

Copper/Polyimide Multilayered Composites

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Incorporation of bis(trifluoroacetylacetonato)copper(II) into poly(amide acid) solutions produces bi- or trilayered composite films upon curing. Internal and near-surface structure may be controlled by choice of curing atmosphere, concentration of dopant, and the specific polyimide precursor monomers. Three polyimide systems were used to determine the effect of monomer molecular structure and polymer glass transition temperature on the microcomposite surface structure. The poly(amide acids) used were produced from two dianhydrides, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA), and two diamines, 4,4'-oxydianiline (ODA) and 1,3-bis(3-aminophenoxy)benzene (APB). The use of BTDA-ODA and BTDA-APB has yielded in general uniform Cu or CuO dispersions of very small particle size resulting from phase separation of the copper additive. In both cases a copper-containing deposit resides at or near the surface that was exposed to the atmosphere during curing. In contrast, the use of BDSDA-ODA produced a highly diffuse copper phase resulting from polyimide/dopant chemical interaction which may account for the increased solubility of the dopant in this polyimide matrix.

Introduction

Polyimides are used in many electrical applications due to their high resistivity ($10^{18} \Omega \text{ cm}$ at 25°C) and exceptional thermal and chemical stability. Yet in certain circumstances, modification of the existing electrical properties may be useful, for instance, in static charge dissipation, in the production of thin-film resistive heaters, and for electromagnetic interference/radio frequency interference (EMI-RFI) shielding. In the past, lowering the electrical resistance of these materials was generally possible only through the heterogeneous incorporation of graphite, metal, or conducting compound (e.g., spheroids, fibers, etc.) within the polymer matrix.¹ In each case significant mass loading was needed to approach the percolation threshold and hence improve electrical conductivity.

In hopes of imparting conductivity to polyimide materials at a lower and more uniform mass loading, polyimide-metal composites in which microscopic metal or metal oxide domains have been incorporated into the polymer matrix by the in situ thermal decomposition of metal-containing additives have been pursued.² Anisotropic structures were produced by carefully choosing the polyimide precursor and curing parameters. In many cases, the anisotropy resulted in reduced surface resistivity, while volume resistivity was unaffected.

Angelo³ first described the doping of polyimide precursors with metal ions in this fashion. One film was described consisting of a homogeneous mixture of (4,4'-diaminodiphenyl)methane, pyromellitic dianhydride, and bis(acetylacetonato)copper(II). A relatively large decrease in the volume resistivity of the thermally cured film was reported. Subsequently, several authors⁴⁻⁶ have described the addition of other inorganic salts and complexes to polyimide precursors. Two patterns of reactivity have been observed: reduction of the additive to the metallic state

or conversion to the metal oxide.

The work of Angelo was later extended by Ezzell et al.,⁷ who studied films resulting from the addition of various Cu(I) and Cu(II) compounds to various polyimide precursors. High-quality doped films were produced that exhibited lower thermal stabilities, higher softening temperatures, and lower electrical resistivities than the polymer alone. Surface segregation and chemical conversion of the dopant occurred during the curing process. Exact structural information regarding the metallic and polymeric components as well as the nature of the polyimide-metal interaction were not reported.

More recently in a preliminary report⁸ we have described the multilayered character of copper-doped polyimides and, in particular, the effect that the curing atmosphere and concentration of dopant has on the final structure of the fully cured polyimide film. Discrete and well-defined copper or copper oxide layers were produced. Partial control of the copper-containing-layer position in the doped film was afforded by variation of the processing conditions. It is the object of this study to describe the structural and thermal properties of copper-modified polyimide films resulting from the in situ thermal decomposition of bis(trifluoroacetylacetonato)copper(II), Cu(TFA)₂. Three polyimides providing a range of glass transition temperatures and chemical structures have been chosen as the host matrices.

Experimental Section

Preparation. The monomers selected for this study were 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA), 4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA), 4,4'-oxydianiline (ODA), and 1,3'-diaminodiphenyl ether (APB). The chemical structure of each monomer employed is shown in Figure 1. Specific combinations of these monomers produced the three polyimides (BTDA-ODA, BTDA-APB, and BDSDA-ODA) that were used in this study. All monomers were obtained from commercial sources. BTDA and ODA were purified as previously described,⁹ while BDSDA was used as received. APB was recrystallized from xylenes (85°C) and vacuum dried before use. Cu(TFA)₂ was synthesized as per literature reference¹⁰ and

(1) Kusy, R. P. *Metal-Filled Polymers: Properties and Applications*; Bhattacharya, S. K., Ed.; Marcel Dekker: New York, 1986; p 1.

(2) St. Clair, A. K.; Taylor, L. T. *J. Macromol. Sci. Chem.* **1981**, *A16*, 95.

(3) Angelo, R. J. E. I. Du Pont de Nemours and Co., U.S. Patent 3,073,785, 1959.

(4) Carver, V. C.; Taylor, L. T.; Furtch, T. A.; St. Clair, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 876.

(5) Khor, E.; Taylor, L. T. *Macromolecules* **1982**, *15*, 379.

(6) Auerbach, A. J. *Electrochem. Soc.* **1984**, *131*, 937.

(7) Ezzell, S. A.; Furtch, T. A.; Khor, E.; Taylor, L. T. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 865.

(8) Porta, G. M.; Taylor, L. T. *J. Mater. Res.* **1988**, *3*, 211.

(9) Boggess, R. K.; Taylor, L. T. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 685.

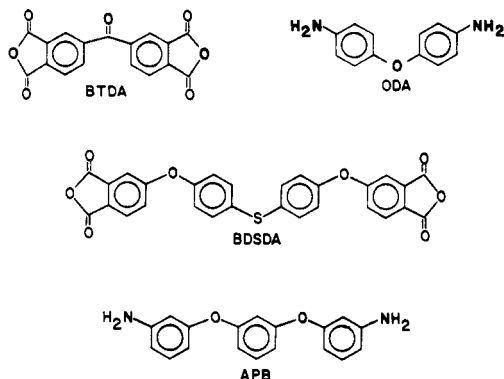


Figure 1. Chemical structure of the monomers used to synthesize condensation polyimides.

purified through sublimation (105 °C) at less than 1 Torr. Reagent grade *N,N*-dimethylacetamide (DMAC) distilled in glass was stored over molecular sieves under a nitrogen atmosphere and sparged with dry nitrogen prior to use.

The precursor poly(amide acid) was formed by the reaction of the appropriate dianhydride and diamine (20% solids) in DMAC. A nitrogen-purged glass septum bottle was charged with the diamine (4.00 mmol) followed by the addition of the respective quantity of DMAC. After complete dissolution, the dianhydride (4.00 mmol) was added, and the consequent pale yellow solution was mechanically stirred for 1 h. Following thorough mixing, $\text{Cu}(\text{TFA})_2$ (1.00 or 2.00 mmol) was added to the resultant poly(amide acid), and the solution stirred for an additional 2 h. Films employing 1.00 and 2.00 mmol of $\text{Cu}(\text{TFA})_2$ will be known as 1 \times - and 2 \times -doped films, respectively.

Thin films were produced by casting the "copper-poly(amide acid)" solution via a doctor blade (18-mil gap) onto a dust-free soda lime glass plate following centrifugation for 5 min at ca. 1500 rpm. The films were precured at 80 °C for 20 min and subsequently thermally imidized under a controlled atmosphere at 100, 200, and 300 °C each for 1 h, respectively. The samples studied in this report were cured in dry breathing air, water-saturated breathing air, or dry nitrogen. After cooling to room temperature, the films were removed from the glass plate by peeling with a razor blade.

Characterization. X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 530 ESCA system using a magnesium anode ($K\alpha = 1253.6$ eV) at 250 w. Samples were attached onto aluminum mounts with doubled-sided transparent tape. The binding energies were referenced to the aromatic C(1s) photopeak at 284.6 eV. Auger electron depth profiles (approximately 30 Å/min via argon ion etching) were recorded with a Perkin-Elmer Phi Model 610 scanning Auger microprobe system. Following placement of the samples onto aluminum mounts, again with doubled-sided tape, the edges of each sample were coated with a colloidal graphite solution enabling optimum electrical contact with the mount to avoid charge buildup.

Scanning and transmission electron micrographs (SEM and TEM) were taken with either a Philips Model 420 scanning transmission electron microscope or a JEOL 100 CX-II transmission electron microscope. Samples prepared for TEM analysis were embedded in Polyscience ultralow viscosity resin and cured for 8 h at 70 °C. Samples were then sectioned to between 500 and 800 Å with a Reichert-Jung ultramicrotome using a Microstar diamond knife. The thin sections were placed on 200-mesh copper or nylon grids prior to analysis. Energy-dispersive X-ray spectra were obtained from the Philips STEM by using a Tracor-Northern 5500 EDAX attachment.

Thermogravimetric analysis was performed with a Perkin-Elmer Model TGS-2 thermogravimetric system at a 10.0 °C/min heating rate with a dynamic air or nitrogen purge (50 mL/min) to determine the thermooxidative and thermal stability, respectively. Elemental analyses were obtained by Galbraith Analytical Laboratories, Knoxville, TN.

Table I. General Properties of $\text{Cu}(\text{TFA})_2$ -Doped Films

polyimide	curing atmosphere	additive level	color ^a	flexibility	PDT, ^b °C
BTDA-ODA	dry air	1 \times	brown	brittle	428 (498, N ₂)
	wet air	1 \times	brown	flexible	432
	nitrogen	1 \times	brown	flexible	438
	dry air	2 \times	gray	flexible	415
	wet air	2 \times	gray	flexible	444
BTDA-APB	nitrogen	2 \times	gray	flexible	420
	dry air	1 \times	gray	flexible	465
	wet air	1 \times	gray	flexible	475 (533 N ₂)
	dry air	2 \times	gray	flexible	494
	wet air	2 \times	gray	flexible	499
BDSDA-ODA	dry air	1 \times	brown	brittle	442
	wet air	1 \times	brown	brittle	467
	dry air	2 \times	brown	brittle	452 (552 N ₂)
	wet air	2 \times	brown	brittle	447
	wet air	2 \times	brown	brittle	447

^a Undoped films are flexible and yellow. ^b PDT: BTDA-ODA = 553; BTDA-APB = 607 (601, N₂); BDSDA-ODA = 580 °C.

Results and Discussion

General Characteristics. Fully imidized nondoped BTDA-ODA, BDSDA-ODA, and BTDA-APB each produced high-quality transparent yellow free-standing films that are very flexible and thermooxidatively stable (>550 °C). BTDA-ODA provides a high- T_g polyimide (285 °C), while BTDA-APB and BDSDA-ODA have T_g 's of approximately 210 and 215 °C, respectively. The addition of $\text{Cu}(\text{TFA})_2$ to each of the prepolyimides yielded reproducible and, in most cases, flexible films (Table I). Due to the casting conditions there were two distinct surfaces of each film. The atmosphere side of each film, except for the doped BDSDA-ODA films, appeared brown or gray with distinct metallic character, while BDSDA-ODA films appeared shiny yet nonmetallic. The glass side of every film was dull brown and in all cases not metallic.

Doping with $\text{Cu}(\text{TFA})_2$ has a pronounced effect on the thermal and thermooxidative stability of each film (Table I). Thermooxidative stabilities are reduced by at least 100 °C as compared to the nondoped analogue. Thermal stability in an inert atmosphere is less reduced (<70 °C). The large difference between the polymer decomposition temperatures (PDT) for the doped films versus the PDT for nondoped polyimides suggests the presence of a dopant-catalyzed decomposition mechanism. Since the presence of oxygen lowers the PDT drastically, an oxidative decomposition pathway, wherein the metal component activates the oxidizing agent, is most likely responsible for reduced stability.

Modified (1 \times) BTDA-ODA Polyimide Film. The surface and near-surface composition of the copper-modified polyimide films was ascertained in part through the use of X-ray photoelectron spectroscopy (XPS).^{11,12} In general, Cu(2p) photopeaks are well-defined with large separation.¹³ In $\text{Cu}(\text{TFA})_2$, copper is in the +2 oxidation state, thereby exhibiting satellite peaks appearing on the higher binding energy side of the 2p_{1/2} and 2p_{3/2} main photopeaks. The absence of satellite structure would indicate a Cu(I) or Cu(0) species.

XPS of the atmosphere side of 1 \times -doped BTDA-ODA films cured in dry air or nitrogen obtained with a takeoff angle of 90° for maximum sampling depth shows insubstantial copper (<0.4 at. %) in any form at or near the

(10) Kidd, M. R.; Sager, R. S.; Watson, W. H. *Inorg. Chem.* 1967, 6, 946.

(11) Dwight, D. *CHEMTECH* 1982, July, 167.

(12) Pantano, C. *Ceram. Bull.* 1981, 60, 1154.

(13) Frost, D. C.; Ishtani, A.; McDowell, C. A. *Mol. Phys.* 1972, 24, 861.

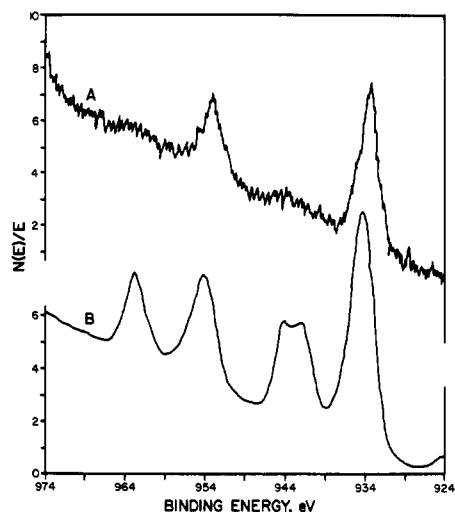


Figure 2. Copper $2p_{1/2,3/2}$ photopeak region of wet-air-cured (A) 1X-doped and (B) 2X-doped BTDA-ODA films.

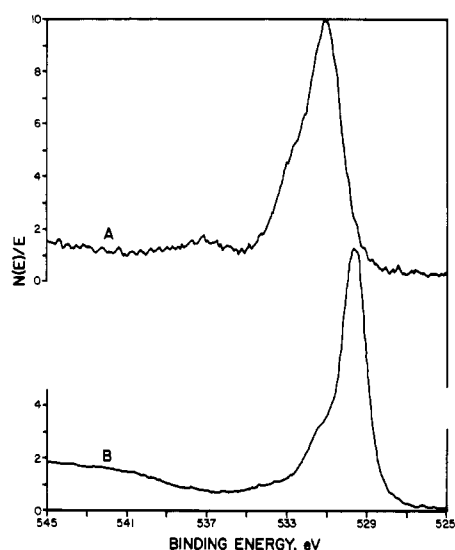


Figure 3. Oxygen $1s$ photopeak region of wet-air-cured (A) 1X-doped and (B) 2X-doped BTDA-ODA films.

surface. Alternatively, the wet-air-cured film reveals the existence of $Cu(2p)$ photopeaks, albeit of low intensity (1.1 at. %), which are devoid of satellite structure suggesting reduction of $Cu(TFA)_2$ to a $Cu(I)$ or $Cu(0)$ species (Figure 2A). The absence of a $F(1s)$ signal provides further evidence that the copper present is not $Cu(TFA)_2$. Reduction of $Cu(TFA)_2$ to Cu_2O would be easily observable through the presence of an oxide oxygen photopeak (<530 eV). Yet, only one oxygen photopeak is observed (~ 532 eV) in the XPS $O(1s)$ spectrum characteristic of both carbonyl and ether oxygen in the polymer backbone as shown in Figure 3A. The nonexistence of an oxide oxygen or appreciable fluorine suggests that the copper species is, in fact, metallic copper. Application of grazing angle (15° takeoff angle) XPS to the film cured in moist air finds copper absent from the surface. Taking into account the decrease in the observation depth of grazing angle XPS, the presence of an organic overlayer residing above the copper deposit is implied. Similar overlayers have been observed for cobalt¹⁴ and gold¹⁵-containing polyimide films.

(14) Rancourt, J. D.; Boggess, R. K.; Horning, L. S.; Taylor, L. T. *J. Electrochem. Soc.* 1987, 134, 85.

(15) Madeleine, D. G.; Spillane, S. A.; Taylor, L. T. *J. Vac. Soc. Technol.* 1987, A5, 347.

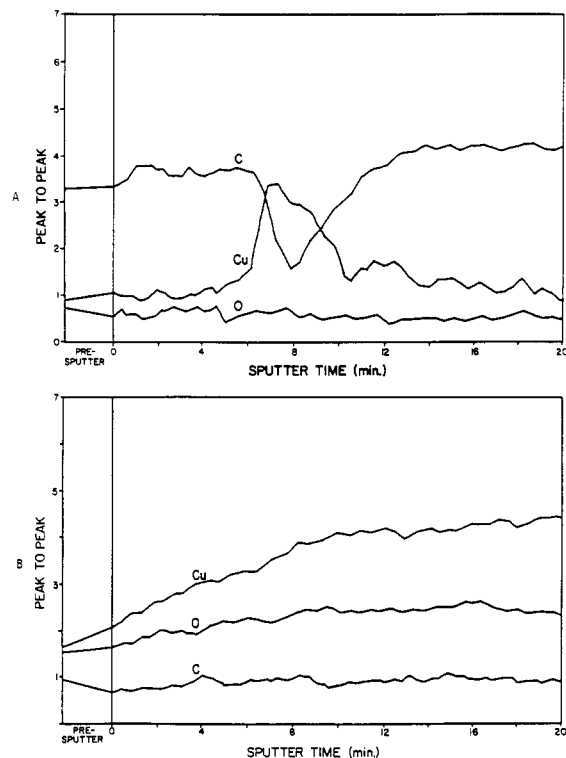


Figure 4. Auger electron spectroscopic depth profiles of wet-air-cured (A) 1X-doped BTDA-ODA and (B) 2X-doped BTDA-ODA films.

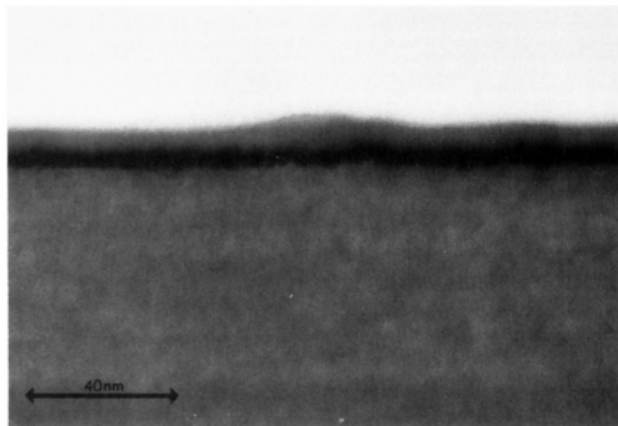
To directly observe the underlying copper deposit by XPS, argon ion etching was employed on the wet-air-cured film in situ prior to analysis. Following a 10-min etch at approximately $5 \text{ \AA}/\text{min}$, the $Cu(2p)$ photopeaks became very intense, indicative of a much higher copper concentration (~ 44 at. %). As in the unetched film, the absence of satellites, fluorine, and oxide oxygen provided evidence that $Cu(TFA)_2$ is reduced to $Cu(0)$. The organic overlayer may be judged to be at least $30\text{--}50 \text{ \AA}$ thick as evidenced by the fact that a Cu signal is observed at a 90° takeoff angle for the unetched film. Despite the fact that the copper concentration is relatively high in the subsurface, significant amounts of carbon, nitrogen, and oxygen are still observed via XPS, which suggests that the copper present in this portion is intermixed with the polyimide matrix.

Depth profiles via Auger electron spectroscopy (AES) in conjunction with argon ion etching of the films cured in dry air or nitrogen do not present any indication of significant copper accumulation within the first 400 \AA of the surface. On the other hand, the Auger depth profile of the film cured in wet air displays the onset of a significant copper layer beginning approximately 5 min into the profile (Figure 4A). A three-layered structure is therefore suggested which has a copper layer positioned between a thin polymeric overlayer and the bulk polyimide. It is known, however, that ion bombardment may cause reduction of metal compounds, including copper in some instances.¹⁶ Therefore, an Auger depth profile was taken of a CuO film that had been vacuum deposited onto a polyimide substrate. The profile of this sample exhibited copper and oxygen patterns characteristic of copper oxide (1:1 at. %), thus furnishing evidence that sputtering and electron- and/or ion-induced copper reduction is slow or negligible at the low sputtering rates used and that the

(16) Kim, K. S.; Baitinger, W. E.; Amy, J. W.; Winegrad, N. *J. Electrochem. Soc.* 1974, 5, 351.

Table II. Morphological Features of Cu(TFA)₂-Doped Films As Deduced from TEM Data

polyimide	curing atmosphere	additive level	overlayer	Cu layer thickness, Å	depletion zone thickness, μm
BTDA-ODA	dry air	1×	yes (60 Å)	45	5.4
	wet air	1×	yes (400 Å)	50	7.1
	nitrogen	1×	yes (350 Å)	60	5.1
	dry air	2×	no	350	2.2
	wet air	2×	no	400	2.4
	nitrogen	2×	no	420	2.4
BTDA-APB	dry air	1×	no	620	15.1
	wet air	1×	no	530	14.5
	dry air	2×	no	700	10.7
	wet air	2×	no	820	12.2
BDSA-ODA	dry air	1×	no		18.7
	wet air	1×	no	200	17.6
	dry air	2×	no		17.6
	wet air	2×	no	300	12.3

**Figure 5.** Transmission electron cross section of the surface region of a wet-air-cured 1×-doped BTDA-ODA film.

elemental copper detected within the film is not an artifact of the process. In many instances, ion sputtering has been known to change or "damage" polymer surfaces.^{17,18} In our studies the carbon signal is used as an elemental tag for the organic component in the Auger depth profile. Profile data should be considered only in a qualitative sense, irrespective of the chemical state of the carbon species and whether damage has or has not occurred.

To obtain a total view of the internal structure, ultramicrotomed cross sections of the films were examined by transmission electron microscopy (TEM). Visual proof of a three-layered structure is observed for the 1×-doped BTDA-ODA film cured in wet air (Figure 5). Surprisingly, similar near-surface structure is observed for the dry-air-cured and nitrogen-cured BTDA-ODA films. The depth at which metallic enrichment occurs for these samples is, however, below that both attempted by AES with concurrent ion milling and achievable by XPS. Thickness of the polymer overlayer and the metallic layer are approximately 60 and 50 Å, respectively, for the wet-air-cured film. The samples cured in dry air exhibited respective layer thicknesses of approximately 400 and 45 Å, while those cured in dry nitrogen had thicknesses of approximately 350 and 60 Å.

The bulk polymer is, regardless of curing atmosphere, void of any other particulate matter to a depth of at least 50 000 Å from the atmosphere side of the films. We term this region the "depletion zone" (Table II). Below this zone spherical agglomerations roughly 3000–5000 Å in diameter are present. Energy-dispersive X-ray analysis of the particles reveals that they are copper in nature.

Whether they consist of elemental copper or Cu(TFA)₂ is unknown since EDAX could detect only elements with atomic number 11 or greater. Similar agglomerates have been observed in CoCl₂ doped polyimides wherein EDAX identified the material as containing Co and Cl.¹⁹ No material in any form has been detected by TEM on the glass side of the 1× BTDA-ODA films or the films yet to be discussed.

Modified (2×) BTDA-ODA and (1×, 2×) BTDA-APB Polyimide Films. XPS applied to the 2×-doped BTDA-ODA film and all Cu(TFA)₂-doped BTDA-APB films reveals strong Cu(2p) photopeaks with satellite structure (Figure 2B). The presence of a Cu(II) species is apparent; yet, the lack of a F(1s) photopeak suggests that copper does not exist as Cu(TFA)₂. Significant amounts of copper ranging between approximately 15 and 40 at. % are observed on each film surface, although substantial amounts of polyimide carbon are still present, which again suggests intermixing. An additional O(1s) photopeak is detected (~529 eV) that is not present in undoped polyimide spectra. The higher binding energy peak can be confidently assigned to the polymer oxygens (carbonyl, ether),²⁰ while the lower energy photopeak is due to the presence of oxide oxygen as shown in Figure 3B. The +2 oxidation state of the copper species along with the 1:1 ratio of the surface copper and oxide oxygen concentrations indicates the presence of CuO on these films. Grazing angle XPS shows no change in the relative atomic concentrations of each element with analysis depth.

Depth profiling with Auger electron spectroscopy assisted by an argon ion etch provided further evidence of a bilayered structure for the 2×-doped BTDA-ODA dry air and nitrogen cured films along with the 1×-doped BTDA-APB wet-air-cured film. On the other hand, the 2×-doped BTDA-ODA wet-air-cured film and all the 2×-doped BTDA-APB films did not show this behavior because the copper-containing deposit could not be penetrated during the 20-min etching period (Figure 4B). In each profile, the oxygen signal intensity steadily followed that of copper throughout the spectrum, indicating that copper is only present only as CuO.

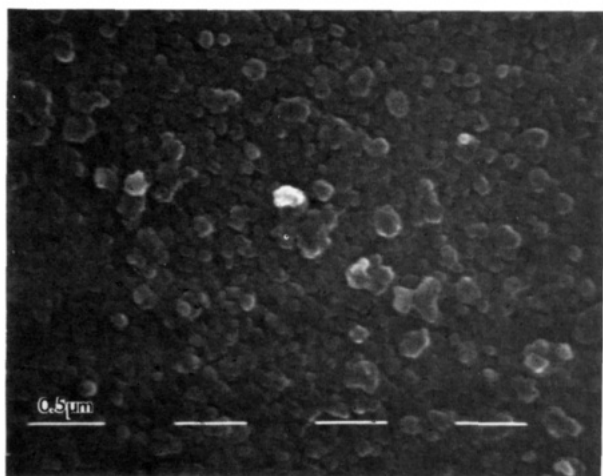
Scanning secondary electron micrographs of the 2×-doped BTDA-ODA film exhibited a rough, granular surface uniform particle size on the order of 400 Å (Figure 6a). This surface morphology suggests that copper is present as the unconventional brown oxide and may pro-

(19) Rancourt, J. D.; Taylor, L. T. *Cross-Linked Polymers*; ACS Symposium Series; Dicket, R. A., Labana, S. S., Bauer, R. S., Eds.; American Chemical Society: Washington, DC, 1988; p 395.

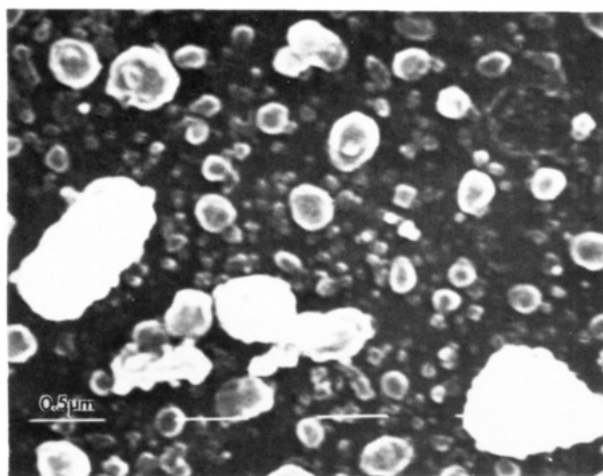
(20) Buchwalter, P. L.; Baise, A. I. *Polyimides: Synthesis, Characterization and Applications*; Mittal, K. L., Ed.; Plenum Press: New York, 1984; p 537.

(17) Briggs, D.; Hearn, J. J. *Vacuum* 1986, 11–12, 1005.

(18) Pantano, C. G. *Ceram. Bull.* 1981, 11, 1154.



A



B

Figure 6. Scanning electron micrographs of a wet-air-cured 2 \times -doped BTDA-ODA film (A) before and (B) after treatment with forming gas (5% H₂/95% N₂).

vide superior adhesive properties.²¹ Micrographs of the 1 \times - and 2 \times -doped BTDA-APB films showed a comparable morphology with a small variation in particle size. Surface structure is unaffected by choice of curing atmosphere. The CuO layer of these films, however, may be partially reduced to elemental copper by reheating the films to 300 °C in a forming gas (5% H₂/95% N₂) atmosphere. Approximately 75% conversion can be realized according to XPS through reduction of the oxide oxygen component from 25 to 7 at. %. Surface reduction results in a change in morphology as observed by SEM (Figure 6B; i.e., upon reduction, the granular particles agglomerate and the surface becomes smoother).

Transmission electron microscopic analysis of ultramicrotomed cross sections visually portrays the bilayered structure of these films (Figure 7). Thicknesses of the CuO layer for the 2 \times -doped BTDA-ODA films range between 350 and 420 Å. The thickest CuO layers were observed in doped BTDA-APB films (Table II). Several trends in these data are noted: (1) within a particular polyimide matrix, the thickness of the copper-containing surface deposit increases with additional concentration of dopant, (2) the increase in copper thickness is accompanied by an increase in the breadth of the depletion zone, and (3) for equivalent doping concentrations and curing con-



Figure 7. Transmission electron cross section of the surface region of a wet-air-cured 2 \times -doped BTDA-ODA film.

ditions BTDA-APB films always contain larger copper deposits and depletion zones than BTDA-ODA films.

Within an identical volume, doubling the dopant concentration would effectively double the potential reservoir of dopant available for the formation of a layer or deposit. The flux of the dopant through a given volume at a constant rate would control the effective size of a zone depleted of the additive. The 2 \times -doped films would necessarily take longer to exhaust the subsurface region over an equivalent curing period than a 1 \times -doped film as long as the total amount removed per unit time is significantly less than the overall local dopant concentration. This being valid, the depletion zone of a 1 \times film should therefore be larger than that of a 2 \times -doped film. The flux of dopant should also be influenced by the glass transition temperature of the polyimide, especially if the additive is dispersed on a molecular scale. TEMs of partially cured films (to 200 °C) do not exhibit additive aggregation in any form. BTDA-APB has a T_g 75 °C below that of BTDA-ODA. Since the T_g is attained earlier for BTDA-APB and a temperature 85 °C greater than the T_g is ultimately reached during cure of BTDA-APB as compared to 15 °C for BTDA-ODA, more material would be expected to become available over the curing period to enrich the surface layer in the BTDA-APB matrix. Consequently, the increase of material reaching the surface and the prolongation of dopant mobility for BTDA-APB should expand the width of the depletion zone.

Modified BDSDA-ODA Polyimide Films. Analysis of the surface and near-surface regions of 1 \times -doped BDSDA-ODA films by X-ray photoelectron spectroscopy revealed weak Cu(2p) photopeak structure (i.e., 1.0 at. % and 2.3 at. % copper for the dry-air- and wet-air-cured films, respectively). If the dopant was homogeneously dispersed, a theoretical volume fraction of 0.3 at. % copper

(21) Slominski, L. J.; Landau, A. *Plat. Surf. Finish.* 1982, June, 96.

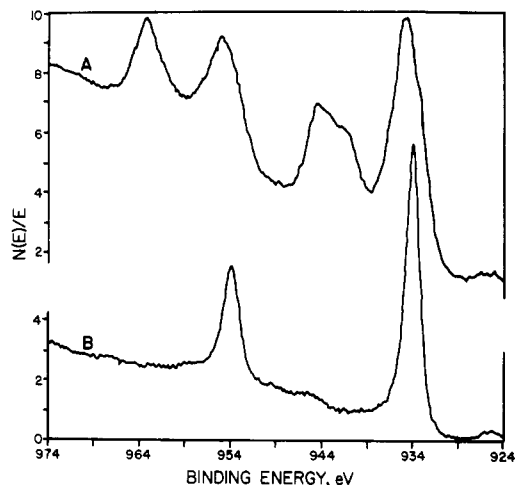


Figure 8. Copper $2p_{1/2,3/2}$ photopeak region of a wet-air-cured 2 \times -doped BDSDA-ODA film (A) before and (B) after argon ion etching.

would be expected. In contrast, the 2 \times dry-air-cured BDSDA-ODA film exhibits negligible surface copper enrichment, while the wet-air-cured analogue contains 6 at. % surface copper. For the 2 \times wet-air-cured film (1) satellite structure is evident, (2) fluorine is undetected, and (3) an oxide oxygen signal is observed. These observations are not apparent for both 1 \times -doped BDSDA-ODA films. Otherwise, each film displays carbon, oxygen, nitrogen, and sulfur photopeaks characteristic of BDSDA-ODA.

A 15-min argon ion etch (~ 5 Å/min) followed by XPS analysis was used to probe the subsurface region of the doped BDSDA-ODA films. The dry-air-cured 1 \times - and 2 \times -doped films showed no change in atomic concentration relative to the presputtered films discussed above, signifying the presence of a homogeneous near-surface region sparsely populated by copper. The 1 \times - and 2 \times -doped wet-air-cured films, on the other hand, exhibited a distinct change in chemical composition following etching. Loss of satellite structure was observed for both samples (Figure 8). The amount of copper present also increased after sputtering to approximately 8 and 21 at. % for the 1 \times - and 2 \times -doped wet-air-cured films, respectively. Fluorine concentration was negligible (<0.3 at. %), as was oxide oxygen. However, a new S(2p) photopeak (~ 163.4 eV) arose at lower binding energy downfield from the polyimide S(2p) photopeak (~ 168.6 eV, Figure 9). Approximately 1.5 at. % sulfur is present on the etched surface of these films. Several inorganic copper compounds have S(2p) binding energies similar to the new sulfur photopeak, CuS at 161.2 eV and Cu₂S at 162.4 eV,²² which suggests an inorganic disposition. It appears that some form of dopant/matrix interaction is present when BDSDA-ODA is used since the sulfur may be obtained only from the polymer backbone. The higher binding energy of the new sulfur species compared to the copper sulfides cited suggests that instead of the sulfur being extracted from the backbone forming some distinct molecular compound, the copper is chelated to the polyimide sulfur present. This is in apparent contrast to the copper-doped BTDA-ODA and BTDA-APB films where dopant/matrix chemical interaction is negligible. The presence of a new sulfur species as well as the loss of Cu(2p) satellite structure suggests that the near-surface region of both films is composed of a mixture of predominantly elemental copper

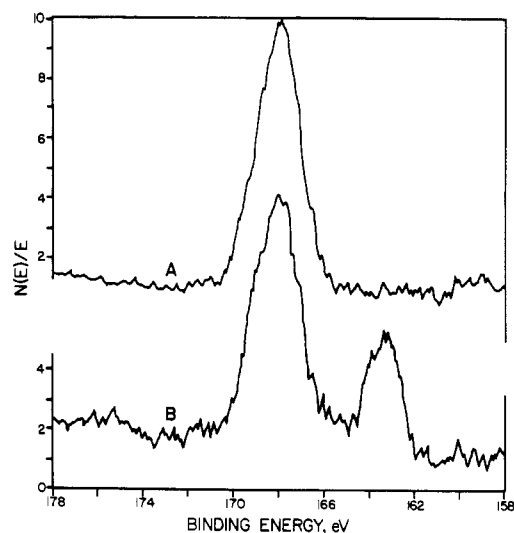


Figure 9. Sulfur 2p photopeak region of a wet-air-cured 2 \times -doped BDSDA-ODA film (A) before and (B) after argon ion etching.

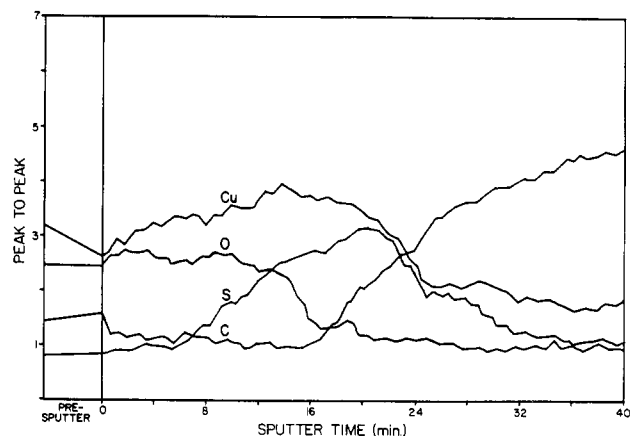


Figure 10. Auger electron spectroscopic depth profile of a wet-air-cured 2 \times -doped BDSDA-ODA film.

and a copper/sulfur component since the limited amount of sulfur present cannot bind the large quantity of copper that exists in this region alone.

AES with ion milling provides a similar view of the surface and near-surface regions to that obtained by XPS. Twenty-minute profiles of the dry-air-cured films display essentially a copper-free region comprised totally of polyimide. Alternatively, the 1 \times -doped wet-air-cured film exhibits a moderate copper concentration with irregular dispersions of sulfur throughout the profile. Similarly, the depth profile of the 2 \times -doped wet-air-cured film is comprised of a copper oxide layer followed by a region composed predominantly of copper and sulfur (Figure 10).

Transmission electron micrographs of the 1 \times and 2 \times dry-air-cured ultramicrotomed films are characterized by large depletion zones (where no dopant aggregation occurs) which span 70–85% of the total film thickness from the atmosphere side of the film. These zones reside above regions of polyimide that contain dispersed copper-containing aggregates (Figure 11). A discontinuous surface composed of discrete copper-containing aggregates approximately 200 Å in diameter is observed for the 1 \times wet-air-cured ultramicrotomed film (Figure 12). The 2 \times wet-air-cured film, on the other hand, displays a rather thick (~ 300 Å) continuous surface layer. Below each surface layer, a large depletion zone is again followed by a region that consists of widely dispersed copper-containing particles suspended in the polyimide matrix. The aggre-

(22) Wagner, C. D.; Briggs, D., Ed. *Handbook of X-ray and Ultra-Violet Photoelectron Spectroscopy*; Heyden & Sons: London, 1977; Chapter 7.

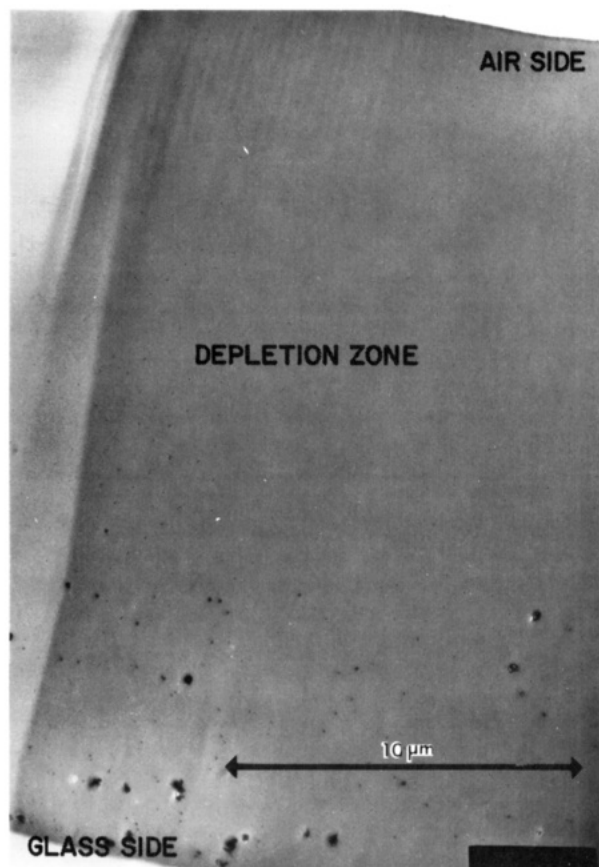


Figure 11. Transmission electron cross section of a dry-air-cured 1X-doped BDSDA-ODA film.

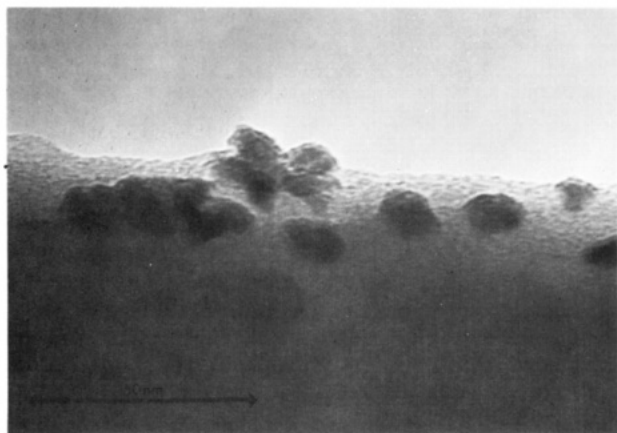


Figure 12. Transmission electron cross section of the surface region of a wet-air-cured 1X-doped BDSDA-ODA film.

gates found below the depletion zones for all doped BDSDA-ODA films are on the order of 800 Å, significantly smaller than those found in the bulk of doped BTDA-ODA and BTDA-APB films. Energy-dispersive X-ray analysis detected both sulfur and copper in the aggregates. Whether the sulfur/copper species coat the particles or form an integral part of the aggregate is unknown.

The large depletion zones observed in all of the doped BDSDA-ODA films are most likely due to copper/sulfur interaction. This interaction would lead to a large amount of dispersed copper, in some form, on a molecular scale, thereby accounting for smaller particles and less aggregation in comparison to the other polyimide systems under study. The large number of thioether groups theoretically available to react with a copper species, which is 4 times the amount of initial additive molecules, could bind to and

restrict additive mobility even at the higher curing temperatures. This immobilization could result in the small amount of internal aggregation that is observed experimentally. The flexibility of the doped BDSDA-ODA films is poor. This, in all likelihood, is due to the interaction between the thioether group and the copper dopant because nondoped films are extremely flexible and the doping of BTDA-ODA and BTDA-APB does not result in embrittlement.

Rationale. It is useful to consider in a qualitative sense how these varied, highly anisotropic metal-containing films are formed, given the fact that the dopant and cure temperature schedule is fixed. A working hypothesis is considered that takes into account the variable polymer matrix and cure atmosphere. Its basis is that the solubility of the dopant is reduced during the thermal conversion of poly-(amide acid) to polyimide, thereby promoting phase separation of a large portion of the additive. $\text{Cu}(\text{TFA})_2$, a partially soluble second component, migrates to or near the atmosphere surface from the bulk during imidization. If the migrating dopant comes in contact with the atmosphere during thermal processing, CuO is formed at the surface. $\text{Cu}(\text{TFA})_2$ may either thermally decompose to copper metal, whereby it is oxidized by reaction with atmospheric oxygen, atmospheric water, or the water of imidization, or $\text{Cu}(\text{TFA})_2$ may interact with the same oxidants to produce CuO directly. Water of imidization is apparently the reactant leading to formation of the CuO observed in the 2X nitrogen-cured BTDA-ODA films. If the migrating dopant approaches the surface but does not come in contact with the atmosphere, either thermal decomposition to metal occurs without subsequent oxidation (BTDA-ODA) or a polymer/dopant interaction takes place (BDSDA-ODA).

Material unable to migrate upward aggregates to form particles analogous to spherulites in a microphase separated copolymer, near the glass side of the film. This may be understood as follows. The portion of the film in contact with the glass substrate is the hottest region, while the surface in contact with the atmosphere is the coolest. This is due to the continual solvent loss (DMAC and the water of imidization) occurring at the atmosphere side of the film. The temperature gradient would cause the percent imidization, which is temperature dependent, to be greater at the glass side of the film during cure, thereby causing a gradient in solubility throughout the bulk of the film. In other words, material would begin to phase separate sooner at the glass side. Surface segregation could occur by having a certain portion of the dopant not yet aggregated seek the more soluble region above it. This would cause a front of additive to eventually reach the air side of the film, where it may further react to form copper and copper oxide.

For any doped film, no more than 5% of the copper initially reacted with the poly(amide acid) is lost throughout the curing process as determined by elemental analysis. This is somewhat surprising since $\text{Cu}(\text{TFA})_2$ sublimates readily at approximately 150 °C at atmospheric pressure; however, in the polymer matrix sublimation does not apparently occur. Since the presence of fluorine in the film is expected to be a tag for unreacted $\text{Cu}(\text{TFA})_2$, an estimate of the conversion of the additive to some other form throughout the bulk can be made by using experimental fluorine elemental analysis. Theoretically, if one measures the volume of aggregated material at and below the surface of a portion of the film on a TEM micrograph, assuming all particles and layers were homogeneous, and if one specified the chemical nature of the aggregates

Table III. Additive Conversion and Volume Fraction of Copper Species

polyimide	curing atmosphere	additive level	exptl		% conversion ^c	V _f	
			% Cu	% F		theoret ^b	exptl ^a
BTDA-ODA	wet air	1×	2.41	1.65	62.1	0.062	0.042
	wet air	2×	4.77	2.37	72.3	0.084	0.056
BTDA-APB	dry air	1×	2.15	1.60	58.3	0.047	0.041
BDSDA-ODA	dry air	1×	1.95	1.16	66.9	0.040	0.005
	wet air	2×	4.27	2.43	68.3	0.069	0.014

^a Volume fraction of particulate matter obtained from TEM. ^b Theoretical volume fraction of particulate matter taking into account additive conversion. ^c Percentage of the initial amount of Cu(TFA)₂ reacted during cure, obtained from elemental analysis:

$$\frac{V_{\text{spheres}} + V_{\text{layer}}}{V_{\text{total}}} = V_f \text{ of particulate matter within the doped polyimide film}$$

$$\% \text{ conversion} = \frac{(\text{Cu}/\text{F})_{\text{reacted}}}{(\text{Cu}/\text{F})_{\text{initial}}} \times 100$$

(Cu(TFA)₂, CuO, Cu), a comparison could be made with the volume of material expected (if evenly dispersed through the film) using the percent additive conversion, the doping level, and the density of the components (see the Appendix). Table III provides the results of these estimates. As shown, the volume of particulate matter observed by TEM could not wholly account for the copper present in the film. Thus, even in the so-called "depletion zone" there exists a significant amount of finely dispersed copper either soluble in molecular form within the matrix or as phase separated particles too small for TEM to detect. Table III also provides information concerning the relative solubility of Cu(TFA)₂ in each polyimide matrix used. The larger difference between the theoretical and experimental volume fractions for the doped BDSDA-ODA films as compared to the other doped matrices supports a higher level of dopant solubility in BDSDA-ODA. A reduced solubility for BTDA-APB as compared to BTDA-ODA is also suggested. The wet-air-cured films display surface deposits denoting some additional effect. It is possible that the increase in moisture from the moist-air purge may decrease the solubility of the additive in the surface region, thereby causing phase separation. It has been reported that atmospheric moisture increases the tensile modulus of fully cured polyimides above room temperature,²³ which may modify the solubility characteristics of doped polyimide films. Otherwise, the effect of curing atmosphere on the ultimate surface structure obtained is minor. It is more likely that the curing atmosphere has a pronounced effect on dopant conversion. The use of wet air should increase the rate of CuO formation from Cu(TFA)₂ relative to dry air and nitrogen curing atmospheres due to surface moisture enrichment. Likewise, curing in dry air should increase the rate of CuO formation as compared to a nitrogen atmosphere.

There exists the likelihood that phase separation may occur at a certain temperature by the continual loss of solvent (DMAC) in the film rather than the imidization process. Partially cured films do not display aggregation below approximately 225 °C. The solubility of Cu(TFA)₂ in DMAC is considerable (>0.2 mol/L), allowing for the possibility of total dissolution even at the higher temperatures present in the film during cure. Several films were doped with bis(acetylacetonato)copper(II), Cu(acac)₂, which has a solubility in DMAC of (~0.01 mol/L). By doping just under the solubility threshold, one would expect that a small loss of DMAC would cause the Cu(acac)₂ to phase separate if dopant solubility did not depend on

the nature of the polymer matrix. Partial curing of these films to 200 °C still produces films devoid of any internal aggregation, while fully cured films exhibit internal spherical particles of small size (~100 Å). The amount of DMAC within the film at 200 °C cannot be sufficient to fully solubilize the additive. We therefore conclude that the matrix itself acts to hold the dopant in solution at least up to a certain percent imidization. Further work is being undertaken to verify the viability of these hypotheses.

Acknowledgment. We gratefully acknowledge the National Aeronautics and Space Administration for sponsoring this research and Michele L. Porta for help in data collection.

Appendix

The experimental volume fraction (V_f) of particulate matter may be estimated from transmission electron microscopy through the following steps:

Calculate the total volume of a portion of a doped polyimide film from a TEM micrograph by using the measured film height, cross-section thickness (obtained from microtoming), and a representative film width.

Calculate the volume encompassed by the surface or near-surface layer if present by using the measured layer height, cross-section thickness, and same width as above assuming the deposit is homogeneous.

Calculate the volume of particulate matter within the bulk of the polyimide assuming each particle is homogeneous and spherical.

From the information above

$$V_{\text{total}} = V_{\text{polyimide}} + V_{\text{spheres}} + V_{\text{layer}}$$

$$\frac{V_{\text{spheres}} + V_{\text{layer}}}{V_{\text{total}}} = V_f \text{ of particulate matter within the doped polyimide film}$$

For example, for a BTDA-ODA/Cu(TFA)₂ 1×-doped, wet-air-cured film

$$V_{\text{total}} = 9.85 \times 10^{-10} \text{ cm}^3 \quad V_{\text{spheres}} = 4.15 \times 10^{-11} \text{ cm}^3$$

$$V_{\text{layer}} = 8.0 \times 10^{-15} \text{ cm}^3$$

$$V_f = \frac{V_{\text{spheres}} + V_{\text{layer}}}{V_{\text{total}}} = \frac{4.15 \times 10^{-11} \text{ cm}^3 + 8.0 \times 10^{-15} \text{ cm}^3}{9.85 \times 10^{-10} \text{ cm}^3} = 0.042$$

Registry No. (BTA)(ODA) (copolymer), 24980-39-0; (BTDA)(ODA) (SRU), 24991-11-5; (BTDA)(APB) (copolymer), 54053-19-9; (BTDA)(APB) (SRU), 54571-76-5; (BDSDA)(ODA) (copolymer), 64391-94-2; (BDSDA)(ODA) (SRU), 119071-97-5; Cu(TFA)₂, 7440-50-8; Cu, 14324-82-4.

(23) Pike, R. A.; Pinto, J. P.; Brunette, C. M. *Recent Advances in Polyimide Science and Technology*; Proceedings of the Second International Conference on Polyimides; Weber, W. D., Gupta, M. R., Eds.; Society of Plastics Engineers, Inc.: Poughkeepsie, NY, 1987; p 92.