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THEORETICAL STUDY OF METAL-POLYIMIDE INTERFACIAL PROPERTIES.

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Abstract

The aim of this work is to achieve a better understanding of metal-polyimide interfacial properties, such as bonding strength between two materials and charge transfer, and assess the consequences for adhesion. The effect of surface modification on adhesion is also discussed. These interfacial studies of PMDA-ODA polyimide with evaporated chromium (Cr), copper (Cu) and nickel (Ni) atoms have been performed using a self-consistent molecular dynamics method with semi-empirical quantum chemistry at the CNDO (Complete Neglect of Differential Overlap) level. All metals were predicted to bond strongly at six-fold rings of polyimide. Despite actual charge transfer between metal atoms and polyimide is small, the bond formation induces charge rearrangement among the polyimide atoms far from the reaction site. The adhesion of polymide to a Ni(100) surface is predicted to be somewhat weaker than that of nickel atoms to polyimide at six-fold sites.

1. Introduction

With an increase of the use of polymers in the microelectronic industry, a microscopic understanding of the mechanism responsible for adhesion between metals and polymers has become of increasing importance. Among the polymers suitable for microelectronic applications, polyimides (PI) have received increased attention due to their thermal and chemical stability, low dielectric constant, high electrical resistivity and relative ease of processing into coatings and films [1]. For all these reasons, polyimides have been widely used in microelectronics as dielectric spacing layers, protective coatings and substrates for metal thin films, replacing traditional inorganic insulators such as SiO_2 in many applications.

In these and other applications good adhesion between polyimide and a metal substrate and between individual metal atoms and a polyimide substrate is required. The mechanism responsible for the adhesion is often not well understood, though chemical bonding at interface is believed to play an important role in adhesion. The interfacial bonding and consequently adhesion are directly influenced by the way in which the interface is formed. Therefore, variations in the preparation of polymers or metal substrates can lead to polyimide/metal interfaces with different adhesive strength. 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. As in other areas, atomistic modelling can play an important role in understanding the nature of bond formation between metals and polyimide.

Since chemical interaction at interface formation leads to the distortion of flexible polymers, it is essential to perform a simultaneous self-consistent calculation of both electronic structure and molecular geometry of the entire absorbate-substrate system.

In order to achieve a better understanding of interfacial properties, such as chemical bonding and charge transfer, we will investigate the interaction of Cr, Cu and Ni atoms with a polyimide fragment as well as polyimide deposited on Ni(100) surface, using a self-consistent quantum chemistry molecular dynamics method. Since polyimide contains a large variety of chemical functions (e.g. benzene rings, ether linkages (C-O-C), carbonyl groups (C=O) and C-N functions) common to other polymers, it is therefore suitable as a model system to study the nature of bond formation at other metal/polymer interfaces. 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 metal-polyimide enhanced-adhesion suggested by the experiments, as a result of polymer surface modification, is also discussed.

2. Method of calculation

The approach we adopt, based on the modified version of the CHEMOS code [2] which extends the original code to transition metals up to copper, combines self-consistent quantum chemistry and molecular dynamics. The quantum chemistry calculations were performed at CNDO (Complete Neglect of Differential Overlap) level using a linear combination of atomic orbitals (LCAO) and a cluster model framework. Molecular dynamics simulations of adsorbate-substrate cluster are performed simultaneously using interatomic forces evaluated from self-consistent electronic calculations.

In the calculations reported here, we have used the set of CNDO parameters from Pople and Beveridge [3], for the elements with only s and p electrons, and the set of parameters given in Table 1, for transition metals. Both sets of CNDO parameters selected leads to convergent open-shell electronic structure calculations. We should note that the CNDO parameters are fixed in advanced, and are not regarded as adjustable parameters.

3. Results and discussion

3.1. Starting geometry

Scanning Tunnelling Microscopy studies of PMDA-ODA polyimide [4, 5] suggest that the polymer chains have the zig-zag form, with the pyromellitimide group lying nearly parallel to the substrate surface. Moreover, X-ray absorption spectra for PMDA-ODA deposited on graphite [6] indicate that the imide and phenyl rings are co-planar and adsorbed parallel to the substrate surface. In modelling both the interactions of metal atoms with polyimide surface and of polyimide with metal surface, we have considered only the specific PMDA-ODA cluster depicted in Figure 1, with hydrogens saturating the dangling bonds.

3.2. Free polyimide molecule

Before any interaction of PMDA-ODA with metal atoms we have relaxed the cluster geometry to equilibrium, starting off with the planar configuration. The oxygen-oxygen distance was found to be 18.0 Å. This distance is close to the length of each segment unit obtained from X-ray diffraction analysis of highly oriented polyimide fibres and films [7]. The calculated bond lengths and bond angles of the PMDA-ODA cluster are given elsewhere [8]. The PMDA-ODA geometry predicted 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 Cr, Cu and Ni atoms with specific groups of PMDA-ODA fragment, as indicated in Figure 1.

In addition, to ensure all adsorbate/substrate systems have an even number of electrons, we have considered the simultaneous reaction of two metal atoms at equivalent sites (rather than a single metal atom) within the polyimide. The interactions of metal atoms with polyimide were 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.

The chemical interaction between transition metals and polyimide leads to a distortion of the polymer fragment both parallel and perpendicular to the molecular plane. Molecular distortion was also predicted for the adsorption of two aluminium atoms on polyimide and trans-polyacetylene [8, 9, 10].

3.3.1. Adhesion energy

Adhesion energies for each adsorption position are given in Figure 2. These results show two important features. First, there is strong adhesion, especially of Cu, with Cr weaker and Ni weakest. Secondly, our results suggest that metal atoms react preferentially with five and six-fold rings (sites II and III respectively). A comparison with experimental data available for Cr and Cu indicates that the calculated adhesion energies for these metals are seriously overestimated [11]. In contrast to experiments that suggest Cr more strongly bound than Cu, our results indicate the opposite. However, their general trends for preferential reaction sites are similar. Since the adhesion energies are strongly dependent on the CNDO parameters set used, any attempt to compare adhesion of different metals to polyimide would be unreliable. Despite the fact that the absolute value of calculated adhesion energies may not be correct, we expect the predicted trends for preferential reaction sites to be reliable.

3.3.2. Metal-induced charge transfer

The chemical interaction between metals atoms and the polyimide fragment leads to charge transfer from or to polyimide, shifting one-orbital energies until the Fermi level of both materials is in coincidence. Table 2 shows the Mulliken charges stored in two metal atoms adsorbed on polyimide for each adsorption position. The interaction of all metal atoms with five and six-fold rings (site II and III respectively) gives rise to charge transfer from polyimide to the deposited metal. The changes in the atomic charge of polyimide atoms due to the interaction of transition metal atoms with polyimide are predicted. The same effect was predicted for metals with only s and p electrons, such as aluminium [8]. Moreover, even when no explicit covalent bonds form the interaction between the metal atoms and the polyimide, the metal still induces charge rearrangements among the polyimide atoms far from the reaction site. We should note that the calculated Mulliken 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. For conjugated polymers such as polyacetylene intramolecular charge rearrangement was also found, with little charge transfer between metal and polymer [10].

3.4. Polyimide on nickel surface

We have simulated the interaction between polyimide and metal surface by considering the adsorption of PMDA-ODA fragment nearly parallel to a Ni(100) surface (represented by a cluster of 17 atoms). The chemical interaction between the functional groups of polyimide and the metal surface leads to a distortion of the molecular fragment (Figure 3).

Our calculations predict that 1.6 electrons are transferred from polyimide to the Ni substrate compared with transfers of 0.02 to 0.48 electrons to isolated adsorbed Ni atoms. These calculations also predict an adhesion energy of 0.49 eV/Å^2 which is lower than the adhesion energy for the adsorption of Ni atoms on polyimide at five and six-fold sites. These results suggest that the adhesion of metal to polyimide surface can be lower or greater than the adhesion of polyimide to metal surfaces, depending on the number and type of metal-polyimide bonds formed at the interface.

In contrast to nickel, the adsorption of polyimide parallel to an Al(100) surface (represented by a cluster of 16 atoms) leads to a negligible charge transfer (0.002 electrons) from polyimide to aluminium surface, though showing a similar adhesion energy [8].

3.5. Modification of polyimide surface

Surface modification techniques such as chemical etching, plasma treatments and ultraviolet irradiation of polymer surface, as well as thermal treatment of metal-polymer system, have been shown to improve adhesion of metal thin films to polyimide, measured by the peel test.

Surface modification studies of polyimides indicate the formation of carbon radicals due to carbonyl oxygen losses. These radicals can either react with each other, resulting in crosslink formation among the polyimide chains, or with the evaporated metal atoms.

We have addressed the effect of surface modification on adhesion by studying the formation of metal-radical bond for Cr, Ni and Cu as well as carbon-carbon bond between two free radicals. Results of metal-carbide bonding are shown in Table 3. Our results suggest that metal-carbide adhesion energy is lower than the adhesion energy for metal atoms adsorbed at six-fold site. A much lower value of 0.2 eV/$\mathring{A}^2$ was predicted for the binding energy of a crosslink between two polyimide chains (represented by their PMDA part) at carbonyl carbon site.

Based on our results, we suggest that any enhancement in adhesion due to surface modification probably result from the formation of a large number of weak crosslinks within the polymer before metal deposition and a few strong metal-polyimide bonds. A simultaneous break of both bond types will lead to increase 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. In addition, the removal of surface contaminants should also improve adhesion, though this question will not be addressed here.

4. Conclusions

We have studied the effects of chemical bonding on the adhesion of both metal atoms on polyimide surface and polyimide deposited on metal surface. Our results suggest that metal atoms react preferentially with five and six-fold rings of polyimide when those chemical groups are present on the surface. Moreover, the metal induces charge rearrangements among the polyimide atoms 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. A somewhat weaker adhesion of polyimide to metal surfaces suggests that, in practice, the polyimide is more likely to adhere to metal oxide rather than clean metal surfaces. We believe that the different adhesion behaviours observed experimentally might be related to the number of bonds rather than the formation of strong bonds.

Our CNDO calculations for transition metals suggest serious overestimates of the magnitudes of adhesion energies. However, we have far more confidence in the adsorption trends and the induced molecular distortions predicted. Self-consistent quantum chemistry molecular dynamics calculations, such as those reported here, can be a useful tool in understanding experiments as well as for providing data which is currently impossible to obtain experimentally.

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Caption of the figures

Figure 1: Schematic diagram of polyimide cluster model used in the calculations reported here. The roman numbers represent the different adsorption positions of metal atoms considered.

Figure 2: Adhesion energy for the adsorption of evaporated chromium (square), nickel (circle) and copper (triangle) atoms on PMDA-ODA fragment at positions indicated in figure 1. The curves are simply a guide to the eye.

Figure 3: Side view of the optimised molecular structure of PMDA-ODA fragment deposited on Ni(100) surface (represented by a cluster of 17 atoms).

Figure 1

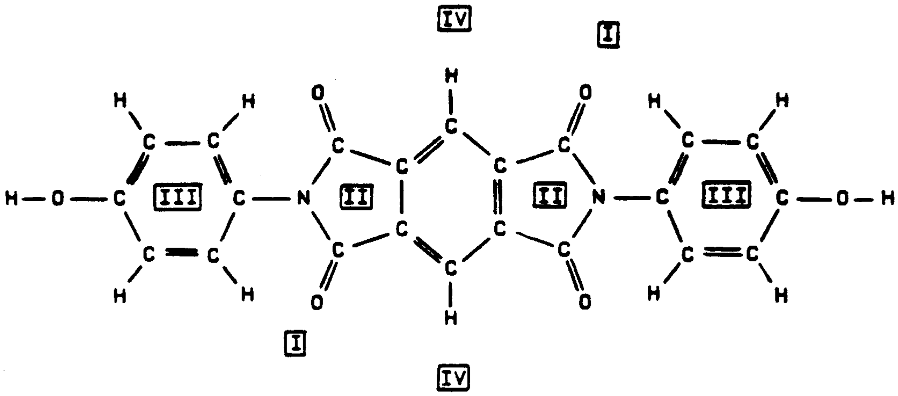
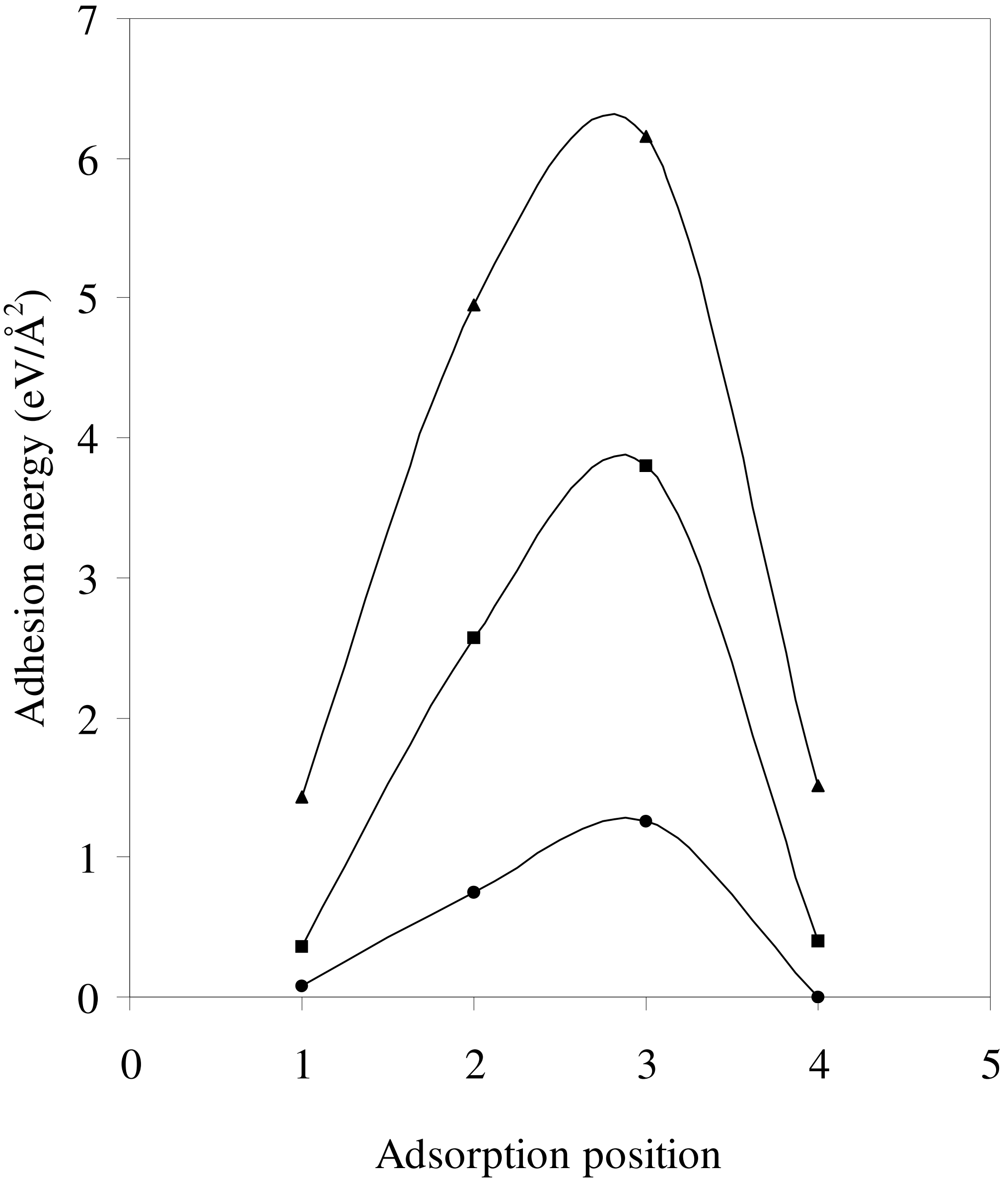


Figure 2



7
6
5
4
3
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3
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Adhesion energy (eV/Å^2)
Adsorption position

Figure 3

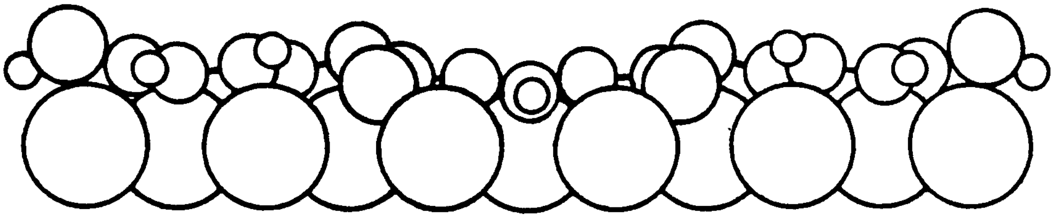

Table 1

CNDO parameters used for several transition metals.

Element	Electronegativity (eV)			Bonding parameters (eV)		Orbital exponent (a.u.$^{-1}$)	
	I_s	I_p	I_d	β_{sp}	β_d	ζ_{sp}	ζ_d
Chromium	3.909	0.876	4.822	-17.0	-23.0	1.663	2.533
Nickel	4.700	1.920	4.970	-7.0	-7.0	2.790	2.790
Copper	4.567	1.347	6.520	-35.0	-30.0	1.482	3.080

Table 2

Charge stored in two metal atoms adsorbed on polyimide fragment at positions indicated in Figure 1.

Bonding position	Charge (electrons)		
	Chromium	Nickel	Copper
I	-0.2193	-0.0667	0.1548
II	-0.1284	-0.1448	-0.2715
III	-0.3027	-0.2416	-0.4984
IV	-0.1865	-0.0130	0.3668

Table 3

Adhesion energy corresponding to the reaction of evaporated chromium, nickel and copper atoms with PMDA-ODA radical.

Metal	Adhesion energy of metal-carbide (eV)
Chromium	3.3
Nickel	0.5
Copper	4.7