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CHEMISTRY AND MICROSTRUCTURE AT METAL-POLYMER INTERFACES

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ABSTRACT

This paper summarizes the present knowledge of the chemistry and microstructure at metal-polymer interfaces formed on PMDA-ODA polyimide. The nature of chemical bonding was deduced from electronic structures observed by photoemission spectroscopies and interpreted by molecular orbital calculations. Bonding at the initial coverages of the metals studied are well described by the formation of metal-polymer complexes as a result of delocalized charge transfer from the metal to the polymer repeat unit. The microstructure was observed directly by transmission electron microscopy and ion scattering techniques. The morphology was found to be strongly dependent on the chemical reactivity of the interface. This correlation between chemistry and microstructure is important for understanding adhesion at the metal-polymer interface.

1. INTRODUCTION

In microelectronics, the large-scale integration of devices necessitates the use of multilayered metallization structures on the chip level and for packaging. Such structures are usually fabricated using alternate metal and insulating layers. This incorporates metal-insulator interfaces throughout the structure, which, depending on the configuration and dimension of the devices, can have varying degree of complexities. These interfaces have to be designed with certain functional characteristics, particularly good chemical and adhesion properties. For this purpose, it is important to understand these basic properties of the metal-insulator interface.

Among the insulators, ceramics and polymers are the most commonly used. Comparing these two classes of materials, the ceramics have the advantage of high mechanical strength and thermal stability. For advanced packaging applications, the ceramic materials have certain undesirable characteristics, including high dielectric constant (about 6-8) and the difficulty in forming line patterns with small dimensions, e.g. less than about 10 microns. These factors restrict the speed and density of the packaging structure. In contrast, polymers generally have low dielectric constants of about 3 to 4 and can be processed by lithographic techniques to yield patterns with dimensions in the micron range, making them well suited for packaging applications.
The current trend in microelectronic packaging is to incorporate polymer layers into ceramic structures to make optimum use of the properties of these two classes of materials. One fundamental concern of such composite structures is the structural integrity, particularly when they are subject to heat treatment or during thermal cycling. The thermal process gives rise to thermal stresses because of the differential thermal expansions of metal, polymer and ceramic substrate. Depending on the material combination, the stress can reach a very high level, exceeding the yield stress of the metal in some cases. To maintain the integrity of the structure under such circumstances, strong adhesion at the interface is needed.

The adhesion strength of an interface is primarily determined by two factors: the intrinsic characteristics of atomic or molecular bonding at the interface and the structural morphology of the interface. The latter can be very important; for example, two polymers with relatively weak molecular bonding can form a strong polymer-polymer interface by promoting the interdiffusion, i.e. interpenetration of polymer segments, at the interface. Depending on the combination of the materials forming the interface, the nature of the bonding can be significantly different. For example, it can vary from a strong and directional covalent bond in semiconductors to a weak van der Waals bond in molecular solids. In this regard, the metal-polymer interface has distinct and interesting characteristics. While the metal is characterized by an ordered atomic structure with close packing density, the polymer has a disordered, loose and interwound molecular structure. The bonding characteristics of such a structural combination is difficult to predict, a priori. In spite of its wide range of applications, the metal-polymer bonding has not been investigated until recently (1-4).

This paper focuses on these two aspects of the interface by reviewing the results of recent investigation on metal-polyimide interfaces. The bonding characteristics have been investigated using surface spectroscopy techniques in combination with theoretical molecular orbital (MO) calculations (3,4,5). The interfacial structure was examined by microanalytical techniques of transmission electron microscopy (TEM) and medium energy ion scattering (MEIS) (6) in combination with Monte Carlo simulation (7). Due to the emerging interest and the increasing activities in studying metal-polymer interfaces, this article is not intended to be a comprehensive review, instead its discussion is focussed on Cr and Cu, two metals with contrasting strong and weak interactions with the polyimide. The emphasis is placed on the current understanding of the microscopic nature of the metal-polyimid interface. For other polymer interfaces, one can refer to other review articles and conference proceedings (8-11).

2. CHEMICAL BONDING AND ELECTRONIC STRUCTURE

2.1 Electronic Structure of Polyimide Surface

UV photoemission (UPS) and X-ray photoemission (XPS) spectroscopies were used to probe the electronic structure of the interface. In UPS, UV photons, which are generated by gas excitation or from a synchrotron source, with energy of about 100 eV or less are used to probe the valence electrons. Since the valence states are directly involved in the formation of the chemical bonds, UPS seems to be ideally suited for probing the bonding characteristics. For metal-polymer interface studies, this is complicated by the fact that the polymer molecule contains various atomic elements and their valence levels usually overlap, making it difficult to identify the specific complex or bonding site responsible for bond formation. In XPS, x-ray photons of energy exceeding 1000 eV are used to probe the core levels which are well separated for the various atomic elements in the polymer molecule. The atomic specificity of XPS is useful in combination with UPS for determining the role of different atomic species in bond formation at the interface.

Both these spectroscopy techniques have very high surface sensitivity since they measure only those electrons within the escape distance of the surface, which is of the order of 10 Å. This restricts the probing depth of an interface to about the escape distance. As a result, most of the spectroscopy studies were carried out during metal deposition on interfaces with only few monoatomic layers of metal coverage. By observing the changes of the spectral features during metal deposition, the spectroscopy techniques enable one to monitor the evolution of the valence and core states during the course of interface formation. Molecular orbital (MO) calculations were carried out to derive the electronic structure of various metal-polymer complexes. By combining the spectroscopy results with MO calculations, the nature of the chemical bonds at the interface can be deduced.
The experiments were carried out in a multitechnique ultrahigh vacuum chamber equipped with a hemispherical electron spectrometer for UPS and XPS measurements. The vacuum chamber has incorporated facilities for ion sputtering, mass spectroscopy, gas exposure, and rapid sample introduction. The samples were fabricated by spinning a thin layer of Dupont 5878 polyimide on a Si wafer. To insure a smooth polyimide surface, a polished Si wafer was used with thin Al layers deposited on both sides. Details of sample preparation have been described elsewhere (3,4).

In order to use spectroscopy techniques to study the interface, the bonding characteristics of the polyimide surface was first investigated (12). Annealing was found to be most effective in obtaining a reproducible surface. As shown in Fig. 1, the three as-prepared samples show subtle differences in surface chemistry which can be detected by UPS. Upon annealing at 360°C for about 1/2 h, the differences disappeared and the spectra converged to one typical of the polyimide surface, as represented by curve d. To verify that the UPS spectrum in curve d indeed represents the valence density of states (DOS) of polyimide, theoretical calculations of the molecular orbital structure of polyimide were carried out. Quantum chemical programs are readily available to carry out self-consistent-field molecular orbital (SCF MO) calculations (i.e., ab-initio) of organic molecules of limited size. Such a program, GAUSSIAN-80 (13) was chosen to study the molecular orbitals of polyimide (5,14).

![Diagram of UPS spectra](image)

**Fig. 1.A.** (a)-(c) UPS spectra from three different polyimide surfaces in the as-prepared state, (d) UPS spectrum after 360°C in situ annealing in UHV, and (e) valence density of states from SCF MO calculations, broadened with 2.0 eV FWHM for comparison with experiment. B. Basic unit of the molecular structure of polyimide.

![Diagram of polyimide structure](image)
The fundamental unit (building block) of the polyimide chain is shown in the bottom of Fig. 1. It consists of two parts: (1) a PMDA part which contains four C=O bonds, a benzene ring, and two N atoms; and (2) an ODA part which consists of two benzene rings connected through the ether oxygen. The agreement between the measured (curve d) and calculated (curve e) valence DOS in Fig. 1 is remarkably good. This agreement indicates strongly that the 360°C in-situ annealing yields a UPS spectrum characteristic of intrinsic polyimide. It also permits us to identify the molecular orbital origin of the spectral peaks. The -10 eV peak consists of three types of carbon orbitals: those associated with the benzene rings, i.e., the C(2p) orbitals lying perpendicular to the molecule, the N(2p) lone pair orbitals (also perpendicular to the molecule), and O(2p) lone-pair orbitals lying perpendicular to the molecule for the ODA part and along the molecular axis for the PMDA part. The peak near -14 eV is composed of the C-C σ bonds, C-O orbitals perpendicular to the molecular plane, and C-H π bonds. The peak structure between 17-20 eV is C(2s). In essence, the -14 eV peak represents valence states bounded together to form the back-bone structure of the polymer, while the -10 eV peak contains the unbounded valence states, which are available to interact with the electronic states of the deposited metal atoms. As seen from subsequent discussions on interfaces, these valence states are primarily responsible for forming the chemical bond at the interface.

Among the core spectra observed by XPS, the C1s spectrum provides the most useful information, so it is relied upon in probing the effect of metal interaction on the polymer chemistry. As shown in Fig. 2, it consists of three peaks reflecting the different chemical environments of the carbon atoms in the PMDA-ODA polymer repeat unit. These include one peak at -288 eV for the carbonyl carbon atoms, one at -285 eV for the aromatic carbons of the 6-member rings in PMDA as well as carbon atoms bonded to oxygen and nitrogen atoms, and one at -284 eV for certain aromatic carbon atoms in the phenyl rings of ODA. The core level spectrum of oxygen exhibits only two peaks derived from the carbonyl and ether oxygens. The spectrum of nitrogen is simpler, consisting of only one peak associated with its single chemical environment in the repeat unit.

![Fig. 2. XPS C 1s spectrum observed for the clean PMDA-ODA surface. The deconvoluted contributions reflect the different chemical environment of the density of states.](image)

The electronic structure of the interface has been investigated for a number of metals, including Cu (2,4,15), Ni (2,16), Al (17), Ti (18,19), and Cr (2,15). In § 2.2 and § 2.3, results are discussed for Cr and Cu to illustrate two contrasting interfaces of strong and weak bonding characteristics.
2.2 Chromium–Polyimide Interface

The spectral series in Fig. 3 illustrates the evolution of the C 1s core states upon Cr deposition. The result indicates that for this strongly interacting metal, reaction occurs immediately upon deposition. With a coverage of only 0.12 Å Cr, the intensity of the carbonyl peak is reduced by about 50% and accompanied by a decrease in the intensity on the high binding energy side of the doublet associated with the PMDA unit. For further depositions of 0.2 Å and 1 Å coverages, the rapid reduction in the carbonyl and PMDA peak intensities continues. With 1 Å coverage, there is a discernible shift of the overall spectrum toward lower binding energy as well as a continued reduction in the emission intensities from the carbonyl and the PMDA fragment. This trend continues for further deposition of Cr. At coverages >2 Å we note a significant change in the C 1s spectrum. The signal originating from the aromatic carbons in the ODA fragment (~284 eV) shifts by ~1.8 eV to lower binding energy, first exhibiting a shoulder and then a peak. This result can be explained as a consequence of continued overlayer formation where coverages above 2-3 Å result in Cr atoms located atop the phenyl rings of the ODA fragment after saturating the interaction with the PMDA fragment. Such a matrixing effect results in interactions which give rise to the observed peaks.

Valence photoemission corroborates the studies described above. Figure 4 displays the changes in the valence spectra with increasing Cr coverage. Even with a coverage of only 0.08 Å a drastic decrease in the ~10 eV peak can be observed, indicating the initial formation of chemical bonds between Cr and the unsaturated valence states of the PMDA fragment while the valence structure near ~14 eV of the back-bone bonding states is largely unaffected. Increasing coverage results in greater reductions of this peak with increasing contributions from emission from the d-levels of the metal overlayer. A rigid shift in the spectra toward lower binding energy is also detected. Since Cr forms a charge transfer complex with the underlying
polymer a dipole can be expected to form which shifts the kinetic energy of the photoemitted electrons. This effect is observed in both core level as well as valence spectra with a shift toward lower binding energy of 1.2 eV saturating above 3-4Å coverage.

The spectroscopy results were interpreted using electronic structures derived from molecular orbital calculations for various configurations of the Cr-polyimide complex (5). Calculations were performed for a number of different complexes involving one chromium atom interacting with the PMDA or the ODA unit. The most stable complex formed was the one with Cr atom sitting above the central six-member ring i.e. at the position of the highest coordination. Another stable complex with PMDA was found with Cr above the center of the five-member ring. The ODA part yields only one such site for complex formation with Cr, namely, the one above each of the two phenyl rings.

For the most stable Cr-PMDA complex, the lowest unoccupied a,\textsubscript{2} π-molecular orbital (LUMO) interacts with the 3d\textsubscript{xy} Cr orbital which is filled and lying in a plane parallel to the plane of the molecule (5). These orbitals are shown at the top of Fig. 5. In the calculation, the distance of the Cr atom above the molecular plane was varied to determine the minimum energy configuration. The resultant bonding orbital is shown at the bottom of Fig. 5. In this complex, the charge transferred from the Cr atom resides mainly at four of the C atoms composing the central benzene ring; two of the C atoms on this ring receive no charge since these C atoms had essentially zero LUMO amplitude. There is also some small amount of charge transfer to the carbonyl C atoms. This transfer of charge shifts the carbonyl C1s levels to lower binding energy as well as causes an intensity reduction in the −288 eV peak. These changes in electronic states can explain the spectral features of the C1s observed with the initial coverage of Cr, i.e. a rapid reduction in the intensities and shift in energy of the carbonyl and PMDA peaks.

Similarly, when the chromium atom is placed above one of the five-member rings there is charge transfer with a resultant shift of the C1s core levels to lower binding energy. Since the chromium atom is not equidistant from all of the carbonyl groups, the C1s carbonyl levels split into inequivalent pairs causing an overall broadening of the spectrum. Such an asymmetry in the charge transfer results in shifts of all the C1s levels associated with the carbon atoms on the central ring.

Results of the molecular orbital calculations can be evaluated by calculating the C1s spectra as a function of Cr coverage. Coverages are simulated with appropriate combinations of clean polyimide and
Cr-PMDA and Cr-ODA complexes. As shown in Fig. 5b, the calculated spectra provide a satisfactory account of the observed results, not only for the peak shifts but also for the overall spectral features.

A model of the interaction of Cr with PMDA-ODA can now be constructed. Cr initially bonds in highly coordinated sites on the PMDA fragment forming a Cr-polymer complex. Increased coverage results in saturation of such energetically attractive sites and forces Cr interaction with the phenyl rings of the ODA fragment. This occurs as the overlayer thickness approaches 1 monolayer. Central to the formation of the Cr-polymer complex is the charge transfer from the deposited Cr atom to the lowest unoccupied molecular orbital of the repeat unit of the monomer. The manner in which charge is transferred from Cr to the various atoms in the polymer repeat unit indicates that the chemical bond between Cr and polyimide is delocalized in nature. A similar mechanism of delocalized bonding can be applied to interpret the spectroscopy results of other metals (see §2.3 for Cu).

2.3 Copper-Polyimide Interface

With respect to the chemical reactivity, Cu represents a contrasting comparison with Cr because of its filled d-electron valence states. Core level studies (15) with increasing Cu coverage produced minimal changes in the observed spectra (Fig. 6a). Even at coverages of up to 3Å the carbonyl signal persists, being reduced only 40% relative to the clean spectrum. The intensity of the $-285\text{ eV}$ peak decreases more rapidly than that at $-284\text{ eV}$ suggesting that Cu interacts primarily with the PMDA fragment. This is similar to Cr except that the reduction in peak intensity is significantly smaller at comparable coverages, indicating a
Fig. 6. a. C 1s spectra for increasing Cu coverage. b. UPS spectra for increasing Cu coverage.

Weaker chemical interaction at the interface. Since Cu is more electron rich than Cr, it is not expected to occupy high coordination sites. Such chemistry weakens the interaction with the underlying polymer and consequently, incomplete coverage due to island formation is observed to occur (4). Similar effect of chemical reactivity on the interfacial structure has been found to be important for all the metal-polyimide interfaces studied so far. This subject will be discussed further in §3.
These observations are consistent with the valence spectra of the Cu covered polymer (Fig. 6b). Although initial Cu interaction with PMDA was observed, as evidenced by the decrease of the $-10$ eV peak, this effect saturates. Even above 2Å coverage the $-10$ eV peak is still observable while at this coverage in the Cr case this peak had completely disappeared. The Cu results can be interpreted in a similar manner as Cr. Although the relative energies of various complexes are difficult to determine accurately due to the weak interaction of Cu, the observed spectroscopy results are consistent with the formation of weak charge transfer complexes predominantly with the PMDA fragment. This shows that the concept of delocalized bonding described for Cr must also be applicable for Cu. Thus the nature of the metal-polymer bonding is different from the localized bonding observed for metal compounds, such as oxides and carbides.

In addition to Cu and Cr, the bonding characteristics to polyimide have been investigated for two other 3d metals, Ni (2,16) and Ti (18,19). Together these studies reveal a consistent chemical trend in which the bonding strength and the chemical reactivity depend upon the number of the d electrons in the metal. The overall bonding characteristics are well described by the formation of metal-polymer complexes. On this basis, Ti is similar to Cr as it interacts strongly with the polyimide while Ni is similar to Cu although its reactivity is somewhat higher. The trend in the chemical reactivity is also reflected in the interfacial morphology obtained with initial metal coverages. Again Ti is similar to Cr with uniform coverages while Ni is close to Cu with island formation. Al, a metal with p valence states, has also been investigated (17). Its bonding strength and chemical reactivity are intermediate between Cr and Cu.

3. INTERFACIAL MICROSTRUCTURE

The microstructure and morphology of the interface have been investigated by cross-sectional TEM (7) and medium-energy ion scattering (MEIS) (6).

Figure 7 shows a cross-sectional micrograph of Cu/PI samples prepared at 300°C with a slow evaporation rate of about a monolayer per minute. Most of the Cu atoms are seen to migrate into the polyimide films to form copper aggregates near the polyimide surface. Diffraction patterns indicate that most of the aggregates single crystals of copper. One interesting aspect of these observations is that the spread in sizes of the aggregates is very small. At this temperature, a number of the Cu aggregates rest at the PI/substrate interface. Apparently, the diffusion length of either the individual Cu atoms or small clusters is sufficiently large so that they form the aggregates and become pinned at this interface. This observation leads one to infer that Cu atoms have a high diffusivity in polyimide and once diffusing inside, they aggregate because the binding energy between Cu atoms is higher than that of Cu to polyimide. This result is a consequence of the weak chemical interaction between Cu and the polyimide and are consistent with the spectroscopy studies.

![Cross-sectional TEM micrographs showing morphologies of Cu/polyimide interfaces formed at 300°C. Deposition rate about one monolayer per minute.](image-url)
Figure 8 shows the microstructures obtained when Cr is evaporated under similar conditions on the polyimide. This micrograph shows clearly that there is no formation of Cr precipitates inside polyimide and intermixing due to Cr penetration. The intermixing, if present, is limited to the resolution of the microscope, i.e., about 10Å.

To elucidate the role of chemical interactions that are expected to be important in the formation of the metal-polymer interface, related Monte Carlo calculations on a model metal-polymer interface have also been carried out (7). These calculations were performed on a two-phase system, simulating the metal-polymer interface. The polymer was idealized by a set of interaction sites with the metal. The interaction sites were allowed to move about, consistent with the energetics of the model. The calculations have been performed on a two-dimensional square grid and the number of interaction sites that one introduces provides a measure of the openness of the polymeric structure. Metal atoms are "deposited" at the top surface and diffuse into the polymer according to the standard Monte-Carlo algorithm. All single metal atom jumps and single polymer interaction site jumps are considered as a function of the interaction energies and temperature. Results of the Monte-Carlo simulation for the Cu/PI interface have been obtained as a function of the deposition temperature and time. Migration and agglomeration of Cu atoms are observed and their characteristics are qualitatively consistent with TEM observation in Fig. 7.

The results of the Monte-Carlo simulation for a more strongly interacting metal reveal that most of the metal atoms get hung up at the surface and are unable to penetrate into the film. Spherical aggregates are not formed at the surface since the interaction with the polymer has been assumed to be stronger than interaction between metal atoms. This result is consistent with the Cr/polyimide interface.

Observations on other interfaces of Al and Ni (17) reveal morphological features intermediate between Cr and Cu. Al is closer to Cr in that it tends to form uniform film on the polyimide in most of the cases studied even though with slow evaporation rate (a few monolayer per minute) and at temperatures of about 300°C, Al atoms have been found to agglomerate to form surface islands. In comparison, Ni is similar to Cu as it tends to diffuse into the polyimide to form Ni clusters, particularly under the condition of a low evaporation rate and a high deposition temperature (7).

4. SUMMARY

In this paper, we have reviewed the results of recent studies on the chemistry and microstructure of the metal-polyimide interface. A basic approach has been used to study the metal-polyimide interface under well-controlled conditions using a combination of analytical techniques. These include the use of photoemission spectroscopy to monitor the valence and core states, TEM and MEIS to observe the morphology and microstructure. These experimental investigations have been complemented by theoretical studies, including molecular orbital calculations to deduce the electronic states of metal-polymer complex and Monte Carlo simulation to derive the interfacial morphology. Such an approach has yielded detailed
microscopic information on the chemical and material characteristics of the metal-polyimide interface. The material reactions such as intermixing and cluster formation, reveal a fundamental nature of this class of interfaces. This aspect of the interface and its correlation to chemistry are important for understanding the mechanical behavior of the interface, particularly for high-temperature polymers, such as the polyimide.

Among the metals studied, the chemical bond between Cu and the polyimide is the weakest, so Cu atoms diffuse readily into polyimide to form clusters. In contrast, Cr bonds strongly to polyimide, giving rise to a high-strength interface with uniform morphology. The difference in the bonding characteristics is reflected in the adhesion strength and stress relaxation behavior of these interfaces.

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