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1991 J. Phys.: Condens. Matter 3 S29

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An electron energy loss study of the vibrations of polyimide layers deposited by Langmuir–Blodgett techniques

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Received 25 April 1991

Abstract. Single monolayer films of poly-*N, N'*-bis(phenoxyphenyl) pyromellitimide deposited on gold and graphite by Langmuir–Blodgett (LB) methods have been investigated by high-resolution electron energy loss spectroscopy. Initially, the vibrational spectra show evidence of the long-chain, aliphatic hydrocarbon units used in the deposition process. However, after heating *in vacuo* these are removed and a spectrum reminiscent of the bulk crystalline polymer is obtained. Of particular interest though is the absence of a strong feature associated with the carbonyl bands. We interpret this as a consequence of an adsorption geometry in which the C=O units of the polymer chain are aligned parallel to the underlying substrate, in general agreement with an earlier NEXAFS study of this polymer deposited on graphite. Further investigations of a five-monolayer film deposited on gold also fail to show a carbonyl feature suggesting that the orientation of the polymer is maintained over this thickness.

1. Introduction

Polyimides (PI) are an important class of polymers which are finding increasing application in the electronic and opto-electronic industries because of a combination of high thermal stability and useful mechanical and dielectric properties. Also increasingly, there is an interest in characterizing the structural and chemical properties of the interface region between polymer materials and, for example, metals. The difficulties associated with the study of insulating materials and in probing buried interfaces are well recognized but several investigations, most frequently using XPS, have been directed at metals evaporated onto polyimide surfaces [1–3] or at thin layers (< 200 Å) of polyimide deposited on metals, either by spin-coating [4, 5] or, alternatively, by vapour deposition [6] of the precursors, followed by heating to cause imidization [7, 8]. In such cases, the polymer chains are unlikely to be orientated in any specific way with respect to the metal surface. Recently, Langmuir–Blodgett (LB) techniques have been used to deposit polyimide films [9–12], up to a few monolayers thick, on gold and highly ordered pyrolytic graphite (HOPG) surfaces. In principle, this method has the advantage of producing layers of controlled thickness and with the polymer backbone aligned parallel to the substrate surface.

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In this study, we have used one sample consisting of a single monolayer LB film of the polyimide, PMDA-ODA [poly-*N,N'*-bis(phenoxyphenyl) pyromellitimide] deposited on HOPG and samples consisting of one and five monolayers of the same polymer, PMDA-ODA, deposited on gold. The former has already been studied by scanning tunnelling microscopy (STM) [11] and NEXAFS [12] with the conclusion that two-dimensionally ordered layers are formed and that the aromatic rings, in both the PMDA and ODA units, are aligned parallel to the surface.

High-resolution electron energy loss spectroscopy (EELS) has been used to obtain the vibrational spectra. EELS has the disadvantage of relatively low resolution, typically 40–80 cm^{-1} , but the considerable advantage that it has the sensitivity, across the complete vibrational spectroscopic range (100–5000 cm^{-1}), to probe even sub-monolayer quantities of adsorbed species [13]. The technique has already been used to study a polyimide spin-coated on gold and polyimide interactions with evaporated palladium and chromium films [2, 3]. The latter study, although at low resolution ($> 160 \text{ cm}^{-1}$), clearly demonstrated the reactivity of the carbonyl sites with the chromium. The work presented here is an extension of our work on the adsorption of polyimide precursors on metal single crystal surfaces.

2. Experimental details

The PI/Au films, loaned by Professor M Grunze, University of Heidelberg, were prepared by LB deposition of the octadecylammonium [$\text{C}_{18}\text{H}_{37}\text{NH}_3^+$] salt of the intermediate polyamic acid of PMDA-ODA i.e. $[-\text{NH}-\text{CO}-\text{C}_6\text{H}_2(\text{CO}_2^-)_2-\text{NH}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-]_n$, onto a gold film ($\sim 2000 \text{ \AA}$) previously evaporated onto a Si{100} substrate with an intermediate Cr layer to assist adhesion. The samples were subsequently heated to achieve imidization. The PI/HOPG films, loaned by Professor A M Bradshaw, Fritz Haber Institute, Berlin, were prepared in a similar manner using the *N,N'*-dimethylhexadecylamine [$(\text{C}_{16}\text{H}_{31})_2\text{NH}_2^+$] salt but with subsequent imidization being promoted by chemical (overnight in a mixture of acetic anhydride, pyridine and benzene) rather than thermal means [10, 11]. All three samples (1 ML-PI/Au, 5 ML-PI/Au and 1 ML-PI/HOPG) were exposed to the air for a considerable time before insertion into the EELS spectrometer which was then baked overnight at approximately 150 °C.

The EELS spectra were measured with the spectrometer (VSW Scientific Instruments Ltd) using electrons of primary energy in the range of 4–10 eV, at a resolution of approximately 9 meV ($\sim 70 \text{ cm}^{-1}$), in both specular and off-specular directions. There was, however, little angular sensitivity in the elastic peak around the specular direction for the PI/Au samples suggesting a low degree of two-dimensional order. The spectra were measured after spectrometer bakeout, without further sample preparation, and then after heating to about 530 K for period of 1 h.

3. Results and discussion

Figure 1(a) shows the EEL spectra obtained from the 1 ML-PI/Au sample following spectrometer bakeout. The spectrum is characterized by four intense features centred at 780, 1100, 1350 and 2950 cm^{-1} . Those at 780 and 1350 cm^{-1} are particularly broad suggesting overlapping bands. On heating to approximately 530 K for 1 h, there are marked changes in the spectrum (figure 1(b)), which then appears very similar to that

obtained by Pireaux *et al* [4] for a polyimide film spin-coated onto gold. Considerable intensity is lost in the region of 1400 and 2950 cm^{-1} . The latter is the region of C-H stretching vibrations and, after heating, the weaker band is centred at 3000 cm^{-1} . After three such 1 h heating periods, the C-H stretching region consists of a weak, sharp feature at 3050 cm^{-1} with a shoulder, weaker still, on the low-frequency side, at 2930 cm^{-1} . The band at 1400 cm^{-1} has been replaced by a high-frequency shoulder on the intense 1100 cm^{-1} band, spanning the region 1300–1600 cm^{-1} . The lower-frequency feature has partially resolved into two bands at 450 and 620 cm^{-1} .

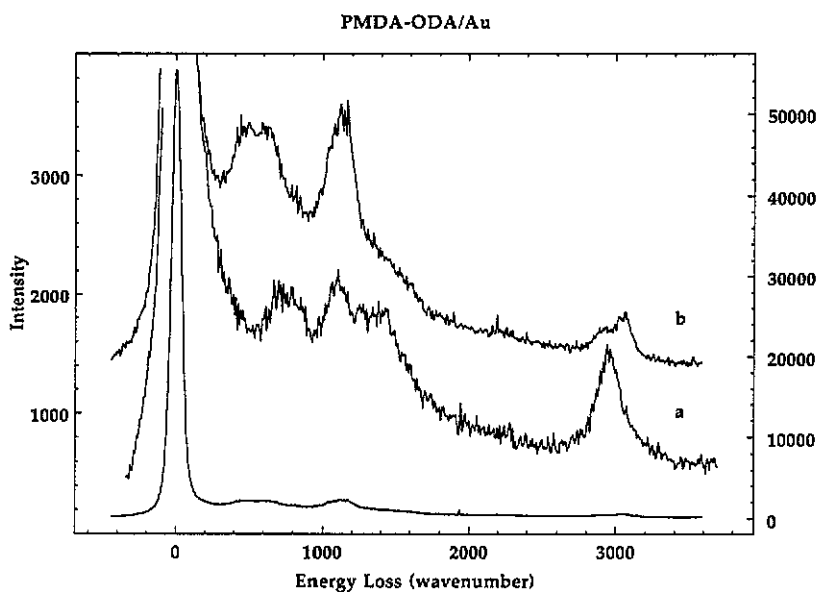


Figure 1. (a) The EEL spectrum of an LB-deposited single monolayer, PMDA-ODA film deposited on gold. The spectrum, 40° off-specular, was obtained after spectrometer bakeout (150 °C) using 8 eV electrons. (b) The EEL spectrum of an LB-deposited single monolayer, PMDA-ODA film deposited on gold. The spectrum, 50° off-specular, was obtained, using 8 eV electrons, after heating the sample to 530 K for 3 h.

The polyimide PMDA-ODA has C-H bonds associated with the aromatic rings of both the PMDA and ODA units. These would be expected to appear above 3000 cm^{-1} . In the pure polymer, there are no aliphatic C-H bonds, which are characterized by stretching vibrations below 3000 cm^{-1} . We interpret the changes, which take place on heating, as being final removal of the long-chain, aliphatic hydrocarbon which was necessary for the LB deposition process. This would be consistent with the changes not only around 3000 cm^{-1} but also around 1400 cm^{-1} , where CH_2 scissor modes occur (1470 cm^{-1} in polymethylene [14]) and above 700 cm^{-1} , where CH_2 rocking modes occur (725 cm^{-1} in polymethylene [14]).

It is noteworthy that no distinguishable C=O feature, anticipated around 1850 cm^{-1} , is seen either before or after heating. It seems likely that gold, as palladium, is too inert to break the C=O linkages, unlike chromium which did cause removal of the C=O features, when evaporated onto a polyimide substrate [2, 3]. We are left with the conclusion either, that the spectrum is dominated by impact scattering excitations because disorder causes the dipole excitations to be diffusely scattered over 2π sr and the C=O modes are very weak in impact scattering or, alternatively,

PMDA-ODA/HOPG

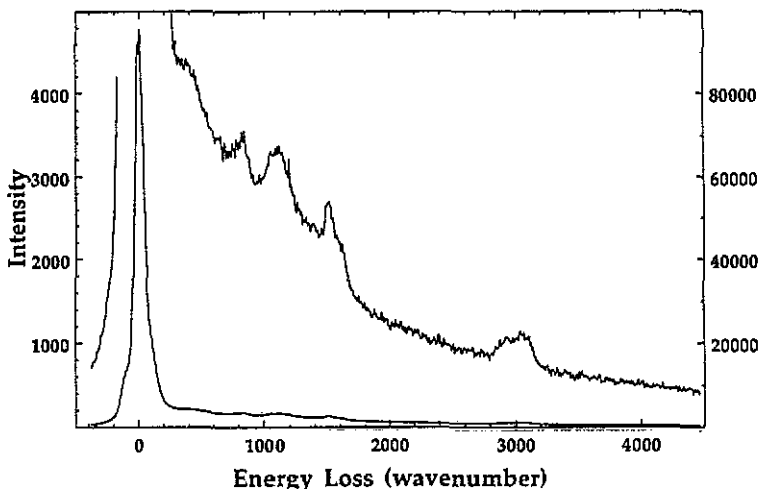


Figure 2. The EEL spectrum of an LB-deposited single monolayer, PMDA-ODA film deposited on highly ordered pyrolytic graphite. The spectrum, 30° off-specular, was obtained, using 8 eV electrons, after heating the sample to 530 K for 1 h.

that the C=O bonds are aligned parallel to the metal surface and their strong dynamic dipoles are screened by image charges in the metal. We favour the latter interpretation since other investigations, on condensed, disordered layers of PMDA (pyromellitic dianhydride) itself, clearly show a strong band at 1850 cm^{-1} , assigned to the C=O stretching vibration [15] and the studies of Pireaux *et al* [4] of the spin-coated polyimide on Au also show a clear C=O band, even though this must be disordered. This orientation agrees with that deduced from NEXAFS studies of the PI/HOPG sample [12]. Spectra of the sample with five, LB-deposited monolayers on gold were essentially identical to those of the single monolayer both before and after heating. This would seem to indicate that the orientation of the PMDA unit parallel to the substrate is maintained over the five monolayers.

There is a severe difficulty associated with an EELS vibrational study of species adsorbed on graphite surfaces [16–18]. This arises because of the semi-metal characteristics of this material. Graphite has an electron-hole (EH) pair excitation spectrum, starting at almost zero energy, which means that there is an intense, long tail on the low-frequency side of the elastic peak in the EELS spectrum which almost swamps the vibrational features of any chemisorbed species particularly in the specular, dipole-scattering dominate-direction. Once again the effect of heating was to dramatically decrease the intensity of the C-H band at approximately 2900 cm^{-1} leaving a weaker band centre at 3050 cm^{-1} and to remove intensity from the 1400 and 750 cm^{-1} regions. Again we attribute this to removal of the long-chain hydrocarbon associated with the ammonium salt used in the LB deposition. Figure 2 shows the spectrum obtained after heating to 530 K for 1 h. More obvious than for the PI/Au samples is the feature at 1600 cm^{-1} which now appears as a more intense, resolved band and also the band at 830 cm^{-1} , although the steeply rising background makes this feature difficult to quantify. The band at 1600 cm^{-1} can be assigned to aromatic ring stretching vibrations [8] or to the asymmetric C-N stretch of the imide unit. Its more obvious presence for the PI/HOPG sample might be related to the greater degree of

order which this sample is known to possess from the earlier STM studies [11].

4. Conclusions

EEL spectra have been obtained for LB-deposited PMDA-ODA films on Au and HOPG surfaces. Initially the samples appear to be contaminated with aliphatic, long-chain hydrocarbon remnants of the LB deposition process. Heating removes this contamination to reveal a characteristic vibrational spectrum, although a strong C=O feature is missing. The absence is attributed to orientational effects in the polymer which allows screening of the dipole activity by substrate electrons. Electron-hole pair excitations strongly affect the ability to collect good quality spectra of species adsorbed on graphite.

Acknowledgments

Professor M Bradshaw of the Fritz Haber Institute, Berlin is thanked for his loan of the PI/HOPG sample. Similarly, Professor M Grunze is thanked for providing the PI/Au samples. The support of the SERC in equipment and a studentship is gratefully recognized.

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