Delocalized bonding at the metal–polymer interface

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This paper summarizes our current understanding of the nature of the chemical bond formed at the interface between a deposited metal atom and an underlying polyimide surface. The approach in these studies is based on the use of quantum chemical calculations to interpret photoemission spectroscopy results. By focusing on the initial reaction between a chromium atom and the PMDA–ODA polyimide repeat unit, the bonding is demonstrated to be delocalized, arising from the formation of a charge-transfer complex between the metal atom and the PMDA unit of the polyimide. Stabilization of the complex involves the transfer of electronic charge from the metal d states of chromium to the lowest unoccupied molecular orbital of the π system of the PMDA unit of the polyimide. The complex proposed is energetically favored over that involving a direct local interaction between the chromium atom and one of the carbonyl functional groups. The distribution of single-particle electron energy levels deduced from molecular-orbital calculations can account for the spectroscopy results. The formation of such delocalized metal–polymer complexes is also inferred from a related study of the chromium/PMDA–PDA interface.

Introduction

Within the past several years, there has been increasing interest in studying the basic properties of metal–polymer interfaces. Several studies have focused on fundamental issues involving the chemical interaction between metal atoms and the polymer surface [1–7]. As with the initial investigations of other technologically important surfaces and interfaces, such as those involving semiconductors, the interpretation of the experimental results, particularly as the interpretation concerns the configuration and energetics of metal–polymer bonds, has aroused considerable interest. To date, the majority of analytical investigations have been carried out spectroscopically. Such work has involved the use of X-ray photoemission spectroscopy (XPS) or ultraviolet photoemission spectroscopy (UPS) to obtain a measure of the core or the valence states of the polymer, respectively. The core-level positions obtained using XPS carry a wealth of information about the local chemical environment of the emitting atom.

The inherent difficulty in interpreting spectroscopic data for a polymer surface or interface arises from the structural and chemical complexities of the polymer. For example, the polyimide family of polymers is composed of aromatic units which are linked via carbon–nitrogen and carbon–oxygen bonds to form the polymer backbone. Wave functions in the vicinity of the Fermi level are delocalized over such aromatic functionalities [8], so when a metal atom is deposited onto the polymer surface, one expects its interaction with the polymer to be delocalized as well. This makes it difficult to assign certain chemical changes that occur during metallic deposition to interactions between metal atoms and the polymeric substrate at specific molecular locations. X-ray studies have revealed that the fully imidized PMDA–ODA

polyimide exhibits a certain type of local smectic order [9]. The molecular structure of the surface has, however, not been characterized in detail. Thus, there is no standard surface, such as in the case of semiconductors [e.g., the Si(111) 7×7 surface], to provide a specific structural framework to investigate the interactions between metal atoms and polymer surfaces. At present, it is clear that in order to understand the spectroscopic results, not only for the clean polymer surface, but additionally for the case involving metal deposition, quantum chemical calculations of the electronic structure and the relative stability of different possible metal–polymer complexes are required. Without the detailed information provided by such calculations, it is difficult to deduce the bonding configurations between a deposited metal atom and the polymer and to rule out configurations which are energetically unfavorable.

Molecular-orbital calculations are also important in providing insight into the core-level shifts expected upon complexing the metal atom with the polymer substrate. It is, for example, well known that similar energy shifts observed in core-level photoemission spectroscopy can have different origins, which in turn can lead to conflicting interpretations.

This paper discusses our present state of understanding of the chemistry of the interface between a metal and the polyimide PMDA–ODA. This understanding has been derived primarily by using quantum chemical calculations to interpret the photoemission data. The discussion is focused on the interface between chromium and PMDA–ODA, as well as on the related polyimide, PMDA–PDA. The latter has a simpler structure than the PMDA–ODA, making possible more direct interpretation of its spectroscopic data. Chromium has been chosen in the discussion because it interacts strongly with the polyimide, allowing an unambiguous interpretation of the results. Furthermore, the interface is technically important and has been under intensive study [1–7].

Interface-sensitive techniques require molecular models upon which interpretation of the data depends. The major point of the present paper is to emphasize the fact that the combination of chromium and a polyimide is unique, so care must be taken in developing molecular models from which a deeper understanding of interfacial properties can be obtained. For example, the standard strategy in interpreting XPS data involving chemical species has been to attribute changes in the spectra induced upon deposition of a metal or other chemical species to well-defined interactions between the deposited species and some clearly identified local chemical group. The theme of our work has been simple and somewhat different. It is based upon the idea that the presence of a large aromatic backbone composing the polymer changes the framework of model building and consequent interpretation. We believe this to be particularly true with regard to chromium, which is known to form complexes involving multiple bonds to ligands in its attempt to satisfy the "eighteen-electron rule." For the chromium–polyimide interface, it is important to consider the possible types of interactions that might occur involving aromatic "delocalized" structures. In particular, we show that all of the XPS data we have accumulated in the low-deposition regime are consistent with chromium atoms interacting with the delocalized π orbitals characteristic of a polyimide structure which has maintained its structural integrity (i.e., has not been subject to any chemistry involving ring destruction). Furthermore, we believe that any attempt to interpret XPS, as well as any other interface-sensitive data concerning the chromium–polyimide interface, will of necessity be incomplete if such delocalized types of interaction, the types described in this paper, are not considered.

Perhaps it should not be surprising that the delocalized structure of the polyimide must be taken into account in interpreting XPS data. In fact, it is not possible to interpret the XPS data taken on a clean PMDA–ODA polyimide surface unless one is prepared to claim that such a surface is composed of numerous oxidized carbon species [8]. Cognizance of the π aromatic character of the clean surface has provided us with the clear understanding that the electronic charge shared by the various atomic species, and in particular by the carbon atoms, is shared according to the distribution of such charge in the delocalized π orbitals of the backbone. It therefore seems a straightforward extension to examine what happens to this delocalized charge upon deposition of a metal, particularly if the metal is chromium. This has been essentially the thrust of our previous work [2–4, 6], which is summarized in this paper.

One should also keep in mind that the surface of the spun-on and fully cured polymer bears little resemblance to any of the aggregate of related organic ligands in the gas phase. In other words, whereas chromium interacting with organic ligands in the gas phase can yield highly stable as well as highly coordinated and saturated gas-phase complexes, the solid surface presents the deposited chromium atoms with a considerably different environment. In the gas phase, the chromium atom or atoms, together with the ligands, can adjust to form low-energy structures which are highly symmetric. We have performed calculations on all of the classic gas-phase zero-valent chromium complexes, i.e., bisbenzene chromium, benzene–chromium–tricarbonyl, and chromium hexacarbonyl. The results revealed that the calculated XPS shifts induced by complexing chromium with these organic ligands parallel the experimentally observed XPS shifts. This has provided us with a check on the adequacy of the set of basis functions used in this work. We believe, however, that calculations on gas-phase complexes do not provide one with significant insight concerning the types of zero-valent complexes which may occur in the solid state. As expected of the polymer, it is

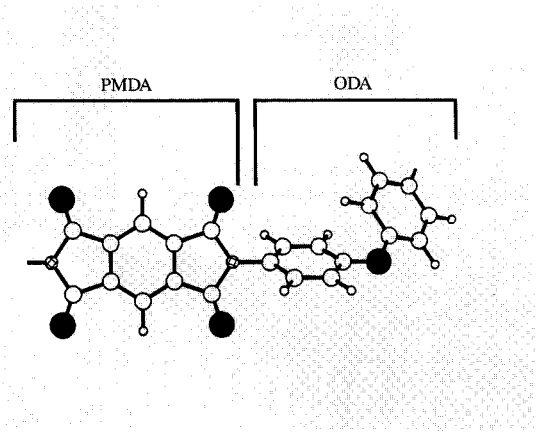

Figure 1

PMDA–ODA repeat unit with 22 carbon atoms (○), 5 oxygen atoms (●), 2 nitrogen atoms (⊗), and 10 hydrogen atoms (⊙).

to a degree disordered, although wide-angle X-ray scattering data have revealed certain local smectic order. In any event, one does not expect the interaction of the polymer with the chromium atom or atoms to be of primary importance in determining the local structural order. One expects, on the other hand, this local order to be determined by the type or types of molecular packing consistent with the nonbonding interactions between the polymeric units. We have modeled such local packing, and have examined its consequences with respect to the interaction between chromium atoms and the polymer and the associated XPS spectrum. These investigations will be discussed in a forthcoming paper [10]. To a large degree, the more detailed results involving polymeric complexes with geometries consistent with polymeric local order are similar to results previously obtained on simple unsaturated one-to-one metal organic ligand complexes. These results on the one-to-one complexes are summarized in the present paper, along with their use in the interpretation of associated XPS data.

Clean PMDA–ODA surface

Interpretation of the XPS spectroscopy results requires the identification of all elemental constituents in the spectra as well as the details of their respective chemical environments. To establish a basis for studying the metal–polymer interface, we first investigate the clean PMDA–ODA surface. In **Figure 1** we show a model of the polymer repeat unit which consists of 22 carbon, 5 oxygen, 2 nitrogen, and 10 hydrogen atoms. A number of details concerning the energetic positions of the carbon core levels can be deduced from a direct examination of this unit. For the four carbonyl (C=O) carbon atoms in PMDA, we expect the 1s core levels to reside at the highest binding energy due to the high electronegativity of the adjacent oxygen atoms which deplete the electronic charge of these carbon atoms. We might also expect that core levels of the carbon atoms bonded to the nitrogen and to the ether oxygen atom in ODA are shifted to higher binding energy for the same reason, although such shifts are expected to be smaller than in the carbonyl case. Finally, we expect that the remaining aromatic carbon atoms, i.e., carbon atoms bonded only to the other carbon atoms in both PMDA and ODA, should reside at the lowest binding energy. Theoretical studies [8] show that the presence of the four carbonyl oxygen atoms results in a shift of the core levels, to higher binding energy, of the aromatic carbon atoms of PMDA relative to those of ODA. Such a shift corresponds to approximately 0.25 eV per carbonyl oxygen atom. Since there are four carbonyl oxygen atoms in PMDA, this results in the PMDA aromatic carbon binding energies appearing 1 eV higher in binding energy than that of the ODA aromatic carbon atom. This therefore contributes to the doublet of the main carbon 1s XPS peak, which has the simple unambiguous feature that the lowest-binding-energy component arises solely from ODA carbon-atom emission, while the higher-binding-energy peak in the doublet arises predominantly from PMDA carbon-atom emission.

A number of simplifying assumptions have been made in the quantum chemical calculation. The first involves the study of the polymer repeat unit alone, as representative of the solid as a whole. This assumption can be justified in studies where bandwidths of the polymeric solid are found to be no more than several tenths of an eV [11]. The lack of significant banding in this material indicates that the π electron system of the repeat unit has small wavefunction overlap with adjacent units. Second, each of the two monomers, PMDA and ODA, is studied separately, with appropriate termination of the end-atom ligands. The PMDA part is planar, whereas the ODA part consists of two phenyl rings twisted with respect to each other and connected by an ether oxygen atom. X-ray studies of related molecular crystals [9] have led one to infer that steric effects result in a torsional rotation of the phenyl ring about the nitrogen–carbon bond by ~60° relative to the PMDA plane. Such a rotation prevents significant overlap of the PMDA π system with the phenyl groups of the ODA part, and hence results in the approximate electronic separability of the π system of the PMDA part of the repeat unit. This electronic separability of the PMDA π system is one essential aspect of our study of the repeat unit. Calculations for the individual monomers have been tested by comparison with a calculation of the entire PMDA–ODA unit, yielding core-energy-level errors of at most 0.5 eV.

Calculations were *ab initio*, and the GAMESS series of molecular-orbital programs were used with an STO-3G basis set of orbitals for the first-row elements. The dotted curve in **Figure 2(a)** shows the calculated carbon 1s spectrum which has been obtained, in the Koopman's approximation, by

Gaussian-broadening the calculated carbon 1s core-level binding energies. The dashed curves give the individual components. A full width at half maximum (FWHM) of 0.9 eV was chosen for the carbonyl- (C=O) and the ether-bonded (C–O–C) carbon peaks, and 1.1 eV for the PMDA and ODA peaks to simulate experimental resolution. Details of the molecular-orbital calculations have been given elsewhere [12]. Results of delta SCF core-hole calculations which take into account final-state effects are given in a forthcoming paper [13]. Calculations of core-hole effects on the XPS spectrum indicate that Koopman's approximation is essentially accurate to within a rigid shift of all core-level positions; thus core-hole or final-state effects should have little effect on the relative core-level positions used in our interpretation.

The calculations assume the presence of a fully imidized surface. Such a surface can be created and maintained in an ultrahigh-vacuum (UHV) system ($P \sim 10^{-10}$ torr) by vacuum curing of the spun-on polyamic acid precursor of the polyimide. Annealing at 320°C for 40 minutes resulted in cycloimidization which involves water evolution and ring closure, converting the acid to the imide. The details have been described elsewhere [14]. **Figure 2(b)** shows the experimental spectrum (solid curve) obtained in grazing-emission-angle geometry. This geometry samples photoemitted electrons emanating from a region closer to the surface than obtained with a normal emission geometry. The experimental spectrum has been fitted with four Gaussians. It is clear that the theoretical calculations result in a good fit to the experimentally observed spectrum.

The nitrogen 1s and oxygen 1s core-level spectra are simpler to interpret than the carbon 1s spectrum because of their simpler chemical environments. The spectrum of nitrogen is the most straightforward to interpret, since its unique chemical environment gives rise to a single peak. The oxygen signal consists of two peaks. The lower-binding-energy peak arises from carbonyl oxygen atoms, whereas the higher-binding-energy peak arises from ether oxygen atoms. These spectra are discussed in the following section, together with the chromium interface results. The details of interpretation of these spectra will be published elsewhere [14].

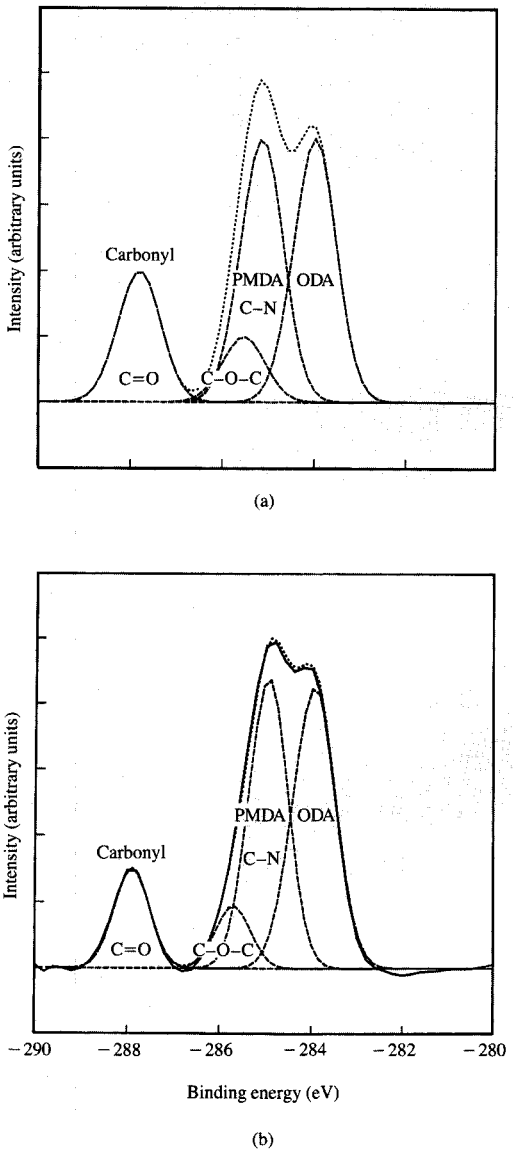

Figure 2

(a) Calculated carbon 1s spectrum of clean PMDA–ODA. The calculated energy levels have been broadened, as discussed in the text. (b) Fits of Gaussians to experimentally obtained spectrum. The assignments shown are discussed in the text.

Chromium/PMDA–ODA interface

The chromium/PMDA–ODA interface was formed by depositing chromium atoms under ultrahigh vacuum ($P \sim 10^{-10}$ torr) at rates sufficiently low to permit reproducible initial coverage of about 0.1 Å to be obtained. Prior to deposition, the polymer surface was carefully prepared to complete imidization in order to ensure a chemically reproducible surface for interface study. This was checked by examining the shape of the main carbon 1s peak, as well as the oxygen 1s and nitrogen 1s signals. In this paper we discuss only the low-to-intermediate-coverage regime up to about 1 Å of chromium coverage.

In our analysis of the interaction of chromium with PMDA–ODA, we examined the interaction of one or more chromium atoms with a single organic ligand. We expect this to be appropriate for the lowest-concentration regimes of the

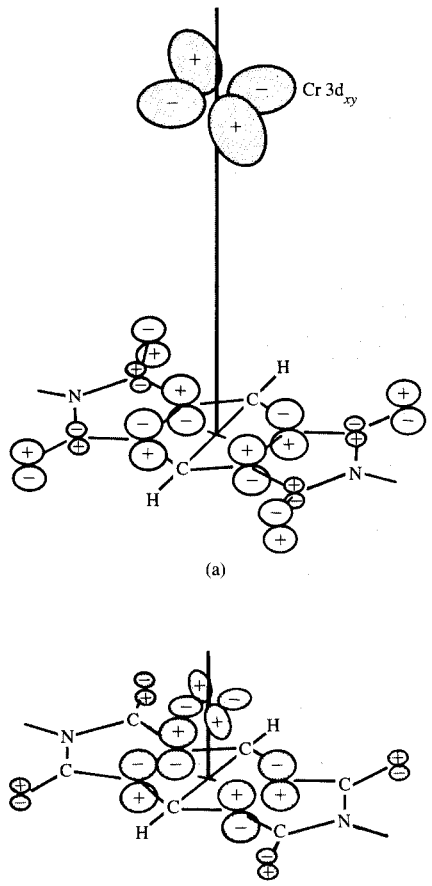

Figure 3

(a) Highest occupied molecular-orbital (HOMO) diagram for the lowest unoccupied molecular orbital (LUMO) of the PMDA monomer when chromium atom is sufficiently distant to be noninteracting. (b) Chromium over the six-member central ring of the PMDA monomer. The phases of the d_{xy} levels add constructively to the π levels of the monomer, giving rise to a stable bonding configuration.

experiments, since at the lowest coverage we have investigated, 0.12 Å, we estimate that on average there is one chromium atom for every three polymeric repeat units. The calculations involved the use of a double-zeta basis set for the chromium atom in order to more accurately characterize the d-levels of the metal atom. The accuracy of the calculations was tested by comparing the results with experimentally determined gas-phase core-level spectra for a number of organometallic compounds such as bisbenzene chromium, chromium–benzene–tricarbonyl, and chromium hexacarbonyl. All of the calculated values were within 0.5 eV of those determined experimentally.

Inspection of the highest occupied molecular orbital (HOMO) of the chromium–PMDA complex and the lowest unoccupied molecular orbital (LUMO) of PMDA yields insight into the metal atom–polymer ligand chemistry that takes place upon deposition. In particular, for PMDA, the LUMO exhibits greater orbital amplitude on the carbonyl oxygen atoms than on the carbonyl carbon atoms [see **Figure 3(a)**]. Significant LUMO amplitude is also observed on four of the carbon atoms in the central benzene ring. Interestingly, we note that there is no significant LUMO amplitude on the nitrogen atoms or on the carbon atoms of the central ring bonded to the hydrogen atoms. These LUMO amplitudes yield insight into the stable bonding configurations one might expect upon deposition of a chromium atom. Sites of high coordination for the metal atom, which permit optimum electron charge transfer into these levels, will be the most energetically attractive and stable. Upon chromium deposition onto the polyimide, we find that a stable configuration is obtained for chromium located in the high-symmetry site above the six-membered ring of PMDA. The $3d_{xy}$ orbitals of chromium can be aligned in such a manner that the orbital phases combine constructively with the π orbitals of the carbon atoms of the six-member ring, as shown in **Figure 3(b)**. For such a chromium–PMDA complex, charge is transferred to the entire aromatic π system of PMDA, with significant charge located only at those PMDA atomic sites having nonzero LUMO amplitude prior to complexing with chromium. One therefore infers that the charge transferred should reside at the carbonyl oxygen atoms as well as the four carbon atoms on the central benzene ring. Such transferred charge density should be absent from the nitrogen sites. The formation of such "charge-transfer complexes" is well documented in the organometallic chemistry literature [15], but they have not heretofore been suggested to be present at the PMDA–ODA chromium interface. Calculations have been performed for one-to-one complexes involving other metal atom locations. Metal sites adjacent to the carbonyl group have been found to be relatively unstable. It is also important to note that highly coordinated sites above the five-membered rings, i.e., those rings containing the carbonyl functionality, also exhibit local energy minima and are therefore potentially stable complexing sites for chromium. We see, therefore, from the calculations described that attractive bonding sites are those for which the chromium atoms are highly coordinated relative to the polymer repeat unit.

The consequences of such bonding configurations can be established by modeling these results and comparing them with experimental core-level spectroscopy, as shown in **Figure 4**. As before, use was made of a grazing-emission-angle geometry. The first deposition of the equivalent of 0.12 Å of chromium results in a number of strong changes in the carbon 1s emission [see Figure 4(a)]. A reduction of about 50% in the carbonyl emission is observed concomitant with

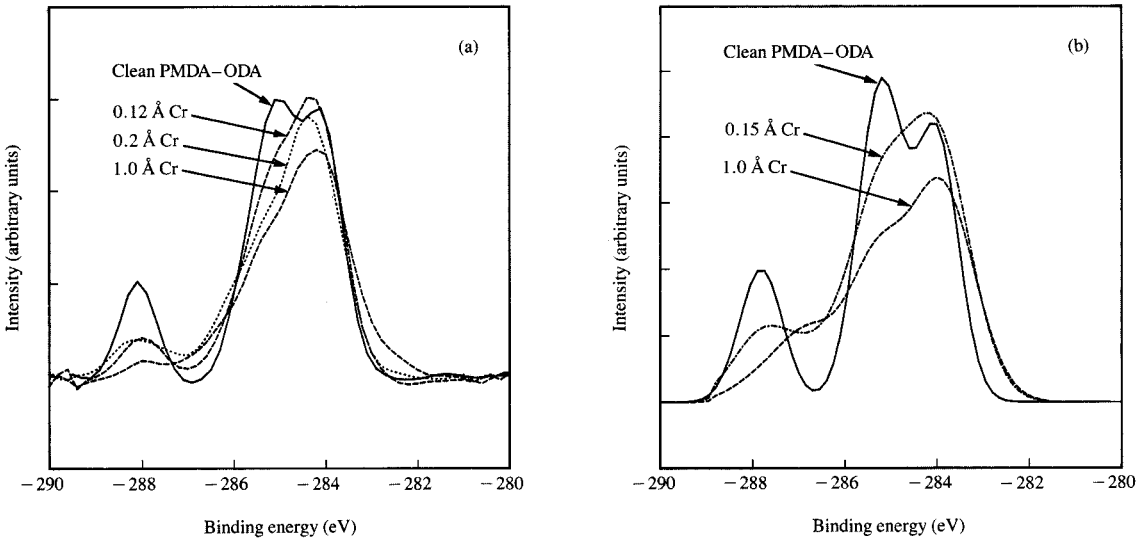

Figure 4

(a) Carbon 1s spectrum as a function of increasing chromium coverage (in equivalent layer thicknesses) on PMDA–ODA. Note that 0.3 Å corresponds to approximately one chromium atom per repeat unit. (b) Calculated carbon 1s emission as a function of coverage.

an emission increase in the valley region between the carbonyl emission and the main carbon 1s peak. Additionally, we note a shift in emission from the high-binding-energy side (−285 eV) of the main peak to lower binding energy, resulting in increased emission at −284 eV. Since we observe such sharp changes in the emission features which arise from PMDA carbon atoms, and we do not observe significant changes in the ODA emission feature at −284 eV, we conclude that initial chromium interaction occurs with the PMDA monomer. The magnitude of the carbonyl emission reduction at −288 eV has led other investigators to conclude that the metal atom initially attacks the carbonyl functionality locally and is perhaps involved in the actual cleavage of carbonyl oxygen atoms from the PMDA unit [1, 16, 17]. We had estimated that a coverage of the equivalent of 0.12 Å of chromium corresponds to approximately one chromium atom for every three repeat units. It appears, therefore, that there is an insufficient number of chromium atoms to account for the observed large changes in the carbonyl carbon 1s intensity in terms of direct attack at the carbonyl functionality or a single carbonyl oxygen-bond cleavage per chromium atom. Instead, the results suggest the presence of a significant number of carbon atoms interacting with each chromium atom. Such a picture is consistent with the interaction of individual chromium atoms with the delocalized π system of PMDA. For such interaction, charge is donated from the chromium to the aromatic PMDA monomer and, therefore, distributed among the atoms composing this monomer. The four carbonyl carbon atoms are then simultaneously affected. As previously mentioned, the calculations indicate that the most stable PMDA–chromium π arene complex consists of a chromium atom at the highly coordinated site above the central six-membered ring of PMDA. Presumably such interaction sites in the polymer will be stabilized by interactions of the chromium atom with the other adjacent ligands. The XPS shifts inferred from the formation of such a complex are consistent with experimental results.

Figure 4(b) shows a calculated XPS spectrum obtained by superposing results from unreacted as well as from reacted species. Molecular-orbital results were utilized from calculations involving chromium atoms interacting with the PMDA ligand at high-symmetry sites above the central six- and five-membered rings of the PMDA monomer. Chromium coverages were simulated with appropriate combinations of clean and chromium-covered repeat units. At 0.15 Å we note a sharp reduction of the −288-eV carbonyl peak, and a concomitant decrease in the −285-eV peak associated with the shift in intensity to −284 eV. Such a result is consistent with the experimental observations in Figure 4(a).

We have also studied the nitrogen 1s and oxygen 1s XPS spectral evolution with chromium coverage in the grazing-emission-angle geometry. As shown in **Figure 5**, nitrogen initially displays a single peak, since there is only one unique nitrogen site within the polymer. Increased coverage results

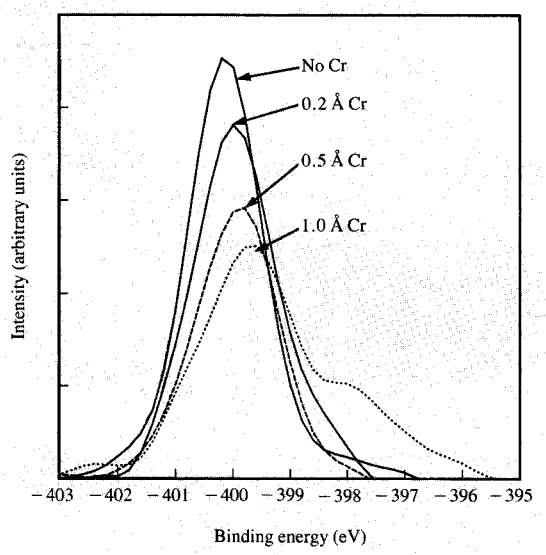

Figure 5

Nitrogen 1s spectrum as a function of increasing chromium coverage on PMDA–ODA. Note that at low coverages only small shifts to low binding energies are observed, consistent with theoretical expectations.

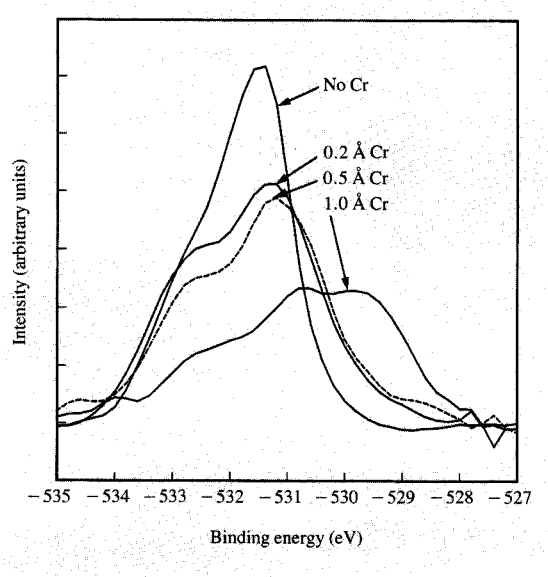

Figure 6

Oxygen 1s spectrum as a function of increasing chromium coverage on PMDA–ODA. Note that there is no shift in the high-binding-energy side of the spectrum, but there are large shifts in the low-binding-energy side associated with the carbonyl oxygens.

in only small shifts of this peak to lower binding energy. This result is consistent with zero LUMO amplitude on the nitrogen atom prior to complexing [see Figure 3(a)]. The lowest unoccupied levels involving nonvanishing orbital amplitude on the nitrogen atoms are located 6 eV above the LUMO. One therefore expects little charge from the chromium atom to be transferred to the nitrogen atom upon complexing PMDA with a chromium atom. However, a small shift is observed, since the nitrogen atoms sense charge transferred to other PMDA atoms as well as the positively charged chromium atom. The absence of any significant shift in the nitrogen 1s peak at low chromium coverages strongly substantiates the presence of a charge-transfer complex involving a PMDA subunit.

For oxygen, as previously described, the XPS (grazing-emission) spectrum (see **Figure 6**) prior to deposition is well fit with two Gaussians; the higher-binding-energy peak results from emission from the ether oxygen atom in ODA, and the lower-binding-energy peak from the carbonyl oxygen atoms in PMDA. At 0.2 Å of coverage, a clear reduction of emission at −531.5 eV from the carbonyl oxygen atoms and a resultant shift of emission to lower binding energy are observed. Concomitantly, we note no significant change in the ether oxygen emission from the ODA monomer. The position of this peak also appears to be pinned, indicating no initial interaction of chromium with the ether oxygen. These results support the conclusion that initial interaction occurs only with the PMDA monomer at low chromium coverage. The results of the molecular-orbital calculations discussed do yield shifts to lower binding energies, consistent with our experimental observations.

Higher chromium coverages have also been studied, but are more difficult to interpret, presumably due to the occurrence of metal cluster formation as well as other complicated chemistry. We have investigated some of the clustering effects by considering two chromium atoms located between two PMDA monomers whose geometrical arrangement involved the slipping of one monomer relative to the other to reflect the nonplanarity of the repeat units. Calculated energy distributions of core levels from such investigations were consistent with the peak shifts to lower binding energies that we observe in the C, N, and O spectra up to about 1 Å of coverage. While all changes in the initial regime of low metal deposition were well described by chemistry occurring only on the PMDA monomer, we observe interaction of chromium with ODA at higher (>3 Å) coverages, where we expect the metal to form a continuous overlayer, as we infer from changes in the ODA carbon atom XPS spectrum that occur at these coverages. Higher-coverage results have been discussed in detail elsewhere [14].

Chromium/PMDA–PDA interface

The replacement of oxydianiline (ODA) with phenyl dianiline (PDA) in the synthesis of the polymer results in the

polymer PMDA–PDA, shown in the upper portion of **Figure 7**. Also shown in Figure 7 is a grazing-emission spectrum as a function of increasing chromium coverage upon deposition onto the fully cured surface of a PMDA–PDA film. The thickness of the PMDA–PDA film was approximately 150 Å; it was deposited by spin-coating onto a silicon wafer covered with a native oxide. The asymmetry of the clean carbon 1s spectrum is as expected, with a greater intensity on the high-binding-energy side of the main doublet peak than was found in the PMDA–ODA case. This can be understood as reflecting the difference in the relative number of inequivalent carbon atoms for the ODA and PDA units. After deposition of the equivalent of 0.16 Å of chromium, there is a significant reduction in the intensity associated with the carbonyl carbon atoms, and a concurrent decrease in the high-binding-energy side of the doublet. This is exactly what was found in the case of chromium on PMDA–ODA, and is again best explained by a delocalized interaction involving the formation of charge-transfer complexes between chromium atoms and the PMDA part of the repeat unit. In this manner, a small amount of chromium can affect several carbonyl carbons simultaneously. As in the case of PMDA–ODA, the initial reaction is at the PMDA part of the molecule.

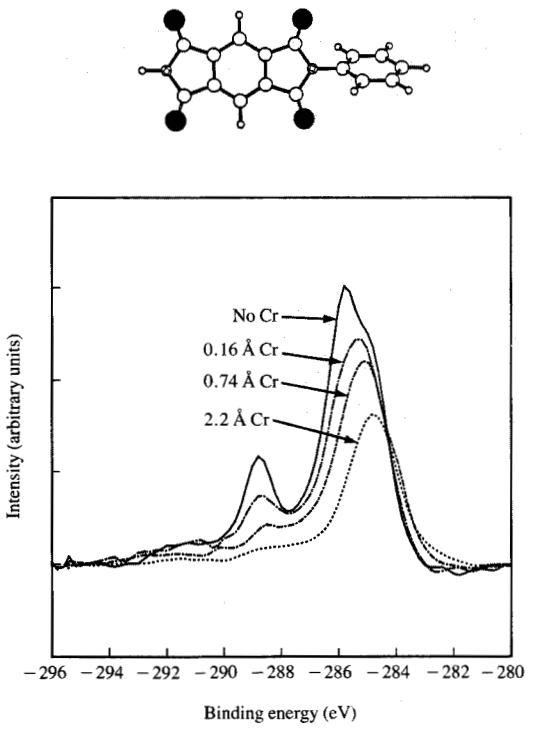

Figure 7

Upper portion: Molecular structure of the PMDA–PDA polyimide repeat unit, showing carbon atoms (○), oxygen atoms (●), nitrogen atoms (⊗), and hydrogen atoms (⊙). Lower portion: Carbon 1s spectrum as a function of increasing chromium coverage on PMDA–PDA.

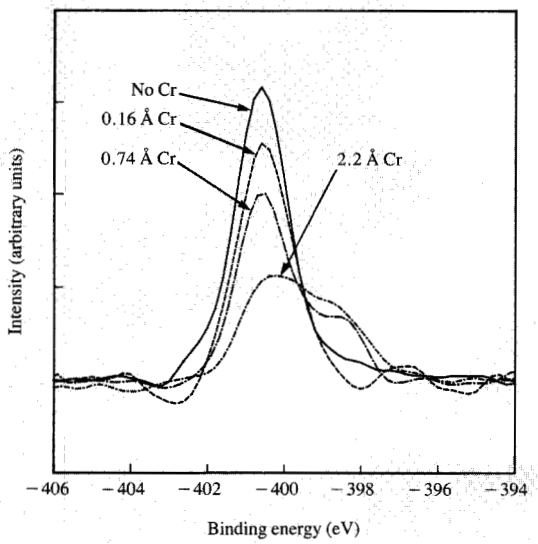

Figure 8

Nitrogen 1s spectrum as a function of increasing chromium coverage on PMDA–PDA.

One high-coverage result in connection with PMDA–PDA should be mentioned, although the details will be discussed in a forthcoming paper [18]. This concerns the coverage dependence of the binding energy shift of the carbon 1s spectrum, which yields a peak at approximately 282 eV. In the case of PMDA–ODA, we have observed that for a coverage of the equivalent of 5 Å of chromium, the peak at 282 eV is equal in intensity to the remainder of the carbon 1s intensity, which is distributed at about 284 eV. This peak at 282 eV can be attributed to the formation of charge-transfer complexes with the ODA part of the molecule [14]. On the PMDA–PDA surface, the onset of this peak has been observed to occur at about 12.5 Å, a coverage significantly greater than the onset observed for PMDA–ODA. This can be understood if the shift is a result of charge-transfer complexing with the PDA part of the repeat unit. There are about half of the interaction sites for PDA compared with a corresponding surface containing ODA; therefore, this peak would arise at about half of the coverage (~5 Å) for PMDA–ODA compared to PMDA–PDA (~12.5 Å).

Figure 8 shows a grazing-emission nitrogen 1s spectrum of PMDA–PDA as a function of chromium coverage. Note that the nitrogen peak does not shift with 0.16 Å of chromium coverage. As in the case of PMDA–ODA, our interpretation

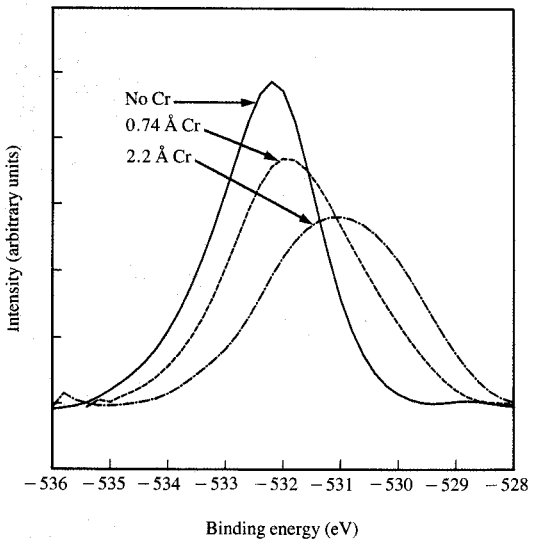

Figure 9

Oxygen 1s spectrum as a function of increasing chromium coverage on PMDA–PDA.

of complex formation is consistent with this result. At 0.74 Å we observe a new peak at a binding energy lower by 1.7 eV. The peak increases in intensity with coverage at approximately the same rate as was found for PMDA–ODA (Figure 4). Its intensity rises as the original peak falls, then begins to drop off as a new peak develops at a binding energy approximately 3.4 eV lower, indicating a smooth transition as the coverage increases.

The dependence on chromium coverage of the grazing-emission oxygen 1s spectrum of PMDA–PDA is shown in **Figure 9**. Here, interpretation of the data should be simpler than for the case of PMDA–ODA, due to the absence of the ether oxygen. In the oxygen 1s spectra for PMDA–ODA, one must attempt to separate the reaction of the ether oxygen peak from that of the carbonyl oxygen peak. Upon initial deposition of chromium (0.2 Å up to 0.5 Å) onto PMDA–ODA, the ether oxygen peak appeared to be pinned and only lost intensity, while the carbonyl peak shifted and broadened to lower binding energy (see Figure 6). In that case, a distinct shoulder begins to develop at a binding energy of about 1.8 to 2 eV below that of the unreacted peak at chromium coverages of 0.5 Å to 1.0 Å. In contrast, the clean oxygen 1s peak for PMDA–PDA in Figure 9 is nearly symmetric, with only a slight asymmetry to higher binding energy, consistent with emission only from carbonyl oxygens at the surface. Initial deposition of chromium broadens the peak and skews it to lower binding energy, so that after 2.2 Å of coverage, the centroid has shifted down by 1.2 eV, with significant asymmetry to the low-binding-energy side. This trend continues with subsequent coverages (not shown); at 11 Å the shift finally reaches about 1.9–2.0 eV, as observed for PMDA–ODA at considerably less chromium coverage.

Discussion

In this paper we have applied the results of quantum chemical calculations to interpret the XPS spectra observed during formation of the chromium/PMDA–ODA polyimide interface as well as the chromium/PMDA–PDA polyimide interface. We have pointed out that although direct local interactions between the chromium atom and the oxygen atoms of the carbonyl functional groups have been previously proposed, calculations indicate that such interactions are not energetically favorable. A major point of the present paper is to emphasize that the assumption concerning the occurrence of "strong chemistry" in the vicinity of the carbonyl functionality during the initial stages of deposition is not a conclusion one need necessarily draw from careful examination of the data. We have shown that the creation of an arene-metal π complex yields results that are consistent with the XPS observations at low chromium coverage. Furthermore, it should be recognized that the formation of such π complexes, during the initial stages of interface growth, is consistent with the large body of observations of metal-atom organic-ligand chemistry. It has been pointed out, for example, by Timms [19] that "the coordination of pi-acceptor ligands to metal atoms is a process of much lower activation energy than oxidative addition. . . ." This is also consistent with the observations of chromium arene complexing with polysiloxanes near room temperature [20].

One important result of the chromium/PMDA–ODA interaction not discussed, since it was observed at high coverages, involves the increased shifting of emission intensity into a new peak at −282 eV [14]. A "handbook" assignment would suggest that this peak is due to formation of "carbides." Calculations we have performed suggest that such shifts can arise from the complexing of chromium atoms with the aromatic rings of the ODA part of the repeat unit. In particular, calculations for chromium positioned 1.6 Å above the phenyl rings of ODA were carried out, and it was found that complexing configurations of this type can yield a 2.0-eV shift to lower binding energy for those carbon atoms not bonded to the ether oxygen or nitrogen atoms, i.e., the carbon atoms with the smallest magnitudes of core-level bonding energies prior to complexing. Changes in the features of associated nitrogen 1s and oxygen 1s spectra are also consistent with the formation of such chromium–ODA complexes. While the details of these results will be discussed elsewhere, it should be emphasized that the lowest carbon 1s binding energy feature at −282 eV observed at high coverages is not inconsistent with the formation of chromium arene complexes involving the ODA unit.

The study of PMDA–PDA was designed to yield a simpler interpretation than PMDA–ODA by eliminating the ether oxygen linkage of the phenyl rings of ODA. Although more carbonyls per unit surface area are available for chromium attack, there is no evidence that chromium chemically interacts with the carbonyl functionality locally or is involved in cleavage of the carbonyl oxygen atoms of PMDA. Instead, the observed results reveal that the overall reaction of chromium with the carbon, oxygen, and nitrogen atoms of the PMDA unit is consistent with the interpretation based on formation of the arene-metal π complex, as for the case of PMDA–ODA.

Finally, it is important to note that while many of the aspects of the interface bonding of chromium we have discussed might be generalized to other systems, the details may be significantly different for other metals. In particular, we have studied the interaction of copper with PMDA–ODA [2, 3, 21]. Since copper has a full complement of d-electrons, its interaction with the polymer is expected to be weaker. Results of initial depositions of copper, however, also suggest a nonlocal interaction with the polymer, in a fashion similar to chromium. The chemistry is considerably weaker, since no more changes in the XPS spectrum were observed after a coverage of several tenths of an angstrom. Coverages of up to 5–10 Å produced no further changes. Aside from the interaction strength, however, there are striking similarities. We note that for both copper and chromium the initial interaction is with the PMDA part of the repeat unit. Sites involving this molecular unit, therefore, provide attractive binding locations for copper as well. Consistent with the observed magnitudes of the spectroscopic shifts, results from TEM as well as from other measurements [21] lead one to conclude that the binding of copper to the PMDA unit is significantly weaker than the binding of chromium to this unit. Similarity in the details of the XPS shifts for these two metals, however, suggests that for copper, as for chromium, the ligand LUMO is involved in some essential manner. For chromium, the partially filled d-levels are actively involved in bonding with the polyimide LUMOs. In contrast, the filled copper d-levels are 2 eV below the s-state and interact, therefore, more weakly with the LUMO of PMDA. This results in weaker bonding and less charge transfer. This difference must play a key role in the strength of the chemical interaction of these two metals with the polymer. Although the details of the metal-atom chemistry may differ between different systems, the delocalized distribution of charge on the polymeric backbone might represent a common ingredient with important consequences for the formation of metal–polymer interfaces.

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