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Vapor Deposition of Polyimide and Polyimide Precursors on Copper

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1. Abstract

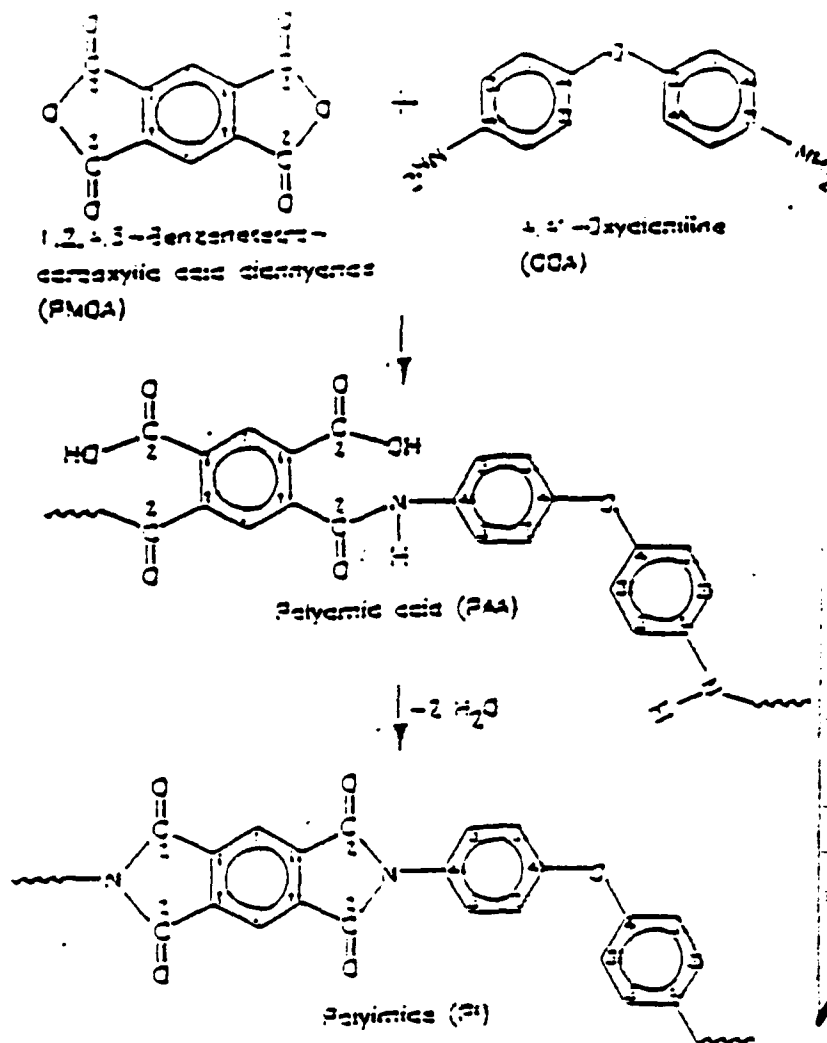
Adhesion between metallic substrates and polymers is an important issue in microelectronic device fabrication and packaging. One of the most widely used classes of polymers are the polyimides which are employed as dielectric spacers in multichip modules and as α -particle barriers in charge sensitive memory devices. In order to study the polymer/metal interface with surface sensitive techniques, the polymer films have to have thicknesses on the order of a few nanometers to obtain chemical and physical information about the interface.

In this article we describe experiments in which ultra-thin films of polyimide were formed on polycrystalline and (111) single crystal copper substrates following heating of a vapor deposited layer of polyamic acid produced by codeposition of 4,4'-diaminodiphenyl ether (ODA) and 1,2,4,5- benzenetetracarboxylic dianhydride (PMDA). The adsorption of the pure components and their subsequent polymerization was followed, in situ, with X-ray photoelectron spectroscopy. Molecular adsorption of the monomers was studied to determine their thermal stability. The composition and adhesion of the thin polyimide film is influenced by fragmentation of precursors at the interface. In contrast to studies on silver and gold surfaces the polyamic acid interacts strongly with the copper substrates leading to a fragmented polyimide layer at the interface after imidization.

2. Introduction

In microelectronics, the application of temperature resistant polymers as insulating interlevel dielectrics has led to increasing interest in their preparation and subsequent adhesion to metal substrates [1]. The most popular of these dielectrics have been the polyimides and, in particular, those formed by the reaction of 4,4'-diaminodiphenyl ether (oxydianiline (ODA)) and 1,2,4,5- benzenetetracarboxylic anhydride (pyromellitic dianhydride (PMDA)). The chemical reaction leading to this polyimide is described in Figure 1.

The two main methods of film preparation are spin coating (SC) and vapor deposition polymerization (VDP). They differ in the way in which the film precursor is applied to the substrate. VDP is a solventless technique in which the evaporated monomers (ODA, PMDA) are codeposited directly onto the substrate whereas spin coating requires that the polymer precursor polyamic acid (PAA) is applied in a solvent.



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Fig. 1 Schematic representation of the reaction between PMDA and ODA to form polyimide. The numbers in the structural formulae are given to facilitate the interpretation of the x-ray photoemission data.

To evaluate the microscopic mechanism in polymer/substrate interfaces the undisturbed interface has to be probed with sufficient sensitivity. In the case of studies using electron spectroscopy, this requires that either the metal or polymer be sufficiently thin to allow elastic electron transport away from the interface and out to the vacuum for analysis. The relative ease with which this has been achieved in studies using metallized polyimides has led to interfaces for metal films deposited on PI being the main source of chemical interface information [2-8]. The difficulties associated with producing an (insulating) organic overlayer of sufficiently thin film thickness (usually $d < 10$ nm) have only recently been overcome. Ultra thin SC films have been prepared on smooth, gold coated Si (100) wafers and the integrity of the film was investigated [9]. Alternatively VDP methods have been shown to routinely produce ultra thin and thin PI films on a variety of substrates [10-13].

It is this VDP class of interface which is of interest in this report. VDP for the formation of polyimide was first described in the production of thick ($d > 1\mu\text{m}$) films [15]. The ability to deposit ultra-thin (monolayer and submonolayer) and thin (monolayer $< d < 10$ nm) films of either monomer on a clean substrate, held at any temperature and investigate the interfacial interaction, is unique to this method. In

comparison, SC requires that the interface be heated to at least 373 K to remove the solvent prior to any spectroscopic investigation. This heating may intrinsically change the interface. Information available from vapor deposited monomer spectra also provide important reference data for the analysis of the more complex spectra arising from thin polymeric films.

The interfacial chemistry and adhesion is directly influenced by the way in which the interface is formed. Therefore, variations in the preparation of the polymer and/or metal will lead to polyimide/metal interfaces with different physiochemical properties. One particularly relevant example of this is the comparison between PI/copper interfaces formed by (i) copper deposition on cured polyimide (PI) and (ii) spin coating of the polymer precursor (PAA) onto a copper film prior to curing to form PI.

Kim and coworkers /2/ measured the adhesion strength by 90° peel tests for (i) and (ii). They found, that in case (ii) adhesion is significantly enhanced as compared to copper deposited onto cured polyimide (i) and they attributed this to the difference in interfacial chemistry, i.e. chemical reaction between polyamic acid and bulk copper (ii) as compared to copper atoms or clusters interacting with cured polyimide. The difference in interface chemistry was also evident in cross-sectional TEM observations /2/. In the case of a sputter deposited copper film onto a cured polyimide film, a sharp boundary was observed, whereas in the case of a polyimide/copper interface prepared by spin coating polyamic acid and subsequent imidization, cuprous oxide (Cu_2O) particles were found distributed in the polymer matrix beyond a precipitation free zone of ~3-20 nm thickness. That copper oxide particles are distributed over a thickness of ~500 nm was also recently found in an XPS study by Burrell et al. /14/ for spun-on polyimide films on copper substrates. In their XPS and IR - Reflection Absorption measurements they attributed a degradation or chemical modification of the thick polyimide films to copper oxide particle formation /14/.

Contrary to the observations made by Kim et al. /2/ on spun-on polyimide films, Kowalczyk et al. /3/ found no copper oxide particles in the polymer matrix in polyimide films produced by vapor deposition (VD). However, if prior to imidization a drop of the solvent N-methylpyrrolidone was applied to the vapor deposited polyamic acid film, copper oxide particle formation in the polymer matrix was observed. Their result clearly showed that the solvent provides mobility for copper oxide particles to diffuse into the polymer matrix, and suggest that initially the polyamic acid functionalities react with the substrate surface most likely forming carboxylate species which decompose during curing and act as a source for copper oxide formation. In this respect we recall our previous results on vapor deposited polyimide films on copper /13/ which showed that it is not possible to produce polyimide films of a thickness less than 4 nm. The thinner films ($d < 4\text{nm}$) showed a strong deviation from the expected polyimide stoichiometry and exhibited x-ray photoelectron spectra characteristic for decomposition products.

The organization of this paper follows the reaction pathway for the formation of PI as described in Figure 1. Comparisons of monomer (ODA and PMDA) adsorption on single and polycrystalline copper substrates will be made and their effect on the formation of the polymer film assessed. The thermal stability of each adsorbate is examined in the context of the importance of the resulting polyimide as a temperature resistant polymer.

3. Experimental

The vapor deposition and XPS experiments were carried out with an apparatus described previously [11]. Tungsten wire was wrapped around quartz tubes containing the pure PMDA and ODA (Aldrich Gold Label) and heated resistively. At sublimation temperatures of between 373 K and 423 K, the resulting evaporation pressures ranged from 2×10^{-6} to 8×10^{-6} mbar. The "measured" deposition temperature was, however, sensitive to the positioning of the chromel alumel thermocouple in this design of oven.

The Cu substrate remained at room temperature during the codeposition process or was cooled down to 200 K in some instances for single monomer depositions. An arbitrary exposure scale, $L = (\text{background pressure in } 10^{-6} \text{ mbar}) \times (\text{exposure time in seconds})$ is used to indicate the extent of deposition. The polymer was formed by heating a codeposited layer of PMDA and ODA to temperatures ranging from 400 K to greater than 600 K for at least 1 hour. No effort was made to maintain a stoichiometric mixture of vapor fluxes during the experiment.

Sample cleaning prior to film deposition was carried out by heating the sample to 800 K in 13 mbar of C_2 followed by 3 mbar of H_2 to remove the surface oxygen. In some instances argon ion sputtering was also used. The $\text{Mg K}\alpha$ x-ray source was operated at 100 W and an experimental resolution of 0.92 eV was measured for Ag 3d emission. The electron binding energies (E_B) were calibrated against the Au 4f_{7/2} emission at $E_B = 84$ eV.

Primary analysis of the XPS spectra arising from the organic depositions involves the determination of peak kinetic energy and integrated peak areas obtained after subtracting a linear secondary electron background. The mean stoichiometry of the film is calculated as a ratio of integrated areas by

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \frac{\sigma_2}{\sigma_1} \frac{E_2^m}{E_1} \quad (1)$$

where N is the number of atoms/unit area for species 1 and 2 and I their core level intensities (proportional to peak area). The relative photoelectron excitation cross sections, σ , are 100, 285 and 177 for C 1s, O 1s and N 1s, respectively [16]. The transmission of the electron spectrometer ($E^{-0.73}$) and electron mean free pathlengths (λ) for organic materials are functions of the kinetic energy E . Combining these leads to the form for E shown in equation 1. The value for m (between 0.5 and 0.71) refers to the thick films ($d > 6 \lambda$) limit and leads to uncertainties of approximately 15% in the relative compositions [17]. Note also that final state effects such as shake-ups effectively borrow intensity from the primary peaks. Calibration spectra of pure monomers were used to assign additional features to incorporate them into the overall calculated stoichiometry.

The absolute peak binding energies are affected by charging within the film. The general trend was shifting to higher E_B with increasing film thickness. This can be explained by charging effects and/or a decrease in the final state screening of the photoionized molecules by metal electrons in the thicker films. Because of the indeterminate nature of these shifts, no corrections have been made to the data reported.

The distributions of bonding environments of the atoms within the films are contained within the XPS line shape. The complexity involved in analysis of lineshapes for polyimide films has been discussed recently [17]. In this paper, assignments of the components within the measured lineshapes are therefore made with reference to previous studies on PI and associated model compounds [11]. Calculated ratios of the various atomic and functional group species are compared with that expected from stoichiometry. The resulting deficits and/or additions are used to infer changes in the film composition.

Film thickness (d) was calculated by attenuation of the Cu 2p_{3/2} or Cu 3p_{3/2} intensity as

$$d = -\lambda \ln (I/I_0) \quad (2)$$

where λ is the mean free path length of the Cu 2p or 3p photoelectrons in the overlayer and has been assumed to have values of $\lambda_{2p}=0.8\text{nm}$ ($E_K=320.2\text{ eV}$) or $\lambda_{3p}=1.3\text{ nm}$ ($E_K=1177.4\text{ eV}$) [18]. I_0 is the intensity measured on the clean surface. The values of d generated from (2) are considered reasonable estimates of true film thickness. A discussion of assumptions involved in (2) has been reported elsewhere [17]. In some instances, up to 99.99% attenuation of the Cu 2p signal ($d < 7\text{ nm}$) could be measured.

4. Results and Discussion

1. PMDA adsorption on Cu(111) at 200 K and subsequent thermal treatments.

In Figs. 2 and 3 we show the C 1s and O 1s spectra of a multilayer film of PMDA(a) and the spectral changes occurring when the film is heated stepwise to 573 K.

The C 1s photoemission of the condensed film ($d > 7\text{nm}$) exhibits two peaks, due to the phenyl ring carbon atoms (C1 in Fig. 1) at $E_B=287.1\text{ eV}$ and carbonyl carbon atoms (C2, Fig. 1) at $E_B=291\text{ eV}$. These peaks are shifted by 1 eV to higher binding energies as compared to a monolayer of PMDA adsorbed on Cu(111) at 200 K indicating decreased final state screening of the core hole and/or charging of the film. The high binding energy tail on the carbonyl C 1s emission (Fig. 2a) is due to final state effects ("shake up") in the photoemission process. The exact origin of this shake up feature, i.e. its association with either the phenyl carbon or carbonyl carbon or both emissions, is not known. For the stoichiometry evaluation, the intensity in the high energy tail was added to the carbonyl C 1s intensity which, if this assignment is not strictly correct, leads to an overestimate of carbonyl groups in the PMDA film.

The corresponding O 1s spectra for the condensed PMDA multilayer is shown in Fig. 3. The unresolved doublet arises from emission from the carbonyl oxygen atoms (O2) at $E_B=534\text{ eV}$ and from the anhydride oxygen (O1) around $E_B=535\text{ eV}$.

The thick film of PMDA condensed at 200 K was subsequently heated to investigate the film stability. The resulting C 1s and O 1s spectra are shown in Figs. 2 b-e and 3 b-e. The reappearance of the Cu substrate signals following treatment at temperatures exceeding 373 K indicates either a considerable reduction in film thickness or film break up into PMDA aggregates. Accompanying this

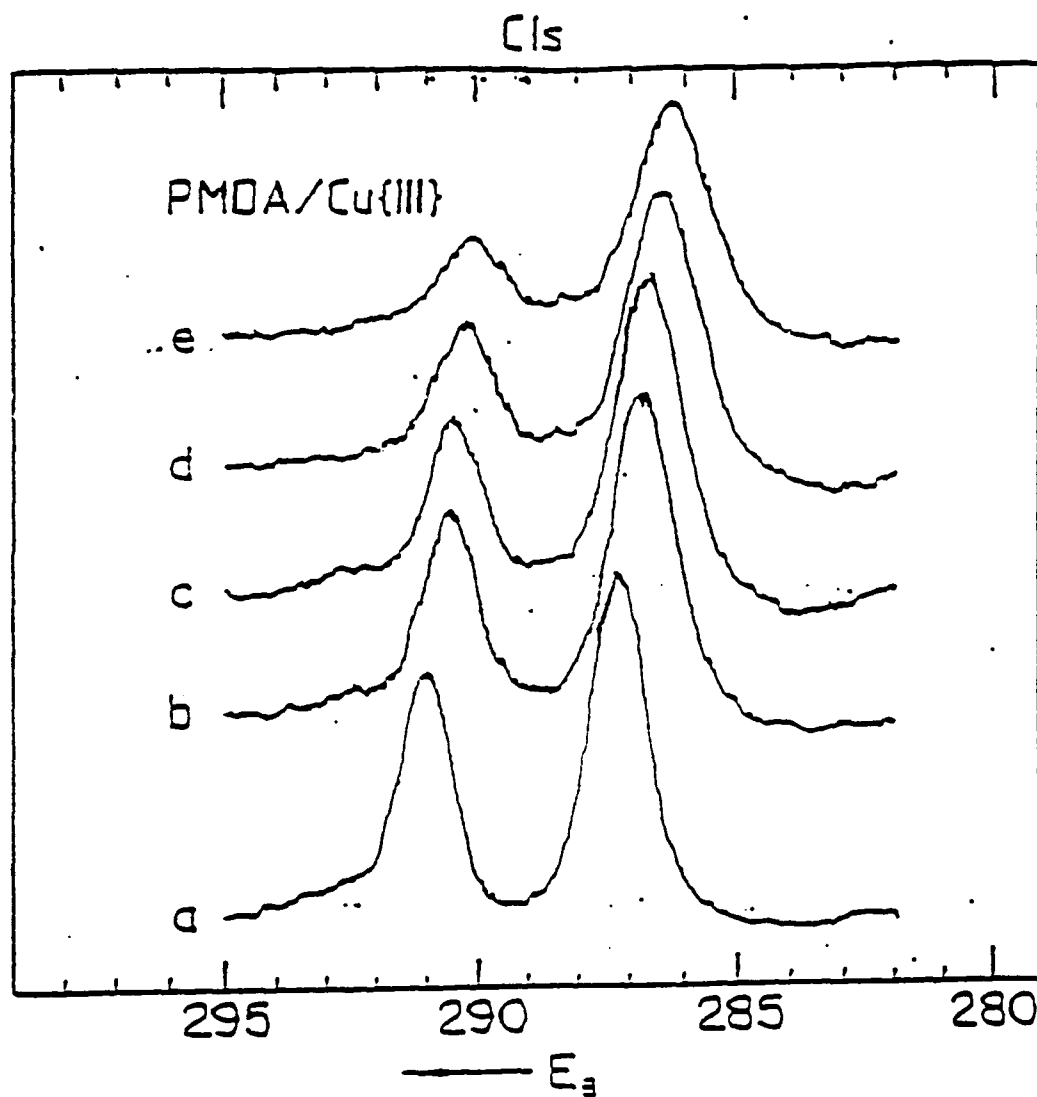


Fig. 2. C1s spectra for thermal treatment of a thick PMDA film deposited on Cu (111): (a) $d > 7\text{nm}$ at 200 K; (b) $d > 7\text{nm}$ following heating to 298 K; (c) $d > 7\text{nm}$ following heating to 373 K; (d) $d \sim 3.4\text{nm}$ following heating to 473 K; (e) $d \sim 2\text{nm}$ following heating to 573 K.

reappearance of Cu is peak broadening of the C 1s and O 1s emission, a shift to lower binding energy by (0.9 eV) and a disproportional reduction of the carbonyl C 1s and O 1s emission. In Fig. 4 we plot the integrated intensity of carbonyl carbon

$\Sigma C_{C=O}(x)$ and total oxygen $\Sigma O(o)$ normalized to total carbon ΣC as a function of temperature and mean film thickness estimated from the increasing intensity of the copper substrate emission. The result for oxygen are calculated in the "thick film" (i.e. $m = 0.7$) and "thin film" (i.e. $m=0$) limit. The lower stoichiometry values indicated by the dots at the lower end of the vertical lines are obtained in the thick film limit, the thin film limit yields the upper dots. To the extent that the PMDA film remains uniform and homogeneous, the composition will be between these limits for $d < 4$ nm. For thicker layers, the thick films limit applies, the thin film limit is valid only for monolayer coverages ($d \ll \lambda$).

The deviation from the expected composition of the condensed film ($\Sigma O=6$) reflects the uncertainties in our stoichiometry evaluation procedure, i.e. the definition of the correct background to be subtracted from the emission envelope and the errors associated with the value of m in eq. 1 used to correct for the energy dependence of the electron mean free path.

The change in lineshape occurs simultaneously with a loss of both carbonyl carbon (C2) and oxygen. The comparatively small decrease in carbonyl carbon compared to the oxygen loss suggests the latter may originate primarily from the anhydride (O1) functional group. Further temperature increases ($T > 500$ K) result in decreases of both carbonyl carbon and oxygen and signify increasing decomposition within the film. There is also evidence for partly ionic oxygen indicative of copper oxide formation at the highest temperature where a low binding energy shoulder appears in the O 1s spectra at $E_B \sim 530$ eV.

Thermal decomposition of the PMDA film is also evident in Infrared reflection absorption (IRAS) measurements. A full account of the technique and the experiments are given elsewhere [19,20]. We give only a brief summary of the results of these IRAS studies. IR spectra of PMDA taken after adsorption at 223 K are representative of molecular PMDA. Heating the adsorbate layer to 300 K results in spectral changes indicating partial fragmentation at the interface, to which the IR reflection absorption technique is most sensitive. At this temperature, however, both carbonyl and anhydride stretching bands are still present in the spectra in addition to a new band at 1708 cm^{-1} which is indicative for a monodentate type bond of the PMDA fragment to the surface. Further heating to 373 K leads to the disappearance of the molecular vibration of PMDA. Considering the selection rules for IR-reflection absorption on metallic surfaces this could either be due to a reorientation of the molecule to lie flat on the surface so that the IR-active carbonyl and anhydride stretches are very weak due to image dipole cancellation or, in view of our XPS data, due to a decomposition of the molecule.

Decomposition of the PMDA molecule when adsorbed at room temperature was described in our previous work [13]. These results are summarized in Fig. 5 where we show the integrated intensity of oxygen (ΣO) normalized to the integrated carbon intensity (ΣC) as a function of exposure.

Comparison of room temperature adsorption of PMDA on copper and silver [11] demonstrates that PMDA does not stick to highly fragmented PMDA. On copper, even at exposures as high as 6000 L there is little increase in the film thickness

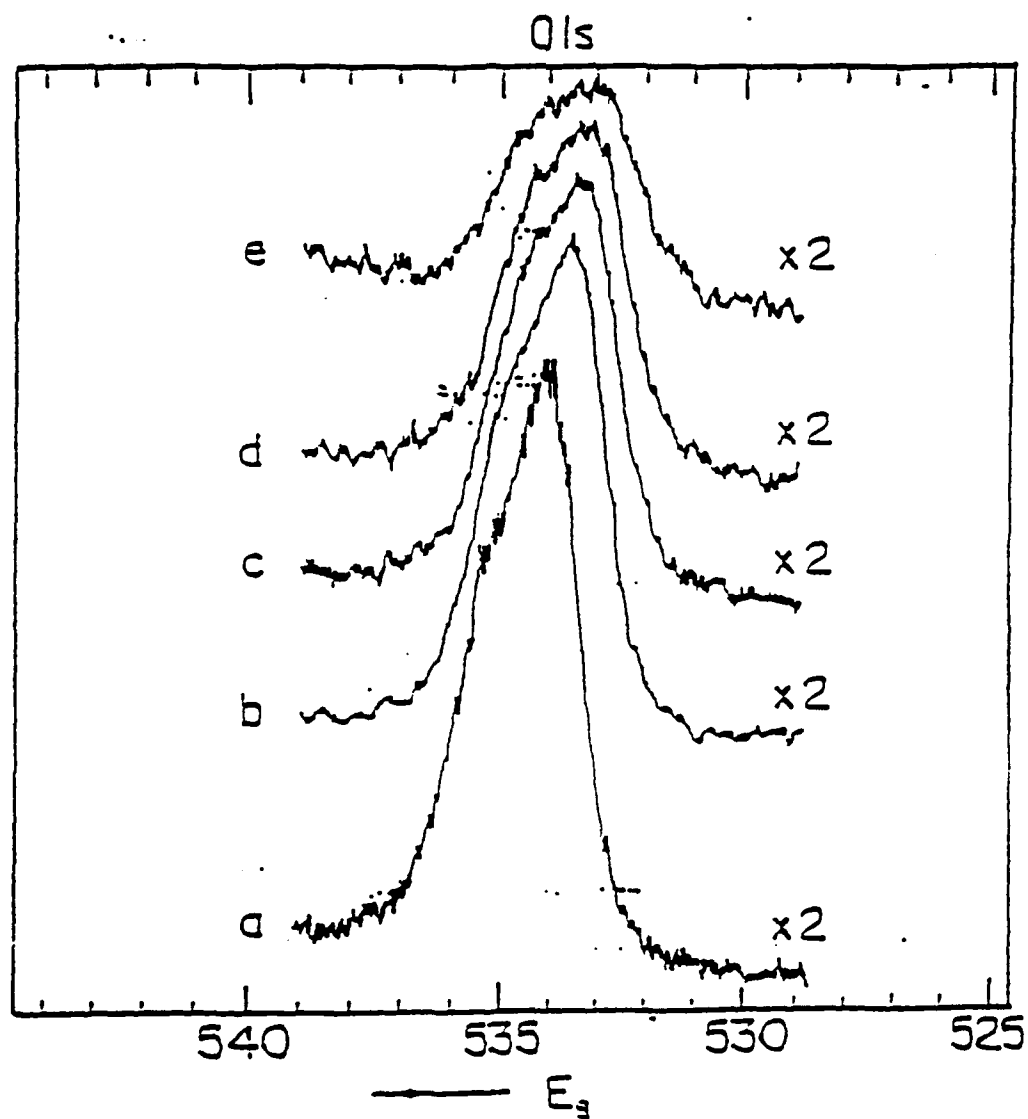


Fig. 3. O1s spectra for thermal treatment of a thick PMDA film deposited on Cu (111): (a) $d > 7\text{nm}$ at 200 K; (b) $d > 7\text{nm}$ following heating to 298 K; (c) $d > 7\text{nm}$ following heating to 373 K; (d) $d \sim 3.4\text{nm}$ following heating to 473 K; (e) $d \sim 2\text{nm}$ following heating to 573 K.

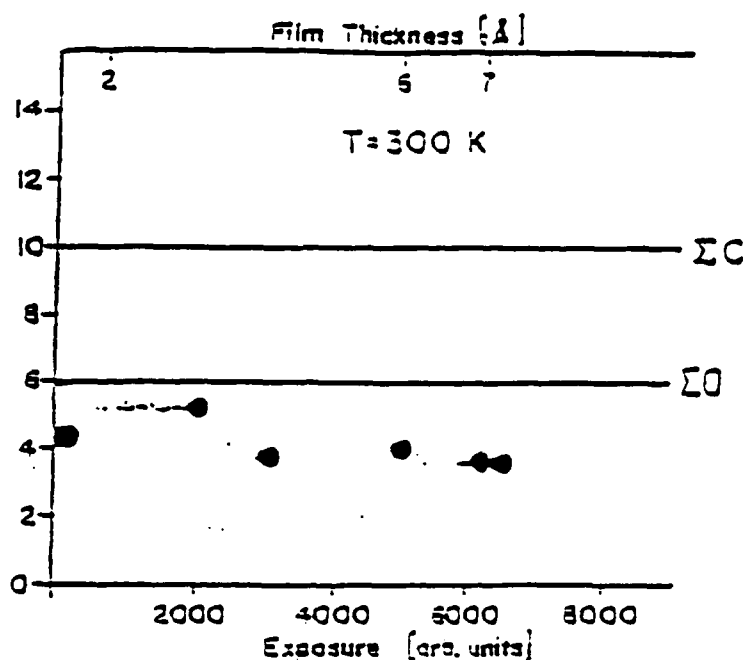


Fig. 4. (b) Total $\Sigma C : \Sigma O : \Sigma C_2$ ratio normalized to 10 PMDA carbon atoms for PMDA deposited on Cu(111) at 298 K

and the non stoichiometric $\Sigma C : \Sigma O$ ratio remains. Molecular adsorption does not therefore appear to occur in room temperature depositions even for very large exposures. Decomposition of PMDA, although to a lesser extent than on copper, has been reported for adsorption of PMDA on silver substrates at room temperature [11]. The partial dissociation involving loss of one CO molecule on silver did not inhibit multilayer molecular adsorption with further exposures [11].

The thermal instability of the interface is highlighted by the obvious difference between PMDA adsorption on a Cu(111) substrate at room temperature where fragmentation occurs without multilayer formation and at 200 K where fragmentation does not occur (these data are not shown here). It seems likely that an ultra thin stoichiometric PMDA film formed on a 200 K substrate would show similar dissociative behavior when heated to 298 K as does the PMDA adsorbed directly on a substrate held at this temperature. Clearly with increasing temperature the interface breaks down. As noted above, the degree of fragmentation at the interface is difficult to ascertain from the XPS measurements because of the thickness of the film and the unknown homogeneity of the layer. In our experiments we probe a weighted average composition of the film, i.e. we cannot distinguish between the signal arising from fragmented monolayers or thicker clusters or islands of PMDA. Heating the film might result in a breakup of the film and nucleation of PMDA crystallites. The observed decomposition

products in our XPS data at estimated film thicknesses of $d \sim 3.5$ nm therefore might arise from an inhomogeneous surface phase.

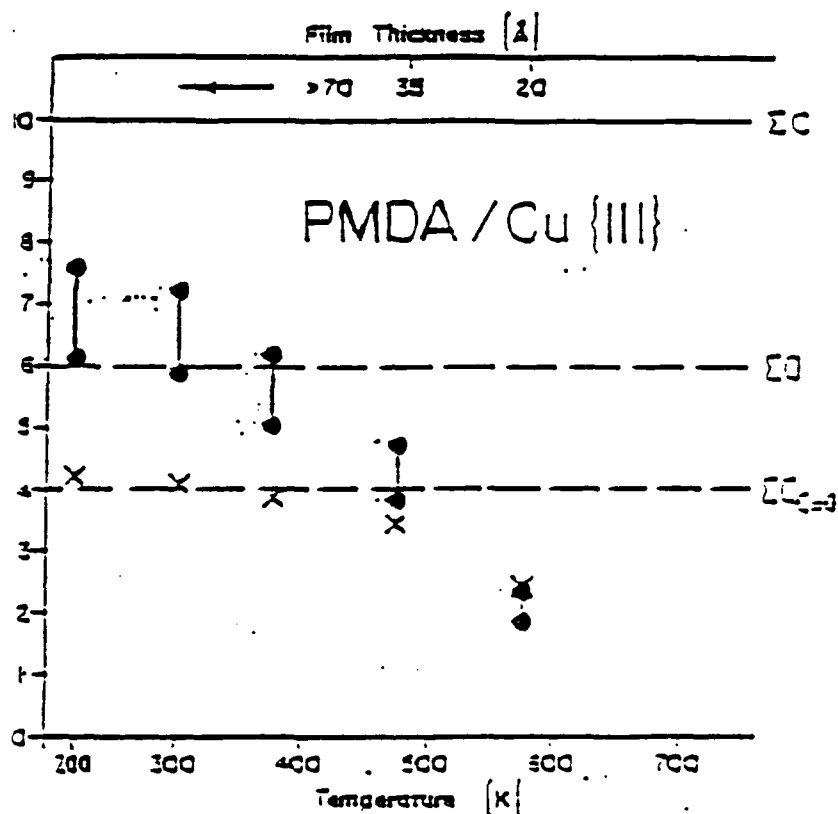


Fig. 5. Total $\Sigma C : \Sigma O : \Sigma C_{C=O}$ ratio normalized to 10 PMDA carbon atoms for thermal treatment of a thick film of PMDA deposited on Cu (111). For the O1s integrated intensities, the higher stoichiometric values were evaluated for the thick film limit, the lower values for the thin film limit (eq. 1). $\Sigma O : \bullet, \Sigma C_{C=O} : \times$

ODA adsorption on Cu(111) held at 200 K

The C 1s and O 1s spectra obtained following from increasing exposure of ODA to a Cu(111) substrate at 200 K are shown in Figures 6-8. In the C 1s spectrum 6a the unresolved doublet originates from the C4 atoms (at higher E_B) and the lower binding energy shoulder corresponds to the C3 atoms. The binding energies remained constant up to exposures of ~ 120 L suggesting that charging is not important up to thicknesses of about ~ 4 nm. Shifts of 0.8 eV to higher binding energies occurs for the thicker films from which spectrum (a) was taken. The lineshape remained constant above $d > 1.1$ nm and indicates that ODA is adsorbing

as a molecular species. The formation of multilayers of ODA without dissociation is also evident in the O 1s spectrum (Fig. 7a). The shift to higher E_B found for the C 1s emission at higher exposure was also apparent in both O 1s and N 1s spectra and reflects charging in the overlayer. The integrated O 1s and N 1s band intensities, normalized to the 12 carbon atoms of ODA, confirm a molecular stoichiometry for all film thicknesses.

Results for room temperature adsorption of ODA up to 1140 L on Cu (111) have been reported previously [13]. The spectra and the stoichiometry of the adsorbate phase suggested a complete dissociation of the ODA molecule upon adsorption.

Heating the thick ODA overlayer condensed at 200 K leads to sublimation and decomposition of the molecules. The C 1s, O 1s and N 1s spectra are shown in Figs. 6, 7 and 8b-e respectively. As the film thins the binding energies shift to lower values due to the elimination of charging. Spectrum d, recorded at room temperature, corresponds to a film thickness $d \sim 4$ nm as judged by the reappearing intensity of the copper substrate photoelectrons.

As shown in the integrated intensities (Fig. 9), the relative concentration of nitrogen decreases at temperatures exceeding 330 K. Yet the O 1s concentration remains invariant, indicating a change in chemical composition of the film. This change is also evident in the line shapes of the C 1s, O 1s and N 1s spectra. The N 1s show only a decrease in intensity, but no clear shift in E_B , whereas a shift and a change in peak shape are observed for the C 1s data. This is paralleled by the shift of the O 1s band to 0.3 eV lower binding energy. Note, however, that the value for the O 1s binding energy (533.5 eV) indicates a non-ionic form of oxygen and is not consistent with copper oxide formation at the ODA/metal interface, since this would give rise to a peak at $E_B \sim 530$ eV [22]. The variation in stoichiometry of the ODA deposit occurs over the temperature range of 330 K - 420 K, at which temperature an average thickness of $d \sim 1.4$ nm is reached. At $T > 520$ K further dissociation is indicated by the parallel decrease in the O 1s and N 1s intensities and results in an almost pure carbonaceous overlayer at $T \sim 700$ K.

Adsorption of ODA at room temperature onto a polycrystalline copper foil was described previously [13]. Formation of a carbonaceous surface species was evident at the smallest exposure. It is only at the highest exposures (2240 L) that the oxygen and nitrogen become discernible. The O 1s spectra indicated, by a weak emission around $E_B \sim 530$ eV, that, besides "organic" oxygen, an oxidic species is formed under these conditions. An evaluation of the stoichiometry of the overlayer after 1140 L exposure results in $\Sigma C : \Sigma O : \Sigma N$ of 12:0.9:0.3. If the oxidic oxygen at $E_B \sim 530$ eV is excluded the ratio is 12:0.7:0.8. Clearly the layer did not consist only of molecular ODA. The fact that the carbon to oxygen ratio is close to the one expected (in particular where the oxidic species is included) but that nitrogen is lost in the initial adsorption process, suggested that the molecule dissociates and releases nitrogen or nitrogen carbon entities. Aniline is one possibility which would also leave an oxaniline species remaining at the surface. Such a reaction scheme has been postulated for the interaction of ODA with silver

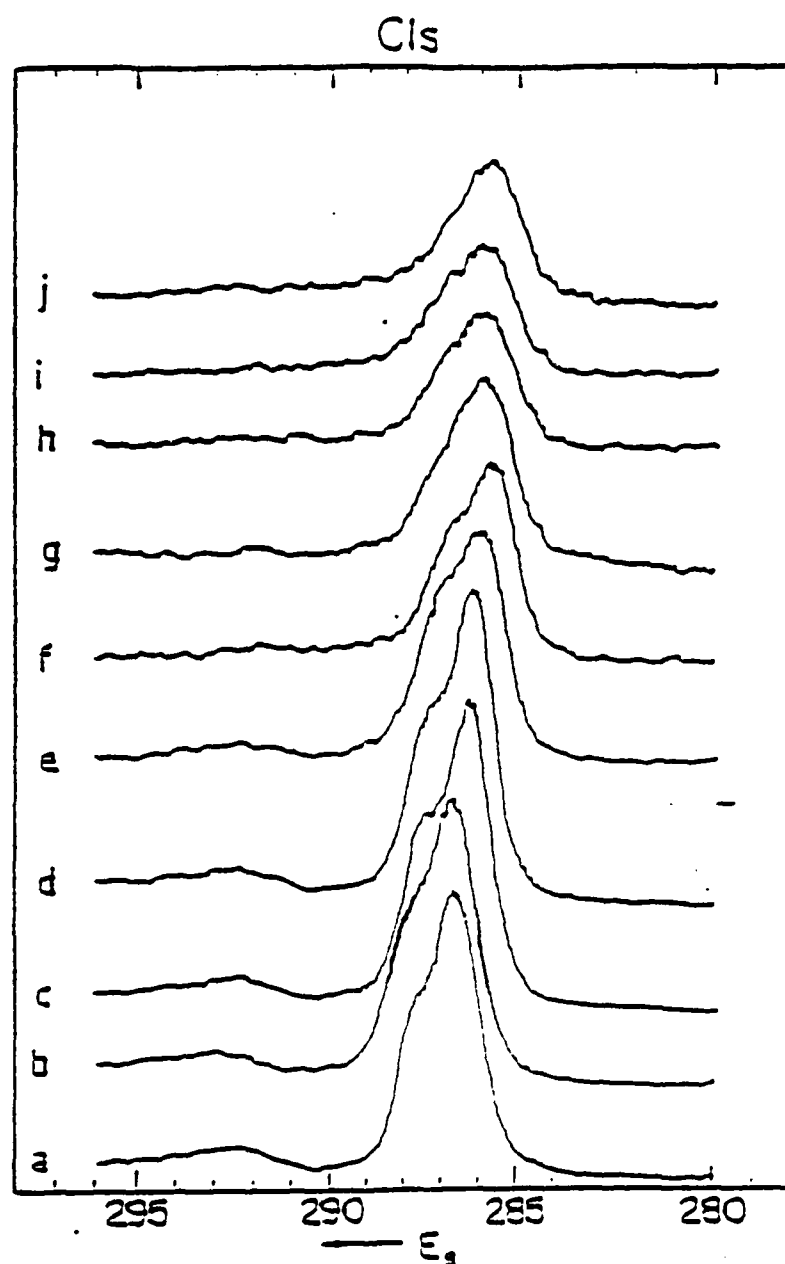


Fig. 6. C1s spectra for thermal treatment of a thick ODA film deposited on Cu(111): (a) Thick film $d > 4$ nm at 200 K; (b) $d > 4$ nm following heating to 223 K; (c) $d > 4$ nm following heating to 273 K; (d) $d \sim 4$ nm following heating to 298 K; (e) $d \sim 2.5$ nm following heating to 323 K; (f) $d \sim 1.8$ nm follow heating to 373 K; (g) $d \sim 1.5$ nm following heating to 423 K; (h) $d \sim 1.3$ nm following heating to 523 K; (i) $d \sim 1$ nm following heating to 623 K; (j) $d \sim 0.9$ nm following heating to 723 K

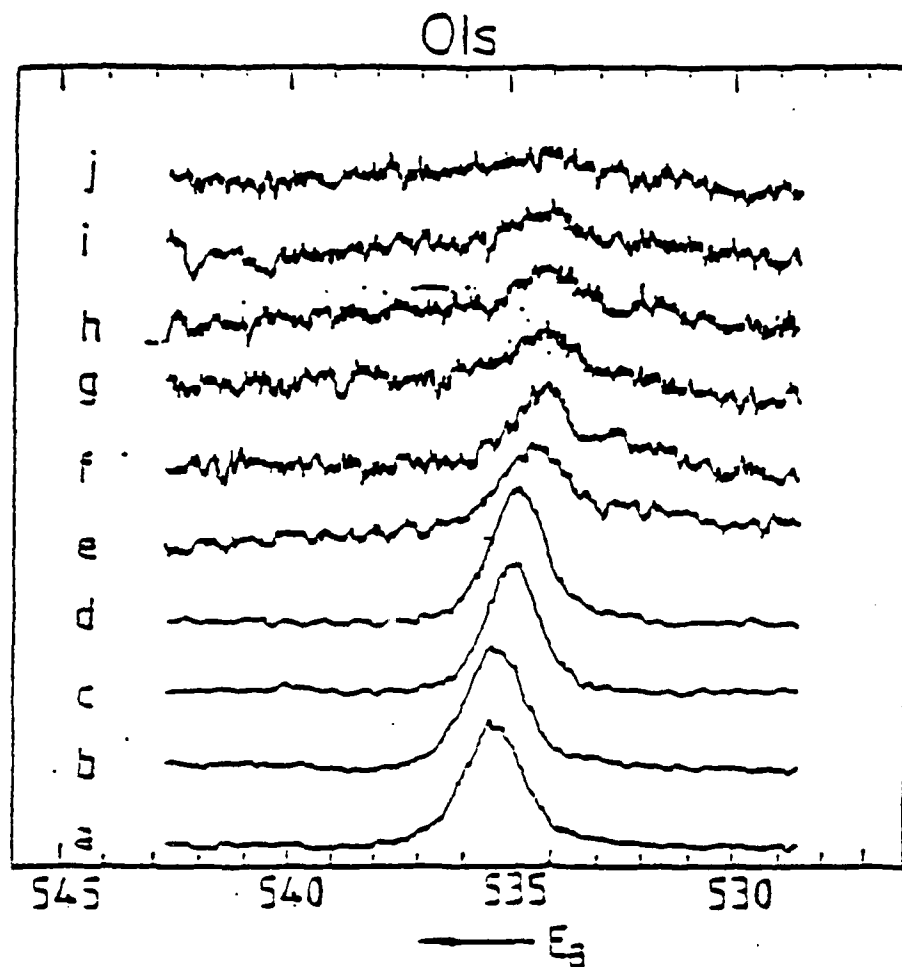


Fig. 7. O1s spectrum of vapor deposited ODA on Cu(111) at 200 K and subsequent thermal treatment of a thick ODA film: (a) Thick film, $d > 4$ nm, at 200 K; (b) $d > 4$ nm following heating to 223 K; (c) $d > 4$ nm following heating to 273 K; (d) $d > 4$ nm following heating to 298 K; (e) $d \sim 4$ nm following heating to 323 K; (f) $d \sim 4$ nm following heating to 373 K; (g) $d \sim 1.5$ nm following heating to 423 K; (h) $d \sim 1.3$ nm following heating to 523 K; (i) $d \sim 1$ nm following heating to 623 K; (j) $d \sim 0.9$ nm following heating to 723 K

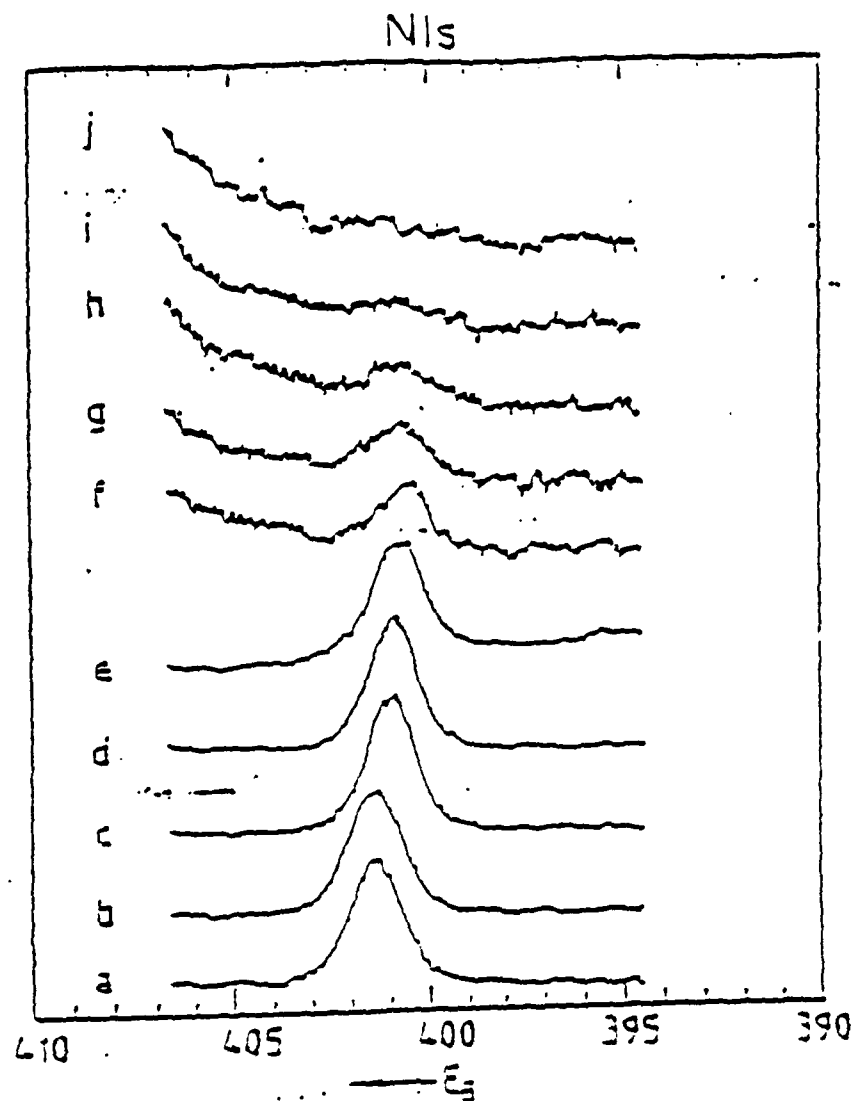


Fig. 8. N1s spectra of vapor deposited ODA on Cu(111) at 200 K and subsequent thermal treatment of a thick ODA film: (g) Thick film, $d > 4$ nm at 200 K; (h) $d > 4$ nm following heating to 223 K; (i) $d > 4$ nm following heating to 273 K; (j) $d > 4$ nm following heating to 298 K; (k) $d \sim 2.5$ nm following heating to 323 K; (l) $d \sim 1.8$ nm following heating to 373 K; (m) $d \sim 1.5$ nm following heating to 423 K; (n) $d \sim 1.3$ nm following heating to 523 K; (o) $d \sim 1$ nm following heating to 623 K; (p) $d \sim 0.9$ nm following heating to 723 K

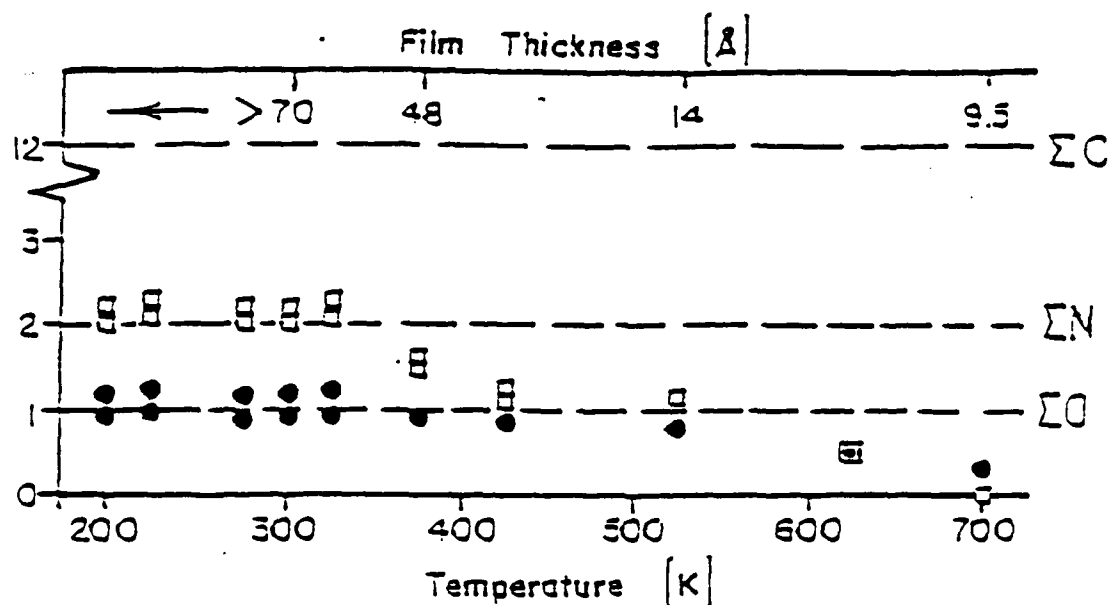


Fig. 9. Total C : O : N ratio normalized to 12 ODA carbon atoms for thermal treatment of a thick ODA film deposited on Cu(111): (●) ΣO ; (□) ΣN ; Upper and lower stoichiometry values correspond to the thin film and thick film limits of eq. 1, respectively.

surfaces [11] but is speculative and needs to be corroborated by other experimental techniques. Since the film thickness after room temperature adsorption does never exceed 0.7 nm it is clear that the dissociation reaction occurs at the interface and precludes multilayer adsorption.

Infrared reflection absorption spectroscopy data for the thin ODA films on clean polycrystalline copper [20] reveal the complete loss of characteristic molecular ODA vibrations at $T \sim 350$ K suggesting that ODA is either completely desorbed or converted into an amorphous carbonaceous overlayer. The disappearance of molecular vibrations in the infrared absorption spectra however, does not necessarily mean that the surface layer loses oxygen and nitrogen completely, as also indicated by the persistence of the N 1s and O 1s photoemission signal up to $T \sim 700$ K. It is therefore probable that the nitrogen and oxygen fragments are incorporated into the organic overlayer but are not active in the infrared absorption experiments. The orientation of the dynamic dipole moments of the fragments with respect to the metal image plane determines their absorbance. The XPS binding energies of the N 1s and O 1s emission indicated that the nitrogen and oxygen atoms in the fragments are not interacting directly with the metal substrate, since this would lead to a further shift to lower binding energy values.

Summary of Monomer adsorption on single crystal and polycrystalline Cu

The PMDA adsorption experiments were only carried out on a Cu(111) surface. The low sticking coefficient at room temperature was accompanied by dissociation of the adsorbate molecules with the loss of carbonyl groups. Multilayer molecular adsorption occurs for deposition on Cu(111) substrates cooled to 200 K. Heat treating a thick film produced sublimation and decomposition within the film.

Molecular adsorption of ODA occurs on Cu(111) surfaces cooled to 200 K. Heating such a layer leads to sublimation and decomposition resulting in the loss of nitrogen and nitrogen carbon entities. Dissociative adsorption occurs at room temperature on both Cu(111) and polycrystalline Cu substrates.

The copper surface appears to destabilize the adsorbates to a greater extent than does polycrystalline silver or gold [11,21]. The inability to form multilayer PMDA or ODA on copper at room temperature highlights this. Obviously copper has a much stronger affinity to fragment the polyimide constituents than the two other noble metals studied in our laboratory. However, from our XPS results we cannot conclude that the copper substrate influences the chemical composition of the films when their thickness is several monolayers. Thickness estimates are based on the assumption that the film is homogeneous with uniform thickness. On silver substrates thermal desorption and IR-Reflection Absorption measurements [20] showed conclusively that thick ODA and PMDA layers condensed at low temperatures form crystallites when the thick films are heated, thus leading to a non-uniform thickness of the layer. In this case, XPS would simultaneously probe both the thick crystalline PMDA and ODA and the decomposed surface layer so that the spectra would reflect an average composition. This inhomogeneous composite layer could lead to the changes in average stoichiometry as well as to the broadening of the peaks observed in the heating experiments. Although this is the most likely interpretation of our results, the possibility that copper atoms or ions diffuse from the interface into the thick PMDA and ODA films and alter their chemical composition cannot be ruled out. Further experiments need to be carried out to resolve this question.

Codeposition of PMDA and ODA on Cu(111)

The C 1s, O 1s and N 1s spectra for PMDA and ODA codeposited on to Cu(111) at room temperature are reproduced in Figs. 10-12(a-d). This layer was then heated slowly in vacuum and resulted in a reduction in film thickness and changes within the XPS spectra as shown in Figs. 10-12(e-j). The variation in spectral lineshape associated with the imidization reaction and the method for deconvolution of these has been reported in detail elsewhere [17]. A similar analysis is used in the following.

Spectra 10-12(a) are taken from the "clean" Cu (111) surface which, however, shows a small oxygen contamination. Subsequently PMDA and ODA were codeposited onto the surface held at room temperature, i.e. both evaporators were operated simultaneously. The first obvious difference from deposition of the pure monomers is that after relatively small exposures a multilayer is formed. This result, that the condensation coefficient for codeposition is by orders of magnitude higher than for pure monomer adsorption, occurs on all substrates studied so far, i.e. Cu, Ag, Au, Ni and SiO₂. The high condensation coefficient remains for thick multilayer film formation; in the example shown here, a formal exposure of 480 L is sufficient to produce a film exceeding a thickness of $d > 7$ nm.

The codeposited layer clearly is not a mixed phase of ODA and PMDA, but consists of polyamic acid (see Fig. 1) as has been discussed previously [11,15]. The C 1s, O 1s and N 1s spectra of the codeposited films (b,c,d) taken after sequential exposures have different lineshapes, indicating that the chemical com-

position varies and is more complex than simple polyamic acid. A stoichiometry analysis showed that spectra b and c have a pronounced deficit of nitrogen, i.e. for spectra c the ratio between $\Sigma C : \Sigma O : \Sigma N = 22 : 6.4 \pm 0.7 : 1.13 \pm 0.05$ compared to the stoichiometric ratio of 22:7:2 for polyamic acid. For spectra (d) an excess of ODA is indicated from the excess of nitrogen and slight deficit of oxygen ($\Sigma C : \Sigma O : \Sigma N = 22 : 5.5 \pm 0.6 : 2.9 \pm 0.25$). Also consistent with an excess of ODA is the $\Sigma N : \Sigma C2 : \Sigma O$ ratio of 2:2.5:3.5 compared to 2:4:7 for polyamic acid [16]. The higher relative carbon content of ODA with respect to PMDA results in a low value for the oxygen stoichiometry.

The initial deficit of nitrogen is not consistent with a PMDA excess because this would also require excess of oxygen due to the higher oxygen/carbon ratio in PMDA as compared to ODA. The result, however, resembles our room temperature adsorption studies of ODA [13], where a pronounced nitrogen deficit of the adsorbed phase was found. Since nitrogen is not contained in this adsorbate phase, some molecular nitrogen species must have been desorbed. The mechanism by which this occurs for pure ODA adsorption and ODA/PMDA codeposition is not known, but the similarity of these two cases highlight the fact that the interfacial chemistry is determined by the functional groups of the organic adsorbates.

The changing lineshapes of the C 1s, O 1s and N 1s spectra b-d following sequential deposition reflect the chemical changes in the ODA/PMDA codeposited layer. The carbon 1s spectrum (b) shows a broad phenyl carbon emission around $E_B = 286$ eV and a broad emission band around $E_B = 290$ eV indicative for carbonyl groups in a variety of chemical environments. In the O 1s emission the high binding energy shoulder at 534 eV is due to hydroxyl oxygen in the polyamic acid deposit. However, only at the higher exposures of spectra (d) does the C 1s, O 1s and N 1s emission become similar to those of solventless polyamic acid produced on silver and gold surfaces by codeposition of PMDA and ODA. The carbonyl intensity is substantially suppressed and broadened while the hydroxyl O 1s emission becomes more pronounced. In the N 1s spectrum (d) the increased width of the peak with the higher binding energy tail indicate that the ODA amino groups are reaction centers in the formation of the polymer (see Fig. 1).

It is the initial bonding of the PAA to the substrate that ultimately determines the fundamental adhesion of the polymer. In previous studies of VDP of polyimide on silver [11] it was postulated that the fragmented monomers acted as anchors for the resulting polymer chain. If this hypothesis is extended to the present case then at the interface only PMDA would contain any functional groups which could react with molecular ODA. As noted earlier, ODA completely dissociates at the room temperature Cu(111) interface with loss of functional groups. The 1.6 nm films of codeposited PMDA and ODA may therefore contain no interfacial ODA. From the lineshape of the C1s spectrum corresponding to 60 L exposure it is clear that the broad carbonyl peak is more pronounced compared to films of increasing thickness. This may originate from PMDA at the interface.

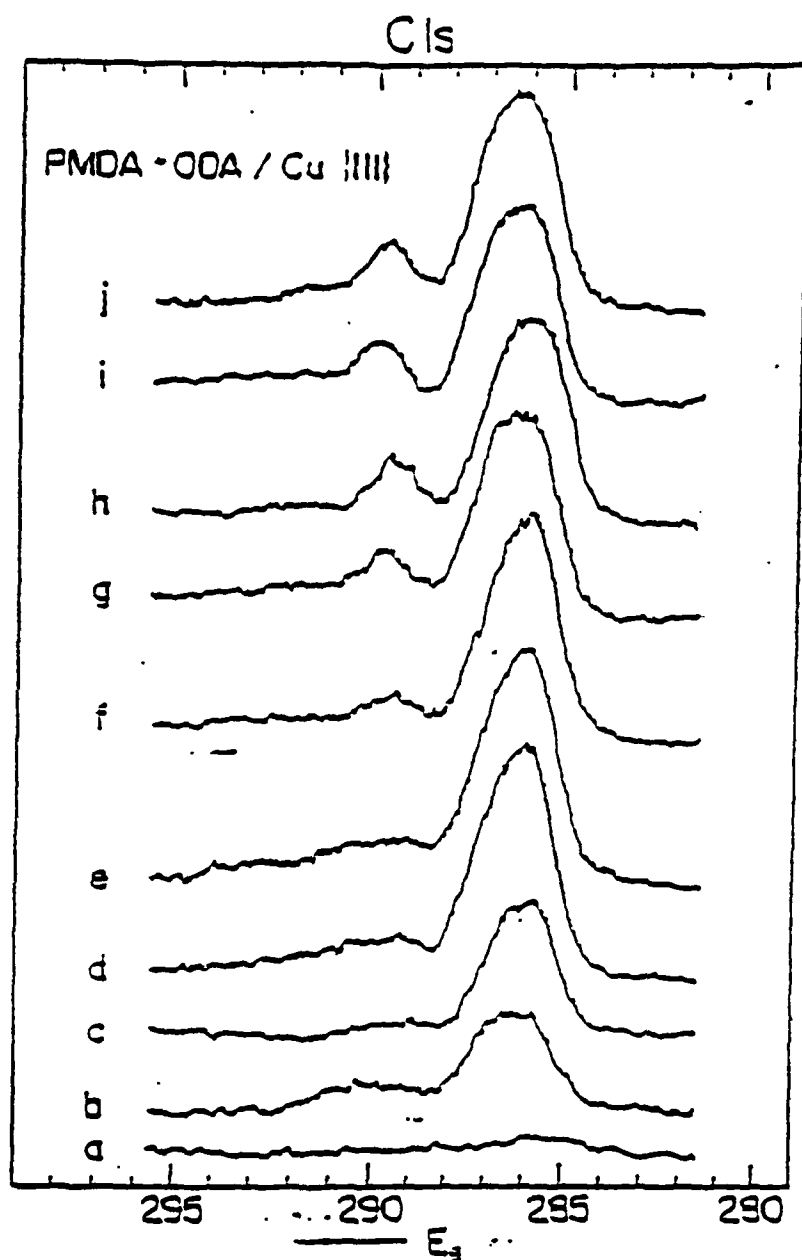


Fig. 10. C1s spectra for the coadsorption of PMDA and ODA on Cu(111) and subsequent heating to form polyimide: (a) Clean substrate (at 298 K); (b) $L = 60$ (at 298 K) $d \sim 1.6$ nm; (c) $L = 180$ (at 298 K) $d \sim 1.7$ nm; (d) $L = 480$ (at 298 K) $d \sim 7.3$ nm; (e) Following heating to 329 K for 1 hr; (f) Following heating to 373 K for 1 hr; (g) Following heating to 423 K for 12 hrs; (h) Following heating to 473 K for 1.5 hrs; (i) Following heating to 573 K; (j) Following heating to 673 K

The fact that multilayers of codeposited PMDA and ODA form at room temperature while neither PMDA nor ODA alone form multilayers suggests that a chemical reaction occurs during codeposition. Accordingly the resulting XPS

spectra are not simply a composite of the monomer spectra. We are unable to determine from the experiments reported here whether the PAA forms at the interface or in the vapor prior to adsorption. The relative size of the polymer does however suggest that Van der Waals forces will play some role in initial adhesion. This would of course increase the initial sticking coefficient.

As the film is heated, the hydroxyl O 1s at $E_B=534$ eV decreases relative to the lower binding energy O 1s emission and the carbonyl C 1s emission is resolved above the background. Concomitant with this is a narrowing of the N1s emission and a shift to higher E_B indicating the onset of imidization. Heating at 573 K and above (Figures 10-12 i-j) does not further change the spectral lineshape which indicates that the curing to form polyimide is complete. The C 1s spectra do not, however, indicate pure polyimide. The peak centered around 286.2 eV does not show the characteristic splitting due to C3 (lower binding energy) and C1 and C4 at higher E_B . Similarly, in the O 1s there is an increase in the lower E_B peak relative to the higher binding energy shoulder. The N 1s peak exhibits a very weak shoulder at lower binding energy, but otherwise shows very little change.

The ratio of the integrated C:O:N intensities during heating is shown in Figure 13 a. As the film is heated there is definite loss of nitrogen due to desorption of excess unreacted ODA. Increasing temperatures lead to imidization and a decrease in oxygen content. At temperatures between 373 K and 473 K there appears to be stoichiometric polyimide.

Figure 13 (b) summarizes the ratio of $\Sigma N:\Sigma O:\Sigma O_2$ integrated intensities and serves to highlight some of the subtleties associated with the reaction. For $T>373$ K the total N:O ratio remains essentially stoichiometric (2:5). In comparison the carbonyl carbon C2 appears to increase as imidization progresses. Much of this initial increase can be attributed to the procedure for background subtraction. Because the broad carbonyl emission in PAA is difficult to separate from the shake-up transitions the latter were initially included in the overall C2 intensity. As the temperature increases, the imidization results in the reappearance of a well defined carbonyl band, which makes the integration much easier. Also, if the phenyl carbons have measurable intensity shake-up transitions, then the carbonyl content will be overestimated at all stages [16]. It is unlikely, however, that the observed large increase in carbonyl can be accounted for in this way. The increase in total carbon relative to nitrogen and oxygen is thus caused by an excess of carbonyl carbon C2.

The lineshape changes indicate that the film produced at 573 K is not pure polyimide but contains a mixture of PMDA and to a lesser extent ODA fragments (the shoulder in the N1s is an indication of this). These excess constituents could be in the form of trapped molecules or terminal groups, but branching and crosslinking might also explain the results. Similar results in very thick films on

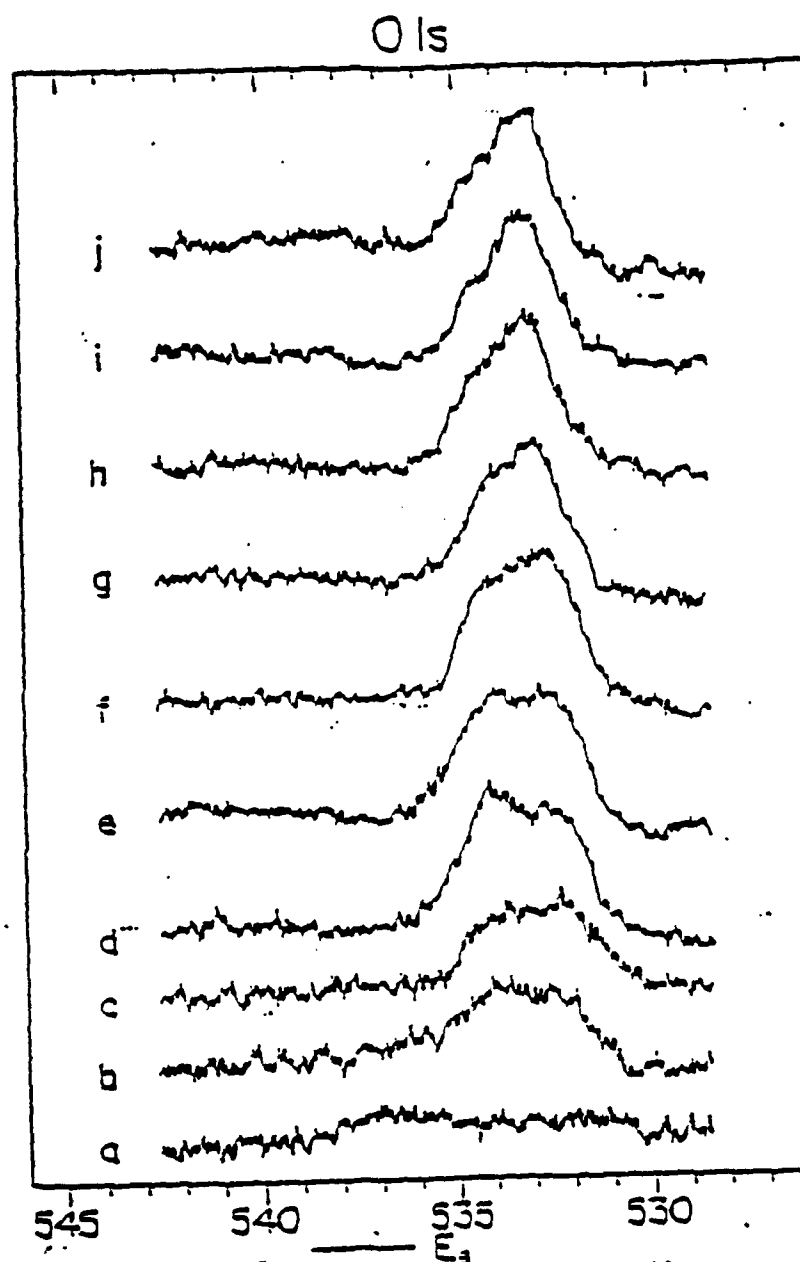


Fig. 11. O 1s spectra for the coadsorption of PMDA and ODA on Cu(111) and subsequent heating to form polyimide: (a) Clean substrate (at 298 K); (b) $L = 60$ (at 298 K) $d \sim 1.6$ nm; (c) $L = 180$ (at 298 K) $d \sim 1.7$ nm; (d) $L = 480$ (at 298 K) $d \sim 7.3$ nm; (e) Following heating to 329 K for 1 hr; (f) Following heating to 373 K for 1 hr; (g) Following heating to 423 K for 12 hrs; (h) Following heating to 473 K for 1.5 hrs; (i) Following heating to 573 K; (j) Following heating to 673 K

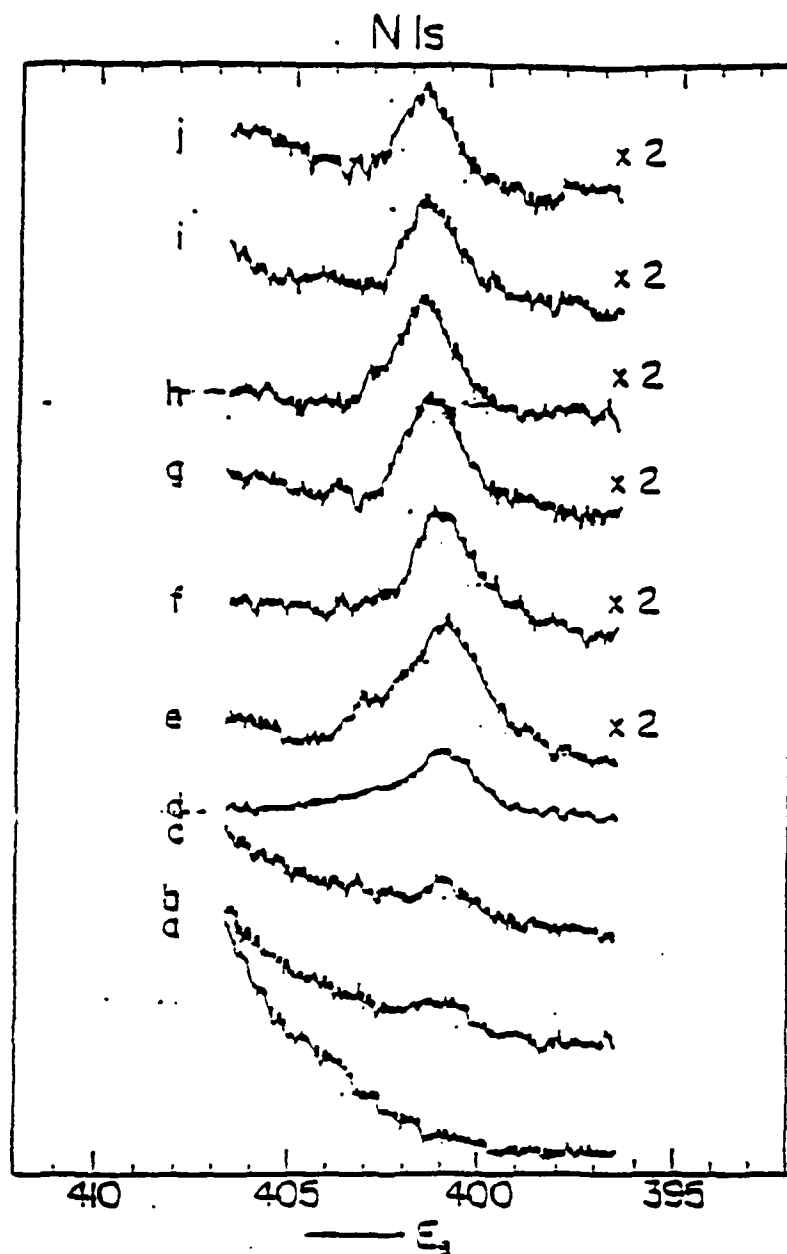


Fig. 12. N1s spectra for the coadsorption of PMDA and ODA on Cu(111) and subsequent heating to form polyimide: (a) Clean substrate (at 298 K); (b) $L = 60$ (at 298 K) $d \sim 1.6$ nm; (c) $L = 180$ (at 298 K) $d \sim 1.7$ nm; (d) $L = 480$ (at 298 K) $d \sim 7.3$ nm; (e) Following heating to 329 K for 1 hr; (f) Following heating to 373 K for 1 hr; (g) Following heating to 423 K for 12 hrs; (h) Following heating to 473 K for 1.5 hrs; (i) Following heating to 573 K; (j) Following heating to 673 K

silver have been reported previously. The dissociation of single monomers on the substrate also suggests that the bulk of the additional carbon in these films could be due to carbonyl carbon arising from the PMDA like fragments in the interface.

Similar results have been reported on polycrystalline Cu[13], for a 4.2 nm thick film. This thicker overlayer did show a much more stoichiometric ratio of C:O:N. The lineshape, however, was also indicative of the presence ODA and PMDA like fragments.

The differences in the polyimide films formed on polycrystalline and (111) copper substrates may then be attributed in part to the interface reaction i.e. to differences in the relative reactive sticking coefficients of PMDA and ODA. If the reactive sticking coefficients of PMDA and ODA leading to carbonyl and nitrogen loss, respectively, are similar on polycrystalline copper but ODA decomposition under the release of nitrogen containing fragments is favoured on Cu (111), the resulting polyimide/copper interface composition will reflect this through an excess of carbonyl groups. Despite having started in the thick polyamic acid film with an excess of ODA, curing has led to an excess of PMDA like species. This is consistent with PMDA and ODA adsorption at room temperature, where the latter is completely dissociated. On polycrystalline Cu the ODA and PMDA were present in much more comparable amounts and the resulting polyimide film composition reflected this.

We can only speculate about the bonding at the polyimide/copper interface at this time. Given the behaviour of PMDA and ODA at $T = 575\text{K}$, we expect that there would in fact be a loss of carbonyl and a breakdown of the polyimide/copper interface into an amorphous carbon layer. However, the polymer has a stabilizing effect and the chemistry at the interface may also be altered due to this.

In previous work [13] the subject of the minimum possible polyimide film thickness was addressed. It was reported that polyimide films thinner than $\sim 4\text{ nm}$ were not possible on polycrystalline Cu while ultra thin films of about 1 nm were possible on polycrystalline Ag. Fragmentation at the interface could be a major cause to this difference. Clearly monomer dissociation is much more pronounced on copper. Figures 9-11a-d show that with increasing exposure an ODA excess is only realized at films with $d > 2\text{ nm}$. If, as suggested previously, this is due to PMDA adsorption being a possible base for future polymer growth then the minimum thickness must take into account the excessive fragmentation at the interface. On silver there is much less fragmentation and the resulting fragments are all available for polymerisation.

In the context of understanding the transmission electron microscopy studies of spun on and vapor deposited polyimide films on copper [2,3] we note that a strong initial reaction occurs between the substrate and both the monomers and polyamic acid. This initial reaction involves covalent and, as has been noted in the PMDA temperature profile, oxidic (partially ionic) bonded copper surface atoms. These then may provide a source for copper ion formation and, subsequent migration into the polymer matrix in the presence of the solvent.

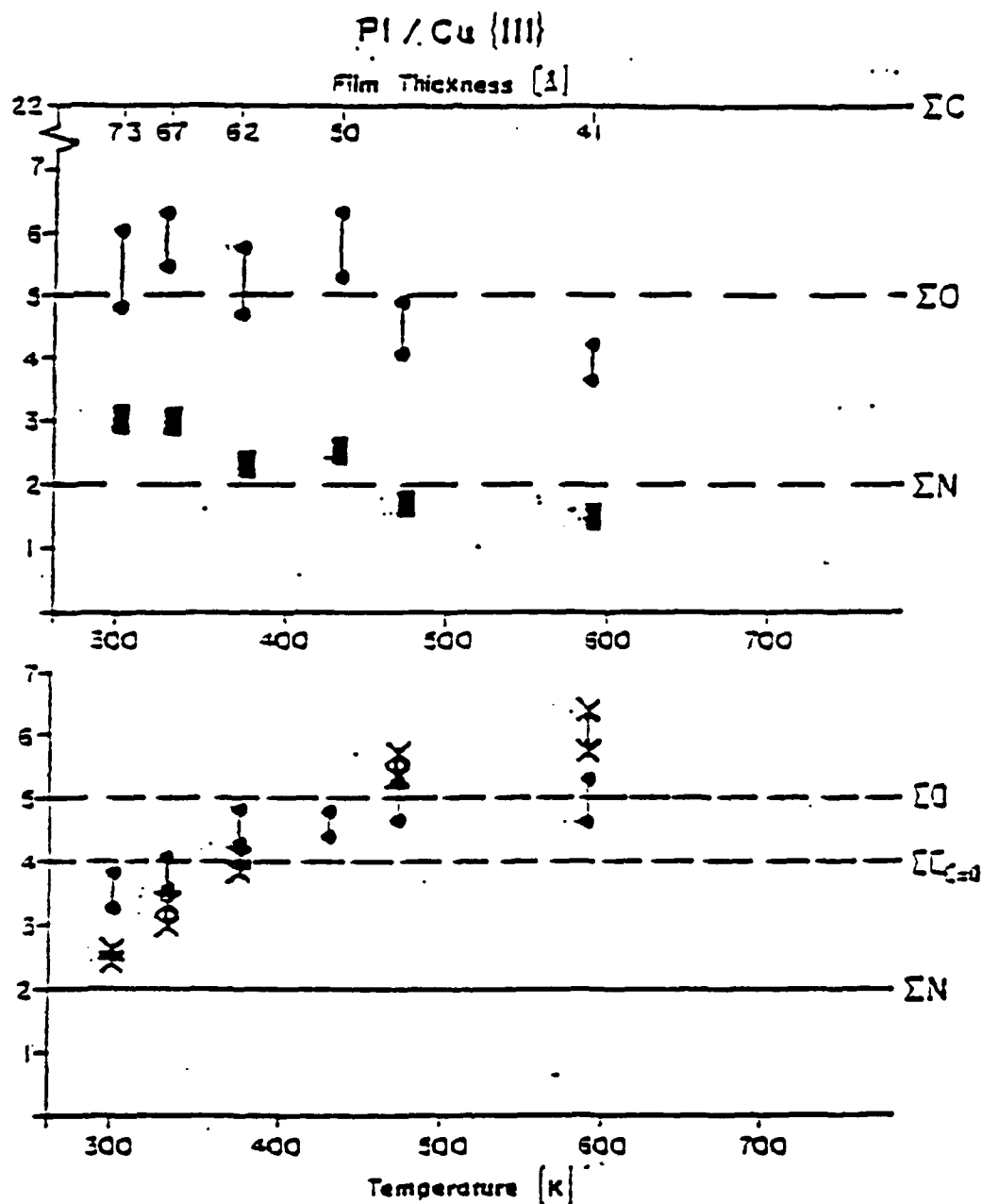


Fig. 13.(a) Total C:O:N ratio normalized to 22 carbon atoms for codeposited PMDA and ODA on Cu(111) at 298 K and subsequent heat treatment. (l) ΣO :• (n) ΣN :[];
 (b) Total O:C2:N ratio normalized to 2 nitrogen atoms for codeposited PMDA and ODA on Cu(111) at 298 K and heat treated; ΣO :• ; $\Sigma C=O$:

Summary

It has been shown that thin polyimide films can be prepared by vapor deposition polymerisation on Cu substrates. The resulting film composition can be related to the initial monomer adsorption. Copper appears to destabilize the adsorbates at room temperature much more than that seen previously on Ag substrates. The minimum polyimide film thickness possible on Cu is found to be about 4 nm and can be explained by the increased degree of fragmentation at the interface.

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References

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1. Polymer Materials for Electronic Applications, A.C.S. Symp. Ser., 184 (1982)
2. Y.-H. Kim, G.F. Walker, J. Kim and J. Park, J. Adhesion Sci. Tech. 1 331 (1987).
3. S.P. Kowalczyk, Y.H. Kim, G.F. Walker, J. Kim, Appl. Phys. Lett., 52, 375 (1988).
4. N.J. Chou and C.H. Tang, J. Vac. Sci. Technol. A, 2, 751 (1984).
5. J.L. Jordan, P.N. Sanda, J.F. Morar, C.A. Kovac, F.J. Himpsel and R.A. Pollak, J. Vac. Sci. Technol. A, 4, 1046 (1986)
6. P.N. Sanda, J.W. Bartha, J.G. Ciabes, J.L. Jordan, C. Feger, B.D. Silverman and P.S. Ho, J. Vac. Sci. Technol. A, 4, 1035 (1986)
7. P.S. Ho, P.O. Hahn, J.W. Bartha, G.W. Rubloff, F.K. LeGoues and B.D. Silverman, J. Vac. Sci. Technol. A, 3, 739 (1985)
8. F.S. Ohuchi and S.O. Freilich, J. Vac. Sci. Technol. A, 4, 1039, (1986)
9. J. Russat, Surf. Int. Anal., 11, 414 (1988)
10. M. Grunze and R.N. Lamb, Chem. Phys. Letts., 133, 283 (1987).
11. M. Grunze and R.N. Lamb, Surf. Sci., 204 (1988) 183.
12. M. Grunze and R.N. Lamb, J. Vac. Sci. Technol. A, 5, 1685 (1987)
13. M. Grunze, J.P. Baxter, C.W. Kong, R.N. Lamb, W.N. Unertl and C.R. Brundle, "Vapor Phase Growth of Polyimide Films" AVS National Symposium, Topical Conference "Deposition and Growth: Limits for Microelectronics", Anaheim, Nov. (1987).
14. M. C. Burrell, P. J. Codella, J. A. Fontana, J. J. Cheva, M. D. McConnell, J. Vac. Sci. Technol. A, 7, 55 (1989).
15. J.R. Salem, R.O. Sequeda, J. Duran, W.Y. Lee and R.M. Yang, J. Vac. Sci. Technol. A, 4, 369 (1986).
16. J.H. Schofield, J. Electron. Spectros., 8, 129 (1976)

17. R.N. Lamb, J. Baxter, M. Grunze, C.W. Kong and W.N. Unertl, *Langmuir*, **4**, 249 (1988)
18. D.T. Clark in "Chemistry and Physics of Solid Surfaces," Vol. 11, Ed. R. Vanselow, CRC Press, Boca Raton (1979)
19. M. Grunze, W. N. Unertl, S. Gnanarajan and J. French, *Mat. Res. Soc. Symp. Proc. Vol. 108*, (1988) 189.
20. S. Gnanarajan, Ph. D. Thesis, University of Maine (1989).
21. T. Strunskus, Diplomarbeit, Univ. Heidelberg (1988).
22. J. P. Baxter, M. Grunze, C.W. Kong, *J. Vac. Sci. Technol. A6* (1988) 1123

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