

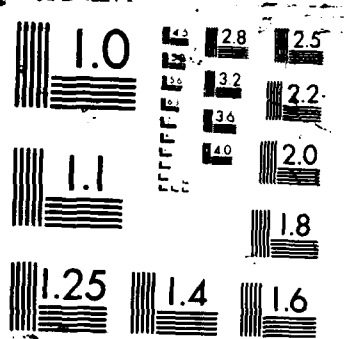
VAPOR PHASE DEPOSITION AND GROWTH OF POLYIMIDE FILMS ON
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS FOR COMPLETING FORM
1. REPORT NUMBER 4	2. GOVT ACCESSION NO.	3. RECORDING CODE DTIC FILE COPY
4. TITLE (and Subtitle) Vapor Phase Deposition and Growth of Polyimide Films on Copper	5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 4	
7. AUTHOR(s) M. Grunze, J. P. Baxter, C. W. Kong, R. N. Lamb, W. N. Unertl and C. R. Brundle	8. CONTRACT OR GRANT NUMBER(s) N00014-85-K-0641	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Laboratory for Surface Science and Technology 9 Barrows Hall University of Maine, Orono, ME 04469	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS R&T Code No. 413a001	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Arlington, VA 22217	12. REPORT DATE November 10, 1987	
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 21	
	15. SECURITY CLASS. (of this report) unclassified	
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in Journal of Vacuum Science and Technology		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) polyimide, vapor deposition, adhesion, copper, XPS, Raman Spectroscopy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See first page		

AD-A189 969

DD FORM 1473 JAN 73

EDITION OF 1 NOV 66 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

88 1 5 096

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OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0641

R&T Code 413a001

Technical Report No. 4

VAPOR PHASE DEPOSITION AND GROWTH OF
POLYIMIDE FILMS ON COPPER

by

M. Grunze, J. P. Baxter, C. W. Kong,
R. N. Lamb⁺, W. N. Unertl and C. R. Brundle**

Prepared for Publication in

Journal of Vacuum Science and Technology

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November 10, 1987



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ABSTRACT

The formation of thin polyimide films from vapor phase deposited 4,4' Oxydianiline (ODA) and Pyromellitic dianhydride (PMDA) was studied by X-ray photoelectron spectroscopy and vibrational spectroscopies. Codeposition of ODA and PMDA onto polycrystalline copper substrates at room temperature, followed by heating in vacuum, led to polymerization and the formation of thermally stable ($T_g \approx 723$ K) polyimide films. Films with thicknesses ranging from ultra-thin (12-30 Å) to several hundred nanometers thick were prepared by this method. Adhesion of the polymer to the surface involve chemical bonding to fragments of PMDA and ODA initially chemisorbed on the clean metal surface. *Keywords: Dielectric Films.*

INTRODUCTION

The formation of thin dielectric polymer films by chemical vapor deposition techniques rather than by spin coating procedures opens the possibility of simplified or alternate manufacturing steps in the microelectronic industry. It is necessary, however, to produce these films with the required electrical and mechanical properties and adhesive strength. Whereas films produced by conventional wet chemical methods are well characterized¹, it would be presumptuous to assume that films formed by vapor deposition techniques, and therefore in the absence of solvents, have the same properties. The absence of the solvent can effect the polymerization process itself and influence the interaction of the film with the substrate leading to an adhesion behavior different from that of spun-on films.

This article describes the results of our experiments on the production of thin polyimide films by codeposition of its respective constituents 4,4' oxydianiline (ODA) and 1,2,4,5 benzenetetracarboxylic anhydride (pyromellitic dianhydride, PMDA) from the vapor phase in a vacuum apparatus. The overall reaction scheme is illustrated in Fig. 1. The principles of solventless preparation of polyimide films were first described in the production of very thick ($> 1\mu\text{m}$) films². Since the thermochemical characteristics of polyimide preclude its vapor deposition, the appropriate constituents which make up the polyimide polymer are co-deposited on the substrate. Under conditions of carefully controlled temperature the coadsorbed molecules will react to form the polymer. The interaction of the constituents with the metal surface and the polymerization process in the co-

deposited layer was followed by X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS) and Raman spectroscopy to determine the interaction with the substrate and the chemical processes during imidization.

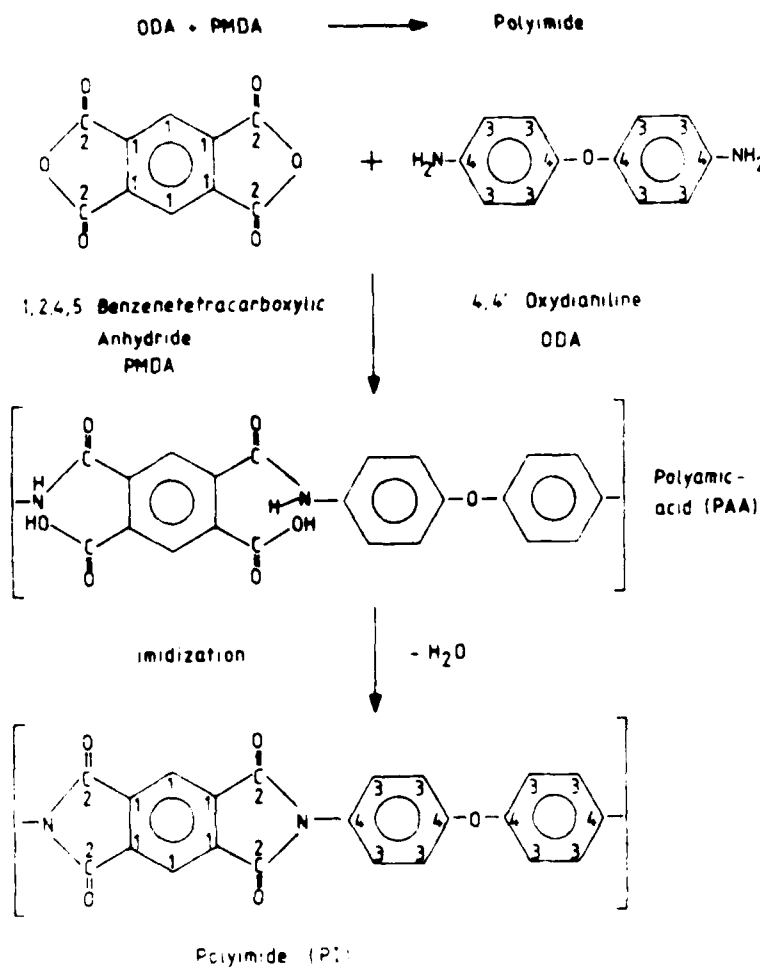


Fig. 1. Schematic representation of the reaction of ODA and PMDA to form polyimide. Labelling of the carbon and oxygen atoms is used to aid the discussion of the XPS spectra.

We first briefly review the pertinent literature on polyimide/metal interfaces. Then we describe our experiments and discuss the chemical characteristics of the films produced by vapor deposition. Finally, we address the nature of the adhesive bond to the copper substrates used in our studies.

1. BACKGROUND

Polyimides (PI) are a class of high temperature polymers that exhibit a unique combination of thermal stability, high softening point and easy processability into coatings or films. In microelectronic device applications, polyimides are used in packaging (e.g. alpha particle barriers, protective overcoats in passivation layers) and as insulating interlevel dielectrics (e.g. pattern delineating material). Polyimide films have usually been applied to the substrate by spin coating. The initial spin-coated layer consists of a solution of the polyimide precursor polyamic acid (PAA) dissolved in a polar solvent. This layer is given a thermal treatment to evaporate the solvent and to imidize the polyamic acid to polyimide.

Reliable adhesion between PI and the substrate is a crucial aspect in all applications. In the absence of extrafacial inhomogeneity (e.g. stress free films) the strength of the adhesive bond is dependent directly on the physics and chemistry of the polymer/metal interface.³ This has prompted a number of investigations to probe the microscopic origins of the bonding which have involved a variety of interfaces and techniques.

Studies involving metallized plastics, where a thin metal film is in contact with a much thicker (usually bulk) fully-cured polyimide phase, have provided the main source of chemical information about the polymer/substrate interface.⁴⁻⁹ For example, room temperature deposition of chromium leads initially to bonding to the PI substrate, possibly via the carbonyl groups, and subsequently with increasing chromium coverage to formation of a carbide like carbon species.¹⁰ Similarly, other electropositive metals such as aluminum,⁷ titanium⁸ and nickel⁴ also appear to react through this carbonyl entity. Copper^{4,6,7} and silver⁴, however, show only a weak interaction with the oxygen in the ether part of the chain.

An alternative method for producing the metal/polyimide interface is spin coating the polymer precursor (PAA) onto a supported metal film, prior to curing and the formation of polyimide. Bulk polyimide/metal interfaces formed in this way⁹ have been shown to produce a marked increase in, for instance, the peel strength of a PI/copper oxide interface compared to conventional metal deposition. The precursor/metal interfacial reaction is apparently much stronger compared to that of the metal/PI where the polymer is fully cured prior to metal deposition. Spin coating has not, until recently,¹¹ been used successfully to generate films thin enough for use with electron spectroscopic techniques because electron propagation away from the interface and out to the vacuum for analysis requires that the insulating films be relatively thin (<100 Å).

It is clear that the way in which the interface is formed is a main factor in determining its chemical and physical properties. While spin-coating and vapor deposition rely upon initial interaction of the substrate with the precursor prior to imidization, formation of a polymer/metal interface by evaporation of the metal onto the fully cured polyimide represents a class by itself. The effect of

the solvent must also be considered in a comparison of spin coated and vapor deposited films. As demonstrated recently by Kim et al.⁹ and Kowalczyk et al.¹² for polyimide/copper oxide interfaces, the presence of the solvent (N-methylpyrrolidone) leads to formation of cuprous oxide particles in the polymer film, whereas interfaces prepared by solventless methods, i.e. vapor deposition of the organic constituents or copper evaporation onto fully cured polyimide, showed no such precipitates.

2. EXPERIMENTAL

The vapor deposition and XPS experiments were carried out in an arrangement consisting of three interconnected vacuum chambers. These were capable of (relatively) high pressure (10^{-6} - 16 bar), high vacuum (to 10^{-9} mbar) and ultra-high vacuum (10^{-11} mbar) conditions, respectively. They were connected via a sample transfer rod which supported the copper samples (1-2 cm²) and was also equipped with both cooling and resistive heating facilities. The temperature was monitored by a chromel-alumel thermocouple. Sample cleaning prior to film deposition was carried out by heating the sample to 800 K in 13 mbar O₂ followed by 3 mbar of H₂ to remove surface oxygen and/or argon ion sputtering. The organic vapor sources consisted of two small quartz tubes (50 mm length, 5 mm diameter) containing the crystalline PMDA and ODA (Aldrich Gold Label), respectively. Thin tungsten wire was coiled around each tube which was subsequently encased in a ceramic block that supported both the wire (heated resistively) and also a chromel alumel thermocouple which was inserted through the mouth of each tube. Prior to deposition, the materials were degassed for thirty minutes at ~393 K. Deposition was carried out in the high vacuum chamber with the sample in the temperature range 200 K-300 K. Optimum deposition conditions were obtained for sublimation temperatures between 373 K and 423 K with concomitant pressures of 2×10^{-6} to 8×10^{-6} mbar. Ultra thin films could be deposited in less than 2 minutes. An arbitrary exposure scale, $L = pt$ [$\times 10^{-6}$ mbar · s] where t is exposure time and p the measured background pressure, is used to indicate the extent of deposition.

In comparison to a similar study with very thick ($> 1 \mu\text{m}$) films,² this present arrangement for co-deposition of organic vapor was significantly simpler in design. In particular, it avoided the necessity of a mixing chamber prior to deposition. No effort was made to maintain a stoichiometric mixture of vapor fluxes during the experiments.

The XPS experiments were carried out in the UHV chamber. The spectrometer contained a Leybold-Heraeus EA11 hemispherical electrostatic electron analyzer and a MgK α x-ray source operated at 100 W. An experimental resolution of 0.92 eV was measured using the Ag 3d emission. The electron binding energies were calibrated against the Au 4f_{7/2} emission at $E_B = 84$ eV.

Analysis of XPS spectra arising from the organic depositions on the metallic substrate involves the determination of peak binding

energies arising for the individual constituents plus determination of the mean stoichiometry from the measured peak areas. The ratio of these is calculated as:

$$\frac{N_1}{N_2} = \frac{I_1 \sigma_2 E_2^{m-0.73}}{I_2 \sigma_1 E_1^{m-0.73}} \quad (1)$$

In eq. 1, N is the number of atoms/unit area with core level intensity I (proportional to the area under the peak) for species 1 and 2. The relative photoelectron excitation cross sections, σ , are 100, 285 and 177 for C 1s, O 1s and N 1s respectively.¹⁴ The electron mean free pathlengths for organic materials and the transmission of the electron spectrometer ($E^{0.73}$) are functions of electron kinetic energy E . A combination of these leads to the form shown in eq. 1. A value for m of zero refers to the limit for ultra thin films. In the case of thick films the correct value of m is not accurately known but probably lies in the range 0.5 to perhaps 0.71;¹⁶ this uncertainty in m results in up to 15 percent uncertainty in relative compositions calculated using eq. 1.

The contribution that final state effects such as shake-ups will have on the integration were discussed in a recent publication with respect to thick vapor deposited films.¹³ Since shake-ups effectively borrow intensity from the primary peaks, uncertainties arise in apportioning these additional intensities. Therefore, calibration spectra of pure PMDA and ODA are used to assign the actual shake-up region in the polyimide spectra.¹⁹

The determination of absolute binding energies is complicated by charging within the film. The general trend observed was shifting of the peaks towards higher binding energies with increasing film thickness and can be explained by a decrease in the final state screening of the photoionized molecule by metal electrons as film thickness increases. Because of the indeterminate contribution of charging to this shift as a function of the film thickness, no corrections have been made to the data presented here.

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

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

where Γ is the mean free path length of the Cu 2p photoelectrons in the overlayer and I_0 is the intensity measured on a clean surface. The main assumptions inherent in eq. 2 are the continuity and homogeneity of the film. We have no information to what extent these conditions are satisfied in the following experiments.

Uncertainties in the choice of Γ have been addressed previously.¹³ The important consideration is, however, its correct order of magnitude rather than any absolute value. The choice of 8 Å for the Cu 2p photoelectrons¹⁵ is considered reasonable in light of previously reported compilations of Γ .¹⁶ The calculated thicknesses report-

ed below are therefore regarded as being suitable approximations. Note that with this value for Γ , films thicker than 37 Å will attenuate the Cu 2p signal to less than one percent of its clean surface value.

The Raman experiments, presented here, were conducted on cured polyimide films which were prepared in the high vacuum chamber and then left exposed to the environment, prior to measurement with the Raman instrument.

3. RESULTS AND DISCUSSION

The overall reaction¹⁷ in the formation of polyimide from ODA and PMDA is shown schematically in Fig. 1. The numbers in the structural formulae are given to facilitate the discussion of the XPS spectra. Initial interaction leads to the formation of polyamic acid which converts upon heating to polyimide.

The following section is concerned with reviewing characteristic features of thin/ultra-thin film spectra for each of the primary constituents, PMDA and ODA. The data for the intermediate (PAA) and the product (PI) are subsequently discussed in light of the analysis of the pure component deposition. This is followed by the examination of a sequence of experiments for determination of the minimum thickness of the codeposited layer necessary to produce a polyimide film.

3.1 ODA AND PMDA

ODA and PMDA were deposited separately on polycrystalline copper substrates to determine the interaction of the two polyimide constituents with the metal surface. The reactivity of the substrate with these will to some extent determine the processes occurring within the codeposited layers and therefore effect the interfacial chemistry between the polyamic acid (and consequently polyimide) and the metal surface.

Figures 2, 3 and 4 show the C 1s, O 1s and N 1s spectra of ODA deposited on polycrystalline copper as a function of exposure. These spectra provide clear evidence for a chemical reaction between ODA and the metal at room temperature.

The adsorption of a carbon containing species is evident for the smallest exposure in Fig. 2, but only at the larger exposures ($L > 240$) is there sufficient oxygen and nitrogen for the adsorbed layer to be detected above the noise level. Spectrum 2c already begins to show the characteristic splitting of the C 1s band for ODA,¹³ whereas the O 1s spectra, Fig. 3c, indicate by the weak emission around 530 eV that besides "organic" oxygen (O 1s emission at $E_B \sim 534$ eV) an oxidic-like species is formed. The N 1s emission corresponding to $L = 240$, however, is too weak to be clearly detected. At $L = 1140$, the C 1s signal increased and a N 1s signal is detected, and there is a small increase in the O 1s spectrum (note the change in intensity scale for the O 1s data between spectra c and d).

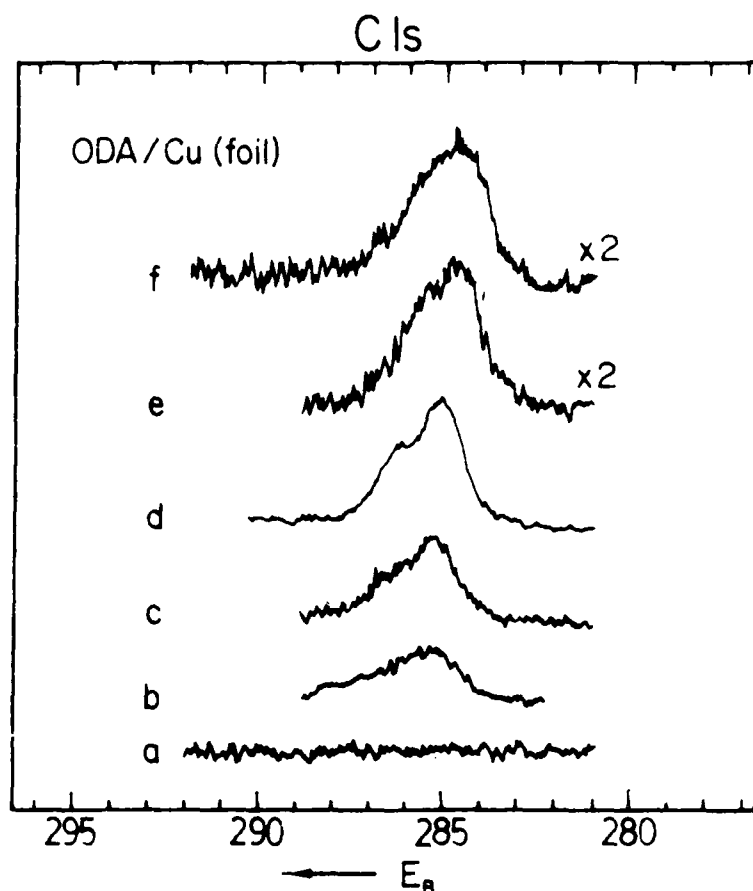


Fig. 2. XPS C(1s) spectra for adsorption and decomposition of ODA on polycrystalline copper. a: clean substrate (298 K), b: $L = 60$ (298 K), c: $L = 240$ (298 K), d: $L = 1140$ (298 K), e: Substrate heated to 346 K, f: substrate heated to 383 K. In trace d the scan speed was decreased from 4 eV/minute to 1 eV/minute and the time constant was increased from 1 s to 5 s.

Heating the sample to 346 K and 383 K (spectra e, f) results in a broadening and decrease in intensity of the C 1s and a decrease in the N 1s peaks and in a reduction of the "organic" oxygen peak located near 534 eV. Some ODA may also sublime.

An evaluation of the stoichiometry of the overlayer after $L = 1140$ results in a total C:O:N ratio of 12:0.9:0.8, if the oxidic oxygen at $E_B = 530$ eV is excluded, the ratio is 12:0.7:0.8. Clearly the layer does not consist of molecular ODA, since the nitrogen content is reduced to about 40% of the expected stoichiometry value of 12:1:2. We therefore conclude that ODA partially dissociates upon adsorption on clean polycrystalline copper. The fact that the carbon

to oxygen ratio is close to the value expected (in particular where the oxidic species are included) but that nitrogen is lost in the initial adsorption process, suggests that the molecule dissociates

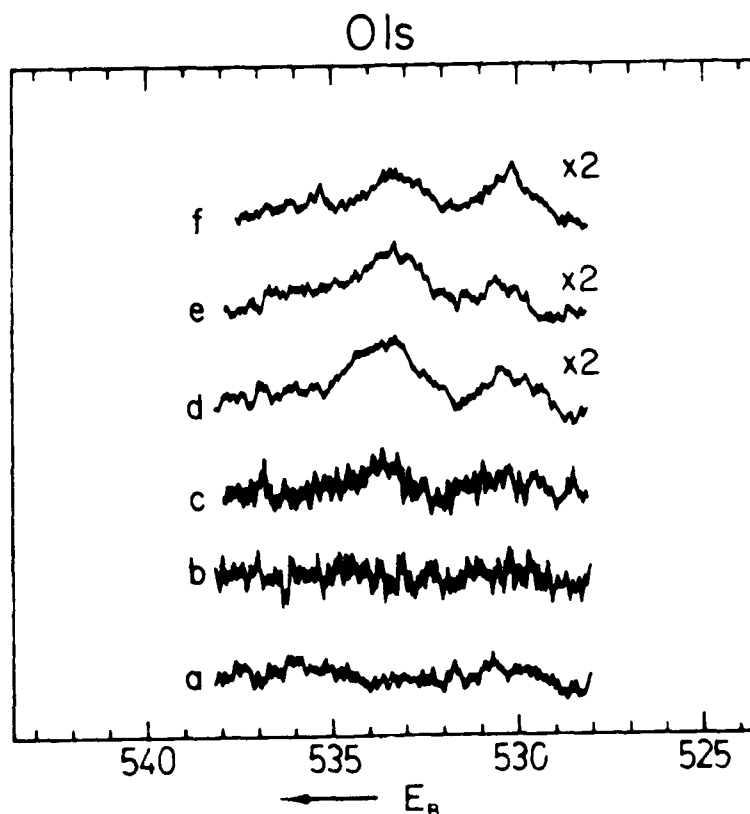


Fig. 3. XPS O 1s spectra for the adsorption and decomposition of 4, 4' oxydianiline on polycrystalline copper. Traces a-f are defined in Fig. 2. In traces d, e, and f the scan speed was decreased from 4 eV/min to 1 eV/min and the time constant was increased from 1 s to 5 s.

via the release of nitrogen or nitrogen carbon entities. A similar reaction scheme has been postulated for the interaction of ODA with silver surfaces¹⁹. As will be discussed elsewhere, heating an ODA layer to $T \geq 380$ K leads to further decomposition leaving primarily amorphous carbon residues on the surface.¹⁸

PMDA deposited at room temperature on a clean Cu {111} surface also decomposes as can be seen from Figs. 5 and 6. Data for PMDA on polycrystalline copper is not available, but it is safe to assume that the chemically more active polycrystalline substrate would show a similar behavior.

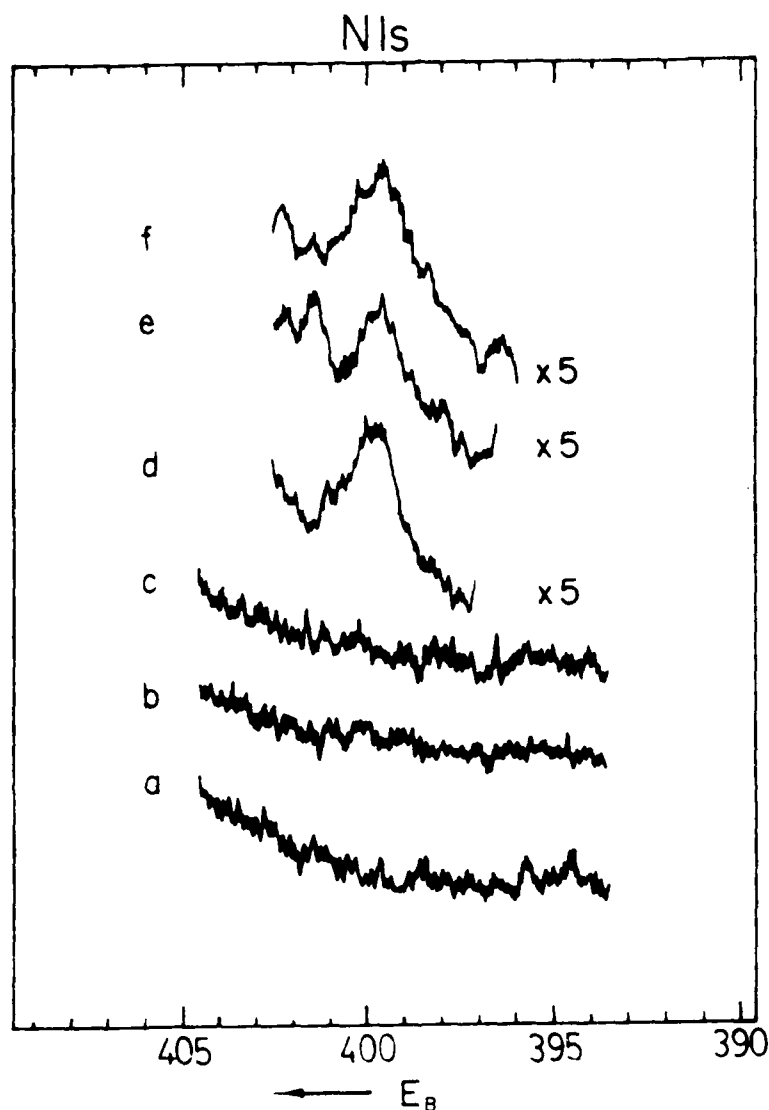


Fig. 4. XPS N 1s spectra for the adsorption and decomposition of 4, 4' oxydianiline on polycrystalline copper. Traces a-f are defined in Fig. 2. In traces d, e, and f the scan speed was decreased from 4 eV/min to 1 eV/min and the time constant was increased from 1 s to 5 s.

Figure 5 shows the C 1s spectra for $L = 30$ and $L = 2040$ at room temperature (Figs. 5a and 5b respectively) and, for comparison, a spectrum recorded after $L = 360$ with the sample held at 200 K (Fig. 5c). The low temperature spectra (Fig. 5c) is for a thick ($d > 40$ Å film) and exhibits the expected¹³ C 1s doublet from the phenyl carbons (C 1 in Fig. 1) and the carbonyl carbons (C 2 in Fig. 1) with a peak area ratio of 6:4. The O 1s spectra (Fig. 6c) corresponding to

the C 1s spectra in Fig. 5c also is indicative of condensed molecular PMDA. The unresolved doublet originates from the anhydride oxygen atoms ($E_B \sim 534.3$ eV) and the carbonyl oxygen atoms ($E_B = 533.0$ eV).

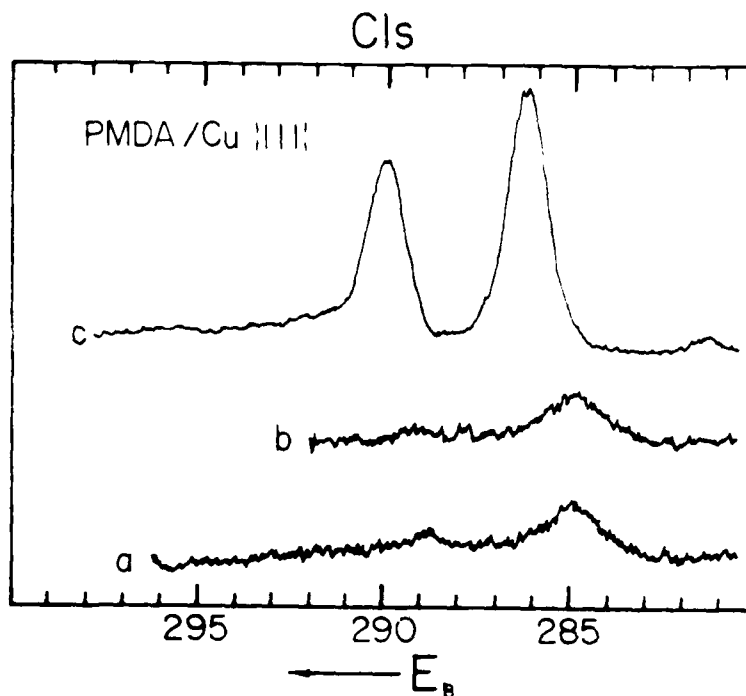


Fig. 5. XPS C 1s spectra of pyromellitic dianhydride (PMDA) on Cu{111}. **a:** $L = 30$ (298 K), **b:** $L = 2040$ (298 K), **c:** $L = 360$, exposure at 200 K. In trace c the scan speed was decreased from 4 eV/min to 2 eV/min and the time constant was increased from 1 s to 2 s.

Thus, the carbon 1s and oxygen 1s spectra Figs. 5a, b and Figs. 6a, b respectively are clearly not consistent with molecular PMDA. The presence of a low binding energy O 1s emission indicates that PMDA oxygen reacts with the surface although the presence of "oxidic" oxygen at $E_B = 530.5$ eV is less clear than in the case of ODA (Fig. 3). The C 1s spectra show a broad low binding energy C 1s emission ($E_B \sim 284.9$ eV) and some residual carbonyl carbon bands ($E_B \sim 289.0$ eV). Clearly, the ratio between phenyl and carbonyl carbon emission of 6:1.7 (in Fig. 5a) is not consistent with adsorbed molecular PMDA, but indicates that PMDA dissociates upon adsorption on the surface. The total C 1s:O 1s ratio of 10:4.6, together with the apparent deficit of carbonyl carbon suggests that PMDA decomposes on the surface with release of one or two CO molecules. The oxygen 1s emission in Fig. 6a and b centered at $E_B = 531.5$ eV is consistent with hydroxyl groups adsorbed on the surface. Formation of hydroxyl species could result from contamination during our deposition experiments,

or by reaction of molecular or atomic hydrogen produced on the hot filaments in the preparation chamber with the PMDA fragments on the surface. From the C 1s spectra it is indicated, however, that PMDA in contact with the clean metal will dissociate.

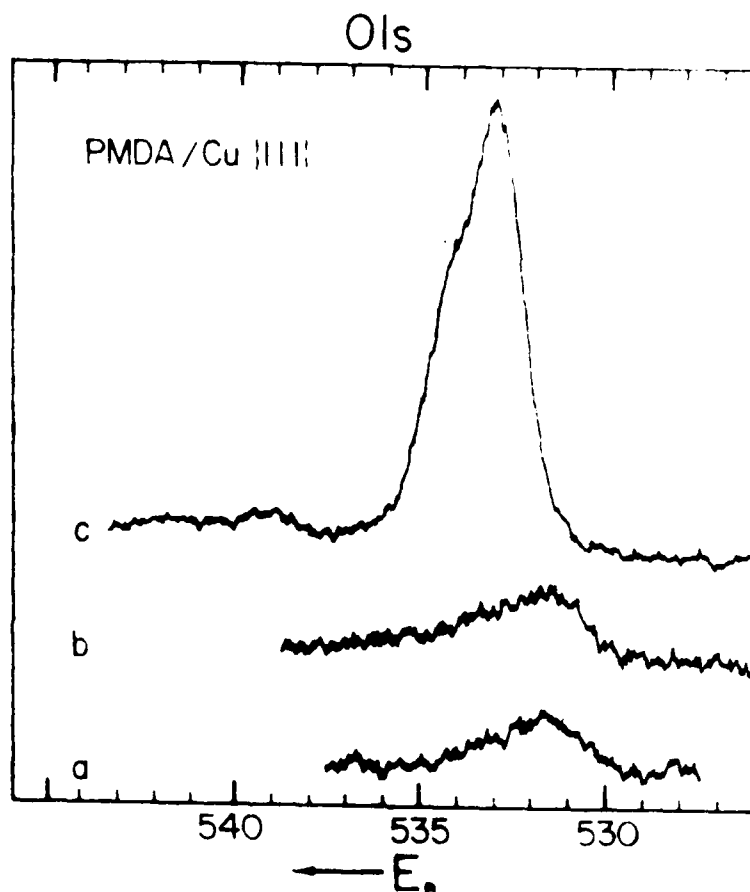


Fig. 6. XPS O 1s spectra of pyromellitic anhydride (PMDA) on Cu{111}. **a:** $L = 30$ (298 K), **b:** $L = 2040$ (298 K), **c:** $L = 360$, substrate temperature 200 K.

3.2 CODEPOSITION OF ODA AND PMDA

The XPS spectra for thin ($d > \Gamma$) and ultra-thin ($d \leq \Gamma$) films of PMDA and ODA on polycrystalline silver substrates have been presented and discussed in detail previously.^{13,19} Deconvolution of the C 1s, O 1s and N 1s bands into the spectral features representative for the different functional groups in the polyamic acid and polyimide chains demonstrated that the resulting polymer films after curing do not consist of pure polyimide exclusively, but must contain a substantial fraction of terminal groups of polyimide chains and/or unreacted ODA molecules. The details of these experiments and dis-

cussion are given in Refs. 13 and 19. Here we only show the general features of the codeposition and imidization process again for a thin film ($d > 40 \text{ \AA}$) of ODA and PMDA codeposited at room temperature onto a polycrystalline copper substrate.

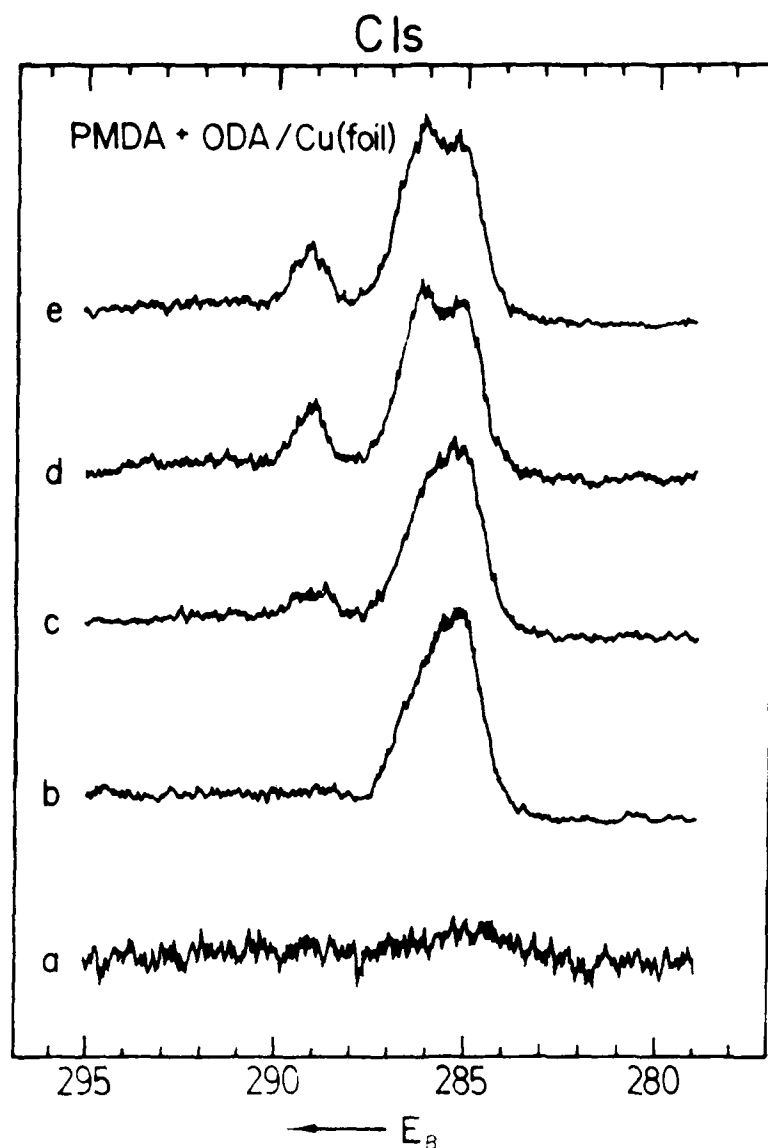


Fig. 7. XPS C 1s spectra for the coadsorption of ODA and PMDA on polycrystalline copper and subsequent heating to form polyimide. **a**: clean copper foil, **b**: $L = 120$ exposure of PMDA and ODA at 298 K, **c**: after heating the substrate for 5 min at 423 K, **d**: heating for 10 min at 573 K, **e**: heating for 10 hours at 573 K. Trace a is magnified by a factor of 2.

The C 1s, O 1s and N 1s spectra Figs. 7b, 8b and 9b are representative of polyamic acid formed by reaction of PMDA and ODA in the adsorbed film. The particulars have been discussed elsewhere,¹³ here we only point out again (i) the absence of a defined carbonyl (C 2) emission, near 290 eV, due to the fact that carbonyl carbons are in a variety of chemical environments, (ii) the pronounced high binding energy shoulder on the O 1s peak attributed to oxygen atoms in

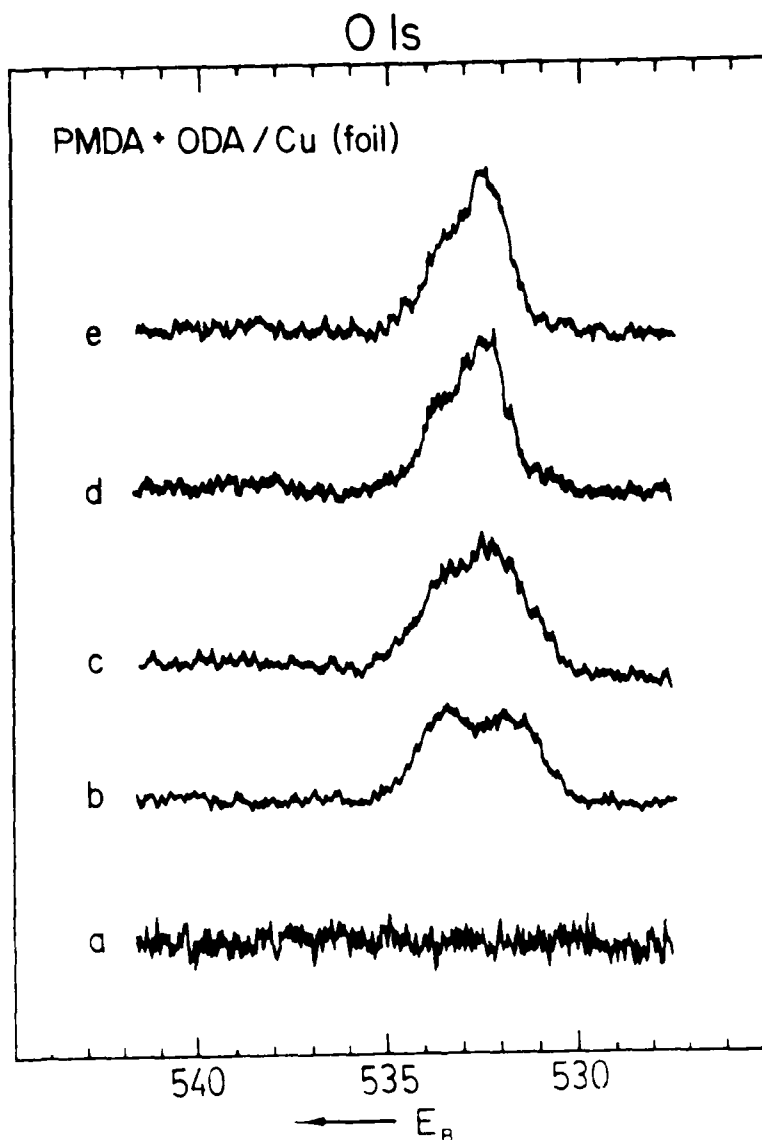


Fig. 8. XPS O 1s spectra for the coadsorption of ODA and PMDA on polycrystalline copper and subsequent heating to form polyimide. Traces a-e are defined in Fig. 7. Trace a is magnified by a factor of 2.

hydroxyl groups in polyamic acid and (iii) the broad N 1s emission indicating a chemical reaction of the ODA amino groups. The stoichiometry of the codeposited layer is C:O:N = 22:4.7:3.2 showing an excess of nitrogen and an apparent deficit of oxygen. In polyamic acid, the stoichiometry is expected to be C:O:N = 22:7:2. An excess of ODA is consistent with the experimental data, since the higher carbon content of ODA with respect to PMDA will give an apparent lower value to the oxygen stoichiometry.

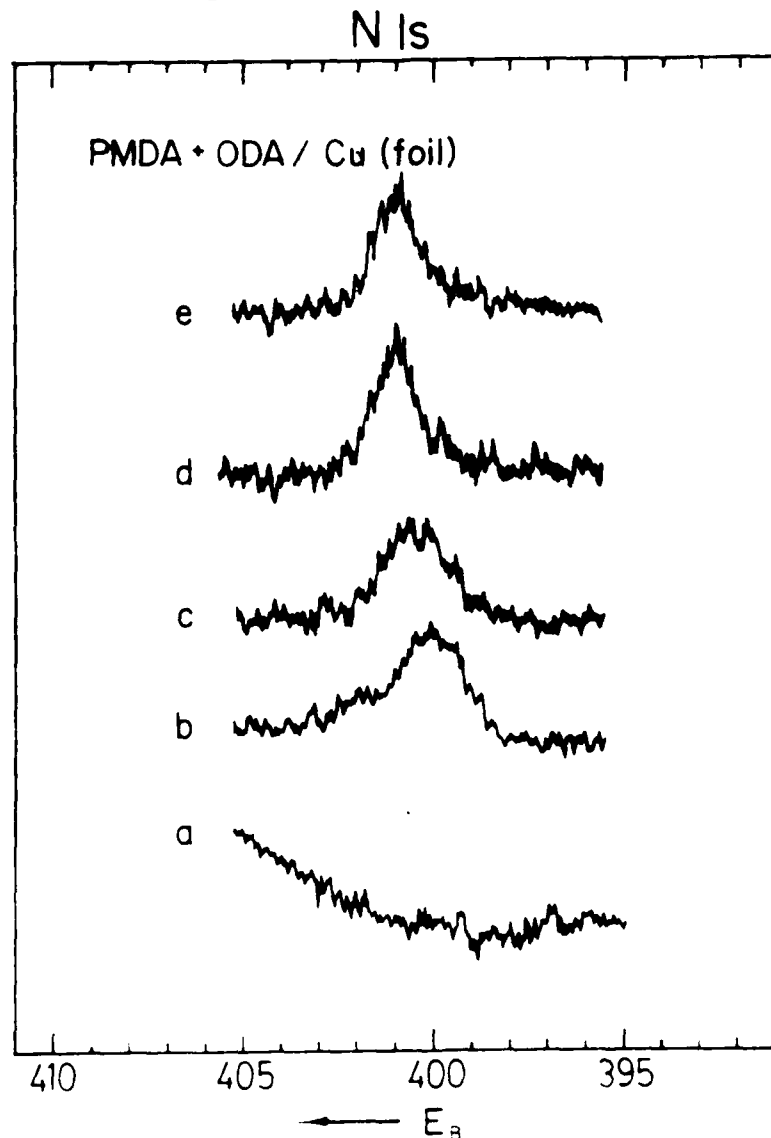


Fig. 9. XPS N 1s spectra for the adsorption of ODA and PMDA on copper and subsequent heating to form polyimide. Traces a-e are defined in Fig. 7.

Heating the film to 423 K for 5 minutes leads to changes in the XPS spectra similar to those observed on silver^{13,19}. In particular, the hydroxyl O 1s emission at $E_B = 534$ eV decreases relative to O 1s emission at the lower binding energies and a carbonyl C 1s emission is resolved again above the background. In the N 1s emission, a shift to higher binding energies is observed indicating the onset of the imidization reaction.¹⁹ Heating to 573 K for 10 minutes then completes the imidization reaction and results in spectra identical to those for a thick polyimide film formed on silver.¹³ In analogy with silver, we conclude that this film even after curing for 10 hours at 573 K does not consist entirely of polyimide. This is supported by the slight deviation of the measured stoichiometry (C:O:N = 22:4.1:1.75) after curing from that of polyimide (22:5:2). In addition, the persistence of a low binding energy tail on the N 1s band indicates the presence of amino terminal groups or perhaps unreacted ODA in the polymer film.

Co-dosed ODA/PMDA on Ag

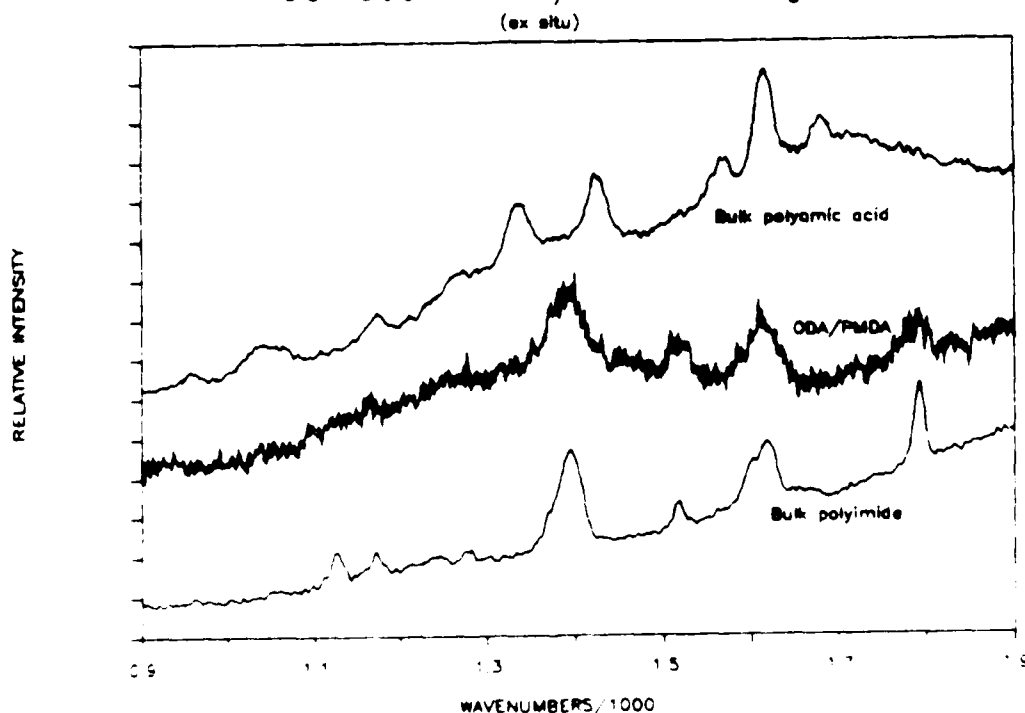


Fig. 10. Raman spectra of polymeric species. The top trace shows a spectra of bulk polyamic acid. The center trace shows a vapor deposited and cured film of about 200 Å thickness on polycrystalline silver. The bottom trace shows the Raman spectrum of a thick polyimide film prepared by spin-coating techniques.

The XPS data shown demonstrate that the core-level photoemission data can be used to follow the deposition and imidization process and can be used to estimate the composition of the final cured films. That these films prepared by chemical vapor deposition indeed are primarily polyimide, follows also from the Raman spectra shown in Fig. 10. Figure 10 compares the Raman spectra of bulk polyamic acid and a spun-on polyimide film with a spectrum obtained from a vapor deposited polyimide film on a polycrystalline silver substrate.¹⁹ This film was cured at 673 K and estimated to be about 200 Å thick based on relative exposure values. The detailed description of these experiments will be given elsewhere, but it is obvious that the vibrational spectrum of the vapor deposited film resembles closely the one for the film prepared by spin coating techniques. However, the vibrational bands in the vapor deposited film (in particular the carbonyl stretching band at 1800 cm⁻¹) are broader. We attribute this to inhomogeneity in the film due to both the uncontrolled stoichiometry of the vapor fluxes and the contribution of the metal/polymer interfacial region.

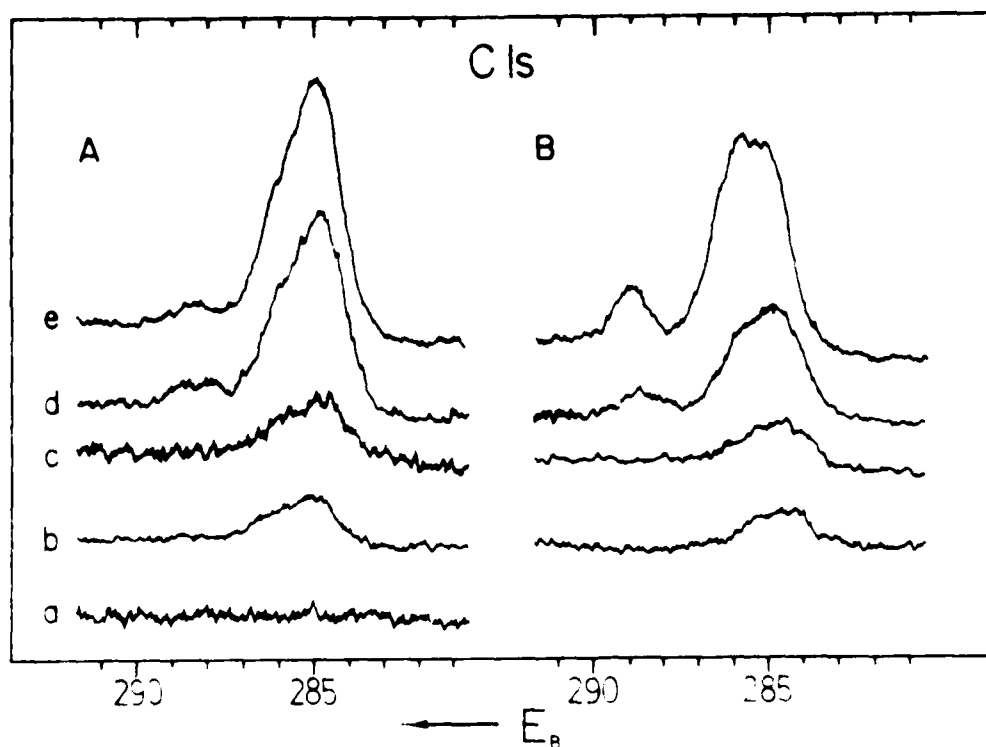


Fig. 11. XPS C 1s spectra of PMDA and ODA codeposited on polycrystalline copper. The spectra on the left (section A) are after deposition at 298 K and the spectra on the right (section B) are after curing the deposit for two hours at 473 K. a: clean surface, b: after L = 20 exposure of the two monomers, c: L = 60, d: L = 300, e: L = 600. Traces b and c part B were taken at a reduced scan speed (2 eV/min) and with an increased time constant (2 s).

We finally want to address the minimum possible thickness of polyimide films prepared by vapor deposition, and the chemical composition of the polymer/metal interface. To study these questions, we performed a series of experiments where polyamic acid films of different initial thicknesses were prepared at room temperature (Figs. 11A, 12A, 13A) and subsequently heated for 2 hours to 473 K to form the polyimide (Figs. 11B, 12B, 13B). Representative C 1s, O 1s and N 1s spectra for four different coexposures and thus different initial film thicknesses and the respective spectra after heating are shown

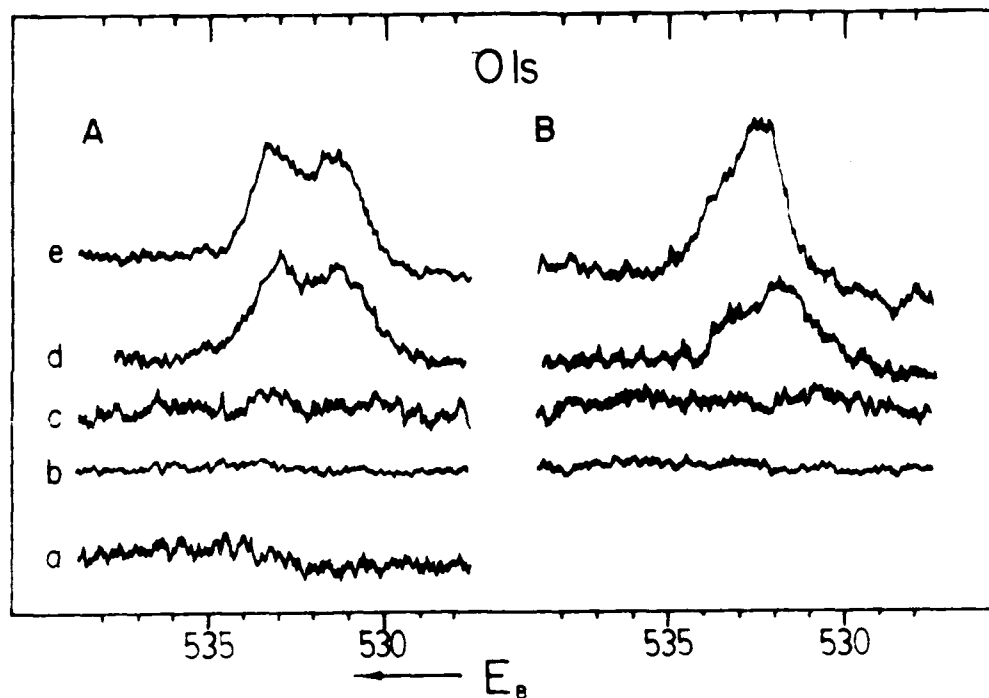


Fig. 12. XPS O 1s spectra of PMDA and ODA codeposited on polycrystalline copper. The traces are defined in Figure 11. Traces b were taken at a reduced scan speed (2 eV/minute) and an increased time constant (2 s).

as curves b, c, d and e in Figs. 11-13. A compilation of the stoichiometries of the different films before and after heating is given in Fig. 14. Spectra b in Figs. 11-13 refer to a very brief coexposure (film thickness $\sim 3 \text{ \AA}$). Only carbon and some nitrogen can be detected after the initial room temperature exposure, indicating that the layer must consist primarily of ODA. Since our fluxes are not calibrated, this result might reflect an excess of ODA in the flux

and/or preferential adsorption of ODA on the polycrystalline substrate. Heating leads to a shift of the C 1s emission to lower binding energies, indicating some decomposition of the film. The somewhat thicker codeposit (spectra c) gives a similar result. A codeposit of 31 Å thickness (d), however, results in C 1s, O 1s and N 1s spectra similar to those expected for polyamic acid.²⁰

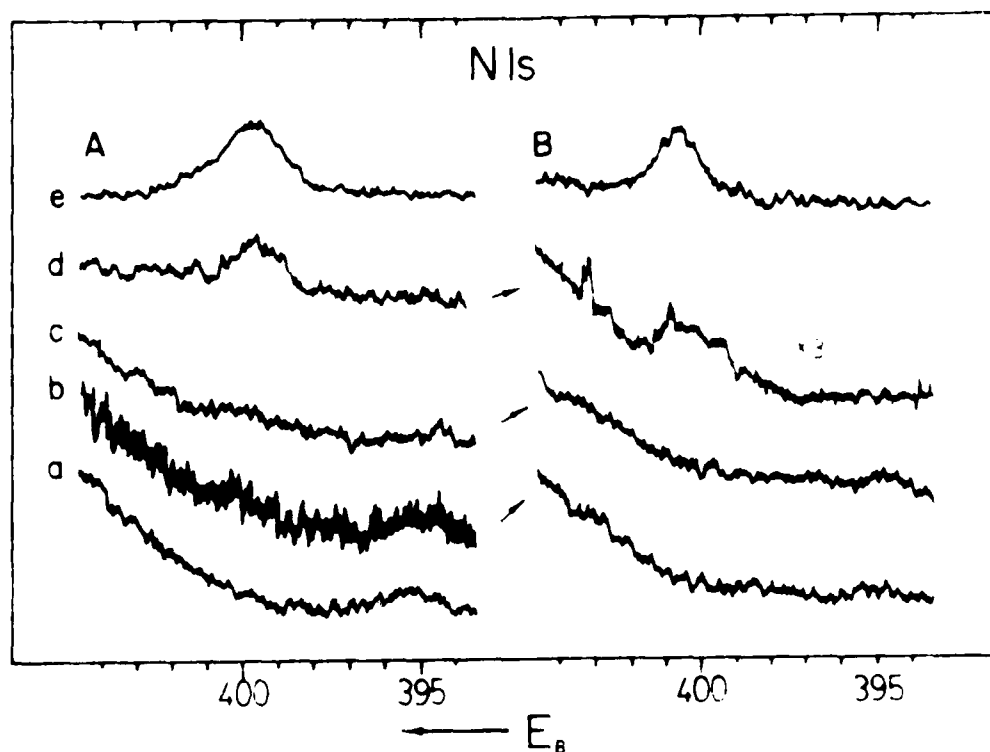


Fig. 13. XPS N1s spectra of PMDA and ODA codeposited on polycrystalline copper. The traces are defined in Fig. 11. In trace b part A the time constant was reduced from 2 s to 1 s.

A broad C 1s carbonyl emission is observed in Fig. 11d as compared to the spectrum in Fig. 7b. We did notice in all of our experiments, that the appearance of the carbonyl C 1s emission in the initial deposits on copper varies strongly, possibly due to different local chemical environments. This variation was not observed for initial deposits on silver. Heating this 31 Å deposit leads to the loss of material (the film thickness decreases to ~11 Å) and to changes in the XPS spectra indicating the presence of organic fragments. It is difficult to identify any spectral features which would unambiguously be defined as due to polyimide. The O 1s emission shows a low binding energy shoulder indicative of oxidic oxygen and, at higher energy, an unresolved doublet which resembles the O 1s from polyimide. Also, the N 1s emission is shifted to slightly higher

binding energies and is indicative of imide nitrogen.

The series of spectra obtained for a deposit of initial thickness $d > 70 \text{ \AA}$ (Figs. 11e, 12e, 13e) heated to 473 K for 1 hour clearly resembles the XPS data for thick polyimide films. The resulting average film thickness for these spectra is about 42 $\text{\AA}$ and the stoichiometry is consistent with that of the thick polyimide film shown in Figs. 7e, 8e and 9e. However, a closer inspection of the C 1s and O 1s lineshapes reveals that both have additional contributions at lower binding energies which are similar to those shown in Fig. 2-7 for initial depositions of pure ODA or PMDA leading to fragmentation.

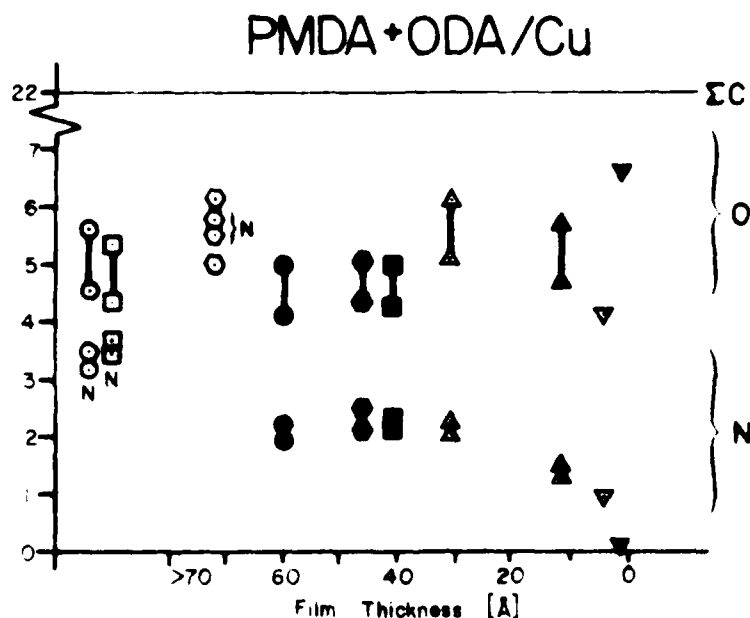


Fig. 14. The stoichiometry of codeposited layers of PMDA and ODA on polycrystalline copper as a function of film thickness reference to a total of 22 carbon atoms. The open symbols are before curing and the closed symbols are after curing. For $d > 10 \text{ \AA}$ the upper and lower symbols connected by the bars refer to the thick film and thin film limit, respectively (see eq. 1). For $d < 10 \text{ \AA}$, only the stoichiometry evaluated for the thin film limit is displayed.

We therefore conclude that the minimum thickness of a polyimide film which can be formed on polycrystalline copper is about 42 $\text{\AA}$ and that there is an intermediate layer at the polymer/metal interface which contains species similar to those observed for fragmented ODA and PMDA. As has been discussed in more detail elsewhere, this intermediate layer is stable at temperatures up to 673 K, whereas

pure ODA or PMDA layers decompose into an amorphous carbon layer at these temperatures.¹⁸ This suggests that the interfacial species are stabilized by the polyimide film, which in turn means that they must chemically interact with the polymer, and that adhesion of the polyimide to the metal substrate occurs through fragmented PMDA and/or ODA.

4. SUMMARY AND OUTLOOK

Polyimide films as thin as ~ 40 Å can be produced by chemical vapor deposition of PMDA and ODA on clean polycrystalline copper substrates. Even thinner films ($d \sim 11$ Å) were obtained on silver substrates as reported elsewhere.¹⁹ Separate adsorption experiments for the pure constituents show that both PMDA and ODA fragment on clean copper surfaces at room temperature; only at temperatures less than 250 K is condensation to form thick films observed. Decomposition of the constituents is also observed in codeposition experiments. Only for sufficiently thick codeposited layers does imidization of the polyamic acid to polyimide occur concurrently with fragmentation at the interface. Adhesion of the polyimide film to the substrate must thus occur via chemical interaction with the fragmented layer.

Our experiments show that chemical bonding is involved in adhesion at the polyimide-metal interface for polyimide films prepared by vapor deposition. The experiments also demonstrate that these films can be made thin enough so that surface sensitive analytical techniques can be used to study their interfaces. This opens possibilities for systematic study of other aspects of microscopic interface chemistry. From a practical viewpoint, we can now begin to study the behavior of interface specific materials such as adhesion promoters.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research and the National Science Foundation through grant No. DMR-8403831. We thank R. Mack, C. Carlin and M. Cook for obtaining the Raman spectra.

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