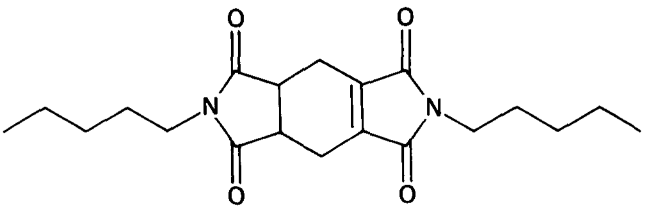


IV

RESULTS AND DISCUSSION

The XPS of C(1s), O(1s) and N(1s) electrons for PMDA-ODA are shown in *Figures 1–3*. Previous workers[1–6,9] have tentatively assigned the various orbitals, and these assignments are confirmed through the use of model polymer systems[10].

Cu–polyimide interactions

The UPS of PMDA-ODA after *in situ* thermal treatment is shown in *Figure 4* (trace A). This spectrum is in good agreement with the calculated densities of state for model systems[3]. Upon the addition of Cu via *in situ* vacuum deposition, the core and valence electrons of the polyimide decrease nearly in proportion, and there is an

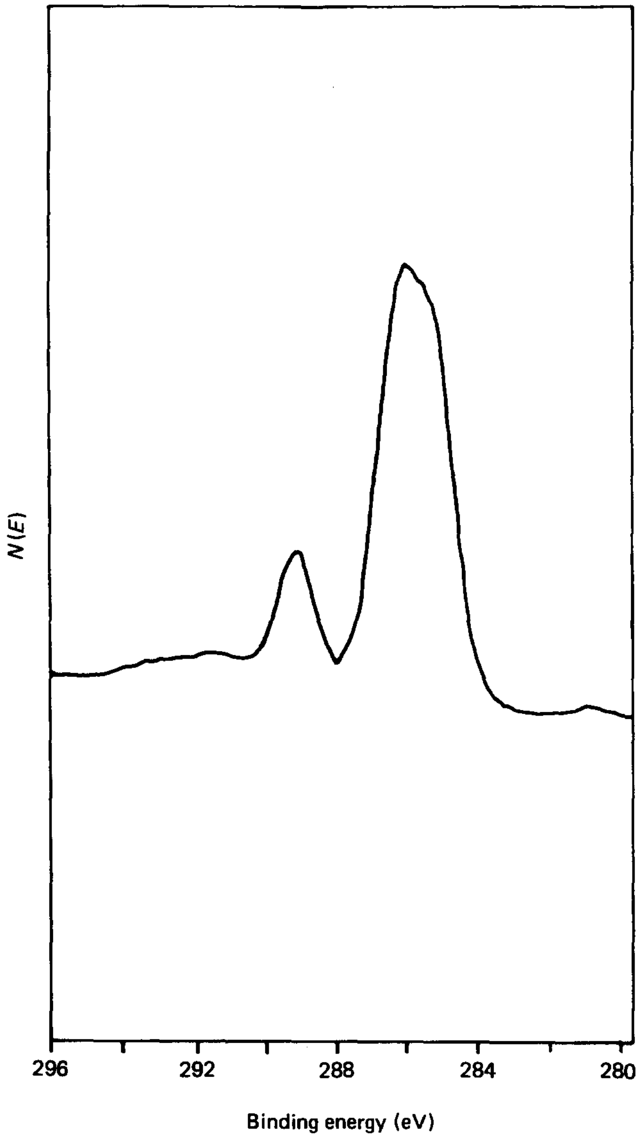


Figure 1 XPS of C(1s) electrons in clean PMDA-ODA

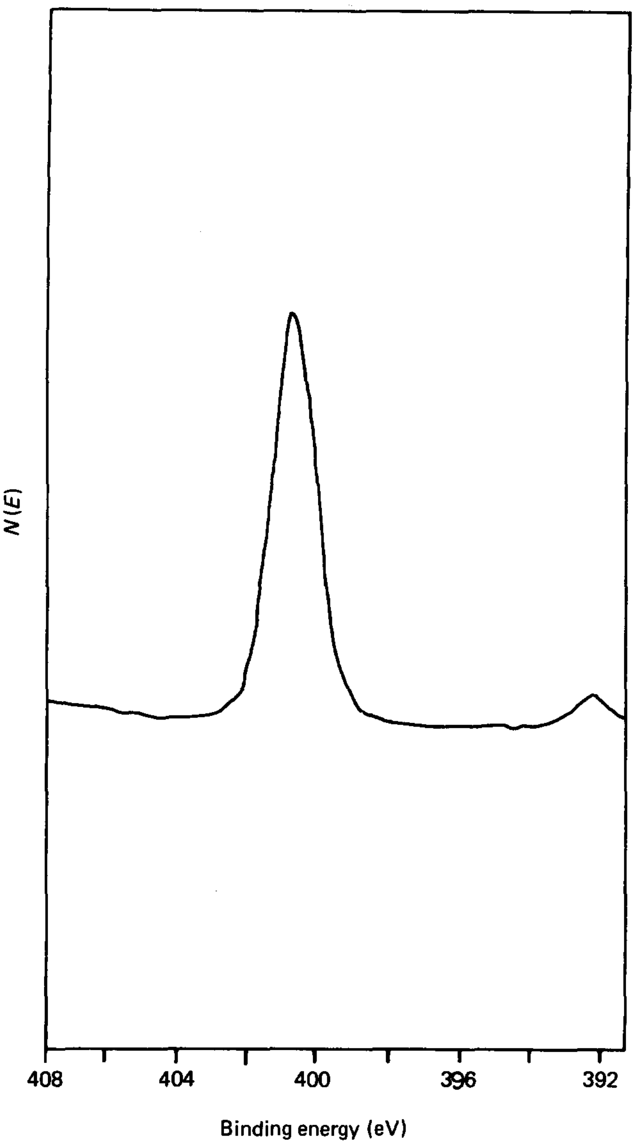


Figure 2 XPS of N(1s) electrons in clean PMDA-ODA

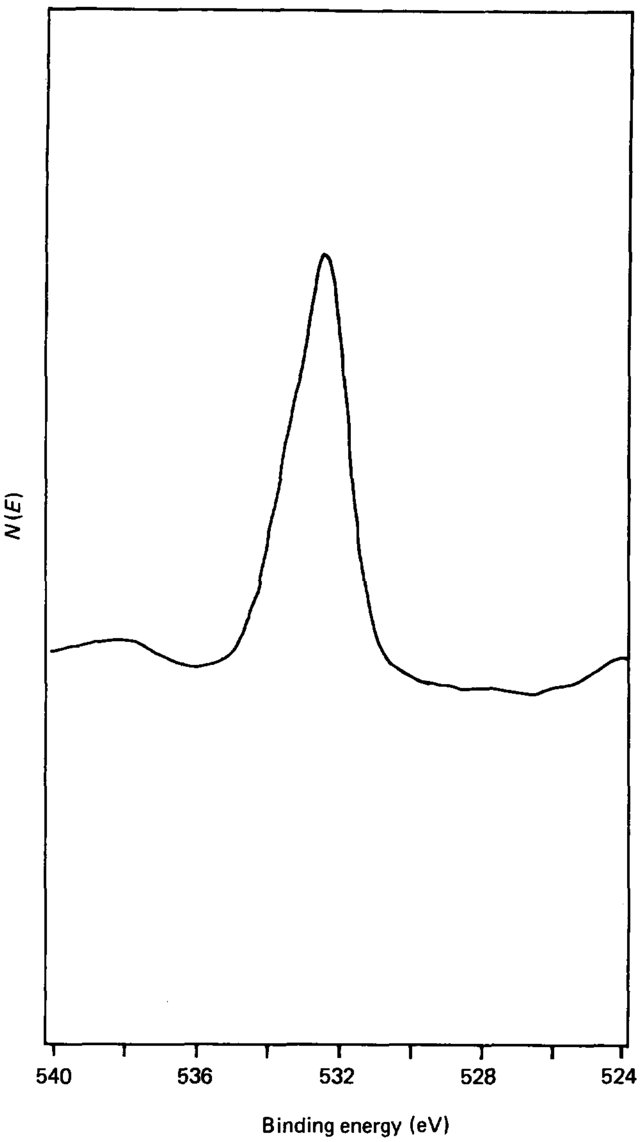


Figure 3 XPS of O(1s) electrons in clean PMDA-ODA

increase in the transition of the Cu(3d) near-Fermi edge as deposition increases, as shown in *Figure 4* (trace B). The proportionality of the changes in the organic peaks suggests that there is essentially no covalent interaction between the Cu and the polymer, and this observation is demonstrated more vividly by the difference spectrum shown in *Figure 4* (trace C), where the polyimide UPS is subtracted from the Cu-deposited spectrum. The overall spectral shape of the negative deflection in *Figure 4* (trace C) is virtually the same as native PMDA-ODA. In addition, there is no change in the binding energy of the Cu(3d) orbitals as deposition progresses, clearly showing the lack of covalent interactions between Cu and the polyimide surface. No change in peak positions or relative intensities in the XPS spectrum of PMDA-ODA is observed with the addition of Cu to the polymer surface, supporting the conclusions drawn from the UPS data.

Sanda[7] and Hahn[3] have published studies suggesting that Cu deposition on PMDA-ODA leads to weak but observable interactions between the metal and polymer. Sanda[7], through the use of monomeric models, described changes in the XPS C(1s) spectra attributed to weak charge-transfer interactions between Cu and 4,4′-diaminophenyl ether. The diamine was represented as a

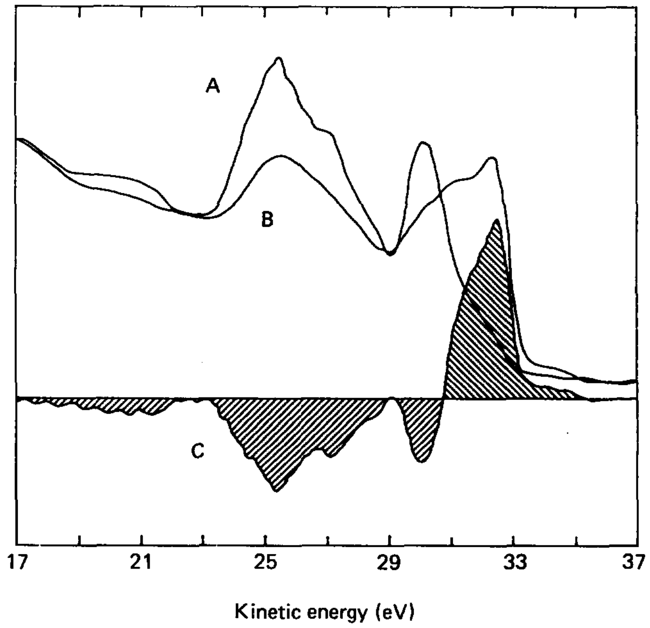


Figure 4 UPS of PMDA-ODA after *in situ* thermal treatment (trace A). UPS of clean PMDA-ODA after *in situ* deposition of Cu (trace B). Difference spectrum of trace B minus trace A showing actual changes in UPS intensity upon deposition of Cu (trace C)

model for the diphenyl ether moiety of the PMDA-ODA backbone, and thus Cu interaction with this species was assumed to be representative of interactions in the polymeric material. Hahn[3] reported that the carbonyl intensity in the XPS C(1s) spectrum decayed more rapidly than did the main carbon band under the conditions used in that experiment. In another model study, Sanda[11] found that deposition of Cu onto poly(phenylene oxide) (PPO) surfaces resulted in a large shift of the ether oxygens to lower binding energy, as determined by XPS monitoring.

In an attempt to clarify the Cu interaction issue, a clean separation of carbonyl oxygens from ether moiety was sought. The polymer PMDA-SDA has thioether substituted for oxyether in the diamine unit. This allows for clean analysis of the S(2p) band in XPS without interference from the carbonyl oxygens. The XPS spectrum of the S(2p) orbitals of PMDA-SDA is shown in *Figure 5* (trace A). Deposition of a monolayer of Cu onto the polymer surface results in no change in lineshape or shift in energy of the sulphur band (*Figure 5* (trace B). This suggests that there is no detectable interaction between the ether moiety and Cu in polyimides.

It has been established that polyimide–Cu adhesion is quite low[1]; these results, and those obtained by others in the field[1–6], suggest that the reason for the low adhesive strengths of polyimide–Cu bonds may reside in the non-covalent nature of these interactions.

Ti–polyimide interactions

In previous studies[1–4], it has been shown that *in situ* addition of Ni, Cr and Al resulted in a decrease in intensity of the C(1s) peak assigned to the carbonyl carbon. The *in situ* deposition of Ti onto the surface of PMDA-ODA shows similar behaviour (*Figure 6*). In this figure, the changes in C(1s) transitions are monitored as a function of Ti coverage. It is clear that there is a marked decay of the carbonyl band and a shifting of the main band to lower binding energy, in addition to the overall decay of the signal corresponding to increased surface coverage up to 32% of the monolayer. *Figure 7* shows the changes in O(1s) XPS peaks as a function of the same coverage of Ti, and it is clear that, with increasing coverage of metal, there is the appearance of a transition with lower binding energy. No significant changes are observed while monitoring the N(1s) orbital. The most dramatic changes in the spectra are observed while monitoring the Ti(2p) band (*Figure 8*). At 19% monolayer coverage, the Ti(2p) transition is found at 458.5 eV binding energy. As coverage increases, this peak broadens and then sharpens yet again at 32% coverage to a new band at 454.7 eV binding energy.

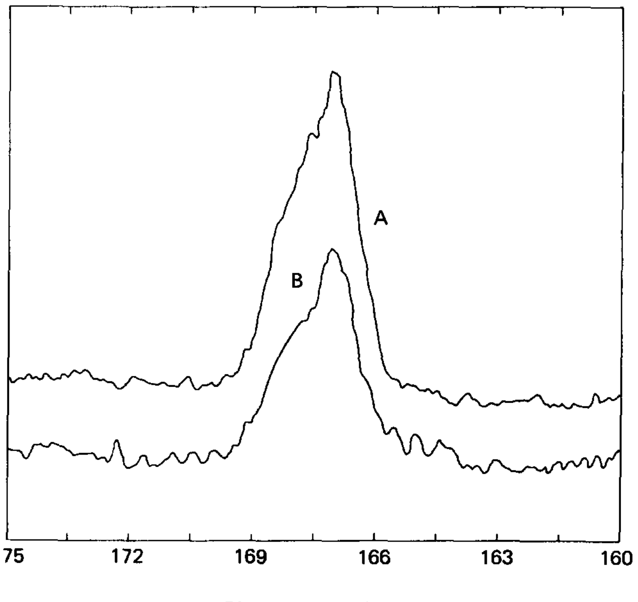


Figure 5 XPS of S(2p) electrons in clean PMDA-SDA (trace A). XPS of S(2p) electrons in PMDA-SDA after *in situ* vacuum deposition of Cu (trace B)

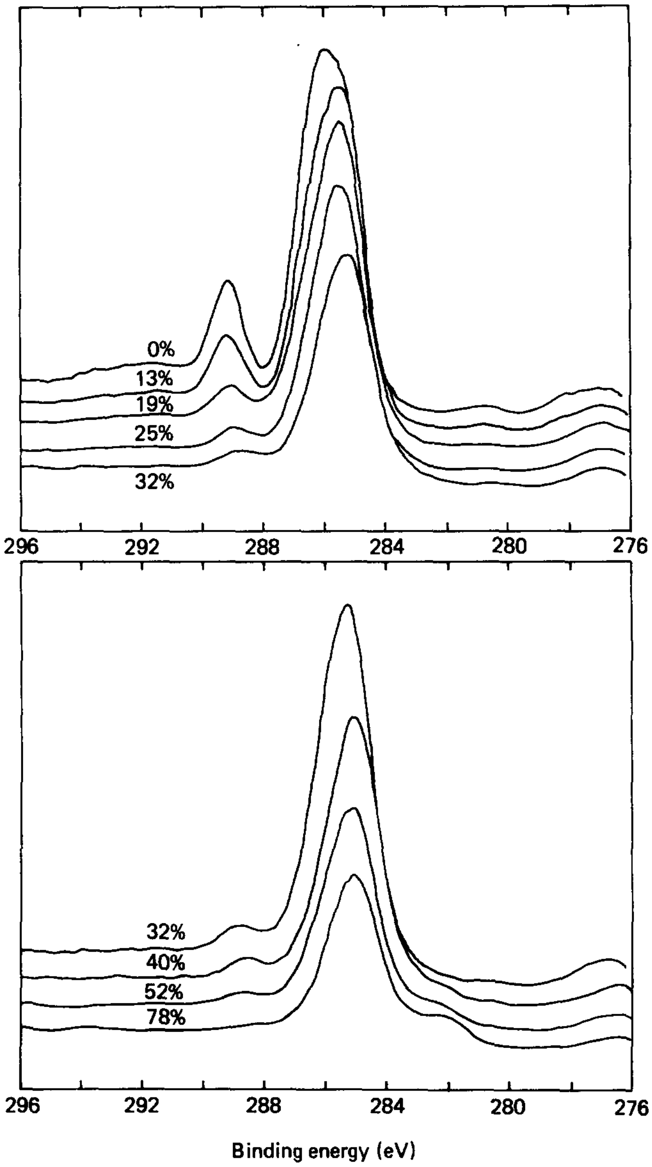


Figure 6 XPS of C(1s) electrons in PMDA-ODA upon *in situ* deposition of Ti. The coverage of Ti is given in per cent of monolayer

The results displayed above have dealt with low coverage of Ti. At Ti coverages greater than 35%, there is the appearance of a new C(1s) species, as shown in *Figure 6*, which has a binding energy 2.8 eV below that of the aromatic carbon group. Increasing coverage results in increasing concentration of this species.

In an attempt to simplify the mechanistic variables, the interactions of Ti with PMDA-PD and PMDA-SDA were studied. PMDA-PD has no ether oxygen, and therefore the interactions of the metal with the carbonyl oxygens can be studied without interference from other

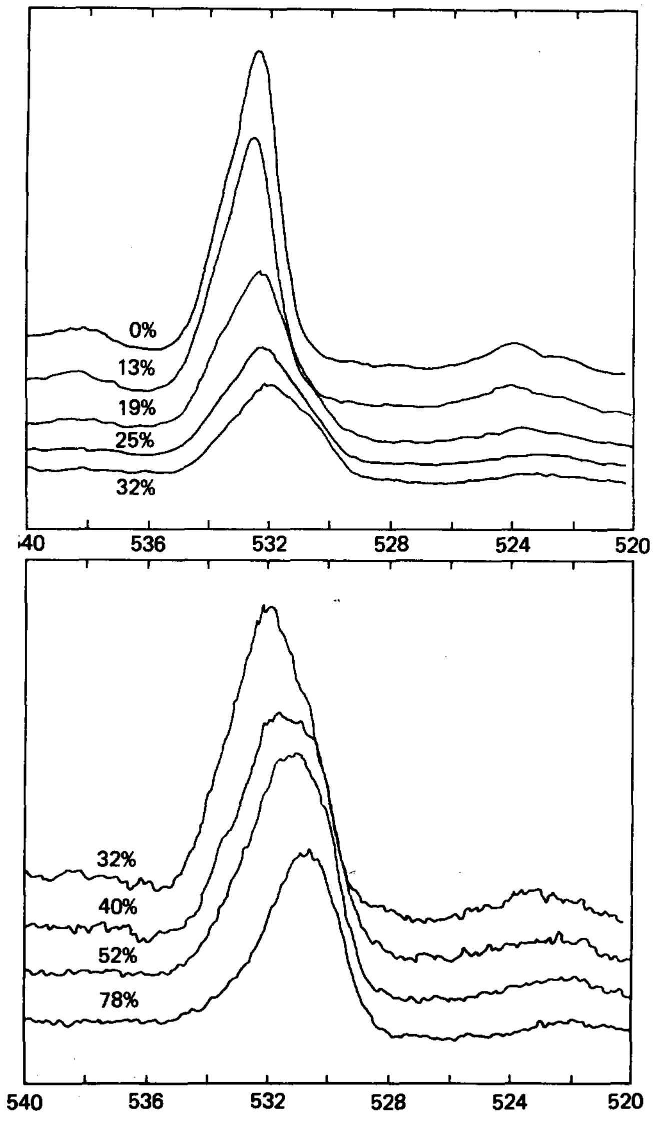


Figure 7 XPS of O(1s) electrons in PMDA-ODA upon *in situ* deposition of Ti. The coverage of Ti is given in per cent of monolayer

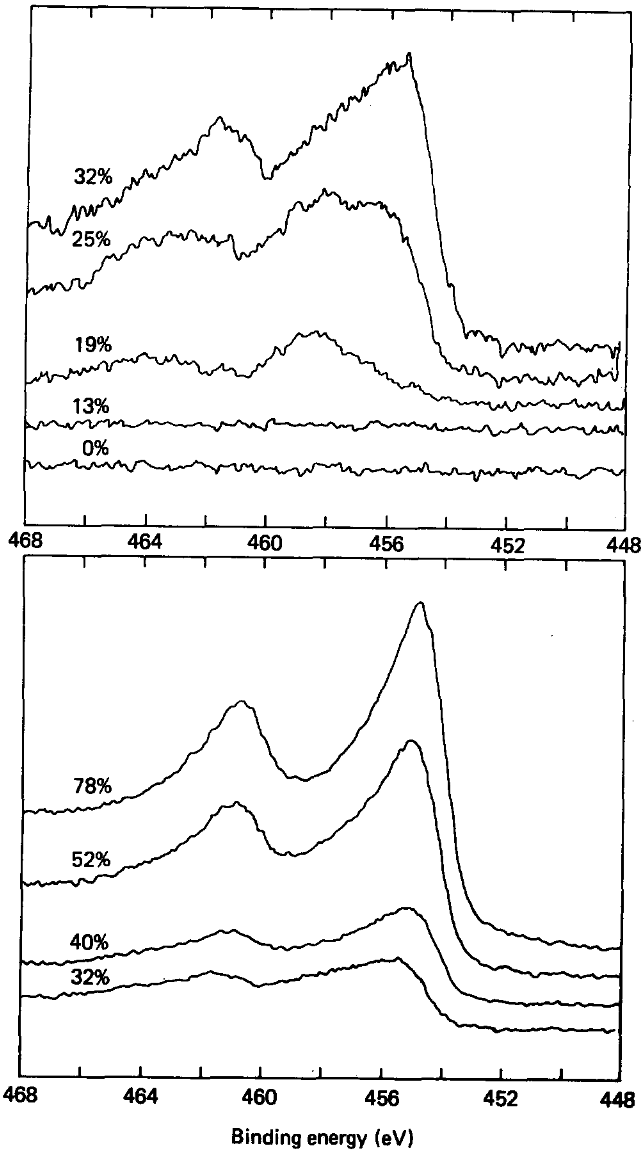


Figure 8 XPS of Ti(2p) electrons upon *in situ* deposition of the metal onto PMDA-ODA. The coverage of metal is given in per cent of monolayer

oxygen-containing groups. PMDA-SDA provides for separation of ether from imide moieties through the introduction of sulphur in place of the ether oxygen.

The deposition of Ti onto a clean PMDA-PD surface was found to proceed in much the same manner as PMDA-ODA. Thus deposition resulted in a decay of the carbonyl band in the C(1s) XPS spectrum along with a shift in the main carbon band to lower binding energy. No change in the N(1s) orbitals was detected. The O(1s) spectrum is of particular interest, and is shown in *Figure 9*. With low levels of Ti deposition (20% of a monolayer), the carbonyl carbon band is found to broaden towards lower binding energy. The difference spectrum in *Figure 9* (trace B) clearly demonstrates the decay of the carbonyl oxygen band, and the shift of this band to an energy 1.6 eV lower than the carbonyl energy. A similar analysis for the deposition of 19% monolayer Ti onto PMDA-ODA reveals a similar peak shift. These results suggest that the addition of Ti at low coverages to polyimides results in the formation of a Ti–O bond with the oxygens of the carbonyl groups of the imide, and that the energy of this species in the XPS is assignable to 530.8 eV. Ti–O bonding is consistent with the UPS results for Ti

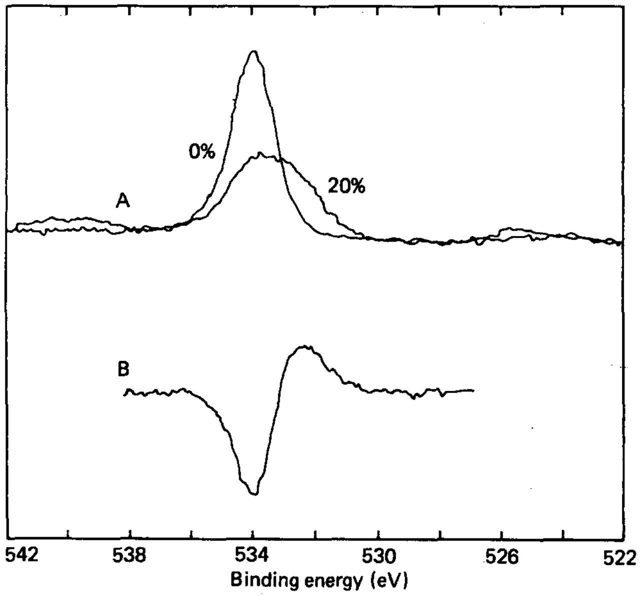


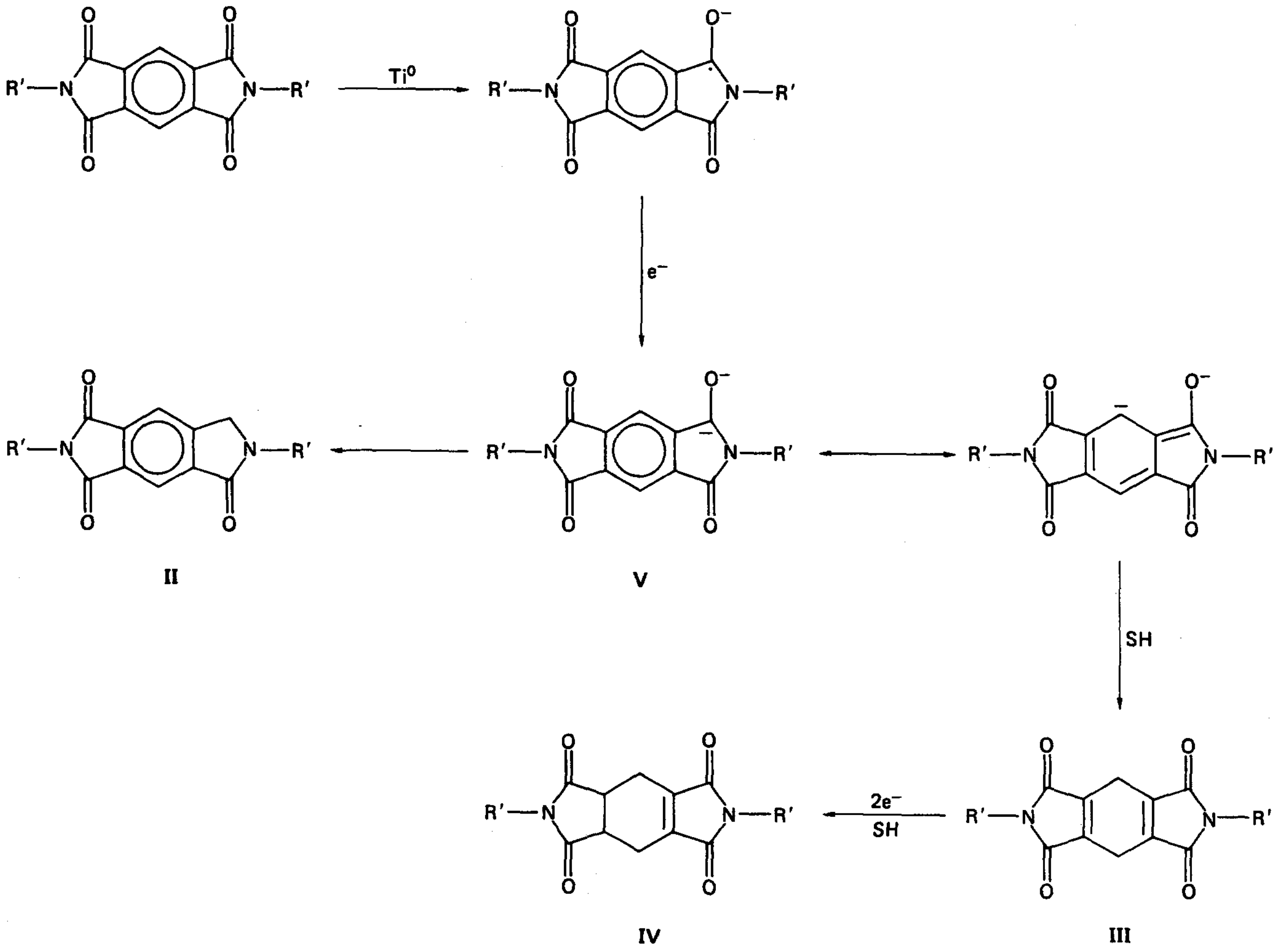
Figure 9 XPS of O(1s) electrons in clean PMDA-PD and with *in situ* deposition of 20% monolayer of Ti (traces A). Difference spectrum of the clean and Ti-deposited O(1s) for PMDA-PD (trace B). BE uncorrected

deposition on PMDA-ODA previously reported[10]. Formation of the Ti–O bond results in an increase in electron density in the carbonyl group, shifting the carbonyl carbons and oxygens to lower binding energy and decreasing the electrophilic character of the imide phenyl ring. An increase in the electron density of the imide ring will decrease the binding energy of the carbons of that ring; this will be revealed in the C(1s) XPS spectrum as a shift in the main band to lower binding energy.

PMDA-SDA is utilized to examine the exclusivity of Ti interaction with the imide unit. As discussed in the section above on Cu/PMDA-SDA reactions, if Ti interacts with the diphenyl thioether moiety of PMDA-SDA, there should be a significant change in the electron density of the thioether S(2p) orbital and thus a shift in the S(2p) XPS band. *Figure 10* shows that as up to 50% of a monolayer of Ti is deposited onto the surface of PMDA-SDA, there is no change in either the band shape or energy of the S(2p) emission. These results imply that there is no detectable interaction between the metal and the diphenyl ether unit in PMDA-SDA, and by analogy in PMDA-ODA.

At Ti coverages greater than 35% of a monolayer, the PMDA-ODA C(1s) XPS band (*Figure 6*) reveals that the carbonyl intensity continues to decrease, but there is also the appearance of a species 2.8 eV lower in binding energy than the main band. This new band continues to grow with increasing metal deposition. The binding energy of this species is consistent with an assignment[12] of a TiC, but more definitive assignment of the carbon can be carried out with Auger lineshape analysis of the C(LVV) 272 eV band. *Figure 11* shows the Auger spectrum of the C(LVV) band of clean polyimide, and of polyimide with increasing amounts of Ti deposition, along with the C(1s) XPS spectrum taken at the same metal coverage. It is clear that, as Ti deposition increases over 35%, there is an increase in the fine structure of the Auger band. This increase in structure is consistent with a conversion from graphitic carbons in the clean and low-metal-covered polyimide to carbidic carbons under high metal coverages. In fact, the Auger C(LVV) lineshape of polyimide with greater than a monolayer of Ti is virtually identical to the published spectrum[13] of stoichiometric TiC. The Auger results, in conjunction with the XPS results, demonstrate that high coverages of Ti result in the formation of Ti–C bonding.

The solution studies described in the experimental section of this work are consistent with the surface analysis, and demonstrate the chemical competence of a mechanism involving initial Ti–O bonding followed by Ti–C bond formation. The three products, **VI–VIII**, can be understood to be formed from a mechanism schematically represented below.



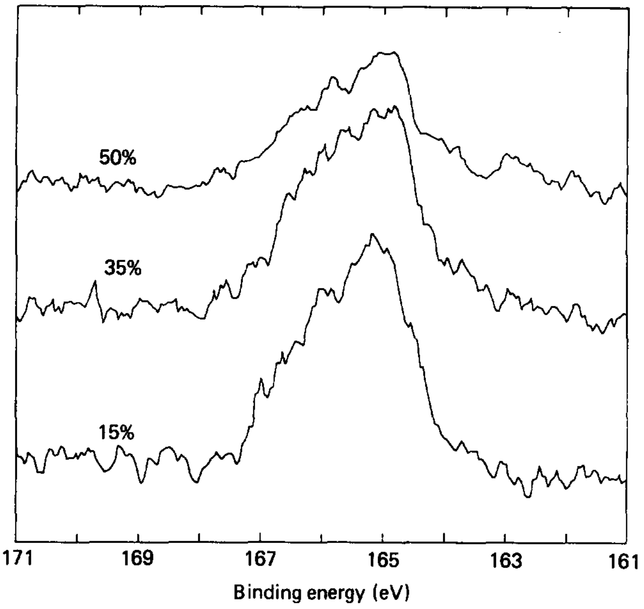


Figure 10 XPS of S(2p) electrons in PMDA-SDA with sequential *in situ* vacuum deposition of Ti, where metal coverage is given in per cent of monolayer

Initial electron transfer from the metal atom to the imide results in the formation of a Ti–O bond. Second electron transfer from either the same or a different Ti atom or ion results in the formation of Ti–C bonding to generate intermediate **V**. This species can be represented by a number of resonance forms, and it is clear that electron density is increased in the imide phenyl groups by this second electron transfer. Protonation of **V** by solvent or work-up gives product **III**, while repeating the two-electron reduction process yields **IV**. The mechanism for the formation of **II** is less straightforward and at this juncture is not understood, yet it is hard to envision a route to **II** which does not involve the intermediacy of **V**. While the formation of these products through a mechanism involving initial Ti–O followed by Ti–C bonding is implied, there experiments are not designed to suggest that these products are formed on the surface of the polymer during Ti deposition.

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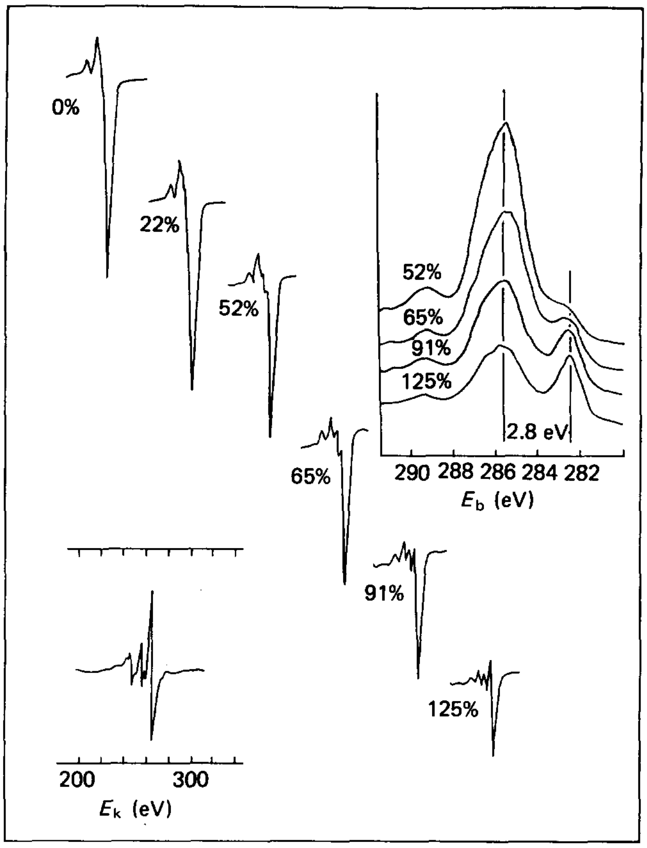

Figure 11 C(LVV) Auger band of PMDA-ODA as a function of sequential *in situ* deposition of Ti, where metal deposition is given in per cent of monolayer. The insert in the upper right allows for comparison of the XPS C(1s) band in PMDA-ODA with identical metal coverages, while the insert in the lower left shows the lineshape of the TiC C(LVV) Auger transition (from ref. 13)

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