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Surface-Semiconductive Polyimide Films Containing Tin Complexes

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ABSTRACT: Tin-containing polyimide films have been fabricated having surface resistivities of 10^5–10^8 Ω/square and thermal stabilities >500 °C. Most of these films are homogeneous, and all appear tough and flexible. A tightly bound layer of SnO_2 on the air-cured, atmosphere side of the film appears to be responsible for the lowered resistivities. Migration of the tin complex during curing followed by reaction with H_2O and possibly O_2 yields the SnO_2 surface layer. Glass sides of films and N_2-cured films are nonconductive. The SnO_2 layer on air-cured films has been found to be photoactive.

Introduction

The modification of polymer properties via incorporation of inorganic species into the polymer has produced many tin-containing polymer systems. Tin compounds have been evaluated and used as additives to PVC[1,2] and in paint formulations. Polymer systems synthesized with tin as a pendant group or in the backbone include polymethacrylates (and polyacrylates),[3,4,7] epoxies,[3] polyethyleneimine,[5] poly(vinyl alcohol),[5] poly(acrylic acid),[5] and polyimide.[6] Objectives of these studies included enhancement of oxidative and photostability, antifouling applications, piezo- and pyroelectric behavior, lowered electrical resistivity, and high-temperature thermal stability.

Previous work in our laboratory has surveyed the effect of incorporation of a variety of Sn(II) and Sn(IV) complexes on thermal and electrical properties of polyimide films.[8] The majority of the tin complexes employed produced materials with surface and volume resistivities within a few orders of magnitude of the unmodified polyimides. The additives $SnCl_2{\cdot}2H_2O$ and $(n\text{-}Bu)_2SnCl_2$ were noted to have a more significant effect upon film resistivity however. The surface resistivities of the atmosphere side of air-cured polyimide films modified with these two additives were found to decrease 8–11 orders of magnitude into the semiconductor range. Volume resistivities did not manifest such a large decrease. Thermal analysis of these tin-modified polyimide films showed in most all cases elevated softening temperatures and only a slight effect on polymer decomposition temperature.

This report will attempt to describe the nature of the semiconductive species responsible for the lowered resistivity that is exhibited by certain of these tin-modified polyimide films. The effect of tin concentration and curing atmosphere upon film electrical properties will be demonstrated. Elevated temperature resistivity and photoconductivity data will also be discussed.

Two polyimide systems (pyromellitic dianhydride–4,4′-oxyaniline (PMDA–ODA) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride–4,4′-oxydianiline (BTDA–ODA)) were chosen for modification by the two previously mentioned tin complexes. Polyimide–metal complex preparations used in this study are listed in Table I.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA) was received from commercial sources and purified by sublimation at 215 °C at less than 1 torr; mp 497 K. 3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BTDA) was received from commercial sources in a polymer pure grade and vacuum dried at 100 °C for 2 h before use; mp 558 K. 4,4′-Oxydianiline (ODA) was obtained commercially and sublimed at 185 °C and less than 1-torr pressure; mp 461–463 K (dec). All tin compounds were obtained commercially and used as received. Reagent grade *N*,*N*-dimethylacetamide (DMAC), glass distilled and packed under nitrogen, was obtained from Burdick and Jackson.

Table I
Thermal Properties of Tin-Containing Polyimide Films

polymer	dopant	cure atm	PDT,[a] °C	AGT,[b] °C
PMDA–ODA	$SnCl_2{\cdot}2H_2O$	air	546	450
PMDA–ODA	$(n\text{-}Bu)_2SnCl_2$	air	534	dec
BTDA–ODA	$SnCl_2{\cdot}2H_2O$	air	544	280
BTDA–ODA	$(n\text{-}Bu)_2SnCl_2$	air	548	404
PMDA–ODA	$SnCl_2{\cdot}2H_2O$	N_2	520	314
BTDA–ODA	$(n\text{-}Bu)_2SnCl_2$	N_2	500	304
PMDA–ODA	$(n\text{-}Bu)_2SnCl_2$	N_2	510	327
PMDA–ODA	$SnCl_2{\cdot}2H_2O$	forming gas	510	327
PMDA–ODA		air	580	405
BTDA–ODA		air	550	286

[a] Polymer decomposition temperature (thermal gravimetric analysis). [b] Apparent glass transition temperature (thermomechanical analysis).

Polymer Synthesis and Modification. Polymer synthesis was performed in DMAC, 15–20% solids concentration. ODA (0.004 mol) was added to a N_2-purged flask with DMAC and stirred until dissolved. The appropriate dianhydride was then added (0.004 mol). Stirring was continued at room temperature for 4–6 h. Doping of the poly(amic acid) was carried out by addition of the tin complex as a DMAC solution (0.001 mol of complex in 1–2 mL of DMAC). The tin-modified poly(amic acid) was stirred for 2–3 h and then cast as a film.

Film Preparation. Poly(amic acid)–tin complex solutions were centrifuged at ~1700 rpm before film coating. Solutions were poured onto acid-cleaned, dust-free soda lime glass plates and spread with a doctor's blade having a 12–22-mil blade gap in order to obtain a film of final thickness 1 mil. These films were then dried in static air at 60 °C for 2 h. Thermal curing at 100, 200, and 300 °C each for 1 h was done to imidize the materials. Curing atmospheres used were forced air, N_2, and forming gas (5% H_2–95% N_2 mixture). After cooling to room temperature, polyimide–metal complex films were removed from the glass plates by soaking in distilled water.

Materials Characterization. Galbraith Laboratories, Inc., Knoxville, TN, performed elemental analyses on tin-modified polyimide films. Thermomechanical analyses (TMA) were performed with a Du Pont Model 990 thermomechanical analyzer on film samples in static air at a 5 °C/min temperature program. Thermogravimetric analyses (TGA) were obtained in static air at a 2.5 °C/min temperature program.

Surface and volume resistivities were measured at room temperature following the ASTM Standard Method of Test for Electrical Resistance of Insulating Materials (D257-66) using a Keithley voltage supply, electrometer, and a three-point probe electrode assembly. Resistivity data at elevated temperature and under dynamic vacuum via a similar procedure were acquired with Keithley electrodes equipped with cartridge heaters and contained in an evacuable chamber. Photoresistivity experiments were conducted with an argon lamp having continuous spectral output equipped with a UV filter. A two-point probe was used with the

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Table II
Surface Resistivities of Tin-Containing Polyimide Films

			surf resistivity, Ω/square		% Sn	
polymer	dopant	cure atm	atm side	glass side	calcd	found
PMDA–ODA	$SnCl_2·2H_2O$	air	2×10^6	6×10^{12}	6.36	6.62
BTDA–ODA	$SnCl_2·2H_2O$	air	1×10^8	6×10^{12}	5.22	4.88
PMDA–ODA	$(n\text{-Bu})_2SnCl_2$	air	8×10^7	5×10^{14}	5.97	4.06
BTDA–ODA	$(n\text{-Bu})_2SnCl_2$	air	1×10^5	2×10^{13}	4.92	3.47
PMDA–ODA	$SnCl_2·2H_2O$	N_2	1×10^{16}	$>10^{18}$	6.36	2.08
PMDA–ODA	$(n\text{-Bu})_2SnCl_2$	N_2	9×10^{13}	6×10^{13}	5.95	1.64
BTDA–ODA	$(n\text{-Bu})_2SnCl_2$	N_2	5×10^{15}	7×10^{14}	4.94	
PMDA–ODA	$SnCl_2·2H_2O$	forming gas	6×10^{10}	3×10^{16}	6.36	2.20
PMDA–ODA	$SnCl_2·2H_2O$[a]	air	7×10^6	4×10^{13}		
PMDA–ODA	$SnCl_2·2H_2O$[b]	air	3×10^7	7×10^{12}		
BTDA–ODA		air	$\sim10^{17}$	$\sim10^{17}$		
PMDA–ODA		air	$>10^{18}$	$>10^{18}$		

[a] 50% additional dopant used. [b] 100% additional dopant used.

probes attached to the film surface with silver paint. A Keithley Model 177 digitial multimeter was used to measure film resistance as a function of irradiation time.

X-ray photoelectron spectra were obtained on either a Du Pont 650 B spectrometer or a Physical Electronics 550 instrument, both equipped with a Mg anode ($\lambda_{Mg\,K\alpha}$ = 1253.6 eV) target. Binding energies of all electrons were measured relative to the instrumental background carbon ($1s_{1/2}$) photopeak, assumed to have a value of 284.0 eV. Auger electron spectrometry/auger ion etching experiments were performed on the previously mentioned Physical Electronics instrument. Gold was vapor deposited on film surfaces prior to analysis in order to alleviate charging difficulties. Argon ion sputter rate was approximated 500 Å/min.

Infrared spectra of the tin-modified polyimide films were obtained with a Nicolet Model 6000 Fourier transform infrared spectrometer using a liquid nitrogen-cooled detector of 4000–400-cm^{-1} range. All spectra were taken via the attenuated total reflectance (ATR) technique, using a Harrick ATR attachment. A 75° angle was employed in order to obtain a spectral penetration depth (into the film surface) of approximately 1 μm.

Results and Discussion

Thermal and Electrical Properties. Thermal data taken for the tin-modified polyimide films are shown in Table I along with those of the corresponding polyimides containing no tin dopant. Apparent glass transition temperature (AGT) appears to vary in an erratic manner with tin-complex incorporation. The effect of curing atmosphere is most striking. Air-cured films exhibit AGT's equal to or greater than that of the polyimide alone, whereas PMDA–ODA doped films when cured in N_2 or forming gas demonstrate much lower (~100 °C) AGT's unlike the one BTDA–ODA film cured in N_2. Polymer decomposition temperatures were seen to consistently decrease upon tin-complex incorporation. However, polymer decomposition temperature for all these materials was 500 °C or greater. The thermal stability of polyimide appears, therefore, not to be compromised by tin-complex incorporation.

Surface resistivity measurements are shown for the tin-modified polyimide films in Table II as a function of cure atmosphere, and in the case of one dopant/polyimide, as a function of degree of tin loading. Values for the unmodified polyimide are also shown. The resistivity values quoted for doped polyimides are average values with a precision of approximately 2 orders of magnitude for independently cast films. The precision for undoped films is less than 1 order of magnitude. For all tin-modified films cured in air, a resistivity decrease into the semiconductor range is noted for the atmosphere side (side of film exposed to atmosphere during curing). A less dramatic resistivity decrease was realized for the glass side of these films. Films cured in N_2 exhibited similar resistivities regardless of the film side and each was close in value to that of the unmodified material. A film cured in forming gas showed a lower atmosphere-side surface resistivity, but again not to the same degree as with the air-cured films.

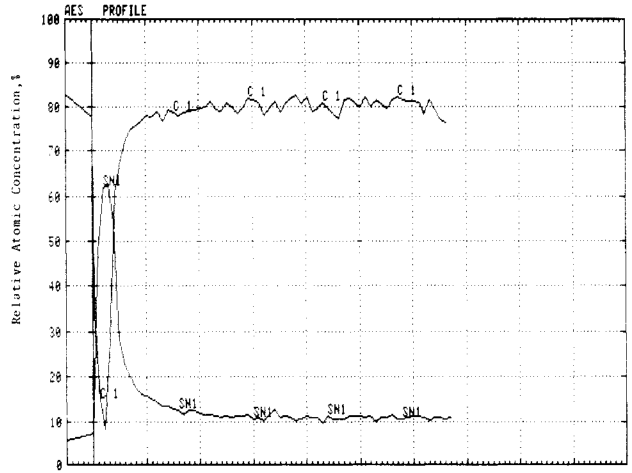

Figure 1. Depth profile of PMDA–ODA/$SnCl_2·2H_2O$ air-cured film monitored by Auger electron spectroscopy. Atomic concentration of C and Sn plotted relative to total surface, C, N, and Sn.

Elemental analyses in Table II show the presence of 1.5–3 times more tin in air-cured films as opposed to N_2 or forming gas cured materials. It is also important to recognize that tin is apparently lost during the curing of all films except one (PMDA–ODA/$SnCl_2·2H_2O$, air cured). More tin is found than calculated for this material, indicating loss of polymer or loss of ligand (Cl or H_2O) by the metal during thermal imidization. X-ray photoelectron spectroscopy (XPS) measurements suggest the latter possibility; vide infra.

The effect on resistivity of increasing the metal complex concentration was evaluated for the PMDA–ODA/$SnCl_2·2H_2O$ doped material. Films were cast and air cured using 1:4, 1.5:4, and 2:4 complex/polymer millimolar ratios. All three of these films were of reasonably good quality. The lowest surface resistivity measured was for the film prepared employing a 1:4 mole ratio. The films prepared with higher metal complex ratios exhibited higher resistivities, as seen in Table II. Apparently a lower resistivity limit of 10^6 is realized for this dopant/polymer pair, and increased tin-complex loading slightly increases rather than decreases resistivity.

Nature of Film Surfaces. Auger electron/argon ion etching spectra (AES) for tin-doped polyimide films are shown in Figures 1–3. All films involve PMDA–ODA polyimide doped either with $SnCl_2·2H_2O$ or with (*n*-

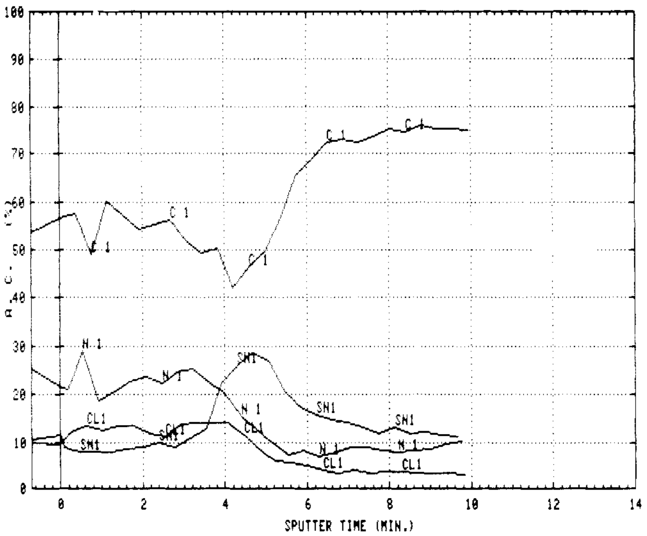

Figure 2. Depth profile of PMDA–ODA/$SnCl_2 \cdot 2H_2O$ nitrogen-cured film monitored by Auger electron spectroscopy.

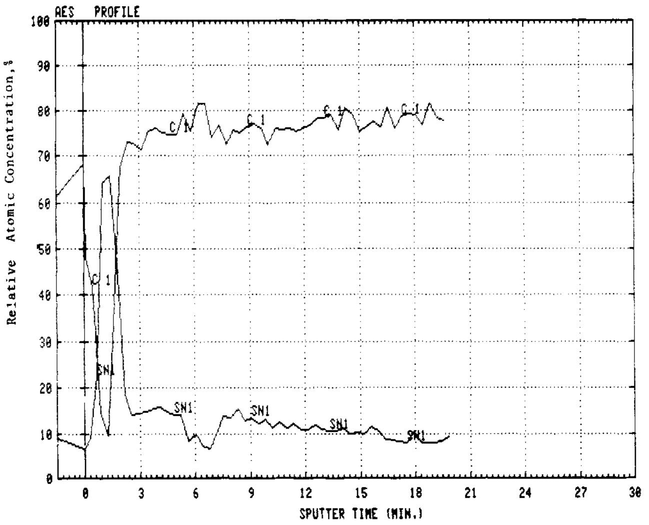

Figure 3. Depth profile of PMDA–ODA/$(n\text{-}Bu)_2SnCl_2$ air-cured film monitored by Auger electron spectroscopy. Atomic concentration of C and Sn plotted relative to total surface C, N, Cl, and Sn.

$Bu)_2SnCl_2$ and cured in either air or nitrogen. The AES profiles that are shown are for the atmosphere side of these films. The AES reflect differences in depth-profile elemental concentrations, which are apparently induced by curing in either air or nitrogen. Elements profiled included tin, chlorine, nitrogen, and carbon. In each figure, atomic concentration is plotted as a function of sputter time, sputter rate being approximately 500 Å/min. Base line atomic concentration varies between 0 and 10%.

Air-cured PMDA–ODA/$SnCl_2 \cdot 2H_2O$ (Figure 1) exhibited a large concentration of surface tin species (about 65 atom %), which sharply decreased upon further depth profiling. Very little chlorine was observed to be present. The same material when cured in nitrogen was found to charge greatly; therefore, a rather thick gold coating had to be applied. Sputtering through the gold coating required slightly over 3 min (Figure 2). A tin concentration of 28 atom % was seen at the surface of this material, which tapers off quickly as sputtering continues into the bulk of the film. Chlorine was again seen to be present in very low quantities. In comparison with the air-cured film, the nitrogen-cured film appears to have much less surface tin species present.

Table III
Binding Energies of Tin-Containing Polyimide Films[a]

material	cure	side	Sn photopetak, BE	
			$3d_{5/2}$	$3d_{3/2}$
		PMDA–ODA		
$SnCl_2 \cdot 2H_2O$	air	atmosphere	485.8	494.2
		glass	486.2	494.6
$SnCl_2 \cdot 2H_2O$	N_2	atmosphere	486.6	495.0
		glass	486.0	494.4
$(n\text{-}Bu)_2SnCl_2$	air	atmosphere	485.8	494.2
		glass	485.6	494.2
$(n\text{-}Bu)_2SnCl_2$	N_2	atmosphere	486.2	494.6
		glass	486.4	494.6
		BTDA–ODA		
$SnCl_2 \cdot 2H_2O$	air	atmosphere	486.3	494.7
		glass	486.8	495.2

[a] Sn $3d_{5/2,3/2}$ binding energies in SnO_2 were measured to be 486.6 and 495.0 eV, respectively. For tin metal, Sn $3d_{5/2}$ binding energy equals 484.5 eV.[11]

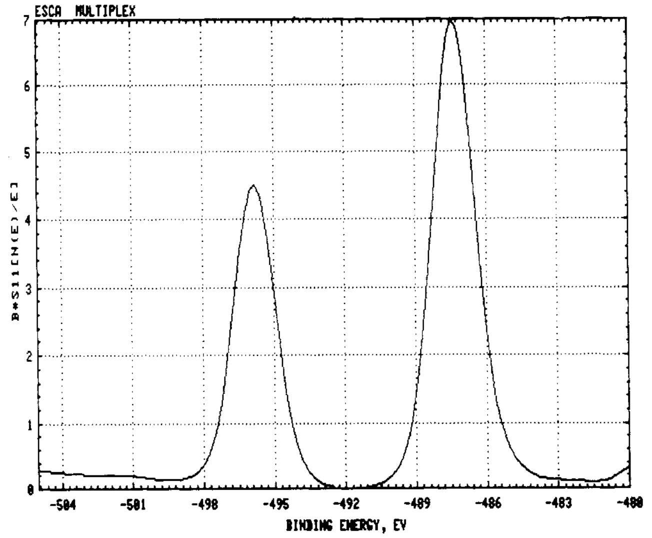

Figure 4. X-ray photoelectron spectrum of Sn 3d photopeak region for the air-cured film derived from PMDA–ODA/$SnCl_2 \cdot 2H_2O$, air-side. See Table III for corrected binding energies.

Although the tin deposit is not as thick, the same trends are exhibited for PMDA–ODA/$(n\text{-}Bu)_2SnCl_2$ air- and nitrogen-cured films as observed for the previous two $SnCl_2 \cdot 2H_2O$ films. A much greater amount of surface tin is present in the air-cured vs. the nitrogen-cured material. Concentration of tin species in the air-cured film was observed to decrease abruptly as sputtering continued into the bulk of the material (Figure 3). Chlorine was undetectable in the air-cured film and was not analyzed in the nitrogen-cured film.

Comparison of these depth profiles lends information regarding the differences between the surfaces of the semiconductive (air cured) films as opposed to the nonconductive (nitrogen cured) films. It is apparent that the air-cured films have a deposit of a tin species concentrated within 1000–1500 Å of the film's surface. The nitrogen-cured films have a surface tin concentration also, but it is much lower in magnitude. These data indicate that the presence of a high tin surface concentration may be responsible for the lower surface resistivities shown by these air-cured films.

Tin binding energies were determined via X-ray photoelectron spectroscopy (XPS) for the previously discussed four materials. Tin ($3d_{5/2}$, $3d_{3/2}$) binding energies for both sides of these materials along with one other tin-modified

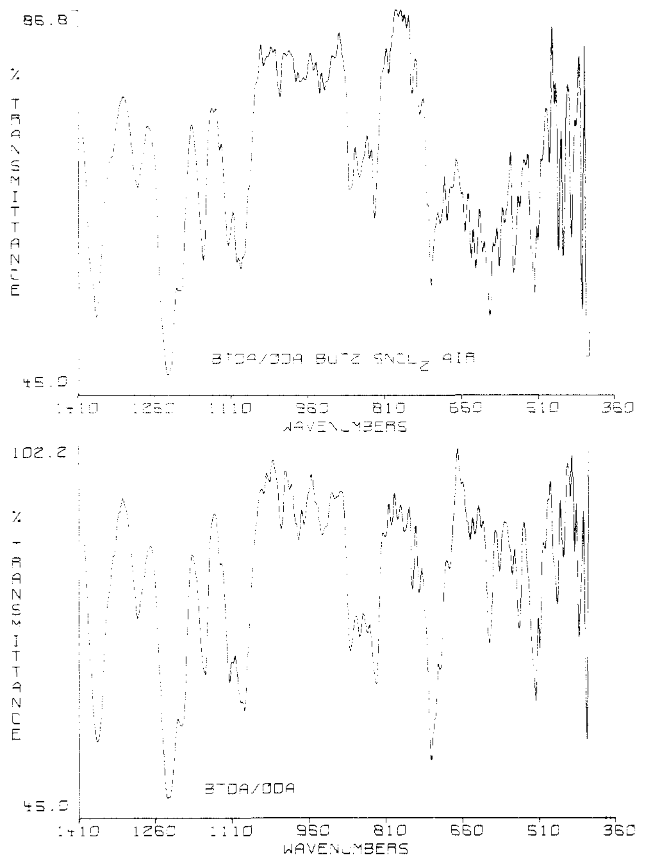

Figure 5. FTIR-ATR spectra of $(n\text{-Bu})_2SnCl_2$-doped and undoped BTDA-ODA air-cured films.

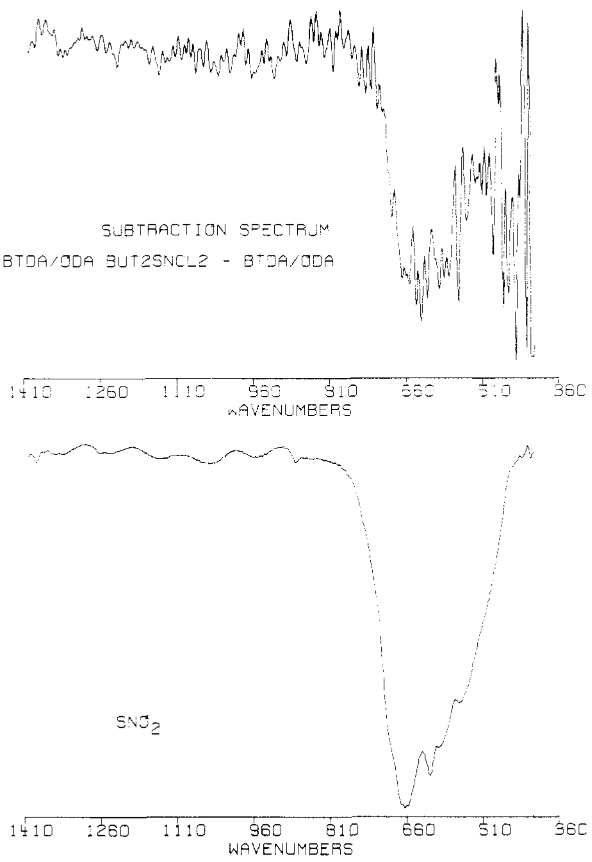

Figure 6. Subtraction FTIR-ATR spectrum of $(n\text{-Bu})_2SnCl_2$-doped and undoped BTDA-ODA air-cured films compared with the spectrum of SnO_2.

polyimide are shown in Table III. Binding energies for all films were found to be essentially the same (within 1.0 eV) regardless of the method of cure or the additive employed (Figure 4). The literature value for the binding energy for tin metal ($3d_{5/2}$) is 484.5 eV.[11] We have measured tin binding energies for tin in SnO_2 and found them to be 486.6 and 495.0 eV. Tin is indicated, therefore, to be in a rather oxidized form on the film surface since all binding energies appear closer in value to that of SnO_2 than to tin metal. A survey of the literature suggests that Sn(II) materials also exhibit binding energies in the same region, but the preferred oxidation state under air-cured conditions is most likely Sn(IV). For nitrogen-cured films, XPS measurements cannot reliably distinguish Sn(II) from Sn(IV). The higher resistivities observed for nitrogen-cured films not only may be due to a lower surface tin concentration but also may be due to a different less conducting tin species.

XPS did furnish some useful, somewhat quantitative information. Air-cured films were found to have much more tin on the atmosphere side as opposed to the glass side, approximately a factor of 100. Nitrogen-cured films also had more tin on the atmosphere side as opposed to the glass side, but only by a factor of 10–30. Air-cured films were found to have more atmosphere-side tin than nitrogen-cured films as previously discovered via depth profiling with AES monitoring. Chlorine was not detectable via XPS regardless of cure environment or film side. One then is forced to conclude on the basis of AES and XPS data that chlorine is not associated with tin on or near the film surface.

Further information regarding the identity of the surface tin deposit found on semiconductive tin-doped polyimide films was obtained via Fourier transform infrared-attenuated total reflectance (FTIR-ATR) analysis. In analyzing the FTIR-ATR spectra of these films, we first noted that there were no dramatic shifts in the vibrational frequency of any polymer IR bands as a result of tin incorportion. Polymer carbonyl frequencies in particular were compared between tin-complex-doped and undoped polyimide. Coordination of tin nuclei to polymer carbonyl moieties has been previously noted to produce a shift in carbonyl stretching frequency of about 50 cm^{-1}.[3] IR evidence indicates no coordination of polymer carbonyl groups with the tin dopant for any films produced in this study, air or N_2 cured.

Although IR band frequencies were found not to change significantly upon tin-complex doping, a marked increase in IR absorption upon tin doping was observed in one spectral region. Figure 5 compares the 1400–400-cm^{-1} region of the semiconductive surface (atmosphere side) of the BTDA-ODA/$(n\text{-Bu})_2SnCl_2$ air-cured film with that of air-cured BTDA-ODA (no additive). A distinct broadening of the bands in the 800–500-cm^{-1} region of the spectrum of the tin-containing film is seen. A subtraction spectrum (polyimide film spectrum subtracted from tin-modified film spectrum) is shown in Figure 6. An absorption is discovered that is unique to the tin-doped film and no doubt accounts for the broadening effect. The FTIR spectrum of a sample of SnO_2, taken on the same instrument, is also shown in Figure 6. It would appear that on the basis of this comparison a concentration of SnO_2 is present near the surface of the $(n\text{-Bu})_2SnCl_2$-modified BTDA-ODA film. Figure 7 provides the same comparison for the PMDA-ODA/$SnCl_2 \cdot H_2O$ air-cured fiilm (semiconductive, atmosphere side) vs. air-cured PMDA-ODA. The presence of SnO_2 again appears to account for band broadening in the 800–500-cm^{-1} region. Figure 8 is a spectrum taken of the PMDA-ODA/$SnCl_2 \cdot 2H_2O$ film,

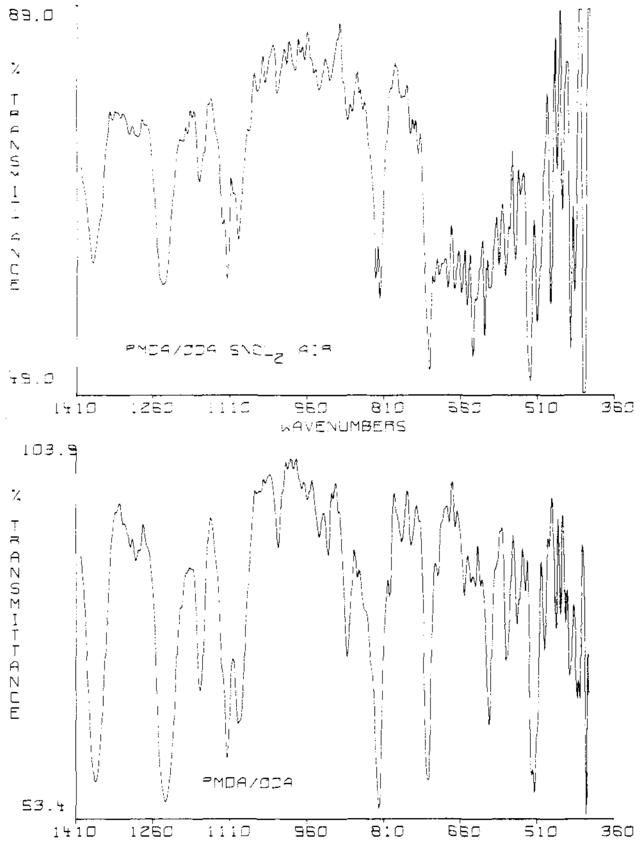

Figure 7. FTIR–ATR spectra of $SnCl_2 \cdot 2H_2O$-doped and undoped PMDA–ODA air-cured films.

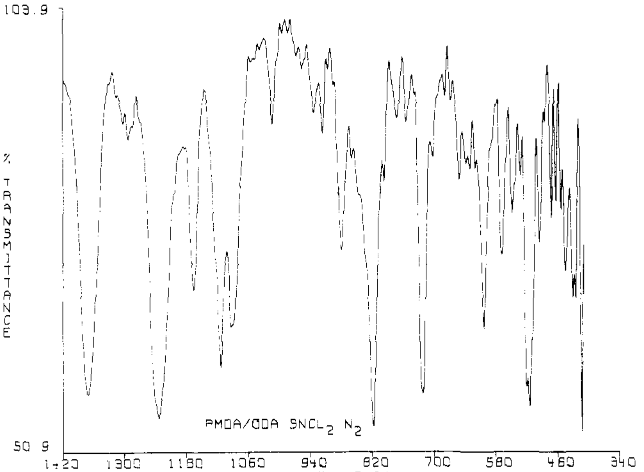

Figure 8. FTIR–ATR spectrum of $SnCl_2 \cdot 2H_2O$-doped PMDA–ODA nitrogen-cured film.

N_2-cured, atmosphere side. Careful inspection reveals no broadening in the 800–500-cm^{-1} region, relative to PMDA–ODA alone. Several rationalizations can be suggested to account for this observation. The surface concentration of Sn as SnO_2 may be so low that it is undetectable via FTIR–ATR and too dispersed to be conductive. Alternatively, the surface Sn may not be "SnO_2-like" and not IR active in the monitored region. In view of the fact that the film was cured in nitrogen, an oxidant source to convert Sn(II) to Sn(IV) is not readily apparent. A form of Sn(II) oxide on the surface of the N_2-cured film seems more likely.

Auger, XPS, FTIR–ATR data indicate migration of tin to the atmosphere side during curing, for both air- and N_2-cured films. Incompatibility of the tin additivies with the polymer system and volatility of the tin additive are no doubt promoting this surface segregation effect. On only one film (BTDA–ODA/$(n\text{-Bu})_2SnCl_2$) is a surface deposit evident by visual inspection; all others have comparatively homogeneous appearances. Surface-semiconductive films are evidenced to have SnO_2 surfaces extending several thousand angstroms into the bulk of the film. The SnO_2 surface is apparently tightly bonded to the polymer since attempts to etch the deposit resulted in destruction of the film. The chemical state of the tin in nonconductive films (cured in N_2), which have a much smaller amount of surface tin, has not been identified.

Well-established tin chemistry can be invoked to rationalize the formation of SnO_2 and loss of chlorine during thermal imidization of these films in air. Reaction of the chlorine-containing tin additivies during curing can be envisioned to occur as follows. For the Sn(II) additive, hydrolysis of the Sn–Cl bond to yield HCl and $Sn(OH)_2$ followed by air oxidation of the Sn(II) to ultimately produce a form of SnO_2 is expected.

$$SnCl_2 + 2H_2O \rightarrow Sn(OH)_2 + 2HCl$$

$$2Sn(OH)_2 + O_2 \xrightarrow{\Delta} 2SnO_2 + 2H_2O$$

For the Sn(IV) additive, hydrolysis is again anticipated initially, thereby freeing HCl. Thermal cleavage of the Sn–C bond to yield n-butane or a higher alkane concurrent with some dehydration can be envisioned to produce SnO_2. The latter proposed Sn(IV) scheme would be likely for both air- and N_2-cured films. The nature of SnO_2 in both cases, however, may be different since air-cured and nitrogen-cured films have dissimilar surface electrical properties.

$$(n\text{-Bu})_2SnCl_2 + 2H_2O \rightarrow (n\text{-Bu})_2Sn(OH)_2 + 2HCl$$

$$(n\text{-Bu})_2Sn(OH)_2 \xrightarrow{\Delta} SnO_2 + 2n\text{-BuH}$$

A different mechanism must be considered for Sn(II)-doped films cured under nitrogen. An initial hydrolysis followed by dehydration (300 °C imidization) to give probably a polymeric form of tin(II) oxide appears reasonable.

$$SnCl_2 + 2H_2O \rightarrow Sn(OH)_2 + 2HCl$$

$$xSn(OH)_2 \xrightarrow{\Delta} (Sn\text{–}O)_x + xH_2O$$

H_2O is generated at >150 °C during imidization of the polymer. More tin was found to be retained by air-cured films than N_2-cured films via elemental analysis. This could be due to oxidation (in the case of Sn(II)) or alteration (in the case of Sn(IV)) of the tin complex in air to the more nonvolatile SnO_2 before evaporation of the tin additive can occur. N_2 curing apparently allows for considerably more volatilization of the complex from the film. It is highly likely for the Sn(IV) additive that polymeric tin species and alkyl side products other than those shown are generated, particularly under N_2 cure. As shown, the Sn(IV) compound could in theory react with H_2O at elevated temperature in the absence of O_2 to give SnO_2. The alkyl–tin bond is unstable at >200 °C[9] and seems to be cleaved in both air- and N_2-cured films.

Resistivity Properties as a Function of Elevated Temperature and Irradiation. Figures 9 and 10 are plots of surface resistivity vs. temperature for two semiconductive tin-containing polyimide films. Both experiments were conducted under dynamic vacuum and both the heating and cooling curves are shown. Resistivities of both films are seen to decrease upon heating. Semiconductive properties are still present after heating in vacuo, indicating ambient atmosphere has little effect upon re-

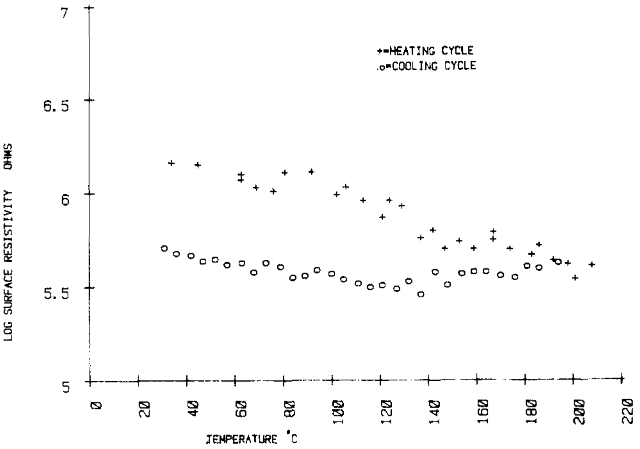

Figure 9. Surface resistivity vs. temperature for air-cured PMDA-ODA/$SnCl_2 \cdot 2H_2O$.

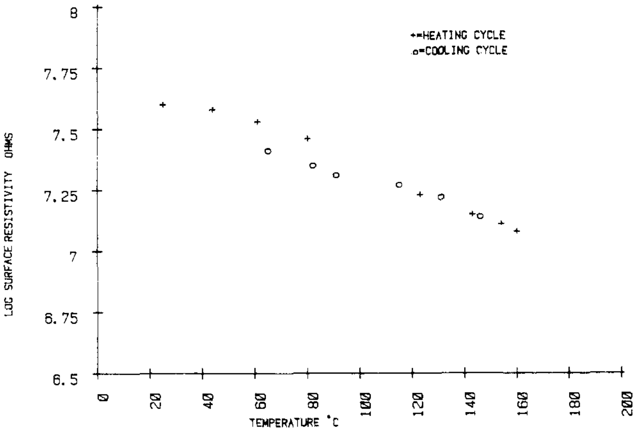

Figure 10. Surface resistivity vs. temperature for air-cured BTDA-ODA/$(n\text{-}Bu)_2SnCl_2$.

sistivity. A hysteresis effect is observed upon cooling in both cases (i.e., lower resistivity values are exhibited by both films after thermal cycling).

SnO_2 has been studied extensively as an electrode material.[10] SnO_2 is an n-type semiconductor, with a resistivity ranging from 10^8 Ω into the conductor region, depending upon the amount and kind of impurities (dopants) present.[10] The hysteresis seen in Figures 9 and 10 could be induced by diffusion of impurities from the polymer into the SnO_2 surface layer during heating. Support for this observation comes from the fact that annealing has been seen to affect the electrical properties of SnO_2 in other studies.[10]

The nature of these semiconductive films prompted a preliminary photoconductivity experiment. Since SnO_2 is an n-type semiconductor, irradiation with a UV source should cause an observable decrease in resistivity. Surface resistivity as a function of irradiation time is shown in Table IV for (i) the semiconductive side of one of our lower resistivity films under full irradiation from an argon lamp and (ii) the same sample under irradiation through a filter transmitting UV but not IR radiation. Data show that the film is photoactive since resistivity decreases by about half upon irradiation. Filtering out the IR radiation showed that the decrease in resistivity was of an electronic rather than a thermal nature. Irradiation of the reverse, nonconductive side of the same film failed to cause any lowering of resistivity. This also ruled out any thermal contributions.

Table IV
Resistivity of PMDA-ODA/$SnCl_2 \cdot 2H_2O$ as a Function of Irradiation

irrad time, min	σ, $\times 10^3$ Ω/square
0	251 (247)[a]
2.5	125 (174)
5.5	122 (162)

[a] Numbers in parentheses are for UV irradiation only (IR filter).

Summary

Air-cured films fabricated from PMDA-ODA or BTDA-ODA polyimide and $SnCl_2 \cdot 2H_2O$ or $(n\text{-}Bu)_2SnCl_2$ have been found to have atmosphere-side surface resistivities from 10^5 to 10^8 Ω/square. Most films are homogeneous and each exhibits good thermal stability. Characterization of air-cured film surfaces reveals a relatively thick layer of SnO_2, which is responsible for decreased resistivity values relative to the undoped polymer. Production of the SnO_2 surface layer is believed to be due to migration and chemical reaction of the tin additive during curing. N_2 curing produces nonconductive film surfaces with much lower concentrations of tin species. Air curing is presumed to allow or to accelerate formation of SnO_2, while N_2 curing allows more substantial volatilization of the added tin complex. Air-cured films exhibit lower surface resistivities upon heating (atmosphere side). Irreversible migration of impurities from the polymer film to the SnO_2 layer lowers resistivity upon annealing in vacuo. The atmosphere side of air-cured films has been found to be photoactive, decreasing in resistivity twofold upon irradiation with a strong UV source.

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Registry No. PMDA-ODA (copolymer), 25038-81-7; BTDA-ODA (copolymer), 24980-39-0; PMDA-ODA (SRU), 25036-53-7; BTDA-ODA (SRU), 24991-11-5; $SnCl_2$, 7772-99-8; $(n\text{-}Bu)_2SnCl_2$, 683-18-1.

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