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MECHANICAL AND SPECTROSCOPIC PROPERTIES
OF METAL-CONTAINING POLYIMIDES

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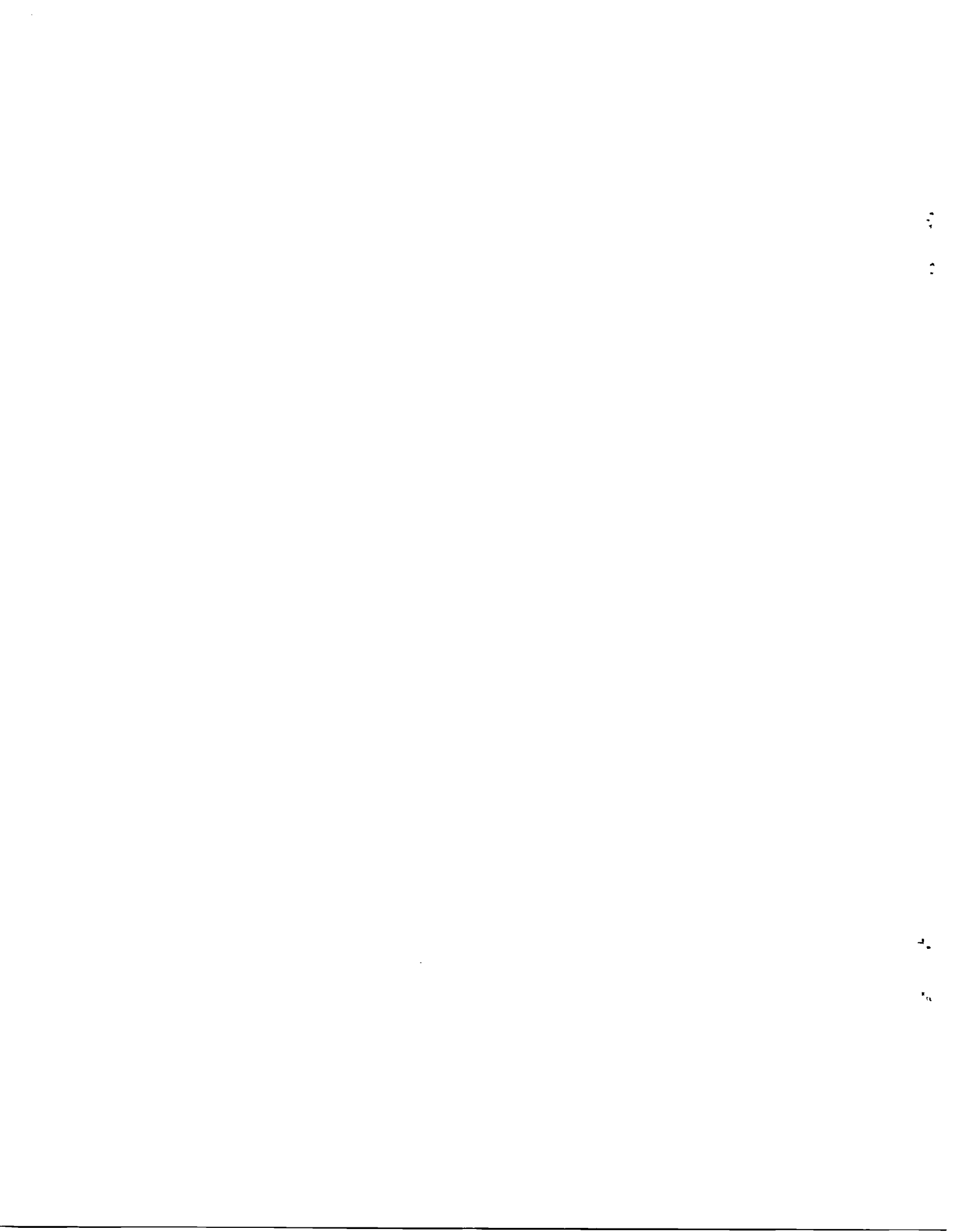
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INTRODUCTION

The continuing demand for materials with a unique combination of properties has brought forth a sizeable research effort¹ concerning polymer modification via incorporation of a variety of non-metallic and metallic dopants into the polymer. The modification of polyimide properties is no exception in this regard. This work had its beginnings approximately 25 years ago when Angelo² briefly reported in a patent the addition of metal ions to several types of polyimides. The object of the invention was a process for forming particle-containing ($<1\mu$) transparent polyimide shaped structures. All of the metals were added in the form of coordination complexes rather than as simple anhydrous or hydrated salts. The properties of only one film (e.g. cast from a N,N-dimethylformamide solution of 4,4'-diaminodiphenyl methane, pyromellitic dianhydride and bis(acetylacetonato)copper(II)) were given. These properties included: %Cu = 3.0%, dielectric constant = 3.6 and volume resistivity = 8×10^{12} ohms-cm. Comparison of metal-doped films with films cast from the neat polymer solution was not discussed. No data were given regarding thermal behavior, adhesive properties or the mode of interaction between metal and polyimide. Unfortunately further patents and published work in this regard are not available.³

Ten years later a report⁴ appeared concerning silver incorporation into the polyamic acid derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline. Both Ag and $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$ were utilized. Films containing 0.25-1.00 gram-atom of Ag per repeat unit were obtained. Electroconductivity was studied as a function of temperature and Ag content. Thermal and electrical conductivities were increased 3-7 times for the polyimide film containing dispersed Ag metal, but no change in properties was noted for the film containing $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$. Prior to this study a patent⁵ was filed covering very similar work (e.g. PMDA, 4,4'-diaminodiphenylmethane and $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$). In this case, the Ag containing polyamic acid complex was converted to the polyimide and Ag metal by heating at 300°C in *vacuo* for 30 minutes. The film was stated to be tough, flexible, opaque and metallic. At this stage the film was not conducting. Further heating at 275°C in air for 5-7 hours, however, rendered it conducting although no resistivity data was reported.

More recently a very brief report⁶ concerning lithium

incorporation into polyimides has appeared. Superior antistatic properties have been found for a soluble polyimide (DAPI-Polyimide) film loaded with either LiNO_3 or LiCl . Physical properties and film smoothness remained unchanged except that electrical resistance was sharply lowered. Conductivity was increased about 20-fold or 2000% over the standard unfilled polyimide. Additional tests showed that the films were very slightly hygroscopic in the presence of lithium ions. This phenomenon was suggested to account for the lowered resistivity. The NASA Brief publication did not state whether the electrical conductivity enhancement was in surface or volume conductivity.

Additional work in the area of metal doped polyimides has centered in our laboratory during the past six years. Our efforts have focused on the extent of polyimide modification by a variety of different metal dopants. Mechanical, thermal and electrical properties have been of interest. Major fundamental questions regarding the distribution and chemical state of metal within the film have been addressed employing various spectroscopic tools. An overview of these investigations provides the framework for this discussion.

OVERVIEW

Synthesis

Polyimides derived from PMDA, IA, or 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA), IB, and either 3,3'-diaminobenzophenone (m,m'-DABP), IIA, 4,4'-diaminobenzophenone (p,p'-DABP), 3,3'-diaminodiphenylcarbinol (DADPC), IIB, or 4,4'-oxydianiline (ODA), IIC, (and to which have been added numerous metal compounds) have been prepared. The synthetic procedure employed involved (1) formation of the polyamic acid (20% solids) in either N,N-dimethylformamide, N,N-dimethylacetamide (DMAC) or diethylene glycol dimethyl ether (Diglyme), (2) addition of the metal complex to the polyamic acid, III, in a 1:4 ratio, (3) fabrication of a film of the polyamic acid-metal compound mixture and (4) thermal conversion (300°C) to the metal containing polyimide, IV. Approximately twenty metals (Al, Au, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pd, Pt, Sn, Ti and Zn) in a variety of forms have been added to the polyamic acid solutions.⁷ Several experimental problems were encountered in following this procedure which limited the number of good quality films obtained. These

problems include: (1) metal complex not dissolving in an appropriate solvent, (2) gel formation or cross-linking of the polymer occurring upon interaction with the metal, (3) polyamic acid precipitating when the metal complex is added and (4) metal promoting extensive thermal oxidative degradation of the polymer film upon curing.

In general metal-doped polyimides derived from BTDA - p,p'-DABP yielded (regardless of the metal) rather poor quality, very brittle films which were due in part to the low viscosity of the resulting polyamic acid solution. Other dianhydride-diamine combinations with specific metal additives yielded high quality flexible films, with ODA as a constituent being most notable. The physical appearance of the thin films (~2 mil) varied considerably with the particular metal dopant employed. Colors range from transparent pale yellow (Li, Sn) to nearly opaque red-brown (Cu, Pd).

With several additives (Cu, Pd) a readily observed deposit appeared after curing on the film side exposed to the curing atmosphere. This difference was very noticeable for the two $\text{Pd}(\text{S}(\text{CH}_3)_2)_2\text{Cl}_2$ containing films BTDA-ODA and BTDA-DABP. While the glass side had a dark red-brown appearance, the air-side possessed a definite silvery, metallic appearance. Re-heating of these films after removal from the glass plate caused the glass-side to also metallize. The metallic looking surfaces could not be produced with DADPC and Li_2PdCl_4 containing films. The presence of oxygen during the imidization process appears crucial, since BTDA-ODA and BTDA-DABP doped with $\text{Pd}(\text{S}(\text{CH}_3)_2)_2\text{Cl}_2$ do not give rise to metallic surfaces when cured in either a dry N_2 , Ar, N_2/H_2 or moist Ar atmosphere.

Determination of an optimum reaction time for preparation of the polyamic acid/metal additive solutions has been necessary in order to (1) minimize any metal catalyzed degradation of the polymer in solution and (2) maximize the solubility of the metal additives into the polymer-DMAC matrix. The optimum reaction time for the polyamic acid/metal additive solutions was ascertained by measuring the intrinsic viscosity of aliquots withdrawn from a continuously stirred reaction mixture at 7, 24 and 48 hour intervals. Aliquots of solution were withdrawn and cast as films simultaneous with the viscosity determinations. It was determined that optimum reaction

time was within 7 hours from start of the synthesis. Intrinsic viscosity and thermal properties generally decreased with reaction time after approximately 7 hours.

Thermal Properties

Thermal properties of metal-ion-containing polyimide films have been studied from three viewpoints: (1) apparent glass transition temperature (T_g), (2) polymer decomposition temperature and (3) weight loss under isothermal conditions. The effect of five different dopants on T_g (Thermal Mechanical Analysis) is indicated in Table I.

Table I. Thermal Properties of Metal/Polyimide Films

Polymer/Metal FILM	T_g (°C)	% Metal	
		Found	Calc'd
Polymer Alone	283	-	-
Polymer + Al(acac) ₃	312	Al=0.9	0.9
Polymer + AgNO ₃	320	Ag=4.0	4.0
Polymer + Li ₂ PdCl ₄	341	Li=0.1 Pd=7.7	0.5 3.8
Polymer + AuI ₃	320	Au=0.2	6.4
Polymer + SnCl ₂	283	Sn=2.7	4.3

T_g increases approximately 30-40°C compared to the polymer alone with the exception of the SnCl₂-containing film. The increased T_g 's do not correlate with added metal content since the mole percent (~9%) of each metal dopant was constant. T_g also does not follow the experimentally determined metal weight percentages. For example T_g

increases 29°C for $\text{Al}(\text{acac})_3$ (%Al=0.9) addition, whereas the T_g does not change for SnCl_2 (%Sn=2.7) doping. Film densities have been measured at 23°C; yet, correlation with T_g is again not obvious. T_g data on copper containing films are quite different from these other metal additives. Figures 1 and 2 compare different dopants with the same curing atmosphere and different curing atmospheres with the same dopant respectively. In the case of different copper dopants, copper(II) films appear to contract prior to softening while the Cu(I) dopant does not. The copper(II) film decomposes near the softening temperature but the copper(I) film does not. This effect is just as pronounced upon considering air and N_2 cured copper(II) dopants. We believe that such polymer contraction near its softening point is unusual and may be caused by a combination of polymer cross-linking and polymer decomposition promoted by copper(II)/oxygen but not by copper(I)/oxygen and copper(II)/nitrogen.⁸

While the softening temperature of these doped polyimides are in general greater than the polymer alone, significant thermal stability has been sacrificed in the AgNO_3 and Li_2PdCl_4 cases (Figure 3). Al, Au and Sn films possess excellent thermal stability, just as the polymer alone, as evidenced by their TGA profiles obtained in air. The lowered thermal stability of the AgNO_3 film may reflect the presence of the highly oxidizing nitrate ion. The film containing Li_2PdCl_4 , of course, possesses two different metals as well as the highest metal weight percentage. In-depth studies with Li dopants alone⁹ have shown reduced thermal stability over polymer alone; however, not to this extent. The Li_2PdCl_4 film exhibits infrared detectable moisture which may also enhance polymer decomposition. A reduction in polymer decomposition temperature occurs on copper ion addition. The contrast between curing atmosphere and copper dopant is not as dramatic insofar as thermal stability is concerned. Air and N_2 cured films yield almost identical polymer decomposition temperatures (Figure 4). In the case of copper(I) and copper(II), the differences are more pronounced. The copper(I) dopant, $[(n\text{-Bu}_3)\text{PCuI}]_4$, exhibits significant low temperature weight loss even though total decomposition occurs at a higher temperature in the copper(I) case relative to copper(II).

These observations on thermal stability are further dramatized by isothermal measurements on several of these films. Originally films were aged at 200°C for 300 hours in an inert atmosphere but none of them lost significant

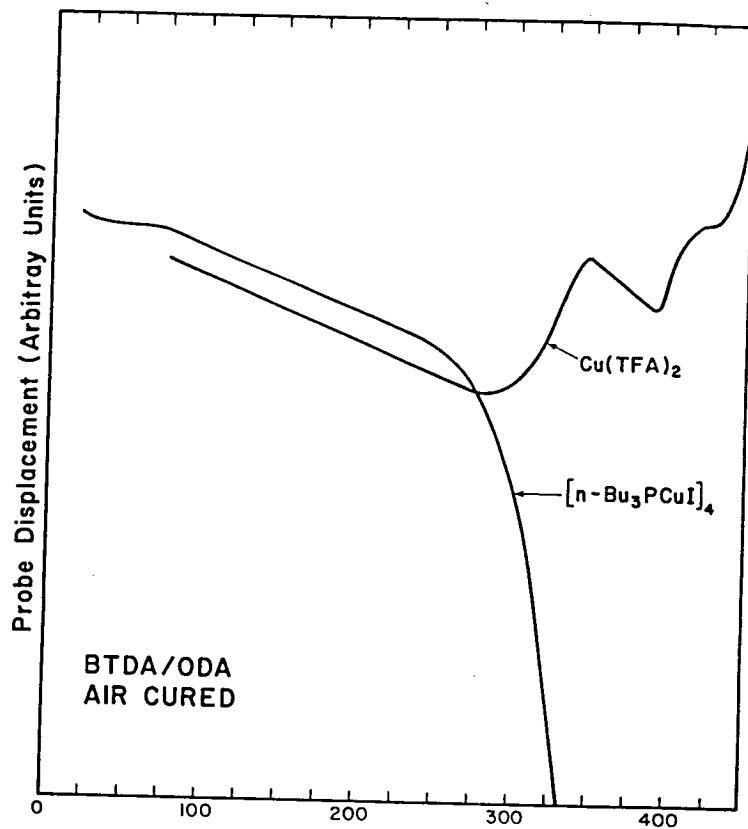


Figure 1. Plot of Thermomechanical Analysis of BTDA-ODA Film (air-cured) Doped with $[(n\text{-Bu}_3\text{PCuI})_4]$ and $\text{Cu}(\text{TFA})_2$.

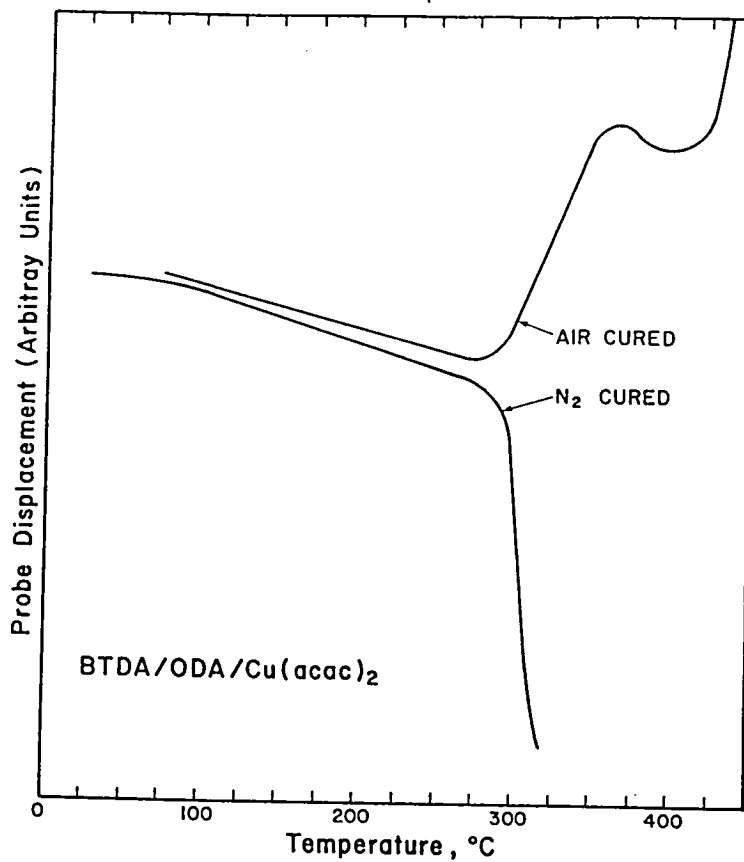


Figure 2. Plot of Thermomechanical Analysis of BTDA-ODA $\text{Cu}(\text{acac})_2$ Film Cured in Air and N_2 .

DYNAMIC TGA OF METAL/POLYIMIDE FILMS
CURED AT 300°C IN AIR

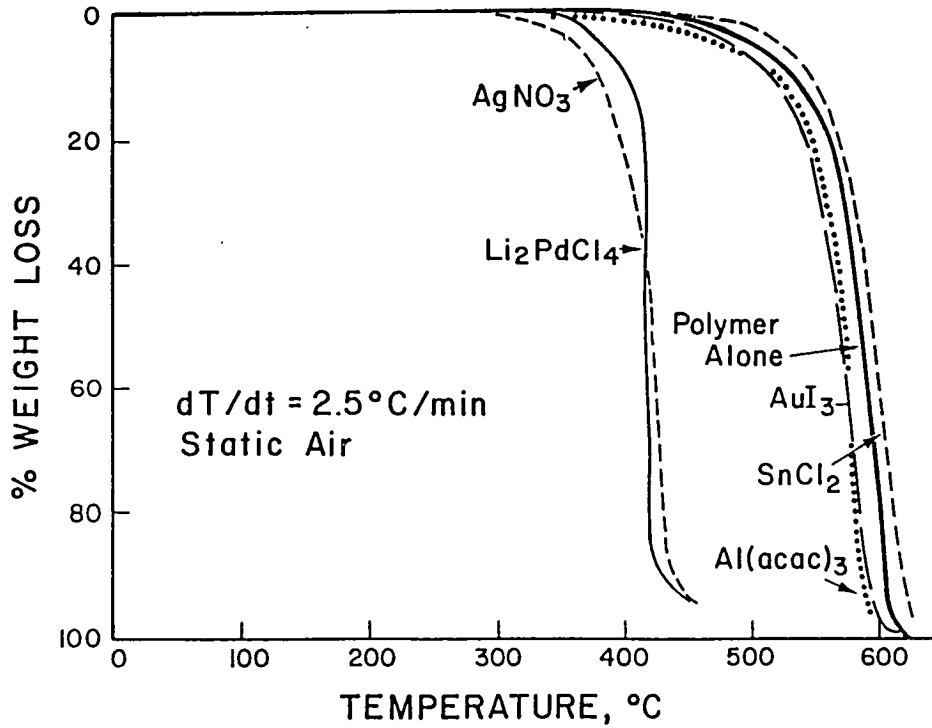


Figure 3. Dynamic TGA of Polyimide/Metal Films Cured at 300°C in air.

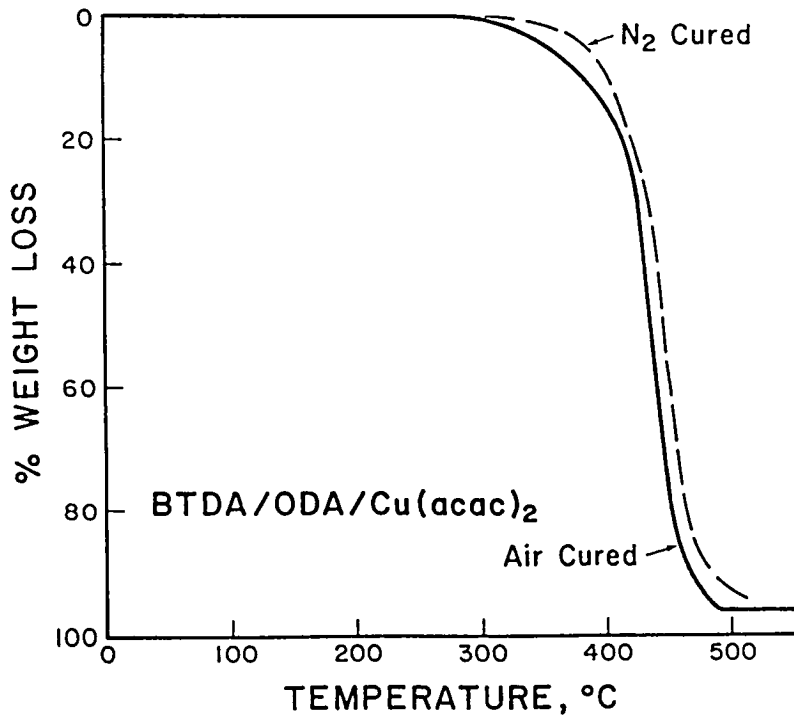


Figure 4. Plot of Thermal Gravimetric Analysis of BTDA-ODA-Cu(acac)₂ Film Cured in Air and N₂.

weight. In order to observe differences in each film, accelerated aging experiments at 300°C were conducted. The Li_2PdCl_4 film was the only film tested that did not survive this environment (Figure 5). Even though AgNO_3 and Li_2PdCl_4 films exhibited about the same polymer decomposition temperature by dynamic TGA, the AgNO_3 film is noticeably more thermally stable by isothermal TGA measurement (i.e. ~4% weight loss after 300 hours).

Reflection upon these thermal properties and the preparative thermal curing (imidization) process employed to prepare these films may reveal in part why several of these films have quite different metal percentages from their theoretical value (Table I). Au, Li and Sn have a much lower metal content than calculated. No doubt vaporization of AuI_3 , LiCl and SnCl_2 occurs during imidization at 300°C in flowing air. The amount of Pd, on the other hand, is double what is predicted. The ready decomposition of the polyimide film when doped with Li_2PdCl_4 indicates that some polymer "break-down" into volatiles occurs during thermal imidization; thereby, raising the %Pd in the film. The curing process apparently affects adversely neither the metal additive nor polymer in the presence of AgNO_3 and $\text{Al}(\text{acac})_3$.

Mechanical Properties

Certain polyimides are known to be excellent adhesives. Doped and undoped polyimides derived from BTDA and m,m'-DABP have been employed in lap shear strength tests employing titanium-titanium adherends. Tests were performed at room temperature, 250°C and 275°C employing either DMAC or DMAC/Diglyme as the solvent. At room temperature, regardless of the metal ion employed, adhesive strength is decreased relative to the "polymer-alone" case (Table II). The choice of metal ion at high temperature testing is critical. The two best cases (i.e. polymer doped with $\text{Al}(\text{acac})_3$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were subjected to adhesive testing at elevated temperatures. Under these conditions the metal ion filled polyimides were superior. The $\text{Al}(\text{acac})_3$ case proved to be exceptional in that it exhibited approximately four times the lap shear strength of "polymer-alone" at 275°C.¹⁰ We feel that this enhanced adhesiveness is due in part to the increased softening temperature of the $\text{Al}(\text{acac})_3$ filled polyimide. These results are somewhat analogous to data collected by St. Clair and Progar¹¹ regarding the use of aluminum metal as a

ISOTHERMAL TGAs OF METAL/POLYIMIDE FILMS
(300° C IN N₂)

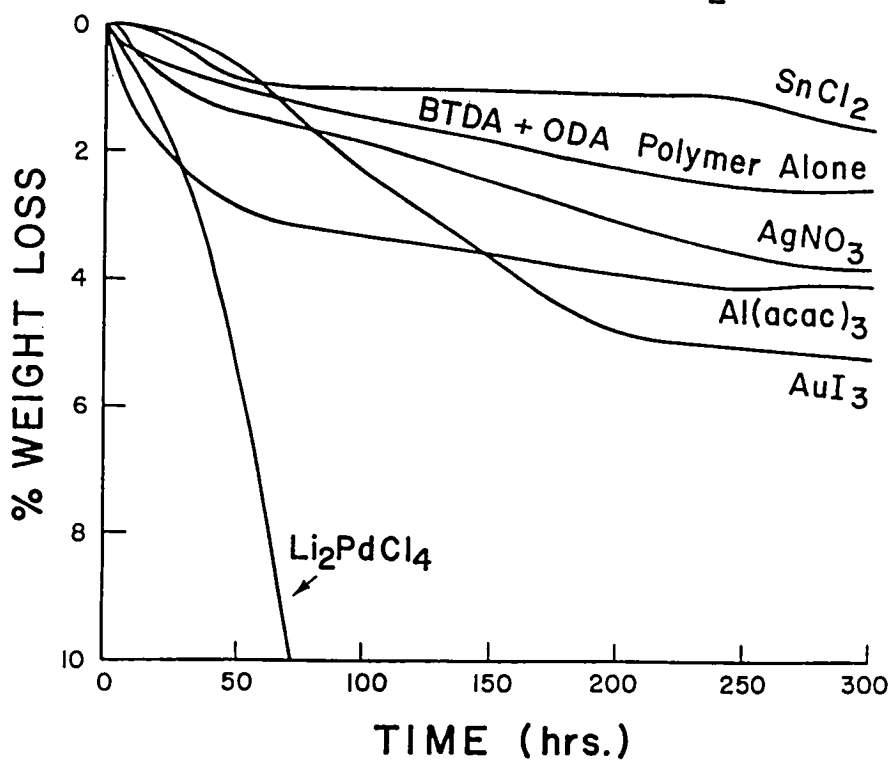


Figure 5. Isothermal TGA's of Polyimide/Metal Films at 300°C in Nitrogen.

Table II. Lap Shear Tests^a, Titanium-Titanium Adherend, BTDA-m,m'-DABP

<u>Metal Ion Added</u>	<u>Lap Shear Strength^b (psi)</u>		
	<u>25°C</u>	<u>250°C</u>	<u>275°C</u>
No metal	2966 (3138)	1573	438 (496)
Al(acac) ₃ ^c	2378 (2400)	1891	1641 (1348)
NiCl ₂ ·6H ₂ O ^c	1800	1332	608

^aNumbers in parenthesis correspond to DMAC/Diglyme solvent mixture.

^bAverage of four tests.

^c0.1g of metal complex (salt) per 4g of polymer (20% solids).

filler with various polyimides. Lap shear strength was found by these workers to double at 250°C with 79% Al filled polyimide versus the unfilled polyimide.

Mechanical properties of several metal-containing polyimide films have been measured.¹² Tensile strengths for these films are given in Table III. Films were pulled in the 0° direction (as cast) at a rate of 0.2 inches/minute at both room temperature and 200°C. With the exception of the AgNO₃ additive, the tensile strengths are excellent. At elevated temperature all metal containing films have surprisingly increased strengths relative to the polymer alone. Incorporation of metal ions into polyimide films in order to improve their space applicability therefore offers a distinct advantage over the addition of heavy metal fillers or carbon microspheres to the polyimide. Fillers and carbon microspheres not only add unwanted weight to the film, but result in greatly lower tensile strengths making them unfit for space applications. Tensile modulus and percent elongation for these films are given in Table IV. Percent elongation for each metal-containing film decreased relative to the polymer alone both at room temperature and 200°C. Although hand-cast films are more subject to flaws and premature breaks, it is reasonable to expect tensile

Table III. Mechanical Properties of Metal/Polyimide Films^a

Polymer/Metal FILM	Tensile Strength (psi)	
	RT	200°C
Polymer + Polymer Alone	16,500	6,700
Polymer + Al(acac) ₃	16,100	7,900
Polymer + AgNO ₃	12,000	8,300
Polymer + Li ₂ PdCl ₄	14,000	10,600
Polymer + AuI ₃	19,100	9,900

^aInstron Tensile Testing

Table IV. Mechanical Properties of Metal/Polyimide Films^a

Polymer/Metal FILM	Tensile Modulus (psi)		Elongation (%)	
	RT	200°C	RT	200°C
Polymer Alone	284,000	178,000	10	26
Polymer + Al(acac) ₃	454,000	257,000	6	6
Polymer + AgNO ₃	486,000	215,000	3	4
Polymer + Li ₂ PdCl ₄	492,000	336,000	4	5
Polymer + AuI ₃	494,000	311,000	8	15

^aInstron Tensile Testing

modulus to increase upon metal incorporation. The moduli of these films are on the order of that of DuPont's Kapton film (400,000 psi). Further evidence of an increase in film stiffness is offered by Young's modulus data (Table V). Regardless of the test temperature or metal dopant, an increase in modulus is observed. A correlation with the weight percentage of each metal was not found (see Table I).

Table V. Mechanical Properties of Metal/Polyimide Films^a

Polymer/Metal FILM	Young's Modulus, $E' \times 10^{10}$ dynes/cm ²		
	RT	100°C	200°C
Polymer Alone	3.52	2.81	2.02
Polymer + Al(acac) ₃	4.49	3.61	2.59
Polymer + AgNO ₃	4.89	3.97	3.10
Polymer + Li ₂ PdCl ₄	4.31	3.67	2.88
Polymer + AuI ₃	4.06	3.39	2.57
Polymer + SnCl ₂	4.66	3.77	2.70

^aAutovibron

Electrical Properties

In light of the excellent thermal and mechanical properties of polyimide films and the great interest currently shown in electrically conducting polymers, considerable effort has been expended in studying the electrical properties of metal-doped polyimide films. The addition of select palladium complexes to polyimides produces one of the more dramatic effects on electrical resistivity. Table VI outlines these results. For BTDA derived films four different combinations of dianhydride, diamine and palladium complex have yielded polyimides with dramatically lowered resistivities when cured in air. More

highly conductive BTDA-ODA films were produced using both palladium additives, Li_2PdCl_4 (LTP) and $\text{Pd}(\text{S}(\text{CH}_3)_2)_2\text{Cl}_2$ (PDS). Surprisingly only LTP gave lowered resistivity values with BTDA-DADPC; while, PDS with the same monomer pair exhibited values equivalent with the polymer alone. The results with BTDA-DABP, however, were totally reversed.¹³

A metallic surface on the air side characterizes the two conducting (BTDA-ODA, BTDA-DABP) PDS films. The three-point electrode method normally used in measuring the surface resistivity of these films is unsatisfactory. A four-point method yielded a surface resistivity of approximately 10^5 ohms for the metallized side. The film side exposed to glass during curing gave a value similar to the polymer-alone. Volume resistivity for these two films was 10^{17} ohm-cm. The PDS additive with BTDA-DADPC and all PMDA films regardless of the diamine gave no metallic surface and no resistivity lowering. This metallic surface is, therefore, apparently not a necessity for conduction, since low resistivity LTP films do not display a metallic surface.

The results on curing the films in a non-oxygenated atmosphere are equally interesting. No metallic surfaces are produced with PDS as an additive and no resistivity lowering is observed. Moist argon and forming gas (N_2/H_2) give the same unchanged results. A nitrogen curing atmosphere, however, does not change the resistivity results appreciably, from the air-cured, low resistivity LTP films. It is significant that in each case, with LTP the resistivity values are always one to three orders of magnitude higher for nitrogen cured films. We, therefore, believe that molecular oxygen is crucial for production of these lower resistivity films, however, the chemistry of LTP and PDS during the imidization process is probably quite different.

No appreciable lowering of volume or surface resistivities was observed with lithium additives except when the dopant was lithium chloride and the monomer pair was either BTDA-ODA or PMDA-ODA.⁹ With the former LiCl -doped monomer pair, the typical volume resistivity range was 10^6 - 10^{10} ohm-cm as compared to undoped films with values greater than 10^{18} ohm-cm. These data, however, were

Table VI. Surface and Volume Resistivities of Conductive Palladium-Containing BTDA-Derived Polyimides^{a,b}

Metal Complex	ODA	DABP	DADPC	Curing Atmosphere
Li_2PdCl_4	9.5×10^5 ohm 2.0×10^6 ohm-cm	NC ^c	1.3×10^7 ohm 1.0×10^7 ohm-cm	Air
$\text{Pd}(\text{S}(\text{CH}_3)_2)_2\text{Cl}_2$	$\sim 10^5$ (ATM) 1.0×10^{17} ohm (GLASS) 1.0×10^{17} ohm-cm	$\sim 10^5$ (ATM) 1.0×10^{17} ohm (GLASS) 1.0×10^{17} ohm-cm	NC	Air
Li_2PdCl_4	5.1×10^7 ohm 8.9×10^7 ohm-cm	NC	2.1×10^{10} ohm 1.4×10^{11} ohm-cm	N ₂
$\text{Pd}(\text{S}(\text{CH}_3)_2)_2\text{Cl}_2$	NC	NC	NC	N ₂

^aResistivity values are quoted for the best quality films. Values for replicate films do not differ by more than one order of magnitude.

^bPolymer alone surface and volume resistivities are 10^{17} ohm and 10^{17} ohm-cm, respectively.

^cNC = No change in resistivity relative to the polymer alone.

obtained for films measured after air-drying. Upon subsequent vacuum drying at 110°C for 12 h, volume resistivities were found to increase to 10^{12} - 10^{14} ohm-cm. Finally, when resistivity measurements were carried out in a drybox after heat vacuum drying, values in the vicinity of 10^{16} ohm-cm were observed. The surface resistivities, likewise, followed the same trend. This suggests that the primary improvement in conduction is due to the ability of the lithium ion to pick up moisture although no noticeable droplet formation was observed on the surface.

For the monomer pair PMDA-ODA, lowering of volume resistivity was only observed when dopant concentration was relatively high. For a film cured in air having 0.65% lithium, the volume resistivity was found to be 1.6×10^{10} ohm-cm. The volume resistivity, however, increased to 7.2×10^{15} ohm-cm on vacuum drying. A film cured in nitrogen containing 0.54% lithium, on the other hand, gave volume resistivities of 4.4×10^6 and 1.9×10^{10} ohm-cm upon air-drying and vacuum drying, respectively. A possible explanation for this observation lies in the brittleness of the air-cured film vs. the more flexible nitrogen-cured film. A more homogeneous distribution of lithium might then be expected in the nitrogen-cured film, which may facilitate better electrical conduction.

The presence of water in the BTDA-ODA-LiCl film was verified by Fourier Transform infrared spectroscopy. The strong IR absorption suggests the presence of a relatively large quantity of water when contrasted to its undoped counterpart, which shows very little evidence for moisture. On extending this examination, we observed a comparable amount of water in all lithium doped films regardless of their resistivity. This implies that a further factor is necessary for reduced resistivity, perhaps the distribution of lithium throughout the film, although scanning electron microscopic study of both types of films to date reveals no major surface differences, where, typically, only a smooth surface was obtained.

Electrical resistivities in several of the copper cases are again slightly lower than for the polymer alone. In all cases the numbers reflect average of values obtained

on multiply cast films. Cu(BAE),* regardless of whether the dopant was added during or after polymerization, consistently gave higher resistivity values than with Cu(TFA)₂.* Imperfections in the 6 cm diameter disks no doubt account for scatter in the resistivity data given similar methods of preparation. The most consistent data were obtained with Cu(TFA)₂ and PMDA-derived polyimide as illustrated by the two independent preparations in Table VII. It is interesting to note that the metallic-looking air side (Cu(TFA)₂ as dopant) always exhibits the lower surface resistivity. The resistivity lowering, however, is not at all comparable to the metallic-looking PDS film surfaces. In those cases where the film is imidized in N₂ the surface resistivity is the same regardless of the film side.

Spectroscopic Properties

X-ray photoelectron spectroscopy (XPS) has proven valuable in studying selected metal-filled polyimides. Measured XPS binding energies (Pd 3d_{5/2,3/2}) for the PDS film show palladium exclusively in the zero oxidation state. This is determined by comparing palladium binding energies in the film with analogous data obtained on PdCl₂ and Pd metal. As expected, the palladium electron count on the side exposed to air during curing (metalized), is considerably higher than for the side against the glass (i.e. Pd(air)/Pd(glass) = 23.4). The corresponding LTP film shows that the palladium on the film surface exists as a mixture of zero and divalent oxidation states. The approximate number of Pd counts is usually quite small relative to the PDS film which is suggestive of a more homogeneous distribution of palladium in the LTP film. This idea is supported by the fact that the ratio of palladium electron counts on the air side to the glass side is nearly unity. Neither of these films exhibits evidence of differential charging at the surface as is suggested with certain Pd-containing films.

*Cu(BAE), bis(acetylacetonate)ethylenediaminecopper(II)
Cu(TFA), bis(trifluoroacetylacetonato)copper(II)

Table VII. Resistivity Data for Cu(TFA)₂ Doped Polyimide Films

Dianhydride	RESISTIVITY		% Cu	
	Volume (ohm-cm)	Surface (ohm)	Calc'd	Found
BTDA ^{a,c}	1.6x10 ¹⁵	2.0x10 ¹⁴ (GLASS) 1.7x10 ¹² (ATM)	2.62	2.76
BTDA ^{b,c}	8.2x10 ¹⁴	>10 ¹⁸ (GLASS) 4.7x10 ¹² (ATM)	2.62	2.82
BTDA ^{a,d}	8.6x10 ¹⁶	4.6x10 ¹⁵ (GLASS) 9.7x10 ¹⁵ (ATM)	2.62	2.61
PMDA ^{a,c,e}	5.6x10 ¹⁴	3.1x10 ¹² (GLASS) 7.3x10 ¹⁰ (ATM)	2.94	4.08
PMDA ^{a,c,f}	4.1x10 ¹⁴	3.0x10 ¹² (GLASS) 9.3x10 ¹⁰ (ATM)	2.94	3.34

PMDA + ODA Alone ^c	>10 ¹⁸	1.0x10 ¹⁶	-	-
BTDA + ODA Alone ^c	>10 ¹⁸	1.0x10 ¹⁷	-	-

^aCu(TFA)₂ introduced after polymerization

^bPolymerization in situ with Cu(TFA)₂

^cAir cured

^dN₂ cured

^ePrep I

^fPrep II

Partial or complete palladium reduction during the imidization process, coupled with significant film resistivity lowering, naturally led to the idea that the presence of zero valent metal and lower resistivities could be correlated.¹⁴ To test this hypothesis two experiments were designed. First, the BTDA-DADPC-LTP film was subjected to an XPS angular dependence study to determine the location of Pd(II)/Pd(0) on the film's surface. Second, the surfaces of LTP and PDS conductive films were etched with aqua regia to free the surface of palladium(0). They were then examined by XPS and remeasured for resistivity.

The result of the angular study are shown in Figure 6. At low incidence angle (θ), the angle between the beam of photoemitted electrons and the sample surface, the number of electrons due to Pd(II) is greatly diminished, compared with those due to Pd(0). Because the sampling depth decreases with decreasing θ , the conclusion is reached that reduction of the metal takes place only on the very surface of the film and that the bulk of the polymer contains a preponderance of Pd(II). The metallic PDS film, of course, showed no Pd(II), even at high incidence angles. The palladium oxidation state in the bulk of this film cannot be determined by this method.

To further test this hypothesis the LTP and PDS films were subjected to surface cleaning with an aqua regia etching solution. Before treatment the LTP film had a volume resistivity of 1×10^{10} ohm-cm and a surface resistivity of 5×10^8 ohm. Acid etching of the surfaces of this film shows a negligible change in these values. XPS of the surfaces of the film before and after etching revealed a small shift in the position of the Pd $3d_{5/2,3/2}$ photopeaks to a higher binding energy which indicated the removal of most of the Pd(0). Etching in aqua regia of the PDS film completely removes the metallic surface and raises the volume and surface resistivities to those equivalent to the polymer alone (Figure 7). Binding-energy measurements show clearly that the acid-etched film contains only Pd(II) at the surface. Elemental analysis of the two films before and after acid etching indicate that a significant amount of palladium is lost from the PDS-doped film in the etching process, whereas in the film doped with LTP a negligible amount of palladium is lost. We therefore might reason that

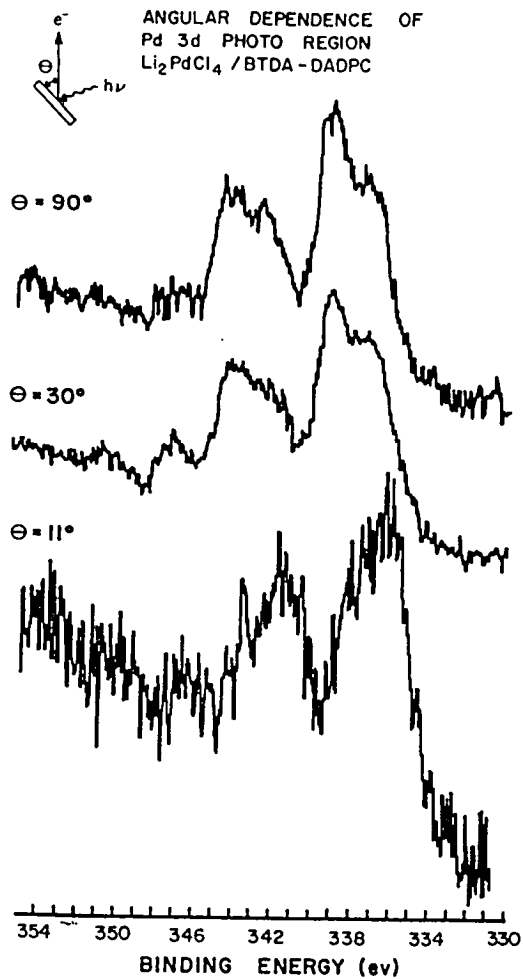


Figure 6. Angular Dependence of Palladium on a LTP-BTDA-DADPC Film.

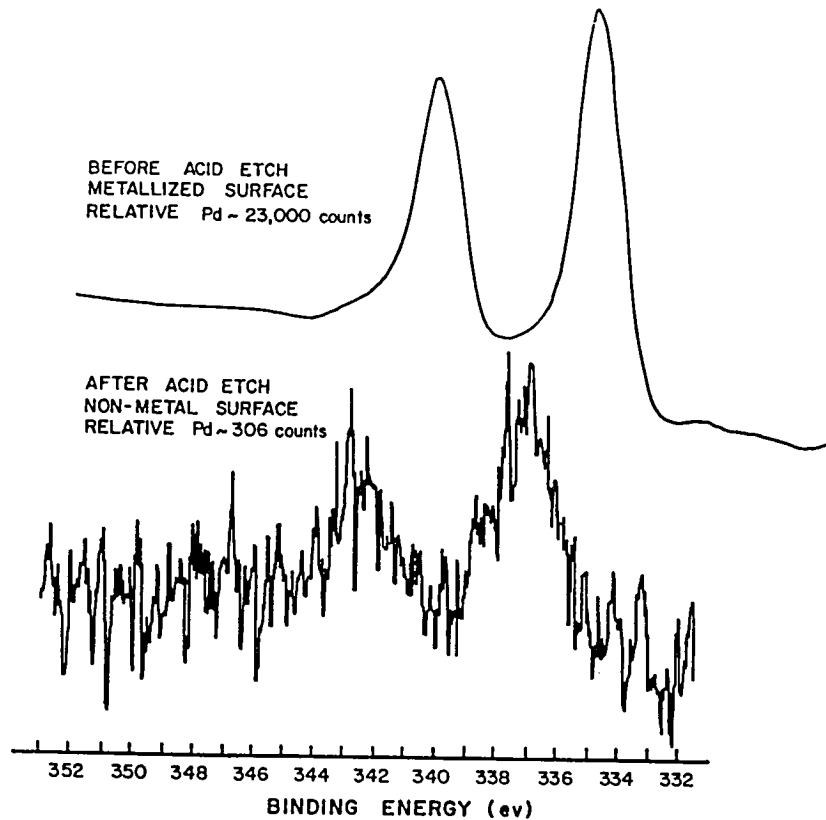


Figure 7. Palladium 3d Photoelectron Region Before and After Chemical Etching of PDS-BTDA-ODA Film Surface.

in PDS films, surface palladium accounts for any lowering of the resistivity. The film behaves essentially as a metal-vapor-deposited polyimide film. The LTP-containing film consequently appears to be the only film that possesses a uniformly lowered resistivity.^{15,16}

Two BTDA-ODA films, one doped with LTP and the other doped with PDS, were subjected to argon ion etching to establish the distribution of dopant components throughout the films. Figure 8 shows a plot of atom percent vs sputter time (min) for a film doped with PDS. Palladium, carbon, sulfur and chlorine were monitored continuously by Auger electron spectroscopy (AES). The estimated rate of ion etching by the Argon ion beam in this experiment is about 500Å/min. The profile shows clearly that most of the palladium in the film lies in the first 1000Å of the film surface and after this point it drops off rapidly to a level similar to that of sulfur and chlorine (residual amounts from dopant complex). The concentration of carbon rapidly rises as the palladium surface is penetrated and the bulk of the polymer is reached by the ion beam. After a distance of about 5000Å all elements have reached constant concentration indicating the film is homogeneous from this point through the film. This agrees with the chemical etching data which suggests that a majority of the palladium is on the surface of the PDS film.

An LTP-doped film was ion etched over a much larger area to make possible the determination of oxidation state of components as the surface is penetrated into the bulk of the film. The film was etched by a rastered ion beam for three thirty minute sequences and XPS information obtained after each time period. The etching rate was estimated to be about 20Å per minute or a total of nearly 2000Å of the surface penetrated. This study clearly shows that after a thin layer of predominantly Pd(0) is penetrated, the film contains a very homogeneous mixture of Pd(0) and Pd(II) in nearly equal amounts. Also present in the film bulk is a uniform mixture of Li⁺ and Li₂O as evidenced by the characteristic photopeaks at 55 eV and 50 eV. Chlorine is also present in residual amounts.

A similar procedure of XPS profiling was carried out on the PDS doped film. Over 4 hours of ion milling was necessary to penetrate the metal layer. After this time an area about 5 mm square had been milled away exposing clearly the dark-red brown color of the polymer film beneath. XPS data acquisition shows clearly that a mixture of Pd(0) and

Pd(II) is present in the film bulk but in concentrations much lower than in the LTP doped film.

The inability of the LTP-BTDA-DABP film to conduct is perplexing in light of other successes with this palladium-dopant. There are, however, indications from XPS that this film is very inhomogeneous with respect to Pd distribution. Figure 9 shows the Pd $3d_{5/2,3/2}$ photopeak for this film. The peaks at 350 and 346 eV are attributed to palladium and are believed to be due to differential charging of the sample surface and are likely to be the result of "islands" of palladium that have been isolated on the surface, thus preventing proper contact with the spectrometer. A scan of several different samples of this film suggests that the degree of this effect varies but is always present. This "islanding" of metal would most certainly be detrimental to any conduction mechanism operable in these films weak signals are again seen for Pd(II) and Pd(0).

These XPS and etching studies have revealed essentially three types of palladium-doped films: (1) those doped with a soluble lithium containing complex (LTP) and are homogeneous and electrically conductive, (2) those with LTP which produce inhomogeneous non conductive films and (3) those that contain a soluble complex (PDS) but exhibit loss of a majority of the dopant upon thermal curing, hence showing no conductivity or at best only surface conductivity.

The conductive films (those doped with LTP) apparently have a mixture of Pd(0) and Pd(II) together with lithium ion. It seem likely that the coupling of Pd(0) and Pd(II) is integral to the conduction process.

XPS has proven useful in the study of lithium speciation in lithium-doped polymers.⁹ Figure 10a shows a typical spectrum obtained for the lithium 1s photopeak. The primary lithium peak for all doped polyimides was found to be around 50.5 eV regardless of the measured resistivity. At higher dopant concentrations, a secondary peak, not always observed and much less intense, appears around 55.0 eV (Figure 10b). According to Povey and Sherwood,¹⁷ the peak at 50.5 eV is characteristic of lithium in Li₂O, while the peak at 55.0 eV is more characteristic of lithium in LiCl. We find no evidence that spectrometer conditions can give rise to photochemical decomposition leading to lithium oxide as suggested by Povey and Sherwood.¹⁷ A film irradiated by

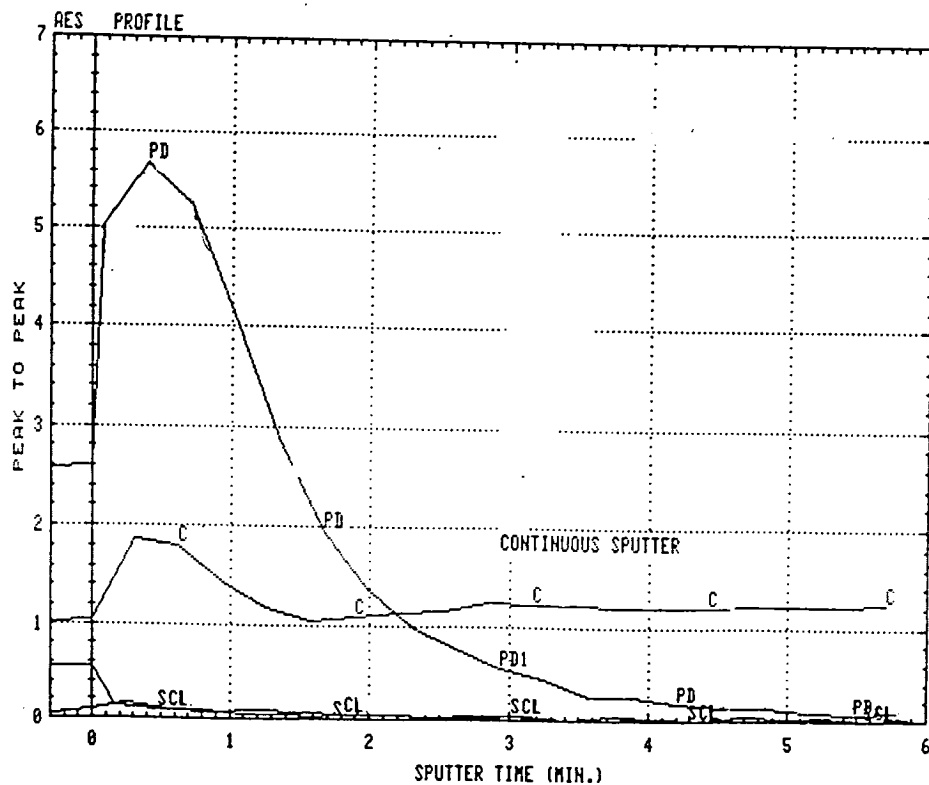


Figure 8. Auger Profile of Pd, C, Cl, and S for a PDS-BTDA-ODA Film.

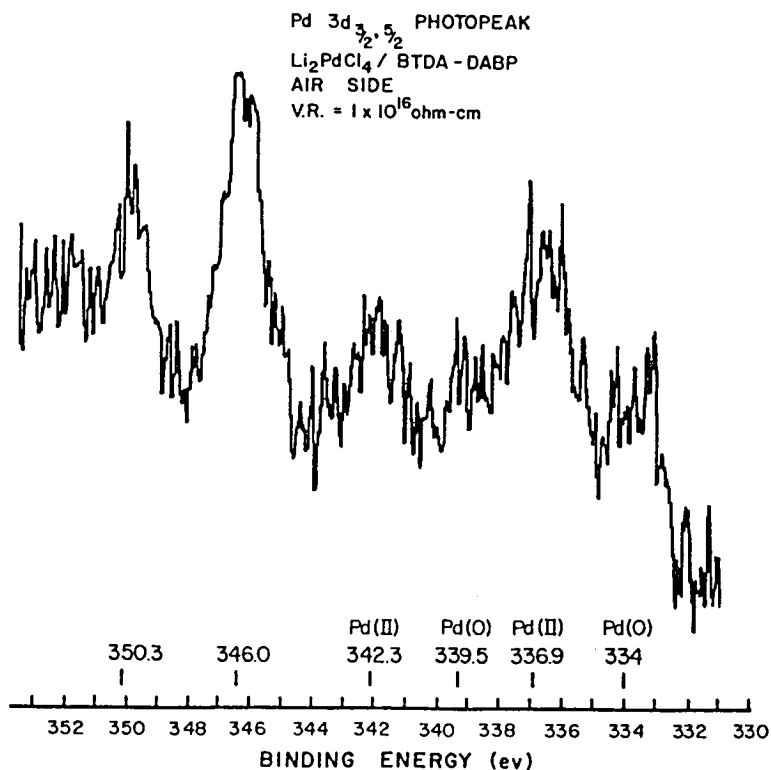


Figure 9. Differential Charging Effects on LTP-BTDA-DABP Film.

x-rays after 30 minutes gave the same spectrum as that of the same film irradiated after 2 hours. This would be unexpected if photodecomposition were occurring during x-ray photoelectron spectroscopic examination. It is reasonable, therefore, to conclude that lithium oxide may be generated during thermal imidization via Li^+ reaction with the released water, followed by hydrolysis and dehydration. Similar lithium XPS observations have been made on films doped with Li_2PdCl_4 . The peak at ~ 55.0 eV which appears only at high lithium concentrations arises when, no doubt, insufficient water of imidization is released to solvate all the lithium ion.

The nature of lithium on the film surface compared to the bulk is of interest. In other words is the "lithium oxide-like" material dispersed throughout the film rather than on the film surface. First of all, the atmosphere side and glass side of each film show a comparable number of electron counts for lithium. This observation is contrary to our palladium findings in that the atmosphere side of the film contains appreciably more palladium than the glass side of the film. Information regarding the lithium content and chemical state inside the lithium doped film has been obtained from angular and depth profile studies. At a 90° x-ray incidence angle, the spectrum of highly doped BTDA-ODA-LiCl is as per Figure 10b. On shifting to an incidence angle of 11° , the secondary peak is diminished significantly relative to the main peak. This suggests that "LiCl" is found only in the matrix of the polymer, whereas, " Li_2O " occupies the surface as well as the bulk. On depth profiling normally doped BTDA-ODA-LiCl for 30 minutes (argon ion sputtering), the shoulder at 55.0 eV which originally could not be discerned has grown to a distinct peak (Figure 11). The ratio of "LiCl" to " Li_2O " through the film appears to be a constant since spectra after 60 and 90 minutes sputtering are similar. One concludes, therefore, that "LiCl" is present in small quantities and that most has been converted into " Li_2O " during thermal imidization.

The nature of the "metallic-looking" surface of copper(II) doped films has been a major question in this investigation.⁸ The surface is produced only when the film is cured in air. Longer (>1 hr @ 300°C) curing times appear to favor formation of the "mirror-like" surface regardless of the copper(II) dopant. Differences in viscosity of the polyamic acid solution and the method of preparation are not crucial, although thicker films seem to adopt the "silvery-looking" surface more readily than thin films.

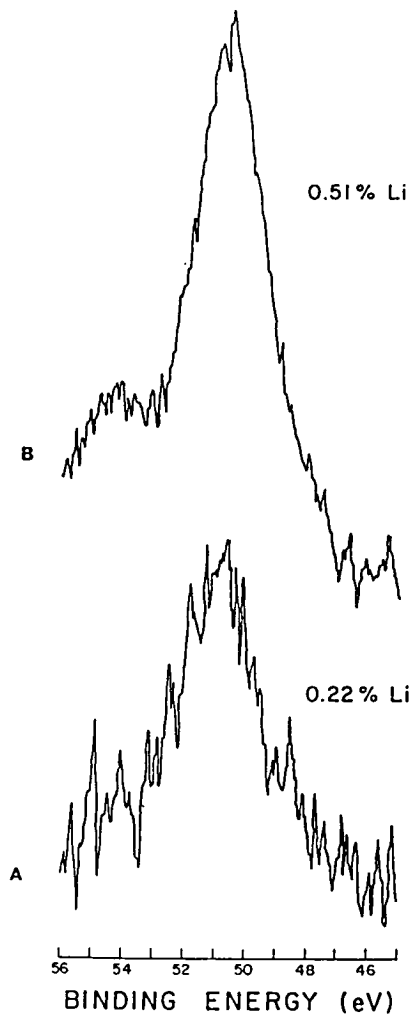


Figure 10. Concentration Dependence of Lithium 1s Photopeak.

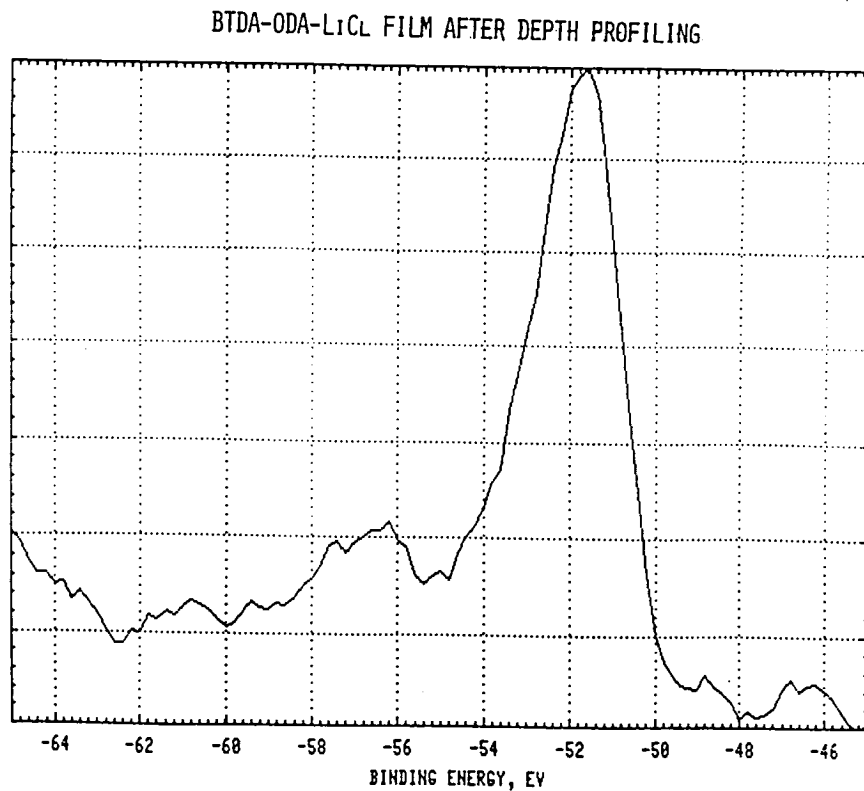


Figure 11. Lithium 1s XPS Region After Depth Profiling of LiCl-BTDA-ODA Film After 30 minutes.

XPS of pertinent photopeaks relative to copper(II) doped films have been measured. The copper 2P photopeak region in all cases affords the most information and interesting features. The $2P_{1/2,3/2}$ main peaks occur in the regions 952.5 eV and 933.0 eV respectively. These values are slightly lower than those observed in the pure copper(II) dopant, but they are higher than in copper metal. Figure 12 dramatizes these findings with $\text{Cu}(\text{TFA})_2$ as dopant in the BTDA-ODA polyimide. The spectrum of the doped polymer is of the atmosphere (air) side of the film. Appreciable Cu(II) is observed, but surprisingly no fluorine could be detected. On the glass side of the film, the opposite conclusions were drawn (i.e. little copper but significant fluorine). Similar findings were made with $\text{Cu}(\text{TFA})_2$ and PMDA-ODA. Since more copper was found on the atmosphere side of the film which also had the "silvery-looking" surface, one may conclude that copper in some form is contributing to this appearance. Binding energy and satellite data suggest a copper(II) rather than metallic copper state. Depth profiling (argon ion etching with auger electron monitoring) reveals the build-up of copper on the surface relative to the bulk polymer. Figure 13 plots atomic concentration versus sputter time for graphite-coated PMDA-ODA doped with $\text{Cu}(\text{TFA})_2$. The inverse relationship of Cu and C concentrations and the absence of F are noteworthy.

The material contributing to the "silvery surface" can also be chemically etched from the polymer film with strong non-oxidizing acid. Depth profiling of the air side of the chemically etched film reveals very little Cu whose concentration is invariant with sputter time. The "silvery" deposit therefore contains significant copper.

Frost and coworkers¹⁸ have documented some forty-six different copper compounds and complexes and have observed three types of XPS satellite splitting patterns which appear to be dependent on the copper ion environment. Type A satellite structure exhibits two satellites in both the $2P_{1/2}$ and $2P_{3/2}$ lines. Type B has two satellites in the $2P_{1/2}$ and two overlapping satellites in the $2P_{3/2}$. One satellite in each photopeak is characteristic of Type C. $\text{Cu}(\text{TFA})_2$ and $\text{Cu}(\text{AcAc})_2$ are of Type A. The XPS spectra change to Type B upon curing of the polymer film. Figure 12 illustrates these changes in satellite structure relative to copper metal which exhibits no satellites. Electronic

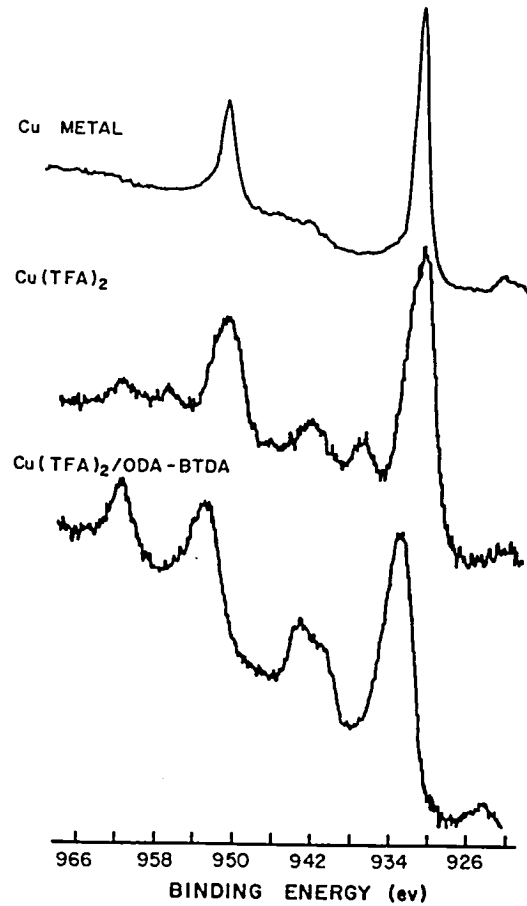


Figure 12. Copper 2p Photopeak Region of Copper Metal, $\text{Cu}(\text{TFA})_2$ and BTDA-ODA- $\text{Cu}(\text{TFA})_2$ Film.

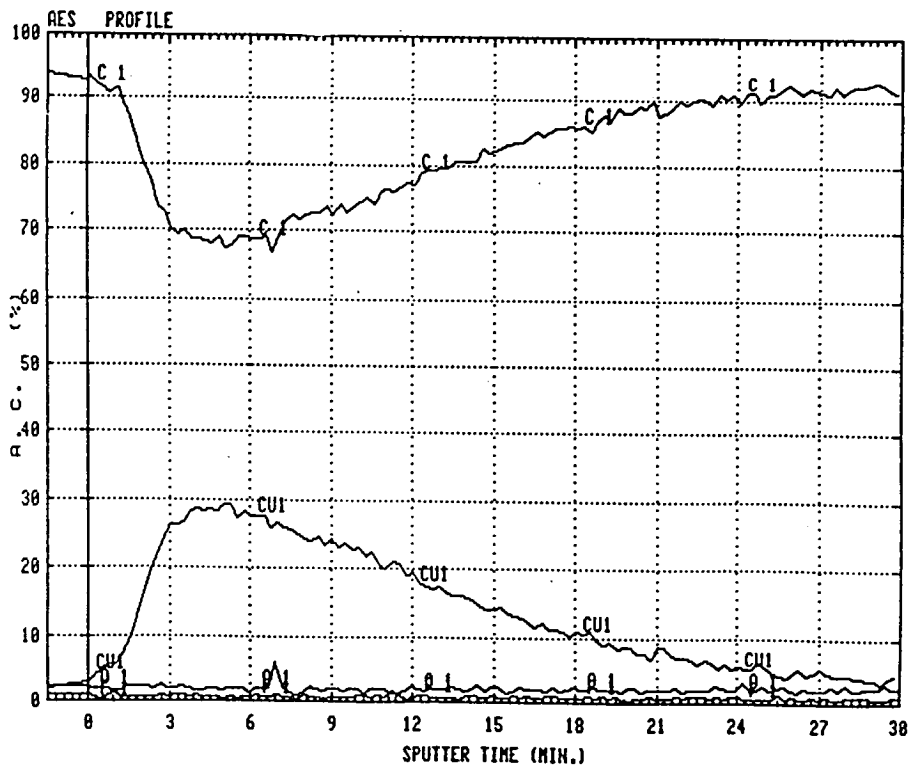


Figure 13. Auger Depth Profile (C, Cu, O, F) of the Air Side of PMDA-ODA- $\text{Cu}(\text{TFA})_2$ Film Before Chemical Etching.

transitions giving rise to these secondary photopeaks are generally believed to be either due to charge transfer between ligand and metal and/or excitation of metal electrons to vacant metal orbitals (i.e. 3d 4s or 4p). The apparent change in satellite structure may reflect a modified environment for copper in the polyimide relative to the dopant. Coordination of copper(II) to the polyimide thermal decomposition of the added metal complex, or hydrolysis of the dopant are possible fates for the metal in these films.

CONCLUDING REMARKS

In Summary numerous properties of polyimides can be modified by incorporation of metal additives at the polyamic acid stage prior to metal imidization. High solubility of the additive in DMAC is required. High quality films are produced in each case which have better thermal stabilities, higher softening temperatures and lower electrical resistivities and increased mechanical strength. The integrity of each additive employed in these studies is not maintained during aerobic thermal imidization. Segregation of the chemically-changed additive is evidenced in some cases by surface deposits on the air-side of each film which may result from either aerobic oxidation, thermal reduction or hydrolysis-dehydration of the metal dopant. Clearly more stable metal additives are needed in order to study the full effects of polyimide modification. Additional study of different metals, different additives of the same metal and various dianhydride-diamine combinations is desirable toward optimizing specific polymer properties. Extension of this research to other electrically neutral polymers would probably be fruitful.

REFERENCES

1. C. E. Carraher and M. Tsuda, Eds., "Modification of Polymers", ACS Symp. Ser., 121 (1980).
2. R. J. Angelo and E. I. DuPont DeNemours and Co., "Electrically Conductive Polyimides", U.S. Patent 3,073,785 (1959).
3. R. J. Angelo, (1976), Personal Communication.
4. N. S. Lidorenko, L. G. Gindin, B. N. Yegorov, V. L. Kondratenkov, I. Y. Ravich and T. N. Toroptseva, AN SSSR, Doklady, 187, 581 (1969).
5. A. L. Endrey and E. I. DuPont DeNemours and Co., U.S. Patent, No. 3,073,784 (1963).
6. M. N. Sarboluki, NASA Tech. Brief, 3(2), 36 (1978)
7. L. T. Taylor, A. K. St. Clair, V. C. Carver and T. A. Furtch, ACS Symp. Ser., 121, 71 (1980).
8. S. A. Ezzell, T. A. Furtch, E. Khor and L. T. Taylor, J. Polym. Sci. Polym. Chem. Ed., 28, 0000 (1983).
9. E. Khor and L. T. Taylor, Macromolecules, 15, 379 (1982).
10. L. T. Taylor, A. K. St. Clair and NASA Langley Research Center, "Aluminum Ion Containing Polyimide Adhesives", U.S. Patent 284,461 (1981).
11. D. J. Progar and T. L. St. Clair, 7th National SAMPE Technical Conference, Albuquerque, NM Oct. (1975).
12. L. T. Taylor and A. K. St. Clair, J. Appl. Polym. Sci., (1983).
13. T. L. Wohlford, J. Schaaf, L. T. Taylor, T. A. Furtch, E. Khor and A. K. St. Clair, "Conductive Polymers", Ed. R. B. Seymour, Plenum Publishing Corp., New York, p. 7, (1981).
14. T. A. Furtch, L. T. Taylor, T. W. Fritz, G. Fortner and E. Khor, J. Polym. Sci. Polym. Chem. Ed., 27, 1287, (1982).
15. V. C. Carver, L. T. Taylor, T. A. Furtch and A. K. St. Clair, J. Amer. Chem. Soc., 102, 876 (1980).
16. L. T. Taylor, A. K. St. Clair, V. C. Carver and T. A. Furtch, NASA Langley Research Center, "Electrically Conductive Palladium Containing Polyimide Films", U.S. Patent 4,311,615 (1982).
17. A. F. Povey and P.M.A. Sherwood, J. Chem. Soc., Faraday Trans., 1240 (1974).
18. D. C. Frost, A. Ishitani and C. A. McDowell, Mol. Physics, 24, 861 (1972).



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16. Abstract The incorporation of specific metal ions into polyimides is described. Detailed studies have included various compounds of copper, lithium and palladium as dopants. Addition of the metal during polymerization or after formation of the polyamic acid precedes the thermal imidization step. With many dianhydride-diamine-dopant combinations high quality variously colored films are produced. Many metal-doped films exhibit (1) improved high temperature adhesive properties, (2) increased electrical conductivity, (3) excellent thermal stability, (4) improved acid/base resistance, (5) increased modulus in flexible films and (6) excellent high temperature tensile strength. X-ray photo-electron spectroscopic study of these films suggests that many of the additives undergo chemical modification during thermal imidization. Palladium dopants appear to be partially reduced to the metallic state, while lithium and copper dopants are probably converted to their oxides. Ion etching experiments with Auger electron spectroscopy monitoring are discussed.					
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