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In this article we discuss the core level spectra of solventless prepared poly(N,N'-(p,p'-oxydiphenylene)pyromellitic acid) or PMDA/ODA polyamic acid (PAA) films with particular emphasis on the chemical composition and on the Ols and Cls "shake up" transitions. Both vapor deposited polyamic acid and the resulting polyimide films show an excess of oxydianiline (ODA) and a deficiency of carbonyl groups. A qualitative analysis of the "shake up" transitions on the Ols and Cls core holes indicate that polyamic acid is in a non-planar conformation. A shoulder in the Nls band at higher binding energy was assigned to positively charged nitrogen and we concluded that a proton is transferred from the amic acid group onto the nitrogen atom of unreacted oxydianiline. The amic acid group of the molecule is the primary site of interaction with evaporated gold atoms and with bulk silver surfaces. In the case of polyamic acid and polyimide films on polycrystalline silver the interfacial bonding is achieved via silver carboxylate linkages.

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Abstract

In this article we discuss the core level spectra of solventless prepared poly(N,N'-(p,p'-oxydiphenylene)pyromellitic acid) or PMDA/ODA polyamic acid (PAA) films with particular emphasis on the chemical composition and on the O1s and C1s "shake up" transitions. Both vapor deposited polyamic acid and the resulting polyimide films show an excess of oxydianiline (ODA) and a deficiency of carbonyl groups. A qualitative analysis of the "shake up" transitions on the O1s and C1s core holes indicate that polyamic acid is in a non-planar conformation. A shoulder in the N1s band at higher binding energy was assigned to positively charged nitrogen and we concluded that a proton is transferred from the amic acid group onto the nitrogen atom of unreacted oxydianiline. The amic acid group of the molecule is the primary site of interaction with evaporated gold atoms and with bulk silver surfaces. In the case of polyamic acid and polyimide films

on polycrystalline silver Infrared-Absorption Reflection experiments indicate that the interfacial bonding is achieved via silver carboxylate linkages.

Introduction

Polyamic acids (PAA's) are the precursor molecules in the formation of polyimides (PI), a class of high temperature polymers widely used in microelectronic applications. Due to their favorable combination of thermal stability, chemical resistance and easy processibility they are replacing cer-amic materials in microelectronic applications. Typically, PI's are processed in their polyamic acid precursor state. The polyamic acid is formed through polycondensation of an aromatic dianhydride with an aromatic diamine by dissolving and mixing the monomeric materials in a highly polar organic solvent (usually N-methyl pyrrolidone (NMP)). The obtained PAA solution is then spin deposited onto the substrate and the solvent is evaporated. Imidization to PI is achieved by subsequent heating in an inert atmosphere at temperatures up to 350 C°.

Curing and imidization of PAA obtained from solution has been investigated by Feger et al.[1]. They demonstrated that complexation of PAA by the solvent NMP has a marked influence on imidization. Only at temperatures high enough for decomplexation and for breaking the remaining hydrogen bonds between PAA and NMP can the highly reactive free groups react to form imide or, in a reverse reaction, to form anhydride. Decomplexation precedes imidization and anhydride formation. Only in the case of excess

NMP in the solution, decomplexation occurs simultaneously with imidization and anhydride formation [1]. An important role of the solvent is to facilitate a high mobility of the polyamic acid moieties and the conformational changes to allow imidization.

Alternatively PAA can be obtained without solvent by vapor deposition polymerization as described first by Salem et al. [2].

In this technique the dianhydride (1,2,4,5-benzene-tetracarboxylic anhydride) and the diamine (4,4'-oxydianiline) are codeposited onto a substrate, where they react to form PAA. Again the transformation to Polyimide is obtained by subsequent heating to temperatures up to 350°C. By comparison to spun on films, initial interaction of the polymer with the substrate occurs in the uncomplexed PAA state. The chemical interaction between PAA and the metal establishes the adhesion of the final polyimide film. This is discussed in this communication for evaporated gold cluster and bulk silver surfaces.

The X-ray photoelectron spectra for both dissolved and solventless polyamic acid have been reported in the literature [2-8]. It has been noted previously by us [5-7], that the spectra for solventless PAA and PI exhibit a pronounced deficiency for the C1s and O1s carbonyl emission. This, together with an analysis of the N1s lineshape and the O1s and C1s shake up features, allows us to derive conclusions on the chemical nature of solventless polyamic acid and to explain its high reactivity towards metals as discussed below.

Experimental

The gold substrates for the vapor deposition experiments were obtained by evaporation from a tungsten basket onto freshly cleaved mica sheets. The gold overlayers were sufficiently thick ($d > 8 \text{ nm}$) to suppress completely the photoemission signal from the underlying mica substrate. Vapor deposition of crystalline PMDA (pyromellitic dianhydride) and ODA (4,4'-oxydianiline) (Aldrich Gold Label) was carried out in the preparation chamber using small quartz test tubes heated resistively with a tantalum wire wrapped around them. Sublimation temperatures were measured by type K thermocouples inserted through the front end of each tube. The temperatures were adjusted to give approximately equal fluxes of PMDA and ODA to the surface. The base pressure of the preparation chamber was in the 10^{-9} mbar range; during deposition the pressure rise was in the 10^{-6} mbar range. After dosing, the samples were transferred in vacuo into the analysis chamber. XPS measurements were performed with a Mg K_{α} anode operated at 100 W. The spectra are calibrated against the Au 4f 7/2 emission with an electron binding energy (BE) of 84.0 eV. No charging corrections were applied. All spectra presented here were recorded with an experimental resolution of 0.9 eV.

The Infrared spectra were recorded with a specially constructed evacuable infrared reflection spectrometer using conventional optics and a grating monochromator. The evacuated spectrometer ($p < 10^{-3}$ mbar) was attached to a small UHV chamber using calcium-fluoride windows. The small UHV chamber was part of a larger surface analysis system. The polymer films were produced in the

vacuum system by vapor deposition and analyzed in ultra-high vacuum without exposure to air.

Results and discussion

1) Polyamic acid

In the following section we focus on some specific features in the core level spectra of polyamic acid and relate them to chemical and structural models for polyamic acid.

a) Carbonyl deficiency in PAA and PI films

Codeposition of PMDA and ODA onto a substrate held at room temperature leads to the formation of polyamic acid (PAA) [5-7]. Since the reactive sticking coefficient of PMDA and ODA forming PAA is substantially larger than for the sticking of the monomers on the bare metal surface, the initial interaction will be predominantly between PAA and the metal. The XPS spectra of the Cls region directly after dosing the gold substrate and after various curing stages are displayed in figure 1a to 1e. The corresponding spectra of the O1s region are shown in figure 2a to 2e. The film thickness of the PAA film (fig. 1a) was 8.8 nm as determined from the attenuation of the gold substrate using $\lambda=2.2$ nm as the electron mean free path for the Au 4f emission at 1170 eV kinetic energy [9]. The lineshapes for PAA as well as for the intermediate curing stages and the final PI film are in good agreement with data reported previously by us and others [2-8].

The main band in the C1s emission around 285 eV binding energy arises from emission of the carbon atoms in the phenyl rings. The features at higher binding energies ($E_B > 288$ eV) in the C1s emission are due to C=O double bonded carbon in carbonyl groups and "shake up" transitions due to $\pi-\pi^*$ excitations in both the aromatic ring systems and in the carbonyl groups. A detailed assignment of the C1s emission for polyamic acid and for polyimide has been reported previously [2-8].

From a semiquantitative analysis as described elsewhere [6] we obtain an O:N:C ratio of 4.7:2.6:22 compared with the stoichiometric ratio of 7:2:22 (normalized to 22 carbon atoms per polyamic acid (or polyimide) repeat unit). Considering the contributions of the ODA and the PMDA monomers to the nitrogen to carbon (N:C) ratio the composition of the poly-amic acid can be calculated independent of the degree of imidization. Using this method we obtain a monomer distribution of 66% ODA to 34% PMDA (or 95% excess ODA) compared with a 50% to 50% distribution expected for stoichiometric polyamic acid (or polyimide). Upon stepwise heating to 350°C most of the excess ODA is desorbed resulting in a polyimide film with an O:N:C ratio of 4.5:2.1:22 (compared with the stoichiometric ratio for polyimide of 5:2:22), corresponding to a monomer distribution of 53% ODA to 47% PMDA (or 13% excess ODA) as calculated from the N:C ratio.

The integrated intensity of the carbonyl carbon emission relative to the integrated phenyl carbon emission for poly-amic acid (around 289 eV in figure 1a) and for polyimide (at 289.0 eV in

figure 1e) after correction for the excess ODA is only 3.4:18 and 3.5:18, respectively, i. e. too small to account for four carbonyl groups per PAA or PI repeat unit. (The integral for the carbonyl groups in polyamic acid was obtained by integrating over the combined carbonyl and shake up region and subtracting the shake up intensity as observed in polyimide). Adding to the carbonyl and phenyl intensity the fraction of shake up intensity as observed in Pyromellitic dianhydride (PMDA) and in Oxydianiline (ODA) i.e. 7.8% (PMDA carbonyl), 10.8% (PMDA phenyl) and 6.2% (ODA phenyl), respectively [27], does not change the carbonyl to phenyl intensity ratios of polyamic acid and polyimide significantly. However, if the fraction of the shake up intensity is higher for the carbonyl groups in PAA or PI than it is in PMDA, we underestimate the carbonyl intensity, if it is lower, the carbonyl intensity could be too high. Taking these uncertainties into account, no quantitative conclusions about the carbonyl deficiencies can be drawn from the C1s spectra alone. The O1s emission of polyamic acid in figure 2a shows a broad doublet around 533 eV. This arises from the carbonyl group emission (lower binding energy) and the hydroxyl and ether oxygen photoemission (higher binding energy) [2,5-7]. The disappearance of the hydroxyl groups due to the formation and desorption of water during the curing process can be clearly seen in figure 2 for the various curing stages. A detailed discussion of the assignment of the bands for the O1s emission of PI (fig. 2e) has been given by Haight et al.[10].

From the deconvoluted O1s spectra (not shown here) we obtain 47% carbonyl oxygen contribution in PAA and a 72% contribution of carbonyl oxygen to the total oxygen content in poly-imide (both corrected for excess ODA). Depending on the degree of imidization the expected carbonyl oxygen contribution should increase to 80% for full imidization. If 90% "imidization" is assumed in the polyimide shown in fig. 2e, we obtain a deficit of 0.5 carbonyl oxygen atoms per PI repeat unit (consistent with the Cls data). We note, that we can not distinguish between complete imidization plus trapping of water and incomplete imidization. Thus the actual degree of imidization can be higher than the 90% given above.

"Incomplete" imidization is further supported by the following considerations: When the amount of ODA monomer in the PI film is calculated from the nitrogen to carbon (N:C) ratio (result independent of the degree of imidization) and the oxygen to carbon (O:C) and the oxygen to nitrogen (O:N) ratio (results depend on the degree of imidization), respectively, a portion of 53% ODA (and 47% PMDA) is obtained from each calculation, and thus the results are in very good agreement with each other. Lower or higher degrees of imidization would give carbonyl oxygen deficiencies in the O1s spectra from zero and up to 1.1 oxygen atoms per PI repeat unit, respectively, but inconsistent results are obtained when the amount of ODA in the film for the corresponding degree of imidization is calculated from the three ratios mentioned above. In summary there appears to be a 12-15%

deficiency of C=O double bonded carbon and oxygen atoms in vapor deposited PAA and PI films.

Higher carbonyl deficiencies have been reported for spin coated polyamic acid [4,8] and polyimide films [4,8,10-12]. The carbonyl group deficiency for spin coated polyimide films has been discussed by Atanasoska et al. [11]. They attribute it to the formation of isoimide groups (as high as 25%), but they also note that there is some contradictory evidence. It is known, for instance, that isoimide groups irreversibly transform to imide groups upon heating to 300°C [13] and only a few percent isoimide are indicated in infra-red spectra of polyimide films [2,13]. A loss of carbonyl groups during imidization can be ruled out, since it is not consistent with the nitrogen to carbon (N:C) ratio in polyimide. Also, no loss of carbonyl groups is found in the case of PMDA multilayer condensation at room temperature and one expects that the carbonyl groups are stabilized by the reaction with ODA. This is supported by the fact that the PMDA loses carbonyl groups at temperatures exceeding 373 K, whereas no loss of carbonyl groups in the PI is observed up to 673 K [15]. Considering the excess of ODA, and apparent deficit of carbonyl C1s intensity found in vapor deposited polyamic acid [5-7], we propose a reaction as shown in Figure 3. The nucleophilic attack of an ODA amino group (3B) at a carbonyl group of PMDA (3A) is accompanied by opening of the PMDA anhydride ring leading to a "protonated" positively charged amide nitrogen and a negatively charged carboxylate group (3C). In the carboxylate group the carbon-oxygen bond order is reduced as compared to a carbonyl

group and the Cls binding energy will be shifted to lower values, resulting in a too low carbonyl Cls intensity, when peak areas are compared. Since the amino nitrogen of oxydianiline is the center of highest basicity (highest proton affinity) in the system, an ammonium salt can be formed through the transfer of a proton from the amide group onto an amino group of free oxydianiline (3D). This ionic form is most likely further stabilized by intra- or intermolecular hydrogen bonding (not shown in figure 3). The transfer of a proton within the molecule leads to the formation of the neutral form of polyamic acid (3E). Further evidence for a proton transfer comes from the N1s spectra in figure 4, showing the amino nitrogen in a thin ODA film (4.8 nm) evaporated at room temperature onto a gold substrate (4a), the N1s spectrum of polyamic acid (4b) and the N1s spectrum taken after imidization and curing at 350 C° (4c). The N1s spectrum of polyamic acid shows a high binding energy shoulder, interpreted by us as positively charged nitrogen. This assignment is in agreement with similar assignments made by Clark et al.[14] in a study of amino acids, dipeptides and polypeptides. Deconvolution of the N1s peak into 3 gaussians gives an intensity distribution of 82%:18% between the main peak (2 gaussians) and the high binding energy shoulder (1 gaussian), respectively. With an ODA to PMDA ratio of 66%:34% (as calculated from the N:C ratio) this corresponds to a situation where 35% of the acid groups are in the carboxylate form. This implies that only one of the two amino groups in excess ODA is protonated and forms an ammonium salt.

If the fraction of acid groups which are in the carboxylate form (35%) do not contribute to the carbonyl intensity, a carbonyl deficiency of 0.7 carbonyl groups per polyamic acid repeat unit follows from the model in fig 3 for PAA. This is close to the 0.6 we found in the analysis of the Cls core level data.

Whereas the proton transfer does not effect the stoichiometry of the final PI when water is eliminated in the imidization reaction (fig. 3F), addition of an excess ODA molecule to polyamic acid could lead to the imine type crosslink formation schematically shown in figure 3G. This would lead to a deficiency of carbonyl oxygen atoms for vapor deposited polyimide and is consistent with our analysis. Mack et al.[16] proposed imine crosslink formation from their Raman spectroscopic studies for vapor deposited polyimides with excess ODA. In accordance with this model we attribute the low binding energy shoulder in the polyimide N1s line (figure 4c) to double bonded nitrogen species. However, the model gives no explanation for the carbonyl deficiency found in spin deposited polyamic acid and polyimide. In this case no excess of ODA is observed and only a very weak shoulder has been reported for the N1s line [4,11].

b) Shake up features in PAA and PI

Analysis of the region around 539 eV in figure 2, where the the $\pi-\pi^*$ shake up satellite of the carbonyl oxygen emission occurs provides additional information about polyamic acid. The intensity in this region increases upon curing as shown by the enlarged scale spectra (compare figs. 2a and 2e). The areas under

the weak shake up features were measured using a linear baseline. A lot of care must be taken defining the baseline. It was chosen in a way that the integrals obtained for the "flat" regions next to the shake up features were vanishing. Deviations of the true background from this background under the shake up feature will give rise to some error in the integrated intensities (estimated by the error bars in fig. 5). The integrated intensities of the oxygen $\pi-\pi^*$ shake up emission and its energy relative to the O1s carbonyl emission (determined from the deconvoluted spectra not shown here) are plotted in figure 5 for various curing stages. Obviously, there is a correlation between the intensity and the corresponding energy of the O1s shake up. We note, that the effect of imidization on the Cls shake up region is substantially less pronounced (compare figs. 1a and 1e).

Qualitatively these spectral changes during imidization can be understood by considering the origin of satellite structures in core level photoemission spectra. The creation of a core hole is accompanied by excitations of valence electrons from occupied states into unoccupied (nonbonding or anti-bonding) orbitals. The energy of these transitions, in our case the $\pi-\pi^*$ transition in the PMDA part of PAA and PI, depends on the localization of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) within the molecule. Depending on the localization the (predominantly) electrostatic interaction with the core hole i.e. screening of the core hole,

is different. Accordingly, the energy of the transition can be larger (when the HOMO is more strongly affected by the core hole) or smaller (in case the LUMO is localized around the core hole) than the excitation energy in the neutral molecule. In extreme cases, such as nitroaniline, the LUMO is pulled below the HOMO in the electrostatic field of the core hole, leading to negative shake up energies in molecules [17]. The spatial distribution or localization of the HOMO and LUMO with respect to the core hole also determines the intensity of the shake up. As discussed by Cederbaum and coworkers [18], the more localized the LUMO is towards the core hole, the smaller is the shake up energy due to the stronger electrostatic interaction and the higher is the intensity. This assumes, of course, that the HOMO is located further away from the core hole experiencing a smaller electrostatic attraction.

Haight et al.[10] performed ab initio calculations to determine the localization of the HOMO and LUMO in the PMDA part of polyimide to explain the spectral changes in their core level spectra when chromium is adsorbed on PI. The LUMO exhibits a much greater orbital amplitude on the carbonyl oxygen than on the carbonyl carbon atoms. There is no significant LUMO amplitude on the nitrogen or on the carbon atoms in the central phenyl ring bonded to hydrogen, some amplitude is found on the carbonyl carbon atom next-nearest neighbor carbon atoms. Accordingly, any changes in charge density on the carbonyl groups would effect predominantly the π^* orbital located around the oxygen atom, but due to the conjugation of the π electron system in a planar

molecule the charge density would be affected also on the central phenyl ring and this would effect the C1s $\pi-\pi^*$ shake up transition. However, in the case when the system is not planar, conjugation is not possible, separating the π electron systems of the carbonyl groups from that of the central phenyl ring. The HOMO and LUMO are expected to be localized mainly on the central phenyl ring and the interaction with the O1s core hole would be strongly reduced, lowering the intensity of the O1s shake up and increasing the energy of the $\pi-\pi^*$ transition due to a smaller conjugated system.

Curing of polyamic acid effects the shake up region in the C1s and O1s core hole spectra differently. Major changes are observed only for the O1s core hole data. This demonstrates that the carbonyl groups and the central phenyl ring in polyamic acid are not conjugated and thus not planar. A non-planar geometry of the PMDA moiety in polyamic acid is also supported by theoretical considerations presented by S. Kowalczyk et al. [19]. During imidization there must be a transition of the PMDA part of the molecule from non-planar non-conjugated in polyamic acid to planar conjugated in polyimide. A "quasi continuous" transition via conformations with an increasing degree of coplanarity and conjugation and corresponding $\pi-\pi^*$ transitions is suggested by the constant half-width (roughly 2.2 eV) of the shake up transition in polyamic acid and polyimide. The half-width of the O1s shake-up in the PAA/PI system is about twice the value found for the planar PMDA molecule (1.1 eV), which indicates that for

a given curing state different conformations in PAA contribute to the O1s shake up satellite.

Changes in the shake up intensity in the C1s and O1s spectra have been observed in the case of chromium deposition on fully cured PI and are interpreted as a charge transfer from the chromium atoms into the PMDA part of the polyimide [10,20,21]. Even at low coverage of one chromium atom for every three PI repeat units there are drastic changes in the XPS lineshapes and both the C1s and O1s shake up intensity are reduced. The phenyl emission shifts from higher to lower binding energy leading to a lineshape qualitatively in agreement with the lineshape observed for PAA and the carbonyl C1s intensity is reduced substantially. In the O1s and N1s spectra broadening of the peaks and for the O1s a split into a doublet has been found for increasing chromium coverages.

The spectral changes occurring upon chromium adsorption on polyimide were interpreted by Haight et al.[10] by a model in which the chromium atom adsorbs over the PMDA phenyl ring and donates charge into the lowest unoccupied molecular orbital (LUMO) of the coplanar system. This will lead to a shift of the C1s phenyl carbon emission to lower binding energies due to increased screening of the core hole and to reduction of the carbonyl bond order thus leading to a decrease in the characteristic carbonyl intensity.

A different interpretation is favoured for the chromium on polyimide data by Jordan et al.[21], who propose that initial attack of chromium and charge transfer occurs on the carbonyl

moiety. Since the charge transferred from the metal is distributed over the planar PMDA moiety of the polyimide, the core level spectra by themselves will not allow a distinction between the two models proposed. However, a careful analysis of the shake up features in the C1s, O1s and N1s core hole spectra might reveal the initial binding site when the amplitude distributions of the LUMO's and HOMO's in the system relative to the created core hole are considered.

2) Interaction of Polyamic acid with metals

In the following we will present some data on the inter-action of polyamic acid with metals which demonstrates the high reactivity of the carboxyl group in solventless PAA.

a) Gold

Sub monolayer evaporation of gold onto a polyamic acid with excess PMDA at room temperature leads to shifting of the PAA core level spectra to higher binding energies by ca. 0.8 eV, to broadening of the C1s and O1s spectra, and a further reduction of the carbonyl C1s intensity and the O1s shake up intensity (not shown here) [15]. As shown in fig. 6, the high binding energy shoulder on the N1s emission is strongly suppressed. The uniform shift of the core levels to higher binding energy can be explained by charging of the surface layer due to photoionized gold atoms and clusters leading to a change in the charge balance of the non-conducting polyamic acid film. This charging effect,

which will vary across the surface and leads to differential charging, can also account for the broadening of the C1s and O1s emission. The changes in the N1s spectra, together with a further reduction of the O1s shake up intensity (not shown here), however, indicate that the gold atoms preferentially inter-act with the amic acid part of the molecule. It can be speculated that gold stabilizes the carboxylic acid group in substitution for positively charged ammonium groups.

b) Silver

The experimental procedures and x-ray photoemission results for the preparation of ultrathin ($d = 1.1$ nm) polyimide films on polycrystalline silver by cocondensation of PMDA and ODA are described elsewhere [5]. In that work our XPS results suggested that the polyimide chains bond to the silver surface via a carboxylate type bonding. This conclusion was derived from an analysis of the results obtained for the interaction of the monomers (PMDA and ODA) and of the resulting ultra-thin polyimide film. Due to the relatively larger thickness of the polyamic acid films as compared to the monomer adsorbate phases and the polyimide film, no conclusions were possible about the reaction of the polyamic acid with the silver substrate.

In figure 7 we show Infrared-Reflection Absorption data for a thin polyamic acid film (a), a thin polyimide film (b) (after curing the PAA film of spectra a) and a thick ($d > 10$ nm) polyimide film (c) on a polycrystalline silver surface.

Transmission and reflection infrared absorption spectra of thick

($d > 1000$ nm) spun-on polyamic acid and polyimide films have been reported previously [22-24]. Salem et al. [2] presented in their pioneering paper the infrared transmission spectra for vapor deposited polyamic acid and polyimide. Except for the relative intensities between the individual absorption bands, our results for a thick polyimide film (Fig. 7c) are identical to those for spun-on and vapor deposited films, showing the unresolved symmetric and asymmetric (strong) $\nu_{C=O}$ stretches between $1700-1800$ cm^{-1} , the $\nu_{1,3}$ (1,4- C_6H_4) ring mode at 1504 cm^{-1} , the $\nu_{(C-N)}$ imide mode at 1385 cm^{-1} , the ν_{C-O-C} stretch mode at 1245 cm^{-1} , and the $(OC)_2NC$ (imide III) mode at 1117 cm^{-1} . A full discussion of the mode assignments is given in the literature [24].

The differences in relative intensities between the bands in our work and those of others as mentioned above have been discussed previously [25] and is due to the preferred alignment of the polyimide chains parallel to the surface plane.

In a grazing incidence ($\theta = 85^\circ$ with respect to the surface normal) infrared reflection experiment the light is almost completely p-polarized at the surface and the electric field is strongly enhanced [26]. Further, due to the dipole-image dipole interaction of the oscillators only those modes will absorb light which have a dynamic dipole component perpendicular to the surface plane. Thus, in the surface near region those modes fulfilling the above requirements will be strongly enhanced. Accordingly, the polymer/metal interface will dominate the reflection infrared absorption spectra in experiments where films are sufficiently thin not to show a strong bulk signal. To which

distance away from the metal the surface enhancement of the electric field and the dipole image-dipole interaction will dominate the reflection spectrum is not known and subject of a present study.

The spectrum of polyamic acid (7a) is dominated by the imide bands between $1200\text{--}1300\text{ cm}^{-1}$ and the $\nu_{1,3}$ (1,4- C_6H_4) ring mode at 1504 cm^{-1} . We note, that there is no pronounced band around 1660 cm^{-1} where we expect the $\nu_{\text{C=O}}$ stretch in carb-oxylic acid, there is rather a broad background absorption indicative of carbonyl groups in different chemical environments. At 1540 cm^{-1} we expect the N-H bending mode and around around 1390 cm^{-1} the amide stretch frequency in PAA.

In silver acetate ($\text{CH}_3\text{COO}^-\text{Ag}^+$) two strong absorption bands are found at 1580 cm^{-1} and 1395 cm^{-1} for the asymmetric and symmetric $\nu(\text{COO}^-)$ stretch. This corresponds to the wavenumber range where we also find absorption intensity for the thin PAA film on silver not present in thick polyamic acid films. We therefore propose, that some fraction of the polyamic acid interacts with the silver substrate via carboxylate type bonds. Intensity appearing in the asymmetric $\nu(\text{COO}^-)$ stretch region as well as in the symmetric stretch region would indicate that the carboxylate is present in a mono-dentate form, since for a bidentate configuration we expect only to see the symmetric stretch, which has a dynamic dipole moment perpendicular to the surface. However, these

spectra were taken on a polycrystalline silver surface and are too noisy to allow a quantitative interpretation.

The interaction of the polyimide chains via carboxylate type bonds is however clearly evident in spectra 7b for the cured polyimide film on polycrystalline silver. In addition to the characteristic vibrational modes of bulk polyimide we find two strong bands at 1600 cm^{-1} and 1440 cm^{-1} not present in the bulk spectra in the thick film (7c). These are interpreted as arising from the polyimide-silver carboxylate type interface bonding as discussed above for polyamic acid. The presence of both the asymmetric and symmetric $\nu(\text{COO}^-)$ stretch could again be due to a preferential monodentate bonding configuration or to the polycrystalline nature of the substrate.

These results demonstrate, that the amic acid site in polyamic acid facilitates the adhesive bond between polyimide and silver as suggested by X ray photoelectron results reported elsewhere [7].

Summary

Vapor deposited polyamic acid and polyimide films show both an excess of ODA and a deficiency of carbonyl groups. In the case of polyamic acid the excess of ODA leads to the formation of ammonium-carboxylate groups. The C1s emission of the carboxylate groups is shifted to lower binding energy and does not contribute to the typical C1s carbonyl emission, leading to a deficiency of carbonyl groups in a quantitative analysis. The presence of a high binding energy shoulder in the N1s emission in polyamic acid

is consequently attributed to positively charged nitrogen in the ammonium groups. Upon curing to polyimide a portion of the excess ODA gets chemically bonded to the imide ring through imine type bonds, leading to a deficiency in the C1s and O1s carbonyl group emission and a low binding energy shoulder in the N1s core hole spectra. Based on the analysis of the shake up intensity on the O1s and C1s core hole emission we concluded that polyamic acid is in a non-planar conformation and that the conformation changes upon curing quasi continuously to a planar polyimide conformation. The carboxyl moiety of PAA acts as a preferential interaction site between polyamic acid and metal atoms (Au) or bulk metal surfaces (Ag) and thus facilitates adhesion between the two materials.

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Figure captions

Figure 1: Cls XPS spectra of codeposited PMDA and ODA on a mica supported gold substrate

- a) after deposition at room temperature (PAA) 8.8 nm
- b) heated to 100 C° for 30 min
- c) heated to 150 C° for 30 min
- d) heated to 250 C° for 30 min
- e) heated to 350 C° for 30 min (PI) 7.1 nm

Figure 2: Ols XPS spectra of codeposited PMDA and ODA on a mica supported gold substrate

- a) after deposition at room temperature (PAA) 8.8 nm
- b) heated to 100 C° for 30 min
- c) heated to 150 C° for 30 min
- d) heated to 250 C° for 30 min
- e) heated to 350 C° for 30 min (PI) 7.1 nm

Figure 3: Schematic Diagram for the reaction of ODA with PMDA
A PMDA; **B** ODA; **C** Ionic form of PAA (intermediate state); **D** Ammonium salt formation in PAA; **E** Neutral form of PAA; **F** PI; **G** Branching of PAA due to reaction with a second ODA monomer

Figure 4: Nls XPS spectra (on a mica supported gold substrate)

- a) Oxydianiline (ODA) thickness 4.9 nm
- b) Polyamic acid (PAA) thickness 8.8 nm
- c) Polyimide (PI) thickness 7.1 nm

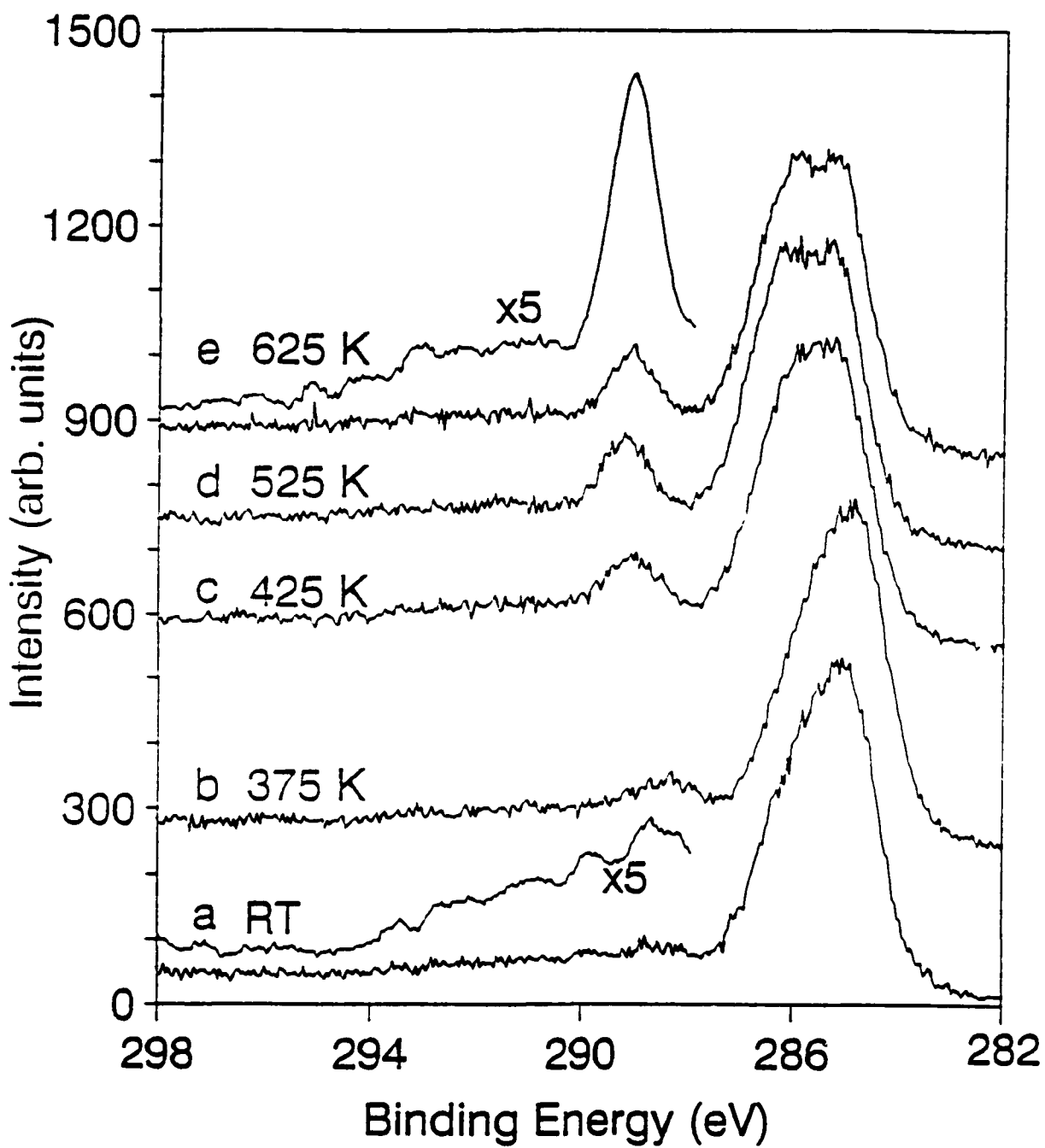
Figure 5: Plot of the integrated Ols "shake-up" intensity (left y-axis) from fig. 2 and energy in eV (right y-axis) relative to the Ols carbonyl emission at various curing temperatures. Error bars are estimated.

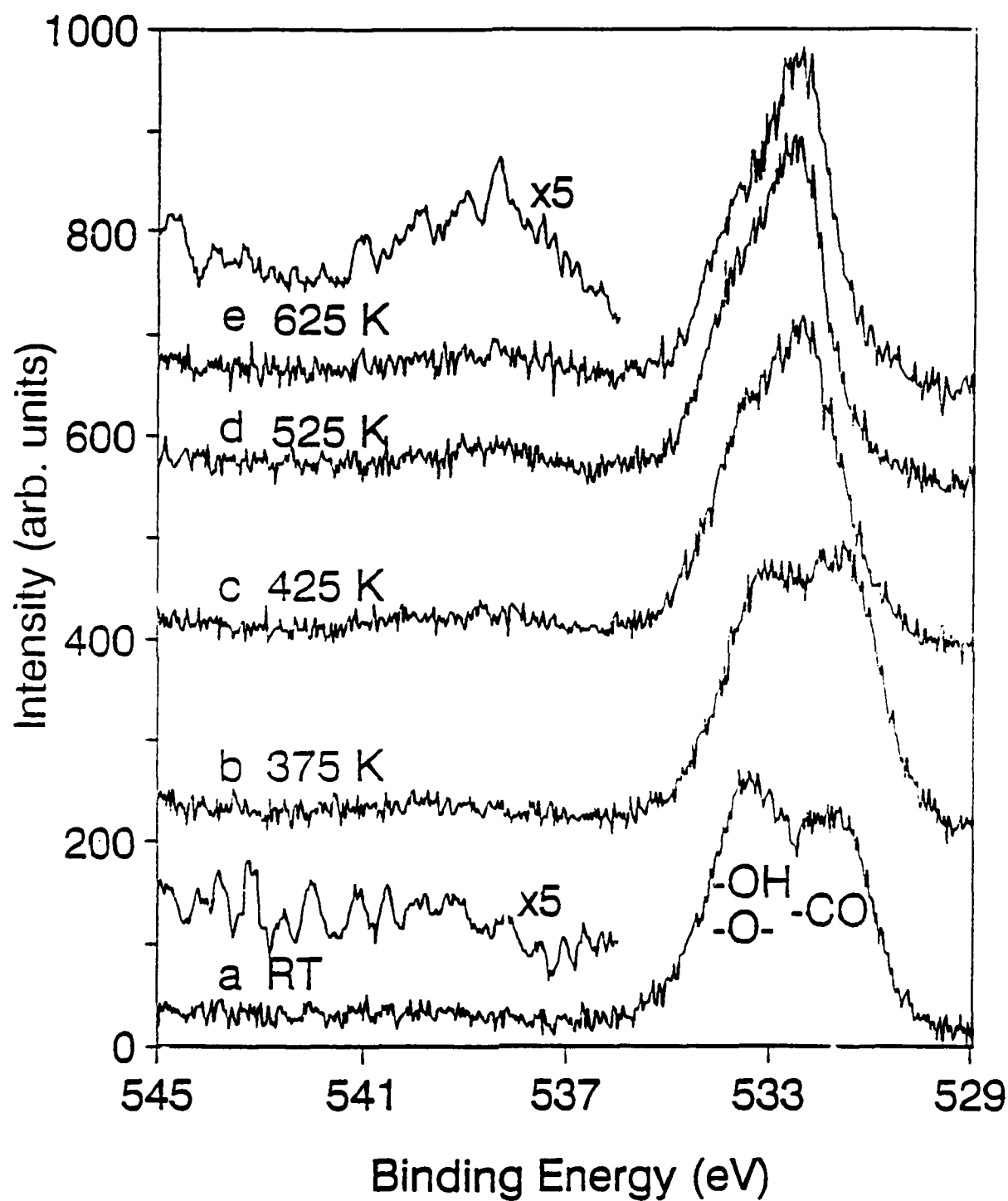
Figure 6: Nls XPS spectra of a thick polyamic acid film

- a) before and b) after deposition of less than a monolayer gold

Figure 7: Infrared Reflection Absorption spectra of

- a) a thin polyamic acid film on polycrystalline silver
- b) a thin polyimide film obtained from a) after curing
- c) a thick polyimide film





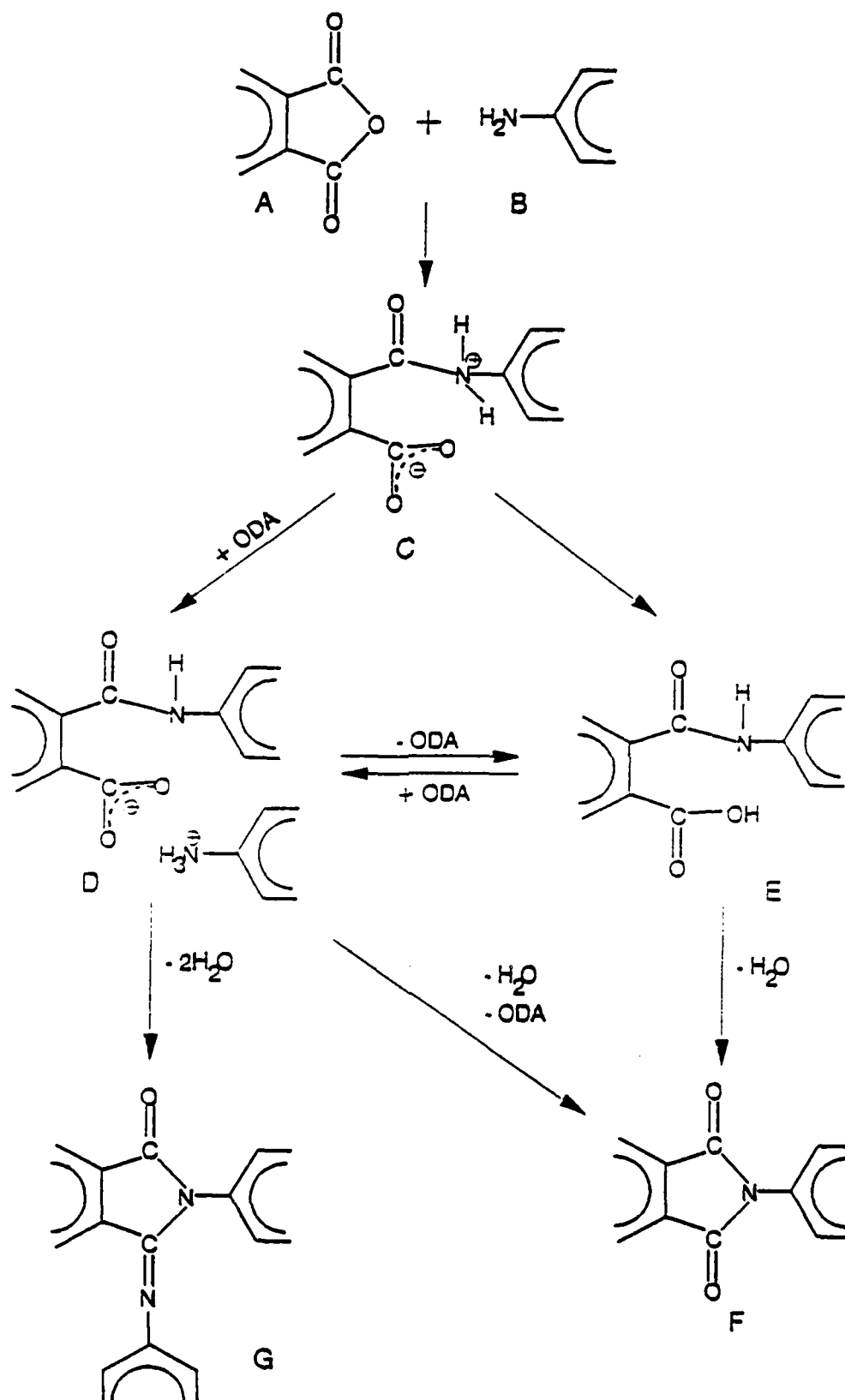
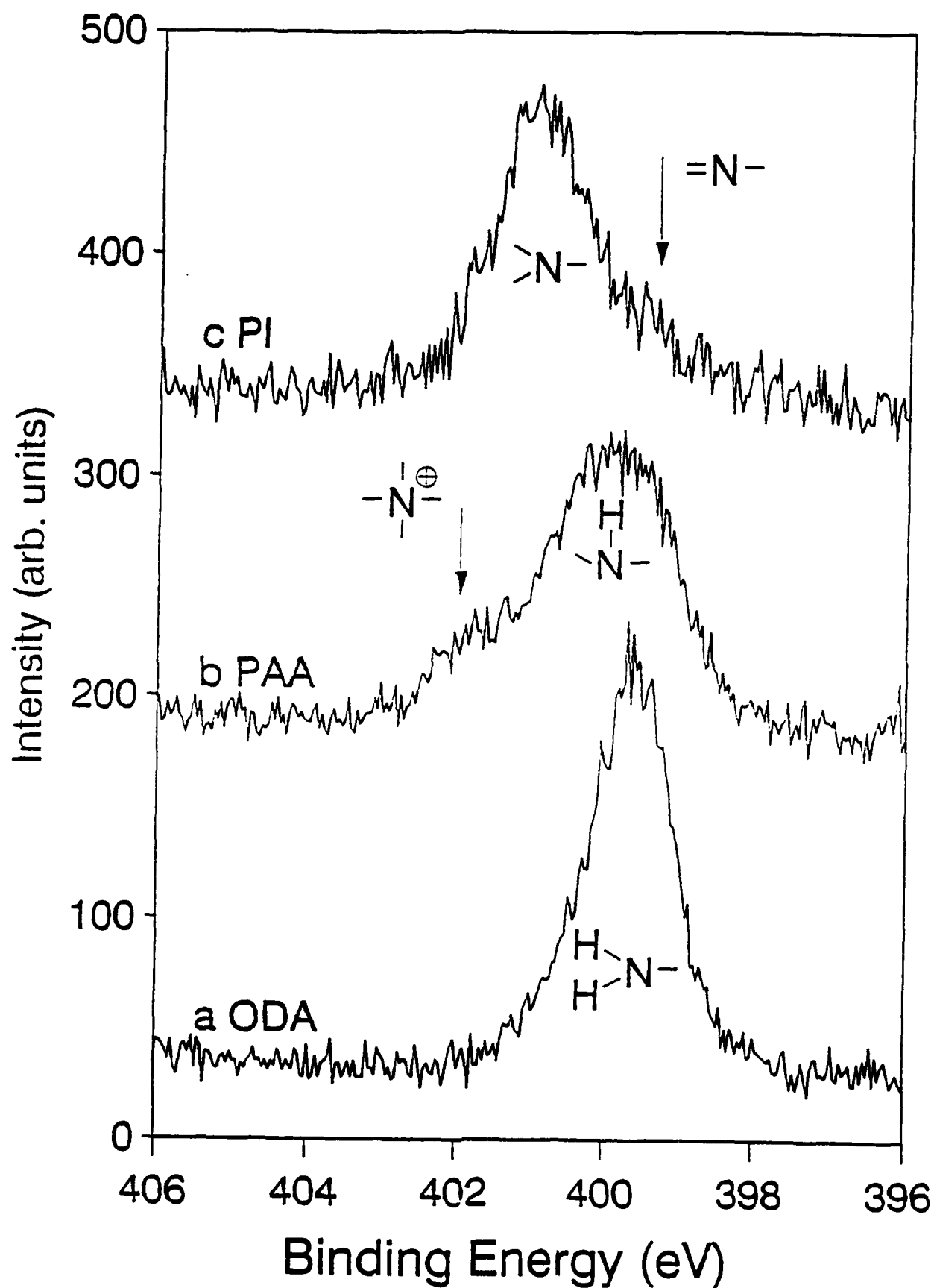
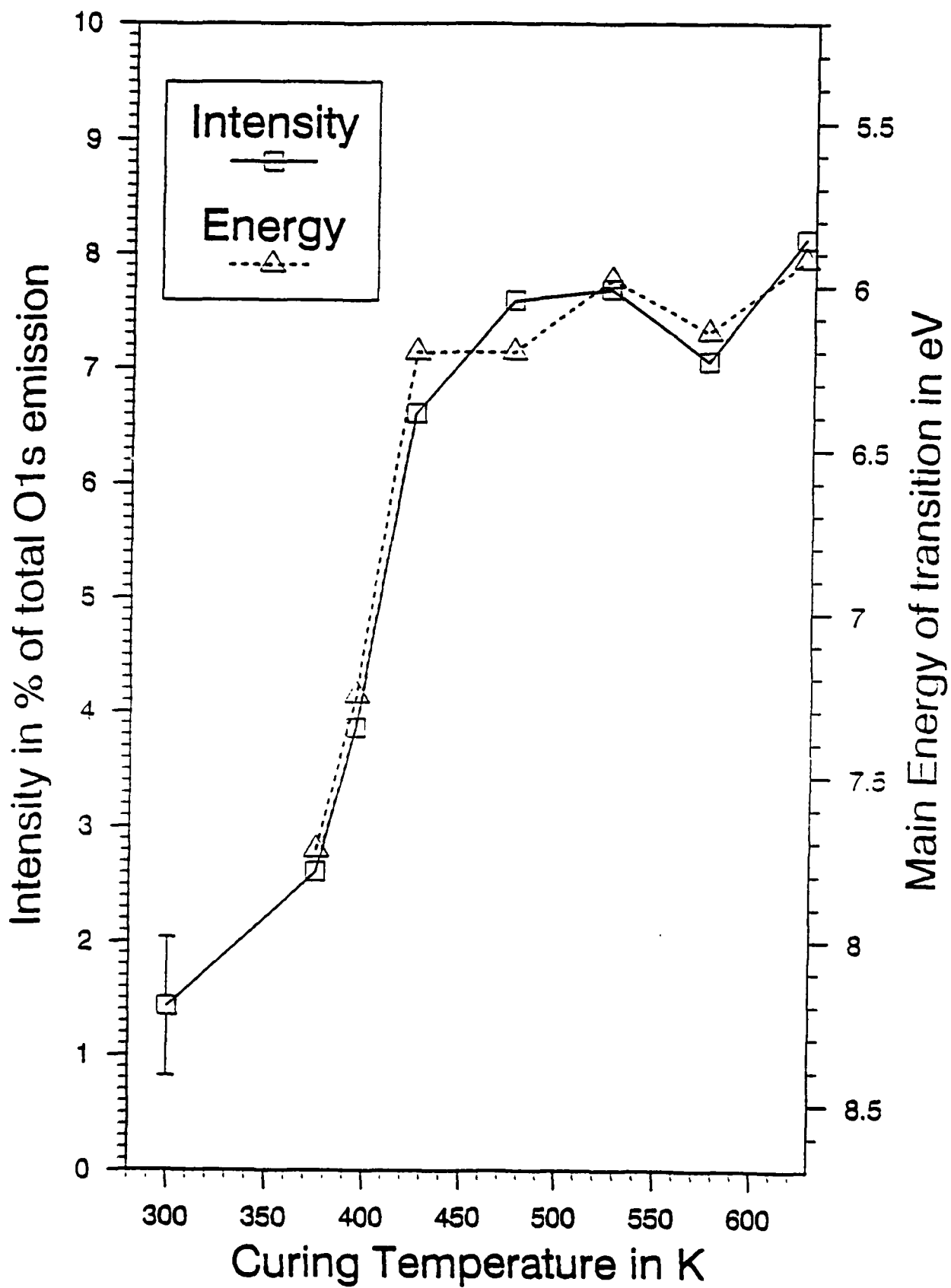


Fig. 3





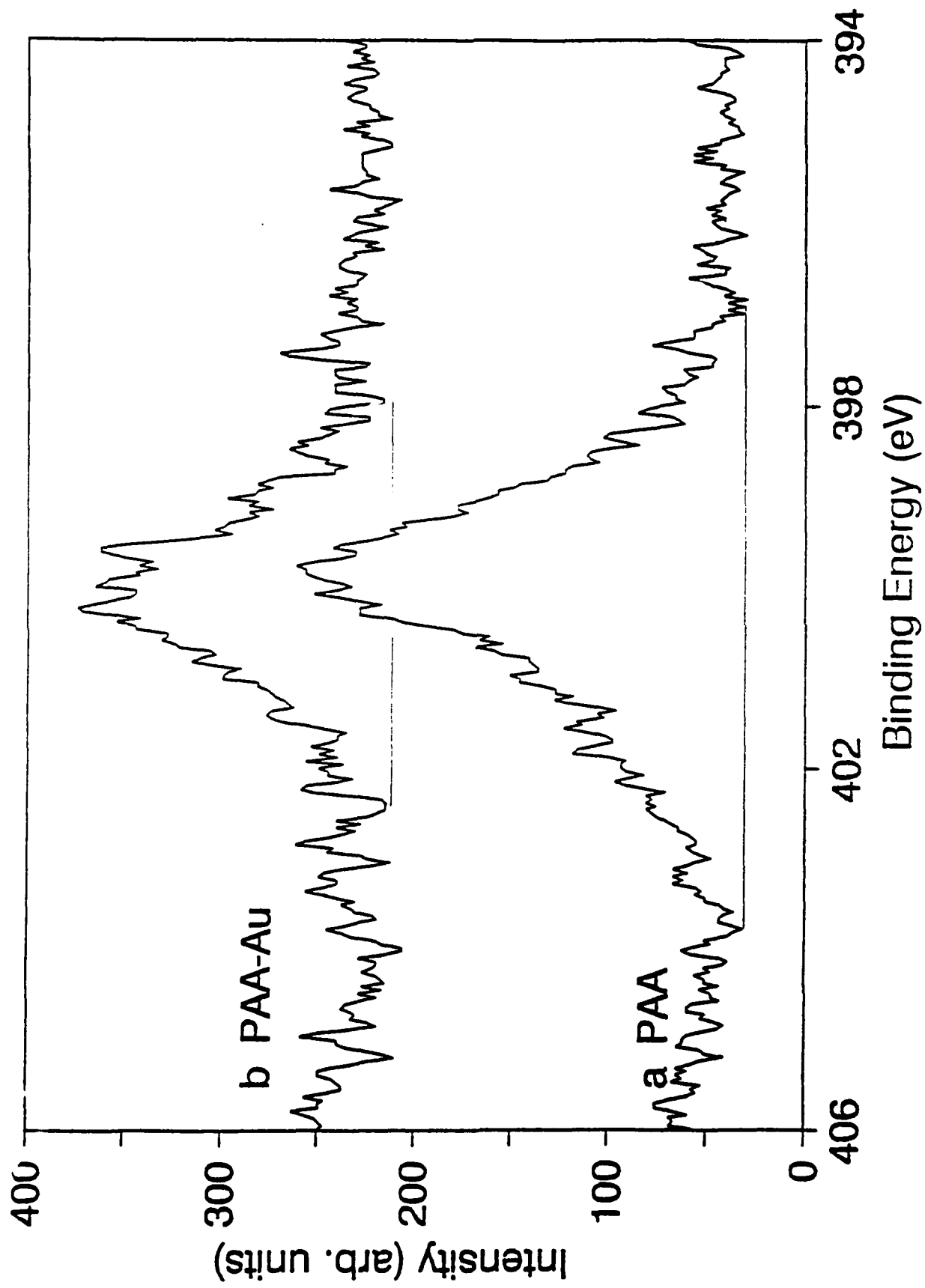
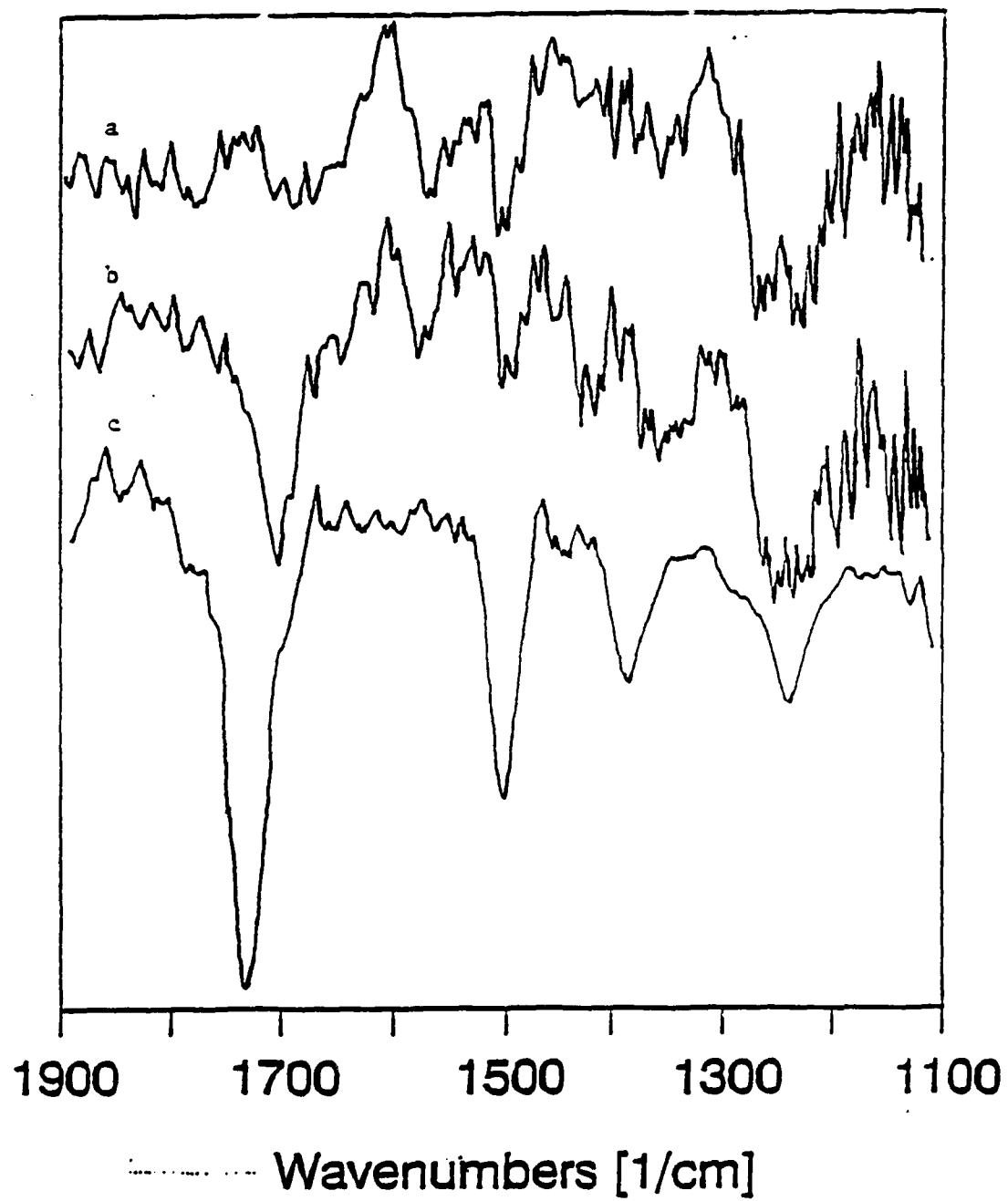
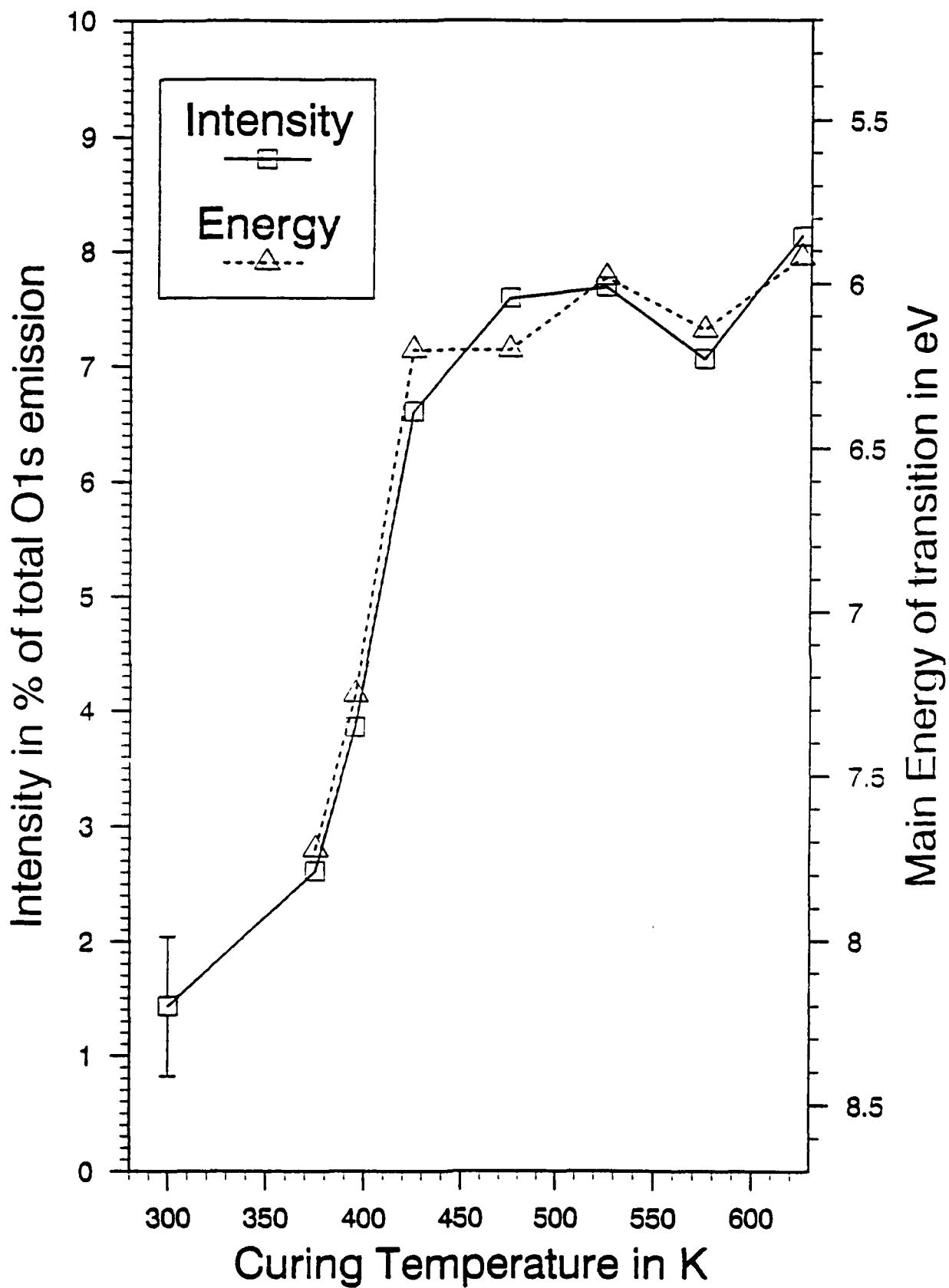


Fig. 6





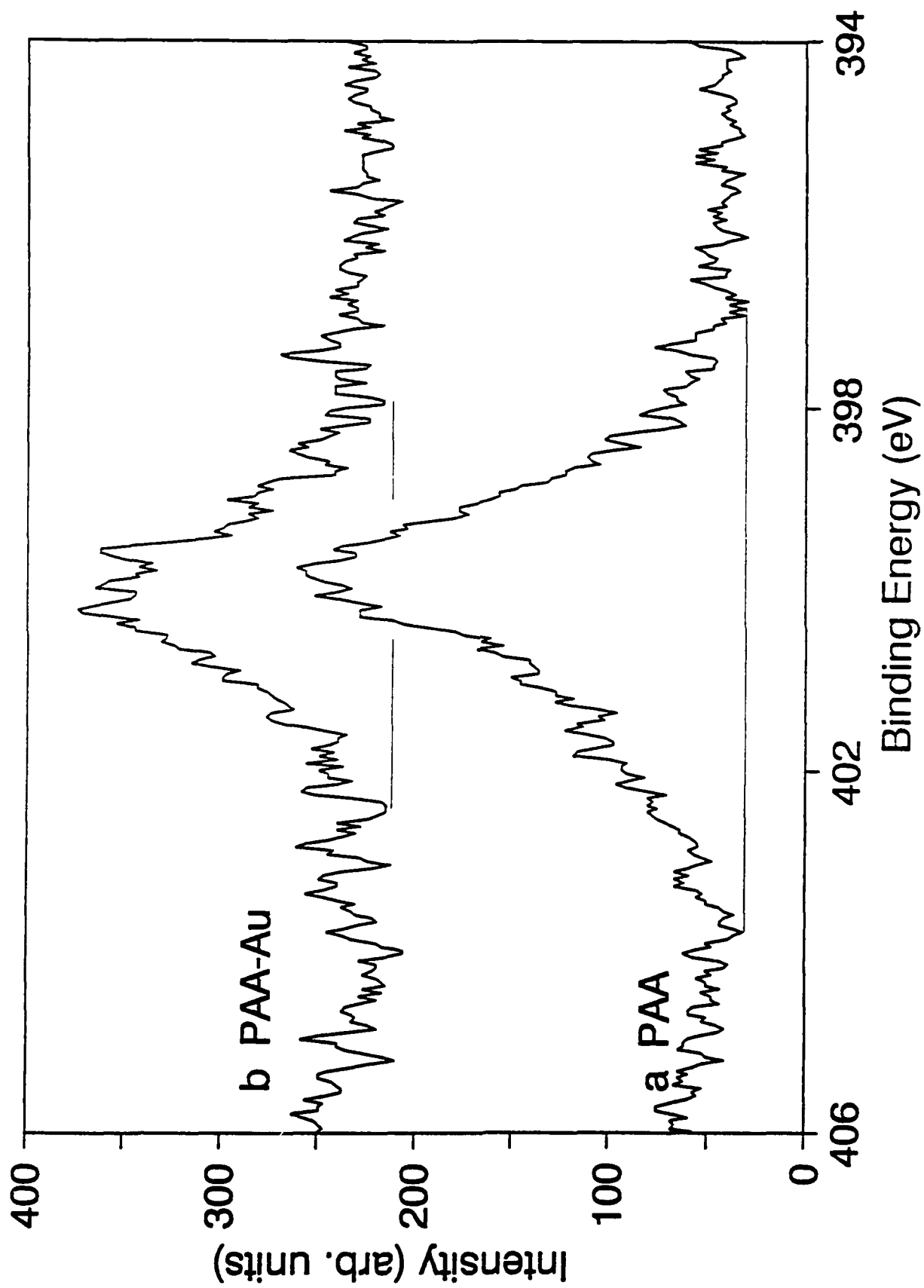
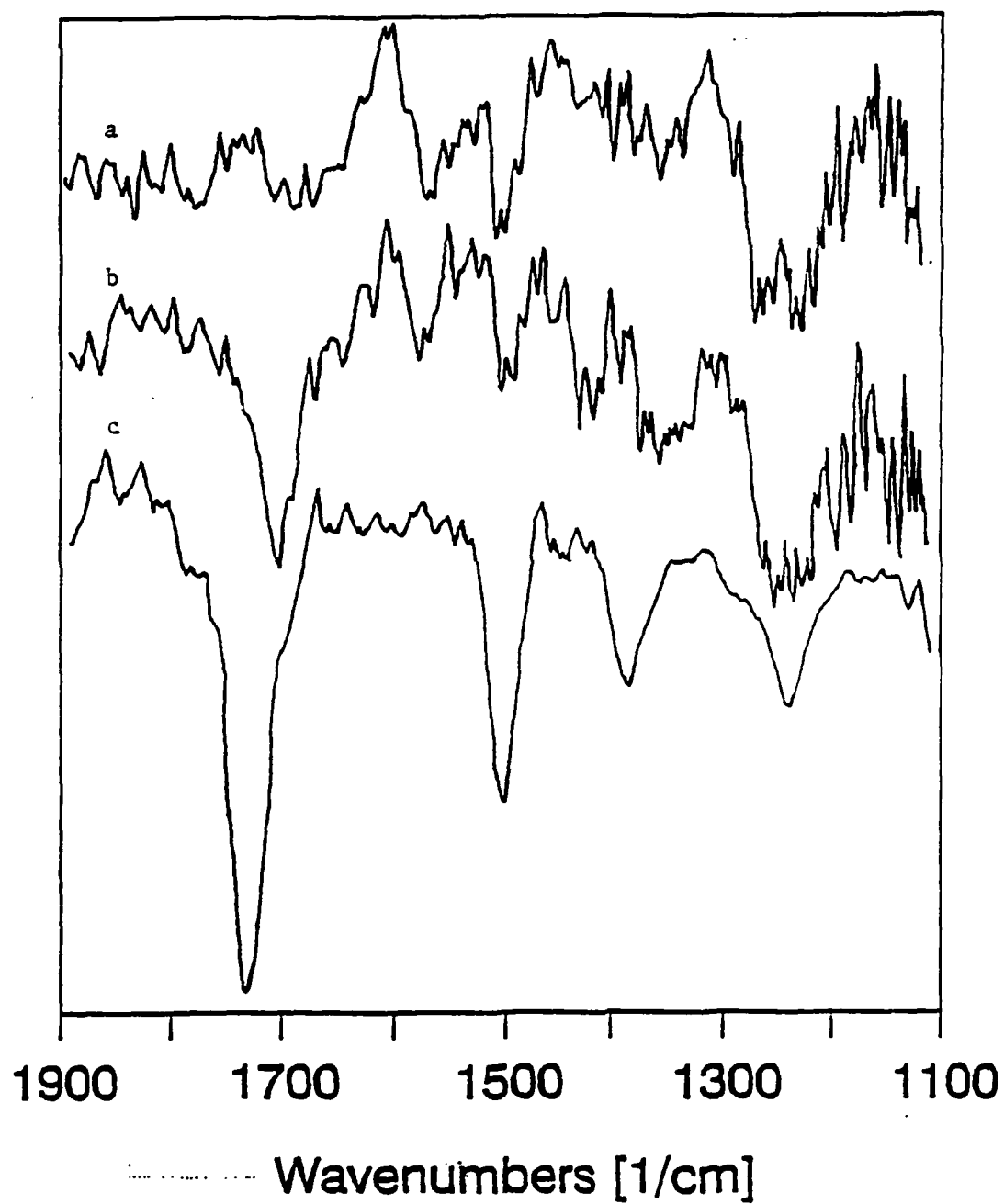


Fig. 6



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