High Refractive Index Polymer Coatings for Optoelectronics Applications

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ABSTRACT

The performance of many solid-state devices including emissive displays, optical sensors, integrated optical circuits, and light-emitting diodes can be improved by applying a transparent high refractive index coating (≥ 1.65) onto the light-emitting or light-sensing portion of the device. Ideally, the coating should combine the excellent durability and easy deposition of a spin-applied polymer coating with the high refractive index and optical clarity of a vacuum-deposited metal oxide coating such as titanium dioxide or zirconium oxide. While some success has been achieved in combining these very dissimilar materials to form transparent hybrid coating systems, for example, using sol-gel or nanoparticle dispersion techniques, the resulting coating systems often require complicated manufacturing schemes and have limited storage stability and reliability.

We have demonstrated two new approaches to development of high refractive index polymer coatings. In the first approach, an organometallic polymer and a conventional organic polymer are combined to form a compatible coating. When cured at elevated temperatures, the organometallic polymer decomposes to form a highly dispersed metal oxide phase that imparts high index properties to the final hybrid coating. The new coatings are transparent and have refractive indices ranging from 1.6 to as high as 1.9 depending on the metal oxide content.

The second approach utilizes our discovery that polyimide materials possess naturally high refractive indices in comparison to most polymer materials. Through careful molecular design, we have developed a new class of polyimide materials having refractive indices ranging from 1.60 to 1.78 at visible wavelengths and exhibiting excellent optical clarity. The new polyimides can be spin-applied to a layer thickness of more than 10 microns in a single coating step and form thermally stable films with good mechanical strength and adhesion to device substrates.

Keywords: LED, optical polymer, optoelectronic, refractive index

1. INTRODUCTION

The performance of solid-state optoelectronic devices such as flat panel displays, imaging sensors, photonic circuits, and light-emitting diodes can often be improved by applying a transparent high refractive index coating (≥ 1.65) onto the light-emitting or light-sensing portion of the device. The more gradual transition from the high refractive index of the active circuitry to the low index of air allows light to be coupled into or out of the device more effectively, increasing its efficiency and/or image quality. Ideally, the coating should combine the excellent durability and easy deposition of a spin-applied polymer coating with the high refractive index and optical clarity of a vacuum-deposited metal oxide coating such as titanium dioxide or zirconium oxide.

Some success has been achieved in combining organic and inorganic materials to form transparent hybrid coating systems, for example, by dispersing a metal oxide sol in a polymer vehicle to form what is commonly termed a ceramer[1]. Similar systems have been prepared using a sol-gel method in which a metal oxide precursor is hydrolyzed and condensed *in situ* to form highly dispersed metal oxide within a polymer matrix to which it is chemically bonded[2]. Film refractive index can be increased into the range of 1.6 to 1.7 using these approaches where the metal oxide component is present prior to coating. However, these approaches are often accompanied by complicated manufacturing schemes and limited coating storage stability and reliability.

We have developed a new approach to the preparation of hybrid coating systems which avoids the problems associated with nanoparticle dispersions and sol-gel techniques. In our approach, the high index metal oxide component forms spontaneously during the curing process of the coating, leaving the polymer and metal oxide phases dispersed at the nanoscale. The resulting coatings have refractive indices ranging from 1.6 to as high as 1.9 at visible wavelengths depending on the metal oxide loading. The coating solutions are stable at room temperature for a minimum of 3 months and can be easily applied by spin coating to form defect-free films that are 0.5 to 2.0 µm thick and that are highly transparent in the wavelength range of 500 to 1700 nm. The cured films are resistant to virtually all organic solvents and most aqueous etchants.

In addition, we have discovered a new class of amorphous aromatic polyimides that possess high refractive indices (1.62 to 1.78) at visible wavelengths and are eminently suitable for optical applications that require thicker coating layers because of their desirable properties, which include:

- High glass transition temperature, or Tg (>200°C);
- Excellent optical clarity at wavelengths greater than 400 nm (> 85% T for 5+ µm coating);
- The ability to be spin-applied from a safe solvent to achieve a coating thickness of 12 µm in a single application;
- A pre-imidized quality, meaning they do not require extended curing at high temperatures;
- Mechanical strength and toughness;
- Thermal stability to >350°C in air.

The new hybrid coatings along with the polyimide coatings are now being evaluated for a wide variety of optical applications.

2. EXPERIMENTAL

2.1 Organic-Inorganic Hybrids

The new hybrid coatings were prepared by combining a polymeric titanium dioxide precursor with a compatible organic polymer in a glycol ether solution. When cast and heated in air, the polymeric precursor decomposes to form highly dispersed titanium dioxide domains within a matrix formed by the organic polymer, or vice versa, depending on the proportions of the two components. The organic polymer contains functional groups that allow primary or secondary chemical bonding between the polymer and the titanium dioxide phase to promote phase compatibility and a high degree of dispersion.

The organotitanate polymer is an analog of poly(n-butyltitanate), or PBT, a well-known commercial product. However, PBT cannot be used directly in the new coating systems because of its extreme hydrolytic instability. Therefore, PBT is first reacted with a chelating compound to convert the tetracoordinate titanium nucleus to a hexacoordinate species before combining the polymer with other components. Hydrolytic stability and coating storage stability are improved dramatically such that the coating can be stored at room temperature for more than 3 months with no detectable change in solution color or viscosity.

The chelated organotitanate polymer and the organic polymer component are compatible in all proportions both in solution and in the cured film as evidenced by their high transparency (see Section 3,“Results”). We found that in practice the final proportion of titanium dioxide in the coating should not exceed about 70%; otherwise, the cured films have a tendency to stress crack during processing.

The new high index hybrid coatings were prepared at different metal oxide–to-polymer ratios (calculated on a w/w basis) by dissolving the organic polymer and the chelated PBT in propylene glycol n-propyl ether, a safe solvent used in photoresist compositions. The resulting solutions, which were clear and free of any gelled materials, were stirred for 4 hours at room temperature and then filtered through a 0.1-µm Teflon endpoint filter to remove particles before coating.

The coating solutions were applied onto quartz and silicon substrates by spin coating at 500 to 5000 rpm for 60 seconds, soft-baked on a 130°C hot plate for 120 seconds, and then cured by baking on a 225°C hot plate for 10 minutes. (This cycle was repeated for some of the compositions to increase film thickness.) The thickness of each coating was then measured with a Gaertner ellipsometer or an Alpha-Step profilometer. Coating transparency, reported as %T for a given film thickness, was measured with a Cary recording UV-visible spectrophotometer, with no corrections being made for scattering or reflective losses. The refractive index of each coating was determined with the aid of a Woollam variable angle spectroscopic ellipsometer (VASE).

The microstructure of different hybrid coating compositions was studied by applying a combination of plasma etching and scanning electron microscopy (SEM). Thin film specimens were prepared on silicon substrates and then subjected to brief fluorocarbon plasma etching to selectively remove the organic material from the surface of the coating. The etching process revealed the metal oxide phase, which was largely unaffected by the etching process, but did not proceed so far into the surface as to cause the metal oxide structure to collapse. The morphology of the exposed metal oxide domains was then determined by high-resolution SEM. The plasma etching conditions are provided below:

- Pressure: 50 mTorr
- Power: 50 Watts
- Gas flow: 20 sccm CF_4
- Platen Temperature: 20°C
- Process Time:
  - Low metal oxide content: 15 sec
  - High metal oxide content: 30 sec

2.2 Optical Polyimides

The polyimide-based coating solutions are preferentially synthesized by first generating the poly(amic acid) in a solvent such as N-methylpyrrolidinone (NMP) or dimethylacetamide (DMAc). Thermal imidization is then done by refluxing the poly(amic acid) solution for about 24 hours, with the use of an azeotroping solvent such as toluene, in order to distill off the water that is generated. The polyimide that is formed is then purified by precipitation into a suitable non-solvent such as methanol, and then dried in a vacuum oven to remove residual solvents. The polyimides obtained have molecular weights (from gel permeation chromatography using a Brewer Science, Inc., proprietary solvent mixture and measured against polystyrene standards) ranging from 50,000 to 80,000 daltons. The polyimide solutions are then prepared by dissolving the recovered solids in a cyclic aliphatic ketone such as cyclopentanone or cyclohexanone in concentrations ranging from 15% to 25% by weight. The resulting yellow or amber solutions are filtered through a 0.2-micron filter to remove any particles prior to coating.

The coating solutions were applied onto quartz and silicon substrates by spin coating at 500 to 5000 rpm for 80 seconds. A soft bake is performed on a 100˚C hotplate for 2 minutes followed by a final bake on a 205˚C hotplate for 1 minute to remove residual solvent. The thickness of each coating was then measured with a Gaertner ellipsometer or an Alpha Step profilometer. Coating transparency, reported as percent transmission (%T) for a given film thickness, was measured with a Cary recording UV-visible spectrophotometer, with no corrections being made for scattering or reflective losses. The refractive index of each coating was determined with the aid of a Woollam VASE.

3. RESULTS

3.1 Hybrid Coatings

The comparative refractive indices for hybrid coatings having different ratios of titanium dioxide and organic polymer are summarized in Table 1. The reported thickness is for one or more applications of the coating on the substrate.

Table 1. Optical properties of hybrid coatings at different titanium oxide-organic polymer ratios.

Composition	*1*	*2*	*3*	*4*	*5*	*6*
Refractive Index (400 nm)	2.01	1.94	1.90	1.86	1.78	1.72
Refractive Index (633 nm)	1.88	1.83	1.80	1.77	1.71	1.66
Film Thickness (microns)	0.88	1.10	1.85	2.15	2.50	4.28
% Transmittance (633 nm)	85.8	86.6	95.7	94.0	96.1	94.5
Metal Oxide-Polymer (w/w)	80/20	75/25	70/30	65/35	50/50	35/65

The hybrid coatings were applied at spinning speeds from 500 to 3000 rpm. However, spinning speeds of 1000 rpm or more are usually desired for obtaining good coating quality on wafer substrates. The cured film thickness values obtained for Compositions 3 (70% metal oxide) and 5 (50% metal oxide) in Table 1 at different spinning speeds are provided in Tables 2 and 3, respectively. The values correspond to a single application of the coatings. The curing process was the same as that used for the compositions in Table 1, i.e., 130°C/120 sec followed by 225°C/600 sec.

Table 2. Cured film thickness for 70% metal oxide hybrid coating versus spinning speed.

Spinning Speed (rpm)	*Cured Film Thickness (µm)*
1000	0.775
1250	0.675
1500	0.605
2000	0.515
2500	0.456
3000	0.415

Table 3. Cured film thickness for 50% titanium dioxide hybrid coating versus spinning speed.

Spinning Speed (rpm)	*Cured Film Thickness (µm)*
500	1.870
750	1.461
1000	1.223
1500	0.977
2000	0.864
2500	0.738
3000	0.655

The ability to use lower curing temperatures for a longer time to achieve the effect of curing the hybrid coatings was investigated for a hybrid coating containing 50% titanium dioxide. The refractive index values obtained at 400 nm and 600 nm after curing on a hot plate at 150°C/60 min or 175°C/60 min are compared in Table 4 versus the standard curing condition of 225°C/10 min.

Table 4. Effect of curing temperature and time on refractive index of 50% titanium dioxide hybrid coating.

Curing Conditions	*Refractive Index (400 nm)*	*Refractive Index (633 nm)*
225°C/10 min	1.78	1.71
150°C/60 min	1.75	1.68
175°C/60 min	1.73	1.66

The wavelength dependence of refractive index for the different hybrid coating compositions was determined by VASE methods. The results for the high and low titanium dioxide content coatings are plotted in Figures 1 and 3, respectively. Likewise, the optical transparency of the coatings was evaluated by determining their transmittance (%T) versus wavelength at different coating thicknesses. The uncorrected %T data for the high and low titanium dioxide content coatings are plotted in Figures 2 and 4, respectively.

Figure 1. Refractive index spectra of high titanium dioxide content hybrid coatings.

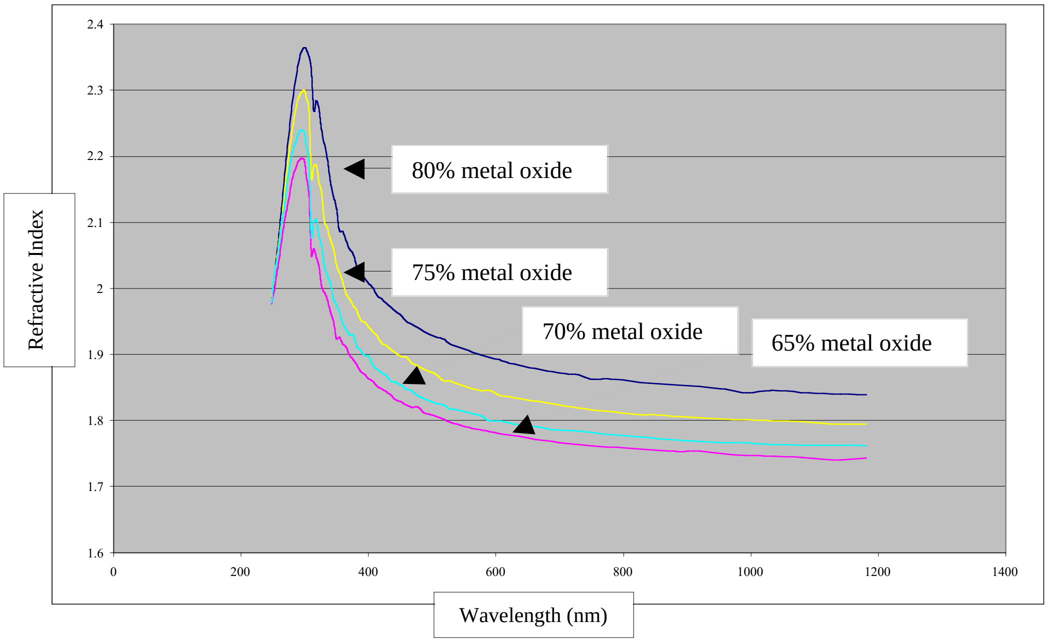


Figure 2. Transmittance for different thickness of 70% titanium dioxide hybrid coating.

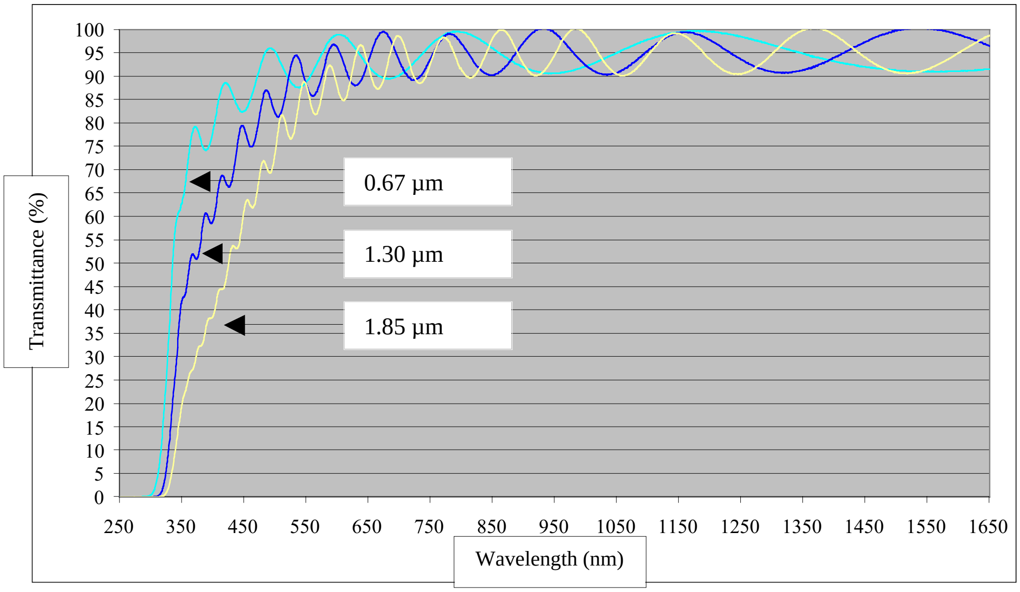


Figure 3. Refractive index spectra of lower titanium dioxide content hybrid coatings.

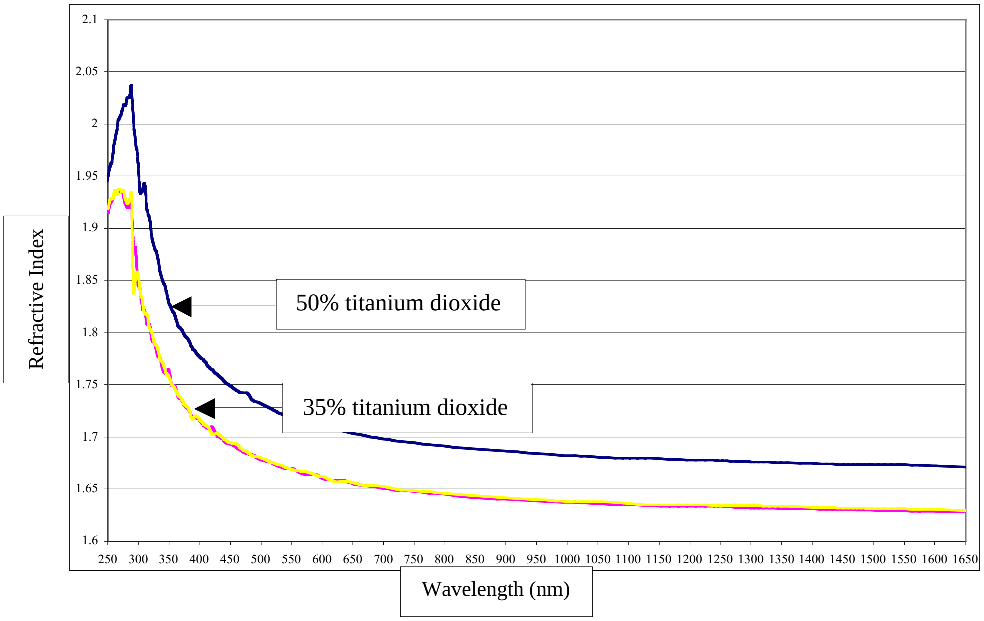
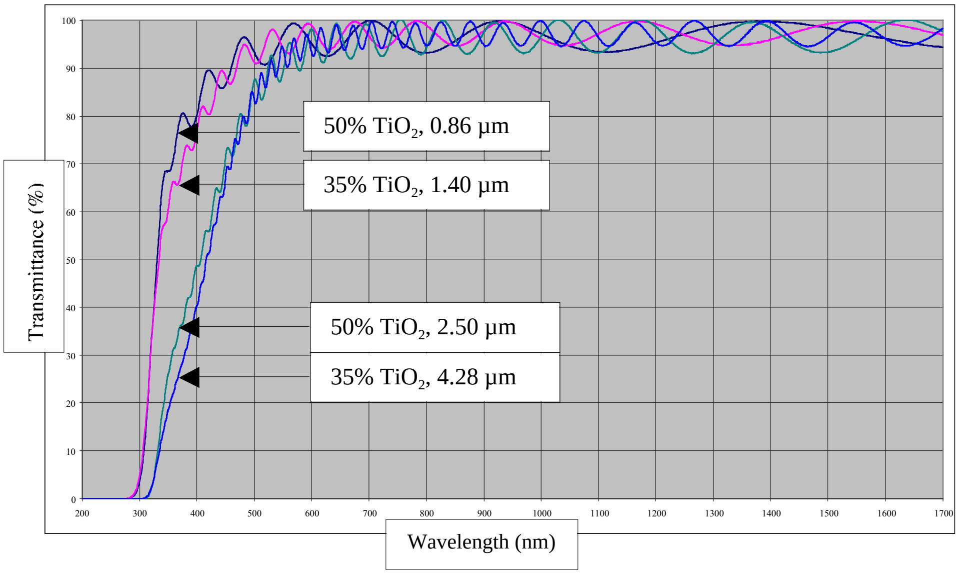


Figure 4. Transmittance of 35% and 50% titanium dioxide hybrid coatings.



The good optical transparency of the coatings suggested the domain size of the organic and inorganic phases was sufficiently small to not scatter visible light, at least not significantly. A combination of surface plasma etching and SEM examination was used to probe the coating morphology at different metal oxide loadings. The microphotographs obtained post-etch for a low and a high titanium dioxide content hybrid coating are displayed in Figures 5 and 6, respectively.

Figure 5. SEM image (100,000X magnification) of plasma-etched surface of low titanium dioxide hybrid coating.

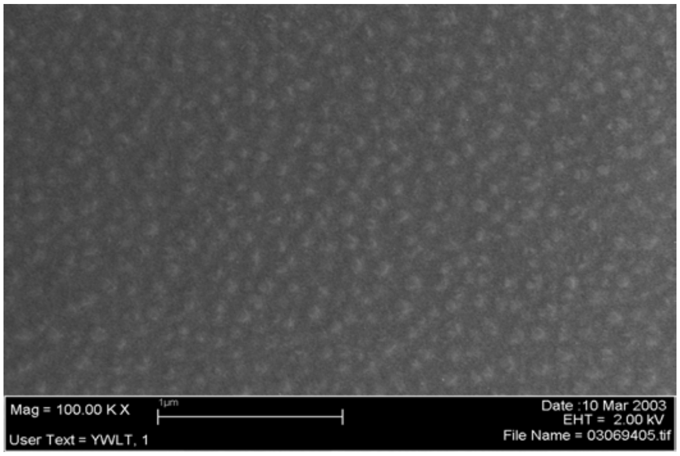
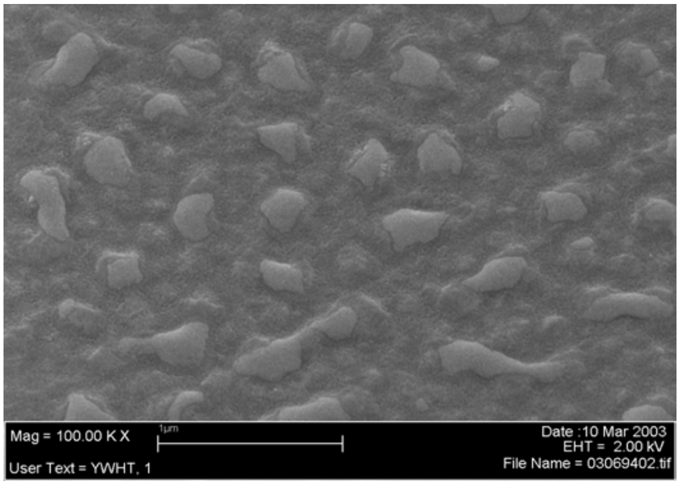


Figure 6. SEM image (100,000X magnification) of plasma-etched surface of high titanium dioxide content hybrid coating.



3.2 Optical Polyimides

In 2002, Eichstadt[3] and coworkers reported that the fully aromatic polyimide (see Figure 7) had a refractive index of 1.662. Using those findings as a starting point, we synthesized a variety of polyimides that took advantage of the processibility imparted by biphenol A dianhydride (BPADA) without overly sacrificing the increased refractive index afforded by the polarizable aromatic groups. We also synthesized BPADA/4,4′-oxydianiline (ODA) using the method described in this paper for use as a reference polymer.

Figure 7. Representative structure of polyimide formed from bisphenol A dianhydride and 4,4′-oxydianiline.

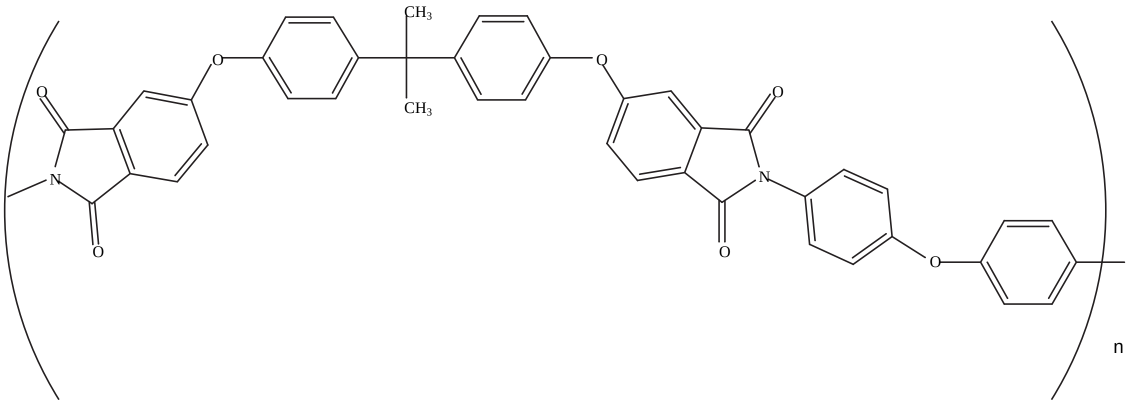


Table 5 shows the comparative refractive index values obtained at various wavelengths. One example, BPADA/9,9-bis(4-aminophenyl) fluorene (FDA), shows consistently higher refractive index values versus the reference compound, while BPADA/2,2-bis(4-[4-aminophenoxy]phenyl) sulfone (BAPS) exhibits slightly lower values across the measured spectrum.

Table 5. Selected refractive index values for polyimide examples.

Wavelength (nm)	*BPADA/FDA*	*BPADA/ODA*	*BPADA/BAPS*
400	1.7935	1.7757	1.7377
450.91	1.7533	1.7329	1.7025
506.12	1.7268	1.7146	1.6817
551.11	1.7132	1.7045	1.6725
604.88	1.702	1.6903	1.6613
652.63	1.7014	1.6853	1.6546
688.89	1.6966	1.684	1.6536
708.57	1.6896	1.6813	1.6471

Figure 8 shows the transmission spectrum curves of the three polyimides, normalized to a thickness of 5 microns. Excellent transparency in the visible to the near-infrared region is shown by all three examples, with transparency of 84% or better at 400 nm, and approximately 95% at 441 nm to 1700 nm.

Figure 9 shows a typical spin-speed curve obtained for a solution of 19% (w/w) BPADA/BAPS in cyclopentanone. These data were obtained following the processing procedure described earlier. The viscosity of this solution was 1770 cSt, as obtained kinematically.

Figure 8. Transmission spectrum curves of three polyimides normalized to a thickness of 5 microns.

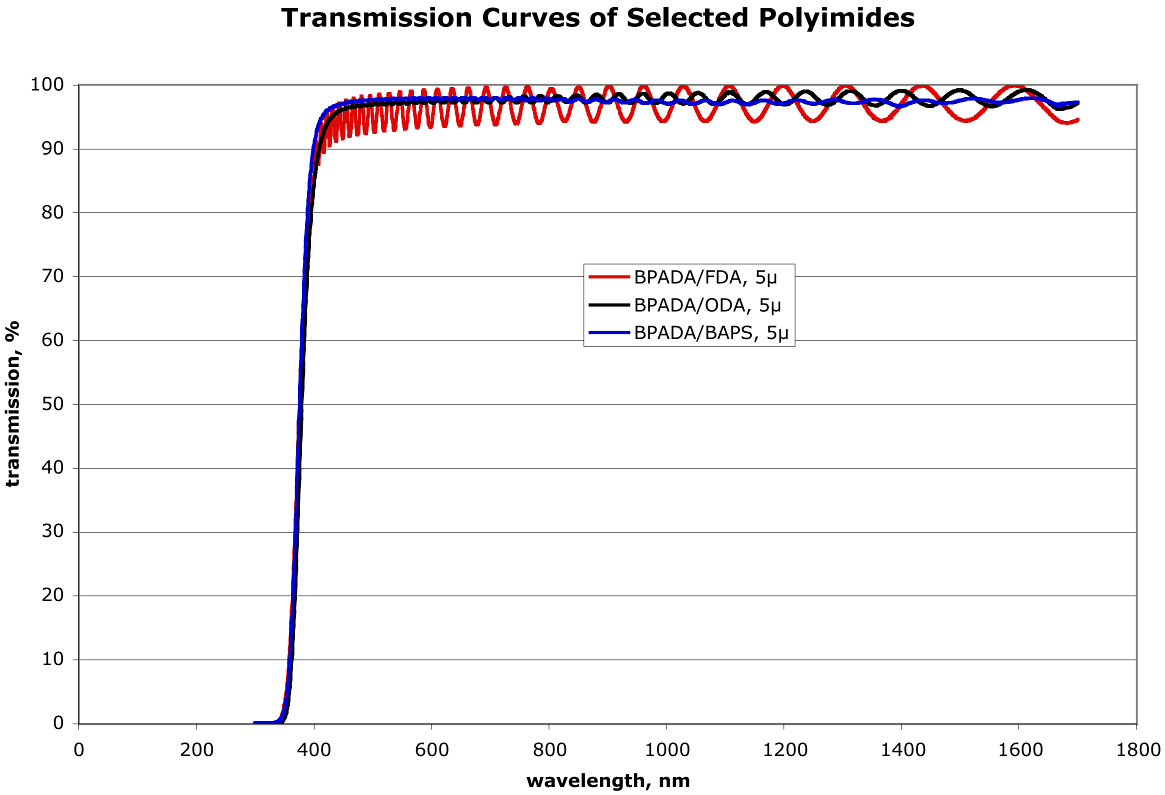
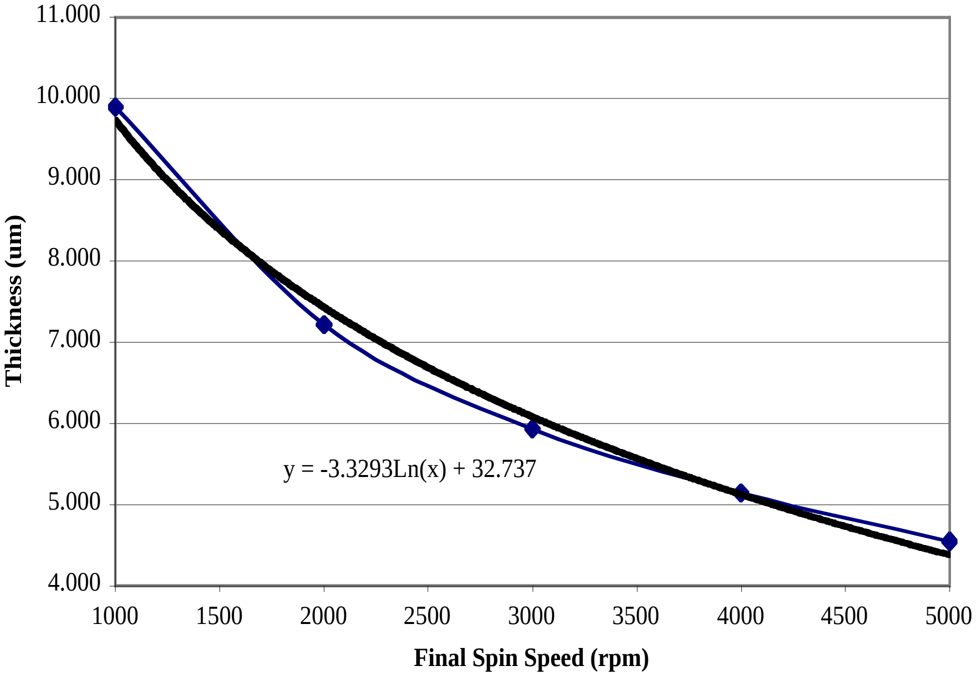


Figure 9. Relationship of film thickness to spin speed.



4.1 Hybrid Coatings

The film thickness versus spinning speed results presented in Tables 2 and 3 indicated that the maximum film thickness achievable for any given spinning speed decreased with increasing metal titanium content, assuming the starting solids levels for the coating solutions were similar. This trend was expected because the high metal oxide content coatings undergo more shrinkage as a result of precursor decomposition and the concurrent release of volatile organic compounds from the film.

The high index hybrid coatings responded well to triplicate application as a means for increasing film thickness. However, it was necessary to cure each layer before the next layer was applied to prevent the first layer from re-dissolving in the coating solvents. Successive curing steps had only a minor effect on the refractive index or optical clarity of previously applied layers.

Using longer curing times at temperatures below 200°C resulted in a slightly lower refractive index than that obtained using the standard curing condition of 225°C/10 min (Table 3). There was an unexpected inversion of the results at 150°C versus 175°C in that the index of the latter sample was actually lower than that obtained at 150°C. Subsequent studies not reported here have shown that a 30-minute bake at 175°C is sufficient for curing the hybrid composition whereas a full hour is required at 150°C. The same studies revealed that curing at 130°C, regardless of the curing time, does not produce the final high index form. Apparently, temperatures below 150°C are insufficient to decompose the chelated organotitanate and produce the metal oxide product. Similarly, the studies showed that curing at higher temperatures (≥ 250°C) produced only an incremental increase in refractive index but noticeably increased discoloration. Therefore, the current generation of hybrid coatings is not recommended for very high temperature applications.

As expected, the refractive index of the hybrid coatings increased directly in proportion to their titanium dioxide content. This observation held true for all wavelengths in the measured range. The refractive index values for coatings with titanium dioxide loadings ranging from 65 wt.% to 80 wt.% (Figure 1) were consistently above 1.7 for all wavelengths. More importantly, refractive indices of 1.8 or higher were achieved throughout most of the visible portion of the spectrum (400 to 700 nm), and values in excess of 1.9 were observed in the 400- to 500-nm segment of the spectrum where many light-emitting devices operate.

The hybrid coatings possessed excellent optical clarity at wavelengths above 500 nm, with good clarity extending into the near infrared. Figure 2 reports the film transmittance of a 70% titanium dioxide hybrid coating at three film thickness values. Some optical loss was observed in the 350- to 500-nm region of the spectrum because of the high metal oxide loading, with the degree of loss increasing steadily with film thickness. Reducing the metal oxide content improved clarity in this region significantly. For example, the transmittance of a film containing 50% metal oxide (adjusted for the same thickness) is about 59% at 400 nm in comparison to the value of 39% obtained for the 70% metal oxide composition at the same wavelength (compare Figure 4). The refractive index values for the 50% and 70% compositions at 400 nm were 1.7765 and 1.8975, respectively, as determined by VASE methods.

The microstructural analysis indicated that at low titanium dioxide content the metal oxide is uniformly dispersed in the polymer matrix as discreet domains that are about 50 to 100 nm in size. As the titanium dioxide content increases, the metal oxide and polymer structure become more co-continuous, with a sponge-like metal oxide phase dominating the morphology at high titanium dioxide content. In this compositional range, the metal oxide features are highly irregular in shape and generally larger, perhaps somewhere in the range of 100 to 250 nm.

4.2 Optical Polyimides

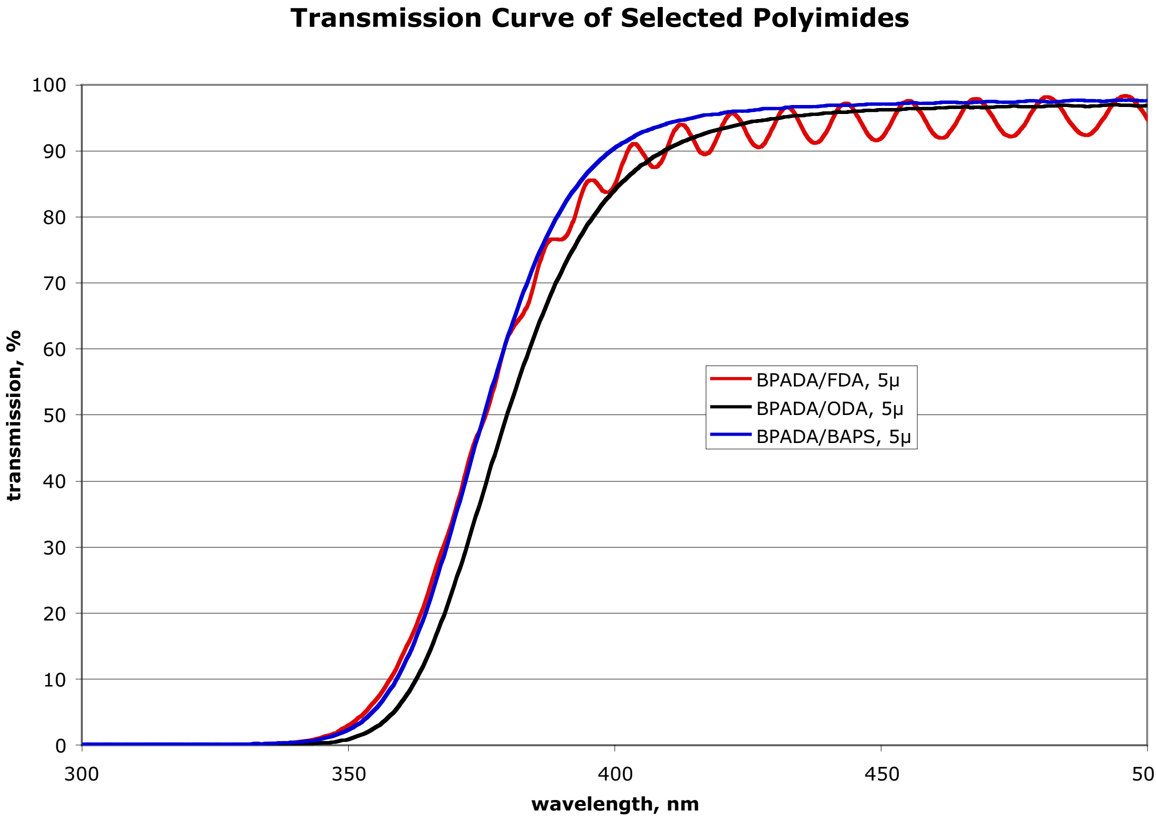
While the fact that many polyimides have high refractive indices compared to other organic polymers is not necessarily a new concept, there have been many drawbacks to their use as optical coatings. These drawbacks include the formation of highly colored species arising from charge transfer complexes. In addition, the highly aromatic nature of most available polyimides limits their solubility to a few aggressive solvents such as N-methylpyrrolidinone, dimethylformamide, dimethylacetamide, or γ-butyrolactone. For example, DuPont's Kapton HN polyimide film has a refractive index of 1.70; it is, however, insoluble and highly colored, as are many other fully aromatic polyimides[4]. Another example is Durimide from Arch Micro, which is a photosensitive polyimide that has been reported to have a refractive index of 1.69 at 633 nm and forms films of up to 50 microns thick in a single application. However, it is available only as a precursor solution that requires curing of up to 350°C for 60 minutes to achieve the desired properties.

The polyimides reported in this work address the issue of poor solubility in aromatic polyimides by the incorporation of highly flexible linker groups in the backbone, such as ether, sulfone, or isopropylidene groups (or a combination thereof). The solubility can also be improved by the use of a bulky organic group that is pendant to the main chain, in this case fluorenyl groups that also contribute to the polarizability (and hence, refractive index). The improved solubility permits higher solids concentration in the prepared solutions, which in turn contributes to greater film thicknesses. The polyimides in this work consistently gave good quality films with a thickness of 5 to 10 microns.

The refractive index values obtained for BPADA/ODA in this study are in good agreement with the reported literature values, despite the difference in the method of measurement (ellipsometer versus prism coupler). This finding indicates that the methodology provides reliable results. In addition, the cyclized imide units are expected to contribute more to refractive index than the corresponding carboxylic acid or ester units. The agreement of refractive index data is indicative of comparable levels of conversion from the poly(amic acid) precursor reported here with the level of conversion from the ester-acid method as reported by Eichstadt[3] and co-workers.

As stated earlier, even higher refractive indices are achievable with polyimides. However, the increase is typically accompanied by color formation as a result of the formation of intra- and intermolecular charge transfer complexes. The transmission data presented show that in the examples presented, color formation is essentially minimized through the judicious choice of aromatic dianhydrides and diamines. This becomes more evident by comparing transmission of the three polymer systems in the wavelengths from 300 to 500 nm (Figure 10).

Figure 10. Transmission of the three polymer systems in the wavelengths from 300 to 500 nm.



BPADA/BAPS and BPADA/FDA show improved shorter wavelength transmission compared to the reference system. In the case of BPADA/BAPS, this comes at the expense of slightly decreasing the refractive index, but in the case of BPADA/FDA, some improvement in index is observed.

5. CONCLUSIONS

The development of robust high index polymer coating systems has not been feasible because of the inherently low refractive index properties of organic polymers. Few organic polymers have refractive indices greater than 1.65 at visible wavelengths, and fewer still have indices of 1.70 or greater. Those high index polymers that have been reported have generally contained a high concentration of large, easily polarized atoms such as bromine, iodine, or sulfur[5], which in turn limits their thermal and chemical stability.

On the other hand, certain metal oxides, most notably those of titanium and zirconium, possess excellent optical clarity when applied as thin films and exhibit refractive indices of 2.0 or more at visible wavelengths. They are usually deposited by evaporation or sputtering and then only as thin films less than 1 micron in thickness. Unfortunately, deposited metal oxide coatings tend to be brittle and may not adhere well to device surfaces without high-temperature annealing, which may in turn degrade device operation.

Sol-gel coating methods have also been used to deposit high index metal oxide coatings from solution[6]. However, the coatings tend to be brittle and can require long, complicated curing schedules. Sol-gel coating solutions also have limited pot life, making the method difficult to practice for commercial device production. More recently, the sol-gel method has been combined with conventional polymer chemistry to prepare inorganic-organic hybrid coatings[2,7] in which the metal oxide phase is formed by *in situ* and chemically bonded to an organic polymer phase to obtain materials with greater toughness and durability. However, these compositions are still prone to the pot life problems and lend themselves best to silicon dioxide incorporation, which does not promote a high film refractive index.

Inorganic-organic hybrid coatings have also been prepared by dispersing nanosized (1 to 50 nm in diameter) metal oxide particles in a polymer vehicle to produce transparent film compositions. Recently reported results[1,8], however, indicate that the refractive indices of these compositions are largely restricted to the range of 1.55 to 1.70 unless very high metal oxide loadings (80%) are utilized. The preparation of these coatings involves many steps, including particle synthesis and purification, surface treatment, and dispersion, often under a non-ambient environment.

We have demonstrated two new approaches to the development of storage-stable high refractive index polymer coatings that offer easy application and broad utility for optoelectronic device applications. The new coating systems provide a host of options for meeting requirements for high refractive index (from 1.6 to as high as 1.9 at visible and near IR wavelengths), coating thickness (from 0.1 to 10+ μm), optical clarity, mechanical strength, and thermal stability.

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