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ALUMINIUM/POLYIMIDE ADHESION

M. M. D. RAMOS[1]†, A. M. STONEHAM[2] and A. P. SUTTON[1]

[1]Department of Materials, University of Oxford, Oxford, OX1 3PH and [2]AEA Industrial Technology, Harwell Laboratory, Oxfordshire OX11 0RA, England

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Abstract—We present a theoretical study of the interactions between isolated aluminium atoms and a polyimide surface and between polyimide and aluminium surface. The effect of surface modification on adhesion is also discussed. Self-consistent geometry optimization and molecular orbital calculations have been carried out within CNDO approximation in a cluster model framework. Our results suggest that aluminium atoms react preferentially with five and six-fold rings of polyimide when those chemical groups are present on the surface. The compound formation is accompanied by charge transfer from the metal atoms to polyimide and charge rearrangement among the polyimide atoms. Madelung potential calculations also suggest considerable core level shifts at polyimide atoms far from the reaction site. The adhesion of polyimide to aluminium surface is predicted to be somewhat weaker than that of aluminium to polyimide.

1. INTRODUCTION

Much remains to be learned concerning the properties even of the technologically important polymers like polyimides. The thermal and chemical stability, low dielectric constant, high electrical resistivity and relative ease of processing into coatings and films have made polyimide an ideally suitable polymer for microelectronic applications such as dielectric spacing layers, protective coatings and substrates for thin metal films [1].

In all these and other applications good adhesion is required between polyimide and a metal substrate and between individual metal atoms and a polyimide substrate. The continued growth of polyimides as insulators has motivated a large number of experimental studies concerning adhesion. The results available are mainly provided by two types of experiments. The first type concerns the adhesion tests such as pull-off, peel, scratch and stretch deformation tests. The second class uses surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and high resolution electron energy loss spectroscopy (HREELS), in trying to identify the nature of the interfacial bonding.

The mechanisms responsible for the adhesion are often not properly understood. One component of adhesion is, of course, the chemical bonding between the organic molecule and the metal. However, the work of adhesion is often dominated by the energy required to break the many weak bonds between polymer molecules as the polymer is pulled away from the metal. Therefore, as de Gennes [2] pointed out, the actual adhesive fracture energies can be two to three orders of magnitude larger than those expected from metal–polymer bonds alone. Using a stretch deformation method, Ho and Faupel [3] have been able to extract adhesion energy values from their experiments. They found that the adhesive energy is only 4% of the total energy input for a complete delamination. This result is consistent with de Gennes' observations.

The interfacial bonding and consequent adhesion are directly influenced by the way in which the interface is formed. A better understanding of the chemical interactions at metal/polyimide interfaces and their consequences for the adhesion has the potential to yield significant progress in the field of adhesion between metals and polymers, with broader technological implications, e.g. in metal-filled polymer composites [4]. Atomistic modelling of interface formation can add to the understanding of adhesion mechanisms and may suggest new methods for controlling or optimizing adhesion.

The aim of this work is to achieve a better understanding of metal–polyimide interfacial properties such as chemical bonding and charge transfer, and assess the consequences for relating the core level shifts to reaction site. We report here a self-consistent calculation of the interaction of aluminium atoms with a polyimide fragment and of polyimide with an aluminium surface. The information that may be gained on the relative reactivities of different functional groups of polyimide should provide qualitative information on the preferential sites for reaction. The possibility of enhanced-adhesion by surface modification is also discussed.

2. METHOD OF CALCULATION

We have performed a simultaneous self-consistent calculation of both electronic structure and molecular

†Present address: Department of Physics, University of Minho, 4719 BRAGA Codex, Portugal.

geometry of adsorbate–substrate system, using a modified version of the CHEMOS Code [5, 6]. The molecular orbital calculations were performed at the CNDO (Complete Neglect of Differential Overlap) level, using a linear combination of atomic orbitals and a cluster model framework. A molecular dynamical method was used in parallel to perform self-consistent geometry optimization.

In the calculations reported here, we have used two sets of CNDO parameters (electronegativity, bonding parameter and Slater orbital exponent for valence orbitals). The first set consists of the parameters selected by Pople and Beveridge [7] to give the best overall fit to minimal basis set *ab initio* calculations (Table 1).

The bonding parameters are calculated using the approximation

$$\beta_{AB} = \frac{K_{AB}}{2}(\beta_A + \beta_B) \quad (1)$$

where the additional constant K_{AB} is chosen to be 0.75 if either of the atoms is from the third row of the Periodic Table and unity otherwise. Preliminary calculations using Pople and Beveridge parameters suggest serious overestimates of the magnitudes of binding energies. Some improvement can be achieved by using CNDO parameters determined by calibration with experimental data. CNDO parameters obtained from experimental results will allow one to take account of the interactions neglected by Hartree–Fock theory (e.g. correlation terms). The present approach is to use the values of Table 1 for electronegativities and orbital exponents and to choose bonding parameters empirically to reproduce the experimental values for the binding energy of diatomic molecules. The validity of this approach depends on the similarity of bonding in small and large systems. The reparametrization procedure followed comprises two steps. First, we determine the parameter β_X [equation (1)] by calibration with the diatomic molecule X_2. Secondly, we determine K_{XY} by considering the diatomic molecule XY (or X_mY_n with m and n small, if the diatomic molecule does not exist). The results are given in Table 2. We should note that the CNDO parameters are fixed in advance from a general approach, and not regarded as adjustable parameters.

Table 1. CNDO parameters from Pople and Beveridge [7]

Element	Electronegativity (eV) I_s	I_p	I_d	Bonding parameter β_{spd} (eV)	Orbital exponent ζ_{spd} (a.u.$^{-1}$)
H	7.176	—	—	−9.0	1.200
C	14.051	5.572	—	−21.0	1.625
N	19.316	7.275	—	−25.0	1.950
O	25.390	9.111	—	−31.0	2.275
Al	7.771	2.995	0.224	−11.3	1.167

Table 2. CNDO bonding parameters fitted to experimental binding energies of small molecules

Element	Basis set	β_{spd}	Molecule	K_{AB}
H	sp	−8.55	—	—
C	sp	−13.70	CH	0.92
N	sp	−18.40	NH	0.97
			CN	1.02
O	sp	−22.50	OH	1.10
			NO	0.99
			CO	1.14
Al	sp	−5.89	AlH	1.05
			Al_2C_2	1.10
			AlN	1.34
			AlO	1.18
	spd	−4.60	AlH	0.98
			Al_2C_2	0.93
			AlN	1.00
			AlO	1.18

3. RESULTS AND DISCUSSION

3.1. Starting configuration

Scanning tunnelling microscopy [8, 9] studies of PMDA-ODA polyimide suggest that the polymer chains have the zig-zag form, with the PMDA part lying nearly parallel to the substrate surface. Moreover, X-ray absorption spectra for PMDA-ODA deposited on graphite [10] indicate that the imide and phenyl rings are co-planar and adsorbed parallel to the substrate surface. A theoretical study of the ultraviolet absorption spectrum for PMDA-ODA [11] also suggests that the pyromellitimide group and its adjacent phenyl rings are coplanar, although a torsional angle between these two groups was taken to be 30 deg due to steric considerations. In order to determine the torsional angle between the PMDA moiety and its adjacent phenyl rings, we have decided to investigate the preferential conformation of polyimide.

Before any dynamic simulation of internal rotation, the system is fully relaxed. The rotation is then simulated by non-damped molecular dynamics using full self-consistent forces at each time-step. In dealing with the rotation around the imide–phenyl bond of polyimide, the atoms placed at one side of that bond are rotated clockwise whilst the other atoms are rotated counter-clockwise. Thus, in addition to the quantum-mechanical force, each atom is subjected to an external force tangential to the circular path. This procedure allows one to perform dynamical rotation with simultaneous geometry optimization. Tangential forces are varied at each time-step to keep a nearly constant angular velocity. Angular velocities of the order of 0.05 deg per time-step are used.

Following the procedure described above, we calculated the potential energy surface for eclipsed and staggered rotation of both phenyl groups of PMDA-ODA polyimide. We have focused our calculations on the monomer-like unit of PMDA-ODA polyimide depicted in Fig. 1, with hydrogens saturating the dangling bonds. Figure 2 shows the energy profile for eclipsed rotation of phenyl groups about the imide–phenyl bonds. A similar energy surface was found for staggered rotation. Our results show

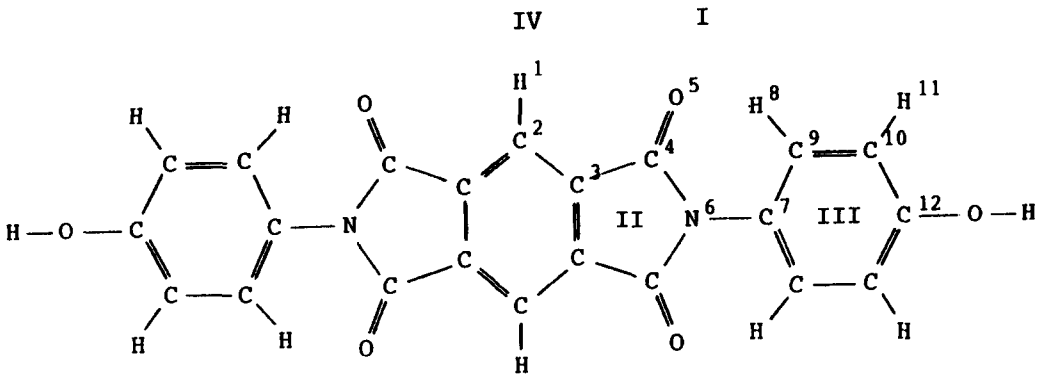

Fig. 1. Schematic diagram of PMDA-ODA cluster model used in the calculations reported here, showing the torsional barriers studied. Some atoms are numbered for easier identification. The roman numbers represent different adsorption position of metal atoms.

negligible difference between whether or not both phenyl groups remain on the same plane as each other (eclipsed conformation) or adopt the staggered configuration. As can be seen from Fig. 2, an orthogonal form of polyimide corresponds to the highest maximum. Moreover, a second maximum energy of 0.003 eV was found for the planar conformation. This small energy barrier is probably due to steric hindrance between the oxygen of the PMDA part and the ortho-hydrogen of the phenyl groups. If the magnitude of the barriers were correct we would expect the smaller barrier to be easily overcome at room temperature leading to an oscillation of both phenyl groups between energy minima. This conclusion still holds even if the barrier height were twice as large. These results suggest a nearly planar conformation for polyimide. Since the conformational behaviour of soft materials is strongly dependent on the environment, polyimide could adopt a somewhat different conformation depending on the processing method used.

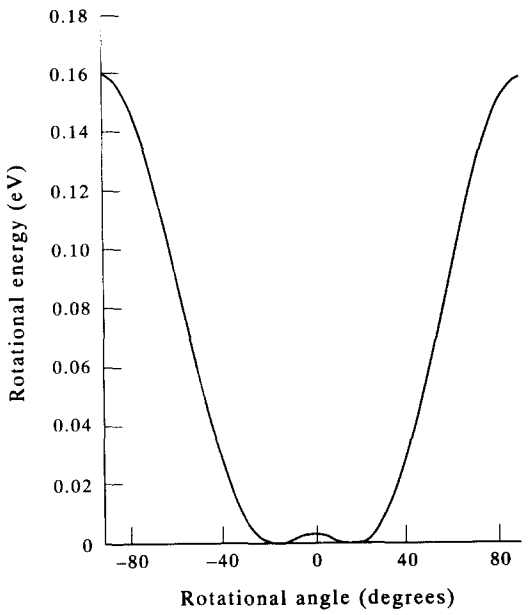

Fig. 2. Potential energy surface for eclipsed rotation of both phenyl groups of polyimide about imide–phenyl bond represented in Fig. 1. When the rotational angle is zero, the molecule is planar.

3.2. Free polyimide molecule

Before any interaction of PMDA-ODA with metal atoms is considered we have relaxed the cluster geometry to equilibrium, starting from the planar configuration. The distance between ether oxygens was found to be 18.0 Å, with chain width 5.1 Å. The oxygen–oxygen distance we found is close to the 15–20 Å between oxygen atoms at successive chain bends obtained from the STM image [9]. According to X-ray diffraction analysis of highly oriented polyimide fibers and films, the length of each segment unit is 18.0 Å [12]. Bond lengths and bond angles of the PMDA-ODA cluster are given in Table 3, where the calculated results are compared with the experimental ones [13]. The polyimide geometry predicted by CNDO compares well with the experimental data reported.

3.3. Metal atoms on polyimide

In order to study the interaction of metal atoms with a polyimide surface we have simulated the bonding of Al atoms with specific groups of PMDA-ODA fragment, as indicated in Fig. 1. In addition, we have considered the simultaneous reaction of two metal atoms at equivalent sites (rather than a single metal atom) within the polyimide in accordance with

Table 3. Bond lengths and bond angles of polyimide

	Bond lengths (Å)			Bond angles (degrees)	
Bond	Calc.	Exp. [13]	Angle	Calc.	Exp. [13]
C2-H1	1.116	1.08	C-C2-C3	117.6	117.0
C2-C3	1.388	1.396	C4-C3-C17	106.9	108.5
C3-C17	1.413	1.413	C3-C4-N6	109.2	105.9
C3-C4	1.457	1.480	N6-C4-O5	122.7	124.3
C4-O5	1.272	1.203	C4-N6-C18	107.7	111.2
C4-N6	1.398	1.414	C9-C7-C21	117.9	120.0
N6-C7	1.409	1.428			
C7-C9	1.395	1.395			
C9-H8	1.118	1.08			
C12-O13	1.353	1.390			

low coverage experiments. The interactions of metal atoms with polyimide was modelled in the following way. Two metal atoms were brought close to the polyimide at the two reaction sites, while the polyimide atoms were kept frozen. When equilibrium was reached for the metal atoms, the entire system was allowed to relax.

3.3.1. Adhesion energy. Adhesion energies for each adsorption position are given in Fig. 3. These results show two important features. First, the reparametrization gives lower magnitude of adhesion energy although the trends are similar. Secondly, our results suggest that metal atoms react preferentially with five and six-fold rings (sites II and III respectively). Other metals such as Cr, Ni and Cu also show similar general trends for preferential reaction sites. Since the adhesion energies are strongly dependent on the CNDO parameters set used, the absolute value of the calculated adhesion energies may not be correct for these transition metals. However, we expect the predicted trends for their preferred reaction sites to be reliable.

3.3.2. Aluminium-induced changes in atomic charges. The changes in the atomic charge of polyimide atoms due to the interaction of the Al atoms with the polyimide are given in Fig. 4. The changes in the atomic charges of Al atoms for each adsorption position is shown in Fig. 5. These results show three main features. First, charge transfer from aluminium to polyimide is predicted for all reaction sites, using the reparametrized CNDO method. These results are in agreement with considerations based on electronegativity differences. Charge transfer in the opposite direction is predicted for the reaction of Al atoms with the six-fold rings (site III) when Pople and Beveridge [7] parameters are used, which may reflect the use of incorrect parametrization. Secondly, our results suggest that charge transfer is not a necessary pre-requisite for compound formation. Thirdly, even when no explicit covalent bonds form in the interaction between the Al atoms and the polyimide, the metal still induces charge rearrangements among the polyimide atoms. The presence of a conjugated system leads to charge delocalization. As a result, charge rearrangement is induced far from the reaction site. We should note that the calculated atomic charges are strongly dependent on the basis of atomic orbitals used to construct the wave function and, therefore, should not be regarded as an accurate description of the electron distribution. However, they provide some understanding of the changes in the electron distribution that accompany metal–polyimide bond formation.

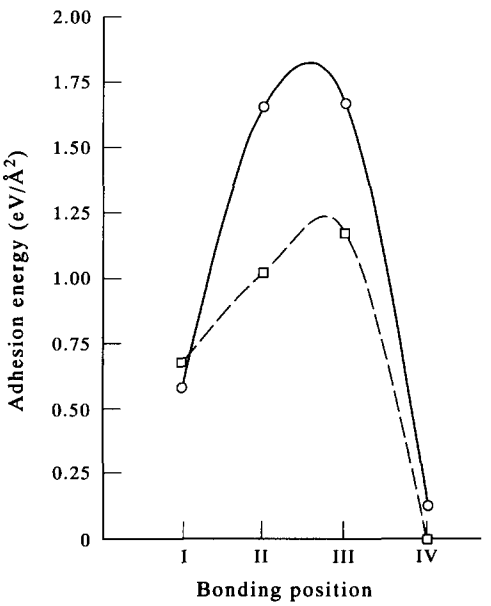

Fig. 3. Adhesion energy of aluminium corresponding to the adsorption positions indicated in Fig. 1: (a) using Pople and Beveridge [7] CNDO parameters (circle), (b) using reparametrized CNDO (square). The curves are simply a gudie to the eye.

3.3.3. Core level shifts. In order to investigate how adsorption position might affect the XPS spectra, we have estimated the changes in core level binding energies of carbon, oxygen and nitrogen atoms due to the interaction of aluminium atoms with the polyimide. Using the point-charge potential method [14], the binding energy of an electron in a core orbital as seen by XPS can be expressed by

$$E_i = E_i^\circ + kq_i + \sum_{j \neq i} \frac{q_j}{R_{ij}} \qquad (2)$$

The reference binding energy E_i° and the constant k are determined from the graph of experimental binding energies versus calculated Mulliken charges for the series of related compounds given by Steiner [15]. The values obtained are given in Table 4.

According to the model above changes in the electronic population of one atom and its neighbours yield core level shifts. Figure 6 shows the core level shifts due to the interaction of aluminium atoms with polyimide. Our results reveal considerable core level shifts for atoms far from the metal adsorption site. These results show that changes in core level binding energy of a specific group of atoms cannot always be associated with metal reaction at that site. Rossi *et al.* [16] calculation for Cr deposited on PMDA-ODA also reveals that core level shifts are more sensitive to the amount of charge transfer than to a specific reaction site. For this reason reaction models based exclusively on XPS data should be treated with caution.

4. POLYIMIDE ON METAL SURFACE

We have simulated the interaction between polyimide and metal surface by considering the adsorption of PMDA-ODA fragment nearly parallel to a Al(100) surface (represented by a cluster of 16 atoms). The chemical interaction between the functional groups of polyimide and the metal surface leads to a distortion of the molecular fragment (Fig. 7).

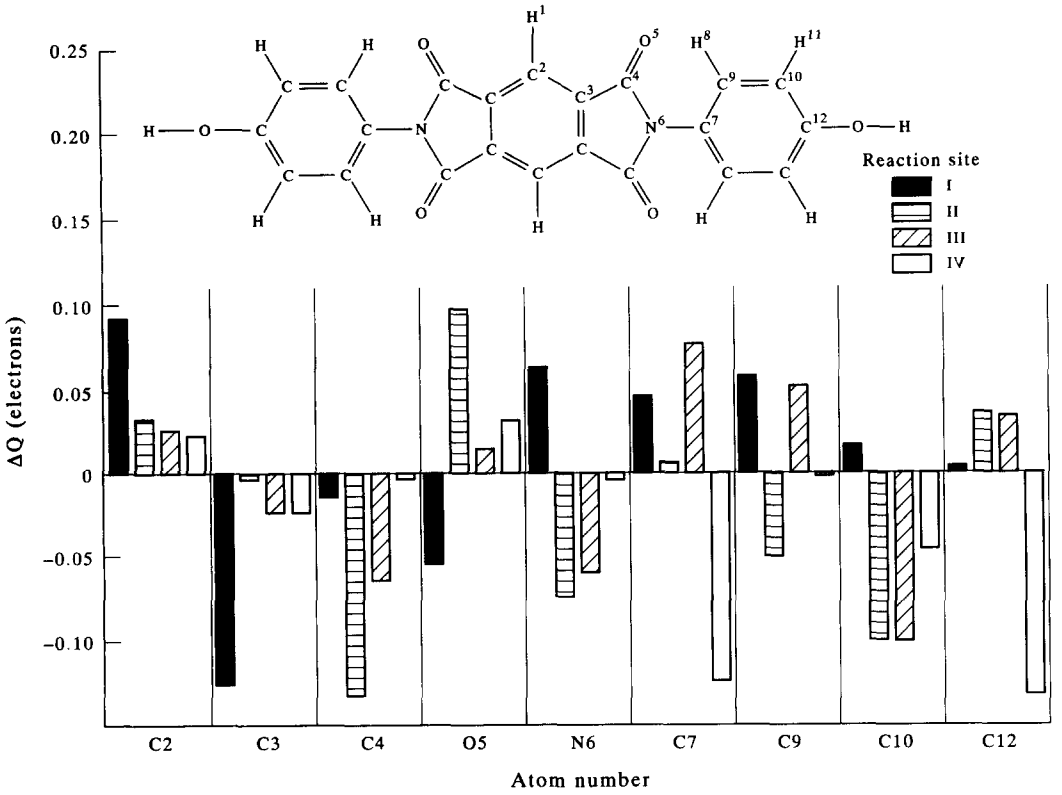

Fig. 4. Change in atomic charges for selected atoms of PMDA-ODA fragment when Al atoms are adsorbed at positions indicated in Fig. 1.

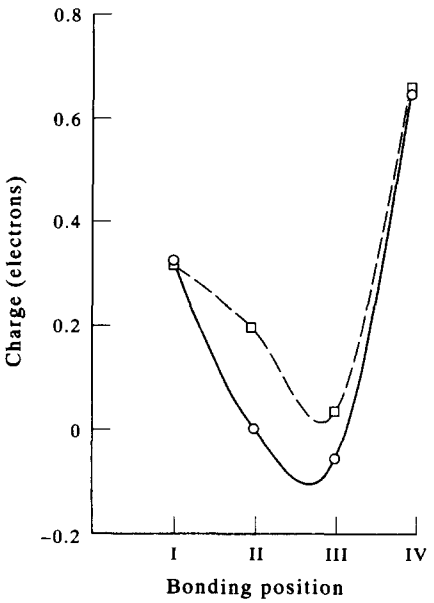

Fig. 5. Atomic charge of aluminium atoms adsorbed on PMDA-ODA fragment at positions indicated in Fig. 1: (a) using Pople and Beveridge [7] CNDO parameters (circle), (b) using reparametrized CNDO (square). The curves are simply a guide to the eye.

The reaction of polyimide with an Al(100) surface leads to a negligible charge transfer (0.002 electrons) from polyimide to metal surface. A value of 0.4 eV/Å^2 was predicted for the adhesion energy, which is much lower than those obtained for adhesion of aluminium atoms on polyimide. The adhesion of aluminium to polyimide surface depends on the number of strong metal–polyimide bonds formed at the interface and could be lower or greater than the adhesion of polyimide to aluminium surfaces. In contrast to aluminium, the adsorption of polyimide parallel to Ni(100) surface leads to greater charge transfer (1.6 electrons) from polyimide to metal surface, though showing a similar molecular distortion.

Our discussion of the adhesion of an isolated polyimide molecule corresponds to submonolayer coverage. We have not investigated the important

Table 4. Parameters for point-charge potential method

Element	k (eV)	E_i° (eV)
Carbon	10.6	292.7
Nitrogen	20.7	419.3
Oxygen	10.7	543.3

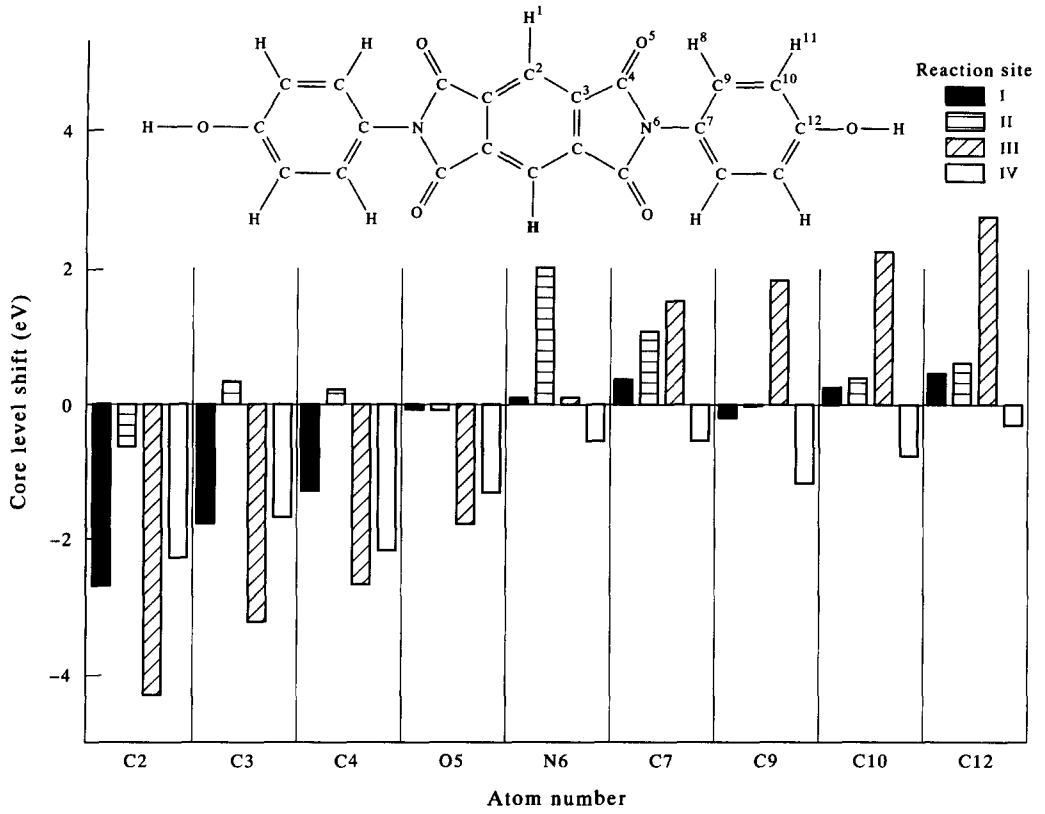

Fig. 6. Core level binding energy shift of selected polyimide atoms induced by the adsorption of Al atoms at positions indicated in Fig. 1.

case of higher coverage, when the substrate is covered with bulk polymer. Clearly, interactions between molecules will affect their conformation. The discussions of [2, 3] suggest that individual interactions between molecules are significantly smaller than the strong metal-polymer binding we find, so it seems likely that the qualitative features we obtain hold for higher coverage. This needs further investigation, especially as there are grazing-incidence X-ray diffraction data showing near-surface ordering [17]. An extension to the bulk case would need to exploit simpler methods too, e.g. molecular mechanics with Lennard–Jones potentials (as in the recent study of polyimide crystal structures [18]). Such simpler calculations can be readily incorporated with our present method, so using molecular dynamics in which the interaction with the metal is treated by self-consistent chemistry but treating interpolymer interactions by interatomic potentials.

5. MODIFICATION OF POLYIMIDE

Surface modification studies of polyimides [19–21] indicate the formation of carbon radicals due to carbonyl oxygen losses. These radicals can then react with each other resulting in crosslink formation among the polyimide chains. These crosslinks will lead to an increase of the surface area which provides additional bonding sites and, moreover, it can produce an enhancement of the surface mechanical strength. The evaporated metal atoms will then react with unmodified parts of polyimide as well as with available free radicals.

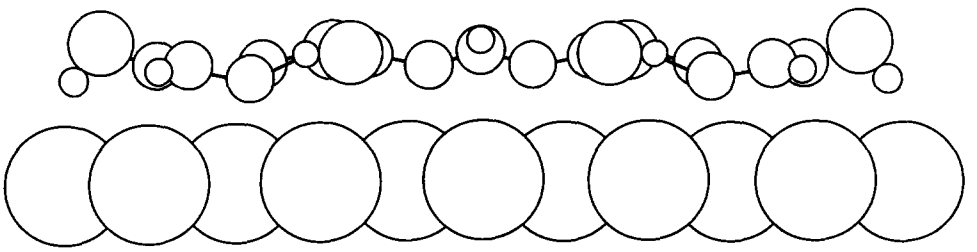

Fig. 7. Side view of the optimized molecular structure of PMDA-ODA fragment deposited on Al(100) surface.

We have addressed the effect of surface modification on adhesion by studying the formation of (1) an aluminium–polyimide radical bond at the carbonyl carbon site and (2) a carbon–carbon bond between two chains. We predict a value of 0.2 eV/Å^2 for the binding energy of a crosslink between two polyimide chains (represented by their PMDA part) at the carbonyl carbon site. The reaction of aluminium atoms with polyimide radicals gives a predicted adhesion energy of 1.4 eV/Å^2.

Based on our results, we suggest that the observed enhancement in the peel strength due to surface modification probably results from the formation of a large number of weak crosslinks within the polymer before metal deposition and from a few strong metal–polyimide bonds. A simultaneous break of both bond types will lead to an increased peel strength. Moreover, surface morphology changes may also contribute to the enhanced peel strength observed, since the textures formed are likely to provide bonding surfaces out of the horizontal plane. In addition, the removal of surface contaminants should also improve adhesion, though this question will not be addressed here.

6. CONCLUSIONS

We have studied the effects of chemical bonding on the adhesion of both aluminium atoms on polyimide surface and polyimide deposited on Al(100) surface. Our results suggest that metal atoms react preferentially with five and six-fold rings of polyimide when those chemical groups are accessible on the surface. Moreover, the metal induces charge rearrangements among the polyimide atoms which lend to core level shifts far from the reaction site. Therefore, one needs to be cautious in interpreting XPS spectra since the correlation of core level shifts with reaction sites is not straightforward. The adhesion of polyimide to aluminium surface is predicted to be somewhat weaker than that of aluminium to polyimide. We believe that the different adhesion behaviour observed experimentally (e.g. surface modification enhanced-adhesion) might be related to the number of bonds needed to be broken in the fracture process rather than the formation of strong metal–polyimide bonds. The experimental observation of the fracture surface within polyimide [22] supports this view.

Whilst we should not regard CNDO binding and adhesion energies as especially accurate, we can have more confidence in the trends and in the molecular geometries predicted. Geometry-optimized molecular orbital calculations, such as those reported here, are a useful tool for microscopic understanding of chemical bonding at metal–polymer interfaces as well as for providing data which is currently impossible to obtain experimentally.

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