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Comparison between the interfacial chemistry of metallized polyimides  
and polyimide films on bulk metal substrates

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Abstract

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elimination of CO molecules from the polymer surface.

Introduction

Aromatic linear polyimides are a class of organic polymers with  
favourable mechanical and dielectric properties for applications in  
electronic devices which can easily be processed into planar films.  
Originally polyimides were introduced in Japan as an interlevel  
dielectric for multilevel metal transistors /1/. Today they are used  
routinely in VLSI devices as multilevel dielectric insulation /2-4/.

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There are also several other applications which emerged in the last 10-15 years. Because of their high absorption coefficient for  $\alpha$ -particles they are used as protective coatings in charge sensitive memory devices. Their mechanical properties and high temperature stability is utilized in composite materials for aerospace uses /5/, and they are tested as high temperature adhesives /6/ as well as lubricants in spacecraft applications /7/. More recent application of some polyimides take advantage of their crystallinity which makes them applicable as orienting layers for LCD devices, or, when crystallization is reduced by adjustment of the curing procedure, as light guide materials /8/.

However, reliable adhesion, particularly in humid environments, remains to be a major issue of concern in the application of PIs. Only recently spectroscopic results on polyimide/metal interfaces have become available which can shed some light on the chemical and physical parameters determining the adhesive bond between polyimide and metallic, oxidic, or semiconducting substrates.

Experiments to determine the chemical interaction between polyimide and metals have concentrated on poly (N,N' - (phenoxyphenyl) -pyromellitimide (PMDA-ODA) and related model compounds. The two commonly used methods to prepare PMDA-ODA polyimide films are spin coating (SC) and vapor deposition polymerisation (VDP). They differ in the way the film precursor (polyamic acid) is applied to the substrate. VDP is a solventless technique in which the monomers PMDA and ODA are codeposited by evaporation onto the substrate where they react at room temperature to polyamic acid. Spin coating (SC) requires that the polymer precursor polyamic acid is applied in a

polar solvent, typically N-methyl pyrrolidone (NMP). 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 film are expected to lead to polyimide/metal interfaces with different physicochemical properties.

In the following the results obtained for the interfacial chemistry of metals deposited onto cured polyimide, and polyimide films deposited by different techniques onto metals and silicon will be compared.

#### Metals deposited onto cured polyimide surfaces

Polyimide substrates were prepared by spin coating polyamic acid onto a substrate followed by solvent extraction, imidization and curing at temperatures exceeding 250°C. The metals were evaporated at room temperature under ultra high vacuum conditions onto the polyimide films and their chemical interaction was followed by x-ray photoelectron spectroscopy (XPS) /9-12,14,15,19,20/, x-ray absorption fine structure (NEXAFS) measurements /10,16/, high resolution electron loss spectroscopy (HREELS) /13/, Infrared- Reflection Absorption spectroscopy (IRAS) /17,37/, and recently also scanning electron tunneling microscopy (STM) /18/. The first systematic XPS study on the interaction of evaporated metals with polyimide surfaces were published in 1984 by Chou and Tang /9/. They studied monolayers and submonolayers of Cr, Ni, Cu and Ag on freshly cured (T=350°C, 30 min) polyimide substrates. They concluded, that Cr and Ni react with the

pendant oxygen in the substrate, whereas Cu and Ag are not forming chemical bonds. They also presented a simple thermodynamic model to predict whether a given metal will form a chemical bond with the polymer during metallization at room temperature. According to this model Al, Mg, Mn, Sn, Ti and V should react with the pendant oxygen in polyimide.

Later experiments indicated that Cr /10/, Ti /11,12/, Al /13,14/ react with polyimide surfaces at coverages around and exceeding one monolayer by polymer bond cleavage and formation of metal oxides, carbides and nitrides. In the case of Cr /10,15,16,20/ and Al /14/ spectroscopic data suggest that the initial interaction between metal and polymer involves a charge transfer with the PMDA part of the polymer. Clabes et al. /10/ compared their XPS data for submonolayer coverages of Cr on PI with chemical and electrochemical reduced polyimide films. Reduction of PI involves electron transfer into the lowest unoccupied orbital (LUMO) of the PI which, according to calculations performed by Haight et al. /15/, has it's highest amplitude on the carbonyl carbon next nearest phenylcarbon atoms and the carbonyl oxygen atom in the PMDA part of the polymer. Clabes et al. interpret their data by postulating that the Cr atom initially interacts with two carbonyl-oxygen atoms of two parallel PI-chains by charge donation into the LUMO of the PMDA parts of the PI macromolecules. A coordination with two adjacent ligands belonging to different monomer unit thus allows the chromium to reach the stable Cr<sup>2+</sup> configuration, which, according to Clabes et al., is not possible through interaction with a single PMDA unit. An initial interaction between the metal (Cr) and the polyimide carbonyl groups was

previously also concluded by Jordan et al. /16,20/ from detailed XPS and NEXAFS studies.

Supported by their "ab initio" calculations Haight et al. /15/ interpreted their XPS data by a chromium/PMDA charge transfer complex where the most stable coordination site for the Cr-atom is above the phenyl ring of the PMDA part of the molecule, analogous to a metal-p-arene complex. The chemical shifts in the C1s, O1s and N1s spectra upon chromium deposition were explained by theoretical calculation based on this model without invoking formation of covalent or ionic bonds. Support for this model was suggested by the fact that the changes in the polyimide C1s, O1s, and N1s spectra are qualitatively the same irrespective whether chromium or copper is deposited.

A direct comparison of the initial interaction of Cr and Cu with spin coated polyimide films was published by Dunn and Grant /17/ using Infrared Reflection Absorption Spectroscopy. Metallization of a 15 nm thick polyimide film with a 1 nm film of chromium or copper was done in a vacuum system at a pressure of  $3 \times 10^{-7}$  Torr during evaporation. After metallization the films were exposed to laboratory air as they were transferred into the infrared spectrometer. In their studies chromium and copper cause similar changes in the polyimide spectra, in particular on the carbonyl stretching band and the out-of-plane C-N-bending vibration of the (O=C)<sub>2</sub>-N group. No evidence for complex formation between the metals and the aromatic rings in the polymer chains as suggested in ref. 15 was observed. Dunn and Grant concluded that for both metals the carbonyl groups on the polymer surface are the primary reaction sites.

Recent experiments by Mack et al. /18/ on copper deposition on polyimide films prepared by vapor deposition, however, suggested that copper interacts primarily via the imide part of the molecule because the XPS N1s emission is comparatively stronger attenuated than the C1s and O1s emission when copper is deposited. We repeated the IRAS experiment published by Dunn and Grant /17/ and the XPS measurement by Mack et al. /18/ for copper evaporation on polyimide films produced by vapor deposition to establish a direct comparison between the two techniques. The polyimide film preparation, the copper deposition and the XPS and IR-analysis (in a single reflection geometry) was done in a UHV-system without exposing the sample to air in between. In the context of this paper the results /37/ are briefly summarized.

In fig. 1 we compare the FTIRAS spectra of the cured polyimide film (a) with the difference spectra between the original polyimide film and the film after the first copper deposition (0.1 nm) (b), the second copper deposition (total of 0.2 nm) (c), and heating the film after the second deposition to 570 K for 15 min. (d). The spectra displayed have been background subtracted. From a qualitative point of view our IRAS results for the 0.1 nm deposition of copper are identical to those of Dunn and Grant, i.e. attenuation of the carbonyl stretching band, attenuation of the imide related bands at 1383, 1248 and 1119  $\text{cm}^{-1}$ , and no obvious effect on the ODA ring stretching mode around 1500  $\text{cm}^{-1}$ . Following the second deposit, however, (fig. 1c) a clear attenuation of the ODA ring stretching mode around 1500  $\text{cm}^{-1}$  is observed. Heating the 0.2 nm deposit of copper further enhances the effect seen in spectrum 1c, in particular for the imide related modes and the ODA ring mode (fig. 1d).

In the XPS data, which are not shown here, we observe a pronounced reduction in the C1s and O1s carbonyl band emission after the 0.2 nm deposit. Concurrent with these changes the phenyl carbon emission is attenuated and a lower binding energy N1s shoulder is observed. A quantitative analysis reveals that the reduction in the carbonyl related C1s and O1s emission is about 100% stronger than of the N1s and phenyl carbon emission. The ratio between the carbonyl carbon and carbonyl oxygen loss is about 1:1. After heating, the 0.2 nm copper deposit, a overproportional reduction in the ODA related C1s phenyl emission and the ether O1s emission is found. The Cu 2p spectra show a binding energy shift between the 0.1 nm and the 0.2 nm deposit to lower binding energies indicating a change in cluster size (or from single atoms to clusters) and, after heating, a small emission from  $\text{Cu}^{2+}$  species. Of particular importance is the fact, that neither the O1s nor the Cu 2p spectra indicate copper oxide formation before heating the film.

Based on these observations, we propose the following model for the interaction of copper atoms and cluster with vapor deposited polyimide surfaces: Initial interaction of copper involves the fivefold planar imide ring of the PMDA part of the polymer. The equal but not homogeneous attenuation of both the asymmetric ( $\sim 1740 \text{ cm}^{-1}$ ) and symmetric ( $\sim 1780 \text{ cm}^{-1}$ ) carbonyl stretch indicate that only some of the carbonyl groups are eliminated, presumable those at the polymer vacuum interface. Complex formation would lead to a frequency shift of the bands, but no evidence for new carbonyl related or imide related bands is found. Copperoxide formation should show up in the O1s and Cu2p spectra. Recalling that the loss in the carbonyl C1s and O1s XPS

emission is overproportional, and that electron-rich nitrogen species are observed in the N1s data, we conclude that copper reacts with the imide ring under elimination of one CO group into the gas phase. Further copper deposition then leads to copper cluster formation (as evident from the Cu 2p data) and adsorption over the ODA part of the molecule. Heating the copper film then enhances the effects seen at room temperature deposition, presumably through copper migration into the polymer selvage.

The results discussed above, taken on vapor deposited polyimide films without exposing the sample to air, are qualitatively identical to those published by other groups for copper deposition on spun or polyimide films and vapor deposited polyimide films. The stepwise mechanism we propose is consistent with results obtained previously, except that elimination of CO in the initial interaction stage was not proposed. However, the FTIRAS results combined with a XPS stoichiometry analysis described above exclude complex formation and copper oxide formation as a major reaction for submonolayer copper deposits.

#### Comparison between copper on polyimide and polyimide films on copper

Polyimide on bulk copper and copper on polyimide are well studied model systems to demonstrate the differences in interfacial chemistry as a function of preparation method. In the following we will summarize the results for the PI/copper interfaces formed by (i) copper deposition on cured polyimide and (ii) spin coating of the polymer precursor polyamic acid (PAA) onto a copper film.

Kim and coworkers /19/ 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 evident in cross sectional TEM observations /19/. In the case of a sputter deposited copper film on 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<sub>2</sub>O) particles were found in the polymer matrix. That copper oxide particles are distributed over a thickness of ~500 nm was reported by Burrell et al. /21/ for spun on polyimide films on copper. In their XPS and IR-Reflection Absorption measurements /21/ they attributed the observed degradation and chemical modification of the thick polyimide films to copper oxide particle formation.

Relatively thick polyamic acid films were spun onto copper substrate by D. Y. Shih et al. /22/. They followed the imidization and curing by sheet resistance, parallel plate capacitance measurements, FTIR and x-ray photoemission. Evidence for the interaction of copper with polyamic acid and for copper oxidation and degradation controlled by the supply of oxygen to the interface was obtained from FTIR and cross-sectional TEM micrographs. Shih et al. reported that the amount of cuprous oxide found in the polymer matrix was significantly less when curing was performed in a reducing gas atmosphere as compared to nitrogen or vacuum curing. They concluded

that Cu-ions are dissolved in the polyamic acid solvent layer in the initial curing stage and subsequently diffuse into the polymer matrix.

To evaluate the role of the solvent (NMP) in the formation of cupreous oxide particles in the polymer matrix during imidization, Kowalczyk et al /23/ studied the PI/Cu interface prepared by vapor deposition by TEM. When the solvent is absent, no copper oxide particles are found in the polymer matrix. However, if prior to imidization a drop of the solvent N-methylpyrrolidone is applied to a vapor deposited polyamic acid film, copper oxide particle formation in the polymer matrix can be observed by TEM /23/. The results of Kowalczyk et al. clearly show that the solvent provides mobility for the copper ions formed at the interface to diffuse into the polymer matrix and eventually react to cupreous oxide.

Results on vapor deposited polyimide films on copper revealed that it is not possible to produce polyimide films of thickness less than 4 nm /24,25/. According to Kowalczyk et al. /26/ this is due to incomplete imidization at the interface caused by carboxylate formation, whereas we believe /25/ that this is a consequence of fragmentation and loss of functional groups of the PMDA and ODA molecules in the interface. Both, the strong initial reaction of PMDA and ODA or of PAA with the copper surface, can provide an explanation for the dissolution of the copper surface and eventual cupreous oxide formation in the polymer matrix facilitated by the solvent.

#### Vapor deposited films as model systems for spin coated polyimide films on bulk substrates

The above comparison for differently prepared polyimide/copper interfaces raises the question to which extent vapor deposited

polyimide films could provide a suitable model to study polyimide/substrate interfaces of practical relevance. Curing and imidization of PAA dissolved in NMP has been investigated by Brekner et.al./27/. They demonstrated that complexation of PAA by NMP has a marked influence on imidization. Only at temperatures high enough for decomplexation to occur can the highly reactive free groups react to imide or, in a reverse direction, to anhydride. Decomplexation precedes imidization when NMP is not in excess. This implies, that for molecules in the interface the decomplexed acid groups can interact with the substrate, possibly in a competitive reaction to imidization. This, however, will occur at a higher temperature than the interaction of room temperature vapor deposited polyamic acid with the substrate. That ultrathin films ( $d < 4\text{nm}$ ) of PMDA and ODA codeposited onto silver /30/, copper /25 / or gold /34 / react instantaneously to form polyamic acid was shown previously by XPS measurements. Recent FTIR experiments reveal that the reaction between PMDA and ODA in the condensed phase start at about 273 K and that at room temperature predominantly polyamic acid is present in the film /37/. Therefore, solventless polyamic acid prepared by vapor deposition onto a substrate is expected to show the same chemical reactivity and reactions occurring with dissolved polyamic acid at temperatures high enough for decomplexation.

For spectroscopic methods to be applied to analyze the polymer/substrate interface the polymer films have to be sufficiently thin. To prepare sufficiently thin polymer films by spin coating was only successful in a few cases. Russat /28/ reported results where polyamic acid dissolved in NMP was spun onto gold resulting in



polyimide film thicknesses ranging between 1.3 to 2.9 nm after imidization and curing. However, the interfacial reaction on gold could not be unambiguously established /28/.

Deposition of polyamic acid by coevaporation of the anhydride (PMDA) and the diamine (ODA) can provide sufficiently thin polyamic acid and, after curing, polyimide films to study the interfacial reaction with x-ray photoelectron spectroscopy /24-26,29-34,/, near edge x-ray absorption fine structure (NEXAFS) /26/ and infrared reflection absorption spectroscopy (IRAS) /33,34,37/. This vapor deposition preparation method to study the interfacial reactions has been applied by our group for copper /24,25/, silver /29-31/ and gold /34/ substrates and by Kowalczyk et al. for Cu, Cr and Si surfaces /26/. The first description of the vapor phase preparation of polyimide films was given by Salem et al. /36/ for thick PI films (d > 10nm). Application of UHV surface studies to such films was first described in reference /29/.

A detailed study of monomer adsorption (PMDA and ODA) interaction with clean silver surfaces /30/ showed that both molecules undergo partial fragmentation upon room temperature adsorption. Spectroscopic analysis of vapor deposited polyamic acid indicates that the reactive sites for the interaction with a silver substrate, as well as for evaporated gold atoms and cluster, are the amic acid groups in the molecule /34/. Evaporated gold atoms and clusters preferentially interact via an electron transfer from the metal to the amic acid part of the molecule /34/. The interaction with a bulk silver surface is believed to involve silver carboxylate formation in either a monodentate or bidentate bonding configuration of the PMDA part of the

polymer chain. This model for the interfacial chemical bond was derived from XPS and IR Reflection absorption experiments for the ultra-thin polyimide films obtained after curing the polyamic acid layers /30,34/. Such a salt-like ionic surface bond would explain the sensitivity of the adhesive bond towards humidity, i.e. it suggests that hydrolysis of the interface bond is a likely cause for adhesive failure.

There are strong similarities in the XPS and NEXAFS data for the case of polyimide vapor deposited onto Cr surfaces and Cr evaporated onto cured polyimide surfaces /26/ suggesting that the same reactions occur in these differently prepared laminar structures. With the highly reactive chromium the formation of carbide, nitride and oxide species are formed in the interface when the PAA/Cr interface is annealed. Due to the variety of the chemical species present it was not possible to identify the polymer/metal bond.

The results for a 0.4 nm thin vapor deposited polyamic acid film on a Si (111)-7x7 surface (the notation 7x7 refers to the clean surface reconstruction) show that three chemical states are induced by the interaction with polyamic acid. This is evident in the Si 2p XPS data and can be explained by more than one geometric adsorption site, more than one functional group being involved in the bond formation, or a stepwise interaction pathway /26/. The C1s data show a very strong attenuation in the carbonyl C1s intensity suggesting that the carboxylic acid groups and the amid carbonyl groups are involved in the interaction with the substrate. Kowalczyk et al. clearly demonstrated in their work that covalent bonds to the silicon substrate are formed in the polyamic acid state.

Typically delamination between polyimide and the substrate is, however, not caused by adhesive failure, but rather cohesive failure in the polymer itself. Although the effect of adhesion promoters (typically aminosilanes) in the formation of a strong interface bond have not been studied by spectroscopic techniques for polyimide laminar structures, it is informative to recall the results obtained for a structural transition of the polymer between a polymer/metal interface and the polymer bulk.

XPS and IR data on silver led to the conclusion that at the surface the polymer chains are oriented away from the surface plane. This geometry is induced by the chemical bond to the surface /30,33/. Small angle x-ray scattering data by Russel /35/, however, prove that for thick polyimide films (d= 75nm) the polyimide polymer chains in spun-on films are oriented parallel to the surface plane. Such an orientation of the polymer chains with respect to the substrate was confirmed by IR absorption reflection studies for vapor deposited polyimide films (d>10nm) /33/. At present it is not known at what distance away from the surface a transition between a nearly perpendicular to a parallel orientation relative to substrate plane of the polymer chains occurs, but it is tempting to speculate that such an orientational change in the polymer is related to the locus of failure in the case of cohesive delamination.

#### Conclusion

With their high temperature stability and easy processibility polyimide based polymers became an integral component in microelectronic device technology. Problems associated with adhesion

in laminar structures have been mainly overcome by a careful control of process conditions, yet our understanding of the interfacial chemistry is still rudimentary and controversial. The application of spectroscopic techniques to identify the chemical composition and bonding at the interface has been established and is now routinely used in basic and applied research efforts. The combination of FTIRAS and XPS can provide new insight into the interfacial chemistry between polyimide and metals as demonstrated for copper deposition onto polyimide surfaces. However, delamination typically occurs by cohesive failure in the polymer. To identify the locus and chemical and/or physical mechanism of cohesive failure remains a challenge for future research.

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Note added in proof:

An excellent overview on the adhesion of polyimides to metal and ceramic surfaces including a summary on adhesion theories and adhesion measurements, by L.P. Buchwalter, came to the attention of the author. This review will appear in the Journal of Adhesion Science and Technology.

### Langmuir-Blodgett Deposition of Polyimide Films

Kakimoto et al. reported the first successful preparation of mono- and multilayer films of polyimide by depositing the alkylamine salt of polyamic acid by the LB technique and subsequently removing the long alkyl chain by thermal or chemical treatment /38/. This technique was also used by Sotabayashi et al. /39/ to deposit polyimide on highly oriented pyrolytic graphite. The PI monolayers formed a regular array of highly oriented polymer chains as evident in the STM images /39/ and the NEXAFS measurements by Schedel-Niedrig et al. /40/. We performed a comparative XPS and NEXAFS study on the orientation and interfacial chemistry /41/ of 1,3 and 5 monolayers of polyamic acid deposited by LB techniques in the form of the octadecyl-ammonium salt and octadecyl-ester and the resulting polyimide films following thermal treatments. The substrate was a Si(100) wafer etched with HF directly before deposition. For polyamic acid and the resulting polyimide films of thickness equal to or exceeding three monolayers NEXAFS measurements indicate a preferential orientation of the polymer chains with respect to the surface plane.

In the context of this short summary we would like to point out the difference in the composition of the silicon surface when the polymer was deposited as the alkylammonium salt or the ester. Fig.2 compares the Si 2p XPS data for a) 5 layers of the alkylammonium salt, b) 5 layers of the ester, c) difference between the salt and the ester films, d) the imidized polyamic acid alkylammonium salt film, e) the imidized ester film and f) the difference spectrum d-e. The oxidation states +1, +2, +3 and +4 of silicon show photoemission at approximately 1, 2, 3 and 4 eV higher electron binding energy than the

Si<sup>0</sup> emission at -99 eV. The relatively stronger emission from higher oxidation states of silicon in spectrum 2 a and in the difference spectrum c demonstrate that for the initial LB deposit the alkylammonium salt of polyamic acid reacts more strongly with the silicon substrate. After imidization, both interfaces show about the same level of silicon in the +4 oxidation state, but the alkylammonium salt deposit exhibits a Si<sup>0</sup> emission extending to lower binding energy values. This lower binding energy shoulder, which is best seen in the difference spectrum 2f, could indicate that some of the silicon surface atoms are in an electron-rich environment, i.e. partially reduced state, at the interface after the ammonium salt of polyamic acid has reacted to polyimide. From our spectra we cannot distinguish between silicon oxide species or silicon in different bonding environments with the polymer.

The Cls, N1s and O1s spectra in agreement with the above observations reveal, that the resulting polyimide films from the two deposits have a different composition in the interface layer when monolayers are deposited. Despite these chemical differences in the interface, both polyimide precursors can be used to grow thick polyimide films by Langmuir Blodgett deposition. This example complements the previous comparison between dissolved and solventless polyamic acid with respect to the observation, that the interfacial chemistry between the polymer and the substrate depends on the method of preparation. In particular the LB technique offers a well controlled experimental procedure to study these effects further.

The results summarized so far refer to studies related to the interfacial bond between polyimide films and the inorganic substrates.

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**Figure captions:**

Fig.1 (1a) FTIRAS Spectra obtained in a single reflection geometry from a vapor deposited polyimide film cured for 30 minutes at 573K.

(1b) Difference spectrum after deposition of a submonolayer of copper (0.1 nm) under ultra-high vacuum conditions.

(1c) Difference spectrum after deposition of a total of 0.2 nm copper on the film in 1a.

(1d) Difference spectrum to 1a after heating the 0.2 nm copper film to 573K for 15 min.

Fig.2 Si 2p XPS data for LB deposited polyamic acid (onto a freshly etched Si(100) surface) and the resulting polyimide films (after thermal treatment for 30 minutes at 250°)

(2a) 5 layers of the alkylammonium salt

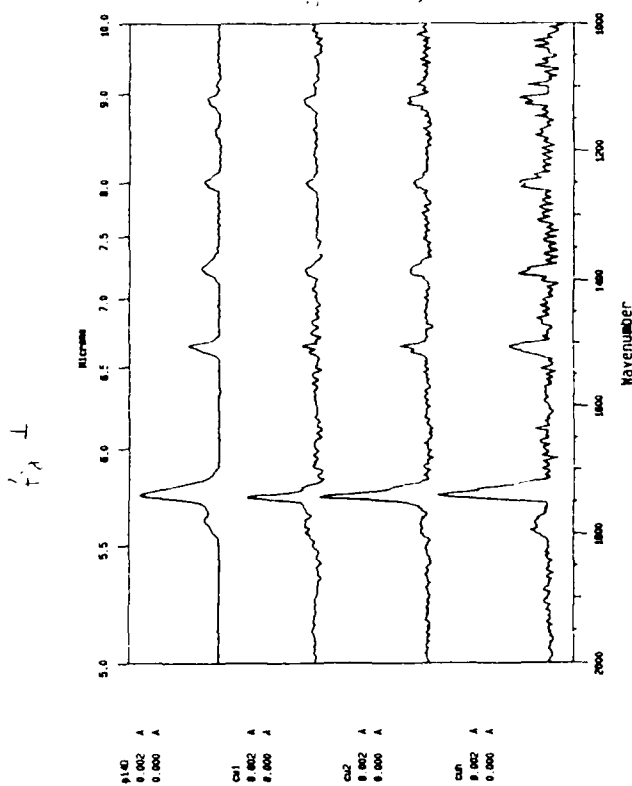
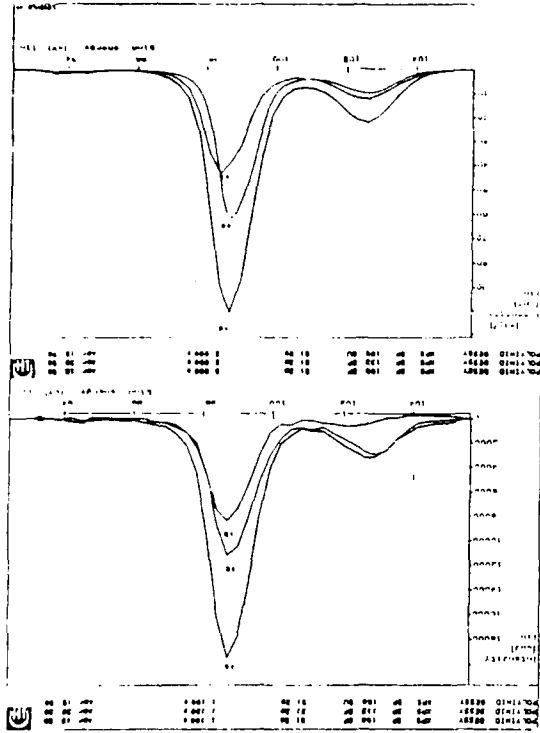
(2b) 5 layers of the ester

(2c) difference between the salt and the ester films

(2d) the imidized polyamic acid alkylammonium salt film

(2e) the imidized ester film

(2f) difference spectrum d-e



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