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The bonding of polyimide precursors to Ni studied by electron energy loss spectroscopy

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Abstract. Polyimides have considerable technological importance in the microelectronics device industry on account of their thermal stability and dielectric properties. The interface between metals and polyimides has been studied most frequently by metal evaporation onto the preformed bulk polyimide. Recently, the microscopic nature of the interface has been probed, by XPS, following vacuum deposition of the precursors to the polyimide on copper and gold surfaces. In this study, we report preliminary high resolution electron energy loss spectra (HREELS) of the precursors, m-phenylenediamine (m-PDA) and pyromellitic dianhydride (PMDA), which are vacuum deposited *in situ* onto a clean Ni(110) surface. Information concerning the nature of the adsorbed species and its orientation at the surface has been deduced. In particular, the dicarboxylic anhydride (PMDA) seems to interact via the C=O bonds of the molecule and we compare this behaviour to that of acetic anhydride adsorbed on the same Ni(110) surface.

1. Introduction

Polyimides play an important role in the microelectronic industry because of their high thermal stability, favourable dielectric properties and the relative ease of processing into coatings and films. Such a technological importance has prompted an increasing number of studies of polyimide interfaces. Obviously, a microscopic understanding of the chemical bonding at the interface is highly desirable if the adhesion properties are to be optimised.

Until recently, virtually all studies on polyimide interfaces have been carried out by metal evaporation *in vacuo* onto polyimide surfaces or cured polyimide films [1]. As an alternative to preforming the polyimide (generally using solvents in spin-coating techniques onto 'inert' surfaces), it has been shown that polyimides can be formed by vapour co-deposition of the precursors onto a metal substrate, followed by heat treatment to cause imidisation [2–4]. Such films have no solvent complications and, furthermore, their thickness is sufficiently small so that the metal–polyimide interface may be probed by surface sensitive techniques.

A typical reaction scheme for the formation of a polyimide is shown in figure 1, using m-phenylenediamine (m-PDA) (or 1,3-diaminobenzene) and pyromellitic dianhydride (PMDA) (1,2,4,5-benzenetetracarboxylic anhydride) as the precursors. In this paper, we present preliminary high-resolution electron energy loss spectroscopic (HREELS) results

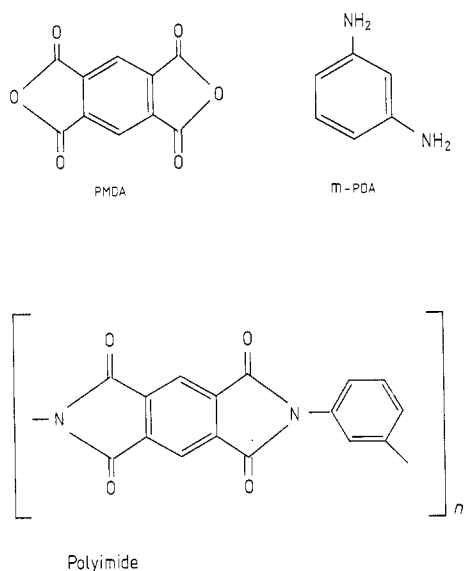


Figure 1. A polyimide repeat unit formed from the two precursors studied in this paper. The precursors are m-phenylenediamine (m-PDA) (1,3-diaminobenzene) and pyromellitic dianhydride (PMDA) (1,2,4,5-benzenetetracarboxylic anhydride).

for m-PDA and PMDA vapour deposited *in vacuo* onto a Ni(110) surface. By firstly studying the bonding of these, and other polyimide precursors, to metal surfaces, it is hoped to improve our understanding of polyimide formation by vapour deposition techniques at metal surfaces. This should then lead to a more detailed microscopic understanding of the adhesion properties of polyimide-metal interfaces.

2. Experimental procedure

Experiments were carried out in an ultra-high vacuum system (base pressure $< 2 \times 10^{-10}$ mbar) equipped with HREELS, low-energy electron diffraction (LEED) and mass spectrometer. The HREEL spectrometer (VSW Scientific Instruments Ltd.) consists of a fixed monochromator and rotatable analyser, both 180° hemispheres with four element lenses, and operates with a resolution of 5–8 meV full width half maximum (FWHM). For these rather disordered adsorption systems, the resolution was routinely 8–12 meV ($64\text{--}96\text{ cm}^{-1}$). HREEL spectra were recorded with incident angles of 50° and off-specular data was collected at an angle of 40° , all angles relative to the surface normal.

The Ni(110) sample was cleaned by standard argon ion sputtering and annealing ($\sim 1000\text{ K}$) procedures. Surface cleanliness was monitored by the appearance of a sharp $p(1 \times 1)$ LEED pattern and the absence of any loss peaks in the tail of the elastic HREELS peak.

The crystalline m-PDA and PMDA samples were kept under vacuum in a stainless steel vacuum line attached directly to the main chamber. Each tube was heated, using external heating tapes, and the temperatures monitored by a chromel-alumel thermocouple wire (m-PDA temperature 50°C , PMDA temperature 120°C). Adsorption was carried out at substrate temperatures of 300 K and 170 K. The acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$) was purified by several freeze-pump-thaw cycles to remove residual dissolved gases and was condensed onto the Ni surface at a substrate temperature of 170 K. For the assignment of the principal vibrational features, infrared spectra (IRS) were recorded for all three samples used.

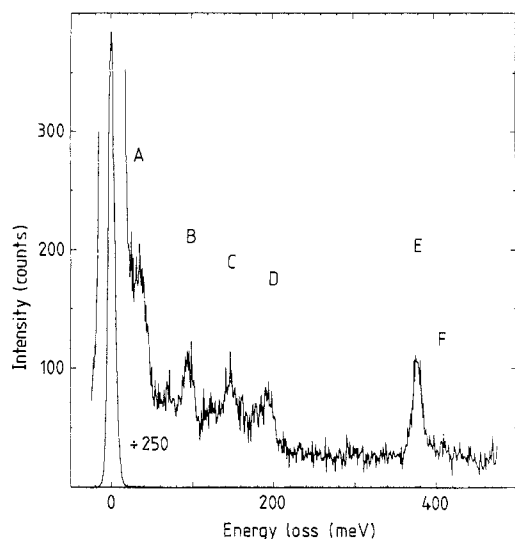


Figure 2. A specular ($\theta_i = \theta_s = 50^\circ$, all angles relative to the surface normal) HREEL spectrum ($E_i = 6$ eV) of the Ni(110) surface after exposure to m-PDA at a substrate temperature of 300 K. Band assignments are given in table 1.

Table 1. Comparison of the vibrational frequencies (in meV) for the HREEL spectra for m-PDA adsorbed onto Ni(110) at 300 K and the IR spectrum for m-PDA. The figures in parentheses are the vibrational frequencies in cm^{-1} and the letters refer to bands in figure 2.

| Assignment | Band | m-PDA-Ni(110) | m-PDA |
|---|------|---------------|-----------------------|
| $\nu(\text{Ni}-\text{N})$ | A | 35 (280) | — |
| $\gamma(\text{C}-\text{H})$ | B | 95 (760) | — |
| $\delta(\text{C}-\text{H})$ | C | 146 (1177) | 146 (1175) |
| $\nu(\text{C}-\text{C})$ or $\delta(\text{N}-\text{H})$ | D | 192 (1536) | 188 (1519) |
| $\nu(\text{C}-\text{H})$ | E | 377 (3016) | 374 (3015) |
| $\nu(\text{N}-\text{H})$ | F | — | 412, 421 (3325, 3392) |

3. Results and discussion

3.1. m-PDA-Ni(110)

An HREEL spectrum recorded in specular scattering geometry (incident electron energy, $E_i = 6$ eV), after exposing the clean Ni(110) surface, at 300 K, to 3×10^{-8} mbar m-PDA for 300 s, is shown in figure 2. Band frequencies were found to be similar for both specular and off-specular scattering geometries and none of the features were found to have an intensity distribution that peaked dominantly in the specular scattering direction. The principal vibrational features are listed in table 1 and the assignments are made by comparison with IR spectra recorded for the m-PDA sample.

The lack of intensity in the spectral region corresponding to the N—H stretching vibration (labelled F in figure 2), in the HREEL spectrum of the adsorbed m-PDA (our off-specular studies show a very small intensity in this region), clearly indicates that deprotonation occurs for room temperature adsorption. This observation is consistent with the photoemission study by Grunze *et al* [5] of the thermal decomposition of ammonia on Ni(100). In their study, ammonia adsorbs as a molecular entity for adsorption temperatures less than 130 K. On increasing the temperature of the nickel surface, partial dissociation was found to occur, leaving an intermediate species containing NH fragments. On heating above 350 K, complete fragmentation resulted in atomic nitrogen being adsorbed on the surface.

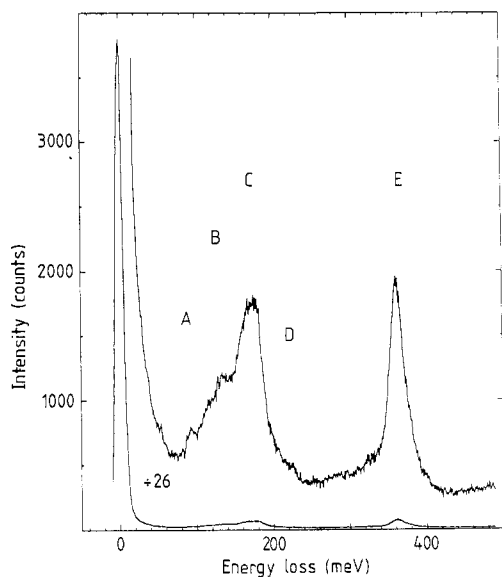


Figure 3. A specular ($\theta_i = \theta_s = 50^\circ$, all angles relative to the surface normal) HREEL spectrum, recorded at 300 K ($E_i = 6$ eV), of the Ni(110) surface after exposure to PMDA at a substrate temperature of 170 K.

Specular HREELS studies of adsorbed aromatic compounds are dominated by the out-of-plane C–H bending mode, when the plane of the aromatic ring lies parallel to the surface [6]. In this orientation, this vibrational mode is strongly dipole active. When the plane of the ring is inclined towards the surface normal however, the C–H bending mode has a much weaker intensity in the specular HREEL spectrum. Figure 2 clearly shows that the out-of-plane C–H bending vibration, $\gamma(\text{C–H})$ (95 meV), has a relatively weak intensity in the specular direction. This implies that the aromatic ring is inclined towards the surface normal.

Therefore, the absence of $\nu(\text{N–H})$ coupled with the low intensity of the C–H bend in the specular direction, leads us to conclude that the m-PDA species undergoes deprotonation at the Ni(110) surface at room temperature, and interacts via one, or possibly both, of its N atoms and is orientated with the aromatic ring inclined towards the surface normal.

3.2. PMDA–Ni(110)

Figure 3 shows a typical specular HREEL spectrum recorded after adsorption at 170 K followed by heating to 300 K. Very little difference was found between specular and off-specular spectra. The spectrum is dominated by features at 94, 134, 171 and 361 meV with, perhaps, a very low-intensity feature at 209 meV. The two features of particular interest are the weakness of the 209 meV (D) ($\nu(\text{C=O})$) band and the much more intense loss at 171 meV (C). These intensities are considerably different from the IR spectrum (not tabulated here) recorded for the PMDA sample, which is dominated by a very strong intensity in the $\nu(\text{C=O})$ stretching region.

For comparison, a much simpler anhydride (acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$) was condensed onto the Ni(110) surface at 170 K. The HREEL spectrum recorded (figure 4) has dominant features which are in strong agreement with the IR spectrum recorded for acetic anhydride (table 2). Clearly, for adsorption at 170 K, molecular acetic anhydride is present and is characterised by dominant vibrational features at 139 meV (B) ($\nu(\text{C–O})$), 171 meV (C) ($\delta(\text{CH}_3)$), 222 meV (D) ($\nu(\text{C=O})$) and 373 meV (E) ($\nu(\text{C–H})$).

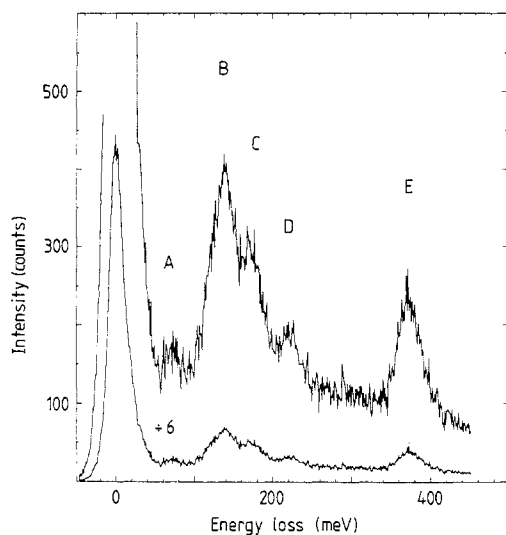


Figure 4. A HREEL spectrum, recorded at 170 K ($E_i = 8$ eV), of the Ni(110) surface after exposure to acetic anhydride ($(\text{CH}_3\text{CO}_2\text{O})$) at a substrate temperature of 170 K. Band assignments are given in table 2.

Table 2. Comparison of the vibrational frequencies (in meV) for the HREEL spectra for acetic anhydride condensed onto Ni(110) at 170 K and the IR spectrum for acetic anhydride. The figures in parentheses are the vibrational frequencies in cm^{-1} and the letters refer to bands in figure 4.

| Assignment | Band | $(\text{CH}_2\text{CO})_2\text{O-Ni(110)}$ | $(\text{CH}_3\text{CO})_2\text{O}$ |
|-----------------------|------|--|------------------------------------|
| Multilayer vibration | A | 73 (584) | — |
| $\nu(\text{C-O})$ | B | 139 (1112) | 138 (1113) |
| $\delta(\text{CH}_3)$ | C | 171 (1368) | 171 (1368) |
| $\nu(\text{C=O})$ | D | 222 (1776) | 217, 226 (1751, 1822) |
| $\nu(\text{C-H})$ | E | 373 (2984) | 366, 278 (2950, 3050) |

On comparing figures 3 and 4, it is clear that since the $\nu(\text{C=O})$ loss at 209 meV (1672 cm^{-1}) is so weak for room temperature adsorption, the PMDA undergoes loss of C=O . Instead, the most intense loss feature is at 171 meV (1368 cm^{-1}) and we assign this as the symmetric O-C-O stretching vibration, $\nu_s(\text{OCO})$, of a carboxylate group. The implication is that bonding to the Ni occurs via the two C-O bonds of the carboxylate group [7]. This is consistent with a decarbonylation reaction which has been proposed by recent XPS studies of PMDA at copper and silver surfaces [3, 4].

4. Conclusions

We have carried out preliminary HREELS studies of the adsorption of two possible polyimide precursors, m-PDA and PMDA, vacuum deposited *in situ* onto a clean Ni(110) surface. For room temperature adsorption, the very low intensity in the N-H stretching region implies that deprotonation of one, or both of the amine groups of the m-PDA occurs. We conclude that the m-PDA bonds via its nitrogen atoms. Furthermore, the relatively weak intensity of the out-of-plane C-H bending mode of the aromatic ring, in the specular scattering direction, suggests that the plane of the ring is inclined towards the surface normal. For adsorption of PMDA at room temperature, the very low intensity in the C=O stretching region, compared with that for molecular acetic anhydride

adsorption at 170 K, suggests that a decarbonylation reaction occurs at the surface, consistent with XPS studies of PMDA adsorbed on silver surfaces. A high-intensity loss feature at 171 meV is observed, and this is assigned to a symmetric O—C—O stretching vibration of a carboxylate species. The implication is that bonding to the Ni surface occurs then via the C—O bonds.

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