Hybrid high refractive index polymer coatings

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ABSTRACT

Thermally curable hybrid high refractive index polymer solutions have been developed. These solutions are stable up to 6 months under room temperature storage conditions and can be easily spin-coated onto a desired substrate. When cured at elevated temperature, the hybrid polymer coating decomposes to form a metal oxide–rich film that has a high refractive index. The resulting films have refractive indices higher than 1.90 in the entire visible region and achieve film thicknesses of 300-900 nm depending on the level of metal oxide loading, cure temperature being used, and number of coatings. The formed films show greater than 90% internal transmission in the visible wavelength (400-700 nm). These hybrid high refractive index films are mechanically robust, are stable upon exposure to both heat and UV radiation, and are currently being investigated for microlithographic patterning potential.

Keywords: high refractive index, hybrid polymer, optical thin film, optoelectronic

1. INTRODUCTION

There has been considerable demand for high-performance high refractive index materials in recent years due to their wide applications in optical devices. The performance of optical devices such as planar waveguides, flat panel displays, optical sensors, high-brightness LEDs, OLEDs, integrated optical devices (photonic crystals), diffraction gratings, and optical data storage has been greatly advanced. Applying a transparent high refractive index coating layer between the active circuitry and air or low refractive index packaging layer onto these devices can often further improve or maximize their performance. The more gradual transition from the high refractive index of the active circuitry to air or low refractive index package layer allows light to be coupled into or out of the device more effectively, increasing its efficiency and/or image quality. With higher efficiency, devices can be made more powerful while consuming less energy. Because some of these optical devices are made from semiconductor materials that have refractive indices as high as 2.5-3.5, the desired refractive index of such transparent coating layers is at least 1.8 over the entire visible region and preferably greater than 1.9. Ideally, a polymer would be the best choice for a coating material if its refractive index is high enough due to its ease of processing and potential low cost. Unfortunately such a polymer does not exist; the polymer with the world's highest refractive index at present is 1.76 and was developed by Sadayori and Hotta of Nitto Denko[1]. Inorganic materials that have high refractive indices and high transparency are to be considered, and transition metal oxides such as titanium dioxide or zirconium dioxide are among the best choices.

Considerable progress has been made on metal oxide–containing materials such as sol-gel coatings and nanoparticle composites[2-5]. However, coatings prepared from these solutions are brittle and subject to cracking, and their applications are limited by their complicated manufacturing process, storage stability, and reliability. Sputtering is the other technique currently being used to generate high index thin films from these metal oxides; however, optical device manufacturers still seek other more cost-effective methods due to the high cost and low throughput of sputtering.

In a previous paper[6] we have reported a new approach to the preparation of hybrid coating systems that avoids the problems associated with nanoparticle dispersions and sol-gel techniques. In that paper we described a method to prepare the titanium dioxide hybrid coating solutions. The organic-inorganic hybrid polymer solution is prepared by first reacting the titanium alkoxide with a chelating agent to convert the highly reactive tetra-coordinate titanium species to a less reactive hexacoordinate species. Other desired polymer components are then added to the stabilized titanium-containing solution and mixed well. As a result of the stabilization, the hybrid polymer solution is stable at room temperature up to 6 months with negligible change in color and viscosity.

The hybrid polymer solution was then spin-coated onto substrates to a desired thickness. A titanium dioxide rich film was generated by thermally decomposing the hybrid coatings at an elevated temperature. The resulting films are transparent and have refractive indices higher than 1.90 in the entire visible region when the cure temperature was 300ºC or higher. A crack-free film over 300 nm in thickness was obtained with a single coating application. Multiple-coating is applicable to obtain a thicker film, and no apparent interface was seen from SEM cross-section images between two consecutive coatings. The hybrid high refractive index films are mechanically robust, are stable upon exposure to both heat and UV radiation, and are currently being investigated for a wide variety of optical applications.

1. EXPERIMENTAL

The hybrid coating was prepared by the following procedure: (1) Dissolve a polymeric titanium dioxide precursor in an alcoholic or glycol ether solvent to form a solution. Weigh the inorganic polymer into a container, then add the solvent to the same container and stir the contents until a clear, homogeneous mixture is obtained, (2) Add the chelating agent to the above solution to convert the tetra-coordinate titanium compound to a hexacoordinate species that is more stable. Slowly add the chelating compound through a dropping funnel into the container while constantly stirring the solution. Stir the contents for an additional period of time after completing the addition to yield the stabilized inorganic polymer solution. (3) Add a compatible organic polymer at desired fraction to the above stabilized solution to form a hybrid polymer coating solution. Stir the mixture for 4 hours to yield a clear and gel-free solution, and then filter it through a 0.1-μm PTFE filter.

The polymeric titanium dioxide precursor and chelating compound used here is an equilibrium product of poly(dibutyl titanate) and ethyl acetoacetate, respectively. Figure 1 shows the idealized structure of stabilized poly(dibutyl titanate).

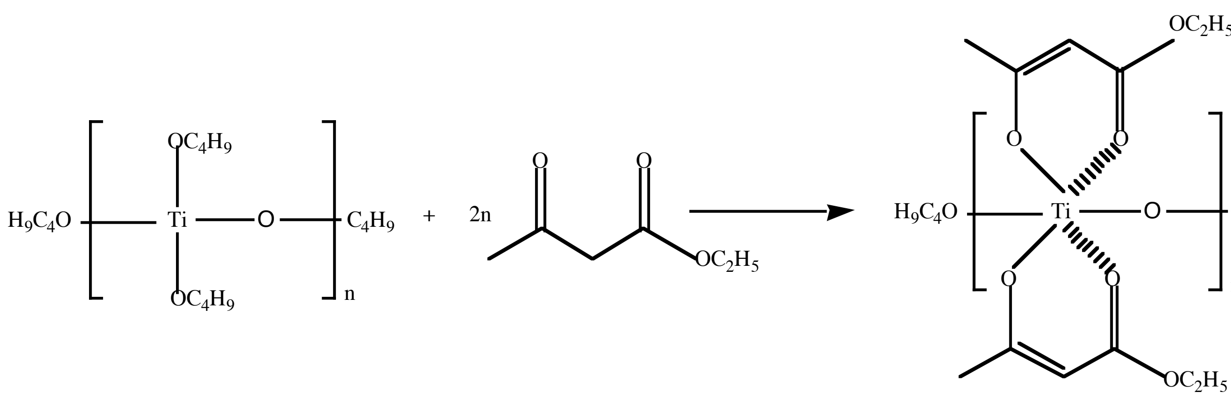

Figure 1. Structure of stabilized polymeric titanium species.

The organic polymers chosen contain multiple hydroxy functionalities. They are so chosen to 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 chelated poly(dibutyl titanate) polymer and the organic polymer are compatible in all proportions both in solution and in the cured film as evidenced by their high transparency.

The coating solutions were spin coated onto quartz, silicon, or other desired substrates by spin coating at 1000 to 5000 rpm for 60 seconds, soft-baked on a 130°C hot plate for 60-600 seconds to remove the solvents, cured by baking on a 225°C hot plate for 60-600 seconds, and then baked again at 300ºC for 60-600 seconds. The resulting coating is a titanium dioxide–rich material with high index (1.9 or higher at entire visible region), high transparency, and resistance to chemical attack. Baking at temperatures higher than 300ºC and for longer times will produce further reductions in film thickness and an increase in refractive index. The intermediate 225ºC bake is not necessary if smoke generation is not a concern or a ramped bake beginning at low temperatures is utilized. This spin-bake cycle can be repeated if a thicker film is desired. Figure 2 illustrates the thermal decomposition process.

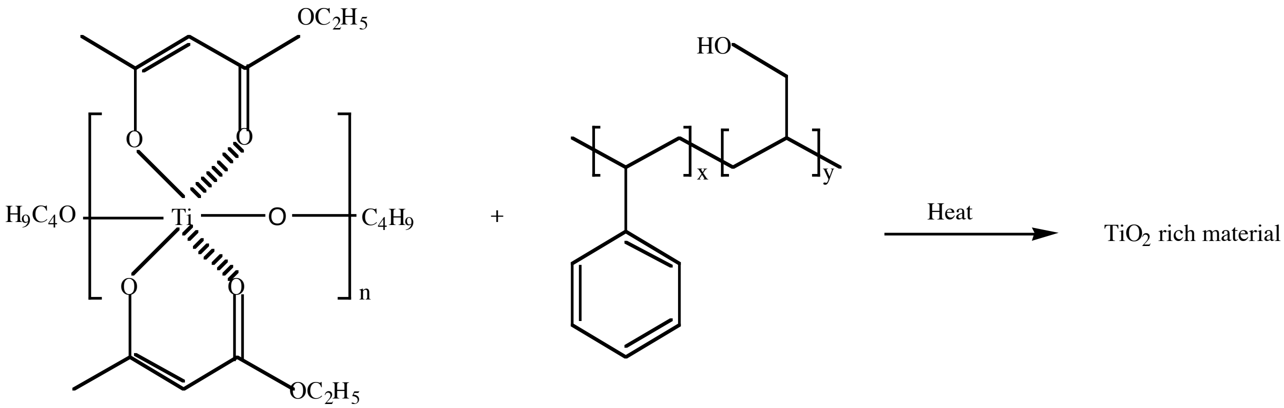

Figure 2. Thermal decomposition scheme of hybrid polymer coating (OptiNDEX A07).

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 Varian Cary-500 UV-visible spectrophotometer, with no corrections being made for scattering or reflective losses. The refractive index spectrum of each coating was determined with the aid of a J.A. Woollam variable angle spectroscopic ellipsometer (VASE®). Cross-section SEM images were taken from an LEO-1560 microscope.

3. RESULTS

In 2003, the authors reported a series of organic-inorganic hybrid coatings having different loadings of titanium dioxide[6]. The calculated titanium dioxide loading ranges from 80% by weight to 35% by weight with curing temperature of 225ºC for 600 seconds. The reported indices for the coatings range from 2.01 to 1.86 for the 80% by weight and 1.72 to 1.66 for the 35% by weight metal oxide coatings in the 400 nm to 800 nm region, respectively. The refractive indices of the coatings with other loadings understandably lie in between these values. Table 1 shows the optical properties of the hybrid coatings; note that composition 4 is also known as OptiNDEX A07, and the film thickness corresponds to double- or triple-coating applications without the formation of cracks.

Table 1. Optical properties of hybrid coatings at different titanium oxide-organic loadings when baked at 225ºC for 600 seconds.

Composition	1	2	3	4	5	6
Refractive index at 400 nm	2.01	1.94	1.90	1.86	1.78	1.72
Refractive index at 800 nm	1.86	1.82	1.78	1.75	1.68	1.66
Film Thickness, μm	0.88	1.10	1.85	2.15	2.50	4.28
Metal oxide content, wt.%	80	75	70	65	50	35

Using the above coatings as the baseline, three new hybrid polymer solutions (OptiNDEX A14, EXP04048, and EXP04054) have been developed that produce coatings with refractive indexes greater than 1.9 in the entire visible region when the coatings are cured at a temperature of 300ºC or higher.

The solutions were applied at spinning speeds of 1000 to 5000 rpm (for 60-90 seconds). However, spin speeds of 1500 rpm or higher are usually desired for obtaining good coating quality on wafer substrates. Figure 3 shows the film thickness versus spin speed for the three new solutions with a single coating application. Thicker films are possible with multiple coating applications.

Table 2 shows the refractive indices of the three new coatings at 400-nm and 800-nm wavelengths and single film coating thickness. Thicker films could be prepared by multiple-coating applications. The full visible refractive index spectrum of the three new coatings is shown in Figure 4, in addition to the OptiNDEX A07 reported previously.

Compared to OptiNDEX A07, the film refractive indices of OptiNDEX A14, EXP04048, and EXP04054 are very similar and increase substantially over the entire spectrum region.

Table 2. Selected properties of the three new hybrid coatings when baked at 300ºC for 10 minutes.

Composition	OptiNDEX A14	EXP04048	EXP04054
Refractive index at 400 nm	2.16	2.15	2.16
Refractive index at 800 nm	1.97	1.95	1.97
Film Thickness, μm	0.24	0.27	0.35
Metal oxide content, wt.%	80	80	80

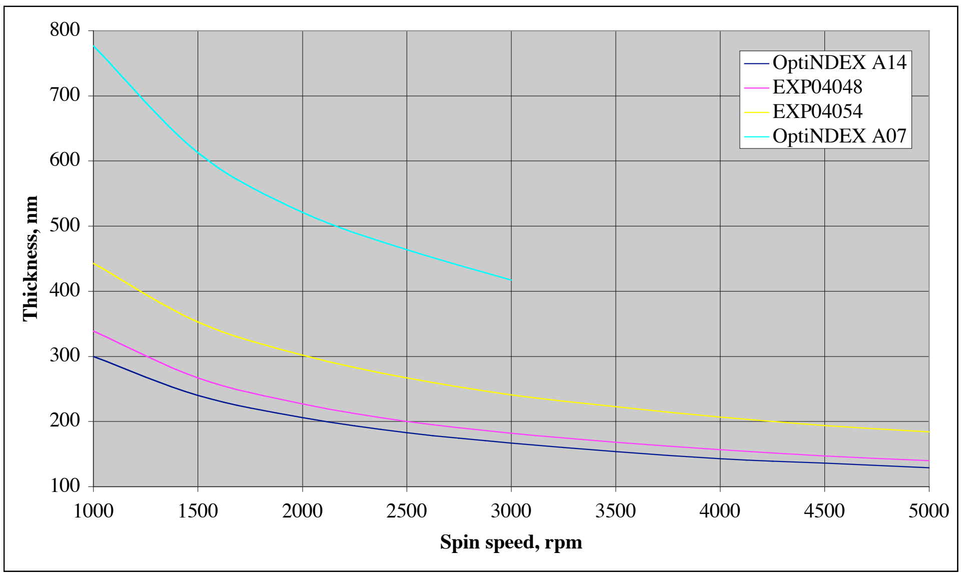

Figure 3. Single-coating film thickness (cured at 300ºC for 10 minutes, 225ºC/10 minutes for OptiNDEX A07) versus spinning speed.

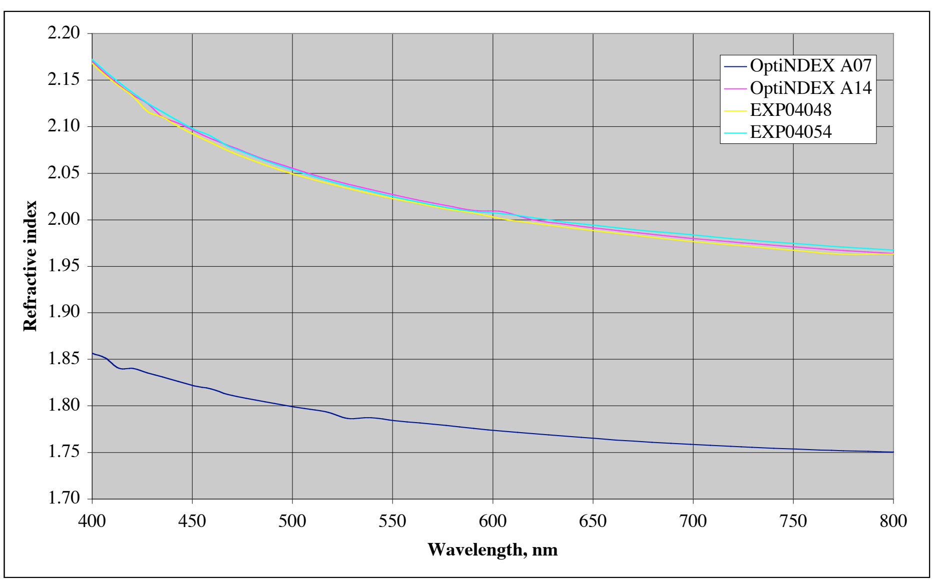

Figure 4. Refractive index spectra of the hybrid polymer coatings.

To further increase film thermal and radiation stability, the film can be baked at higher temperature if necessary and with no damage to the substrate. The refractive index of higher temperature baked film has a small change, and no loss in transparency was observed.

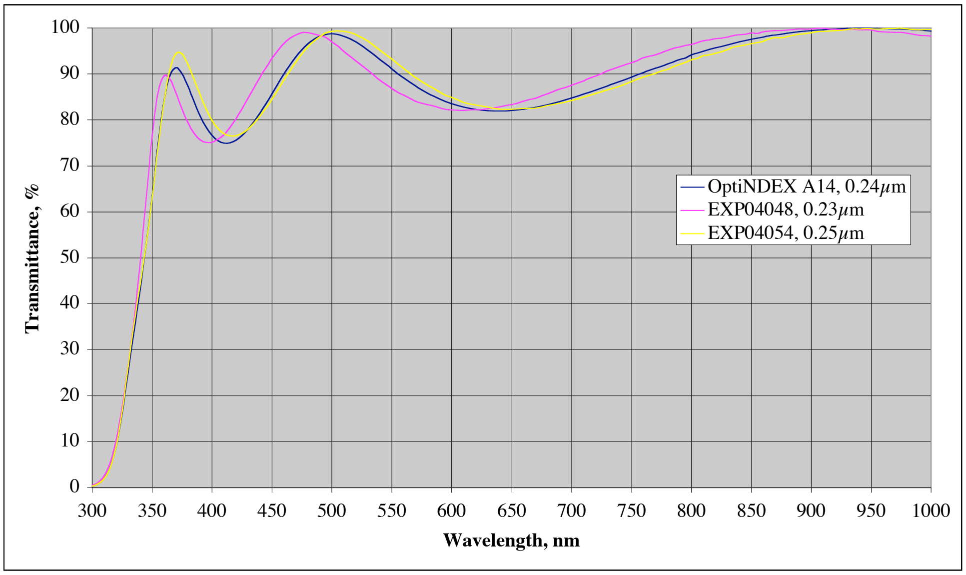

Figure 5. Film transmission curves of the three new hybrid formulations.

Films prepared from the three new solutions have excellent transmission over the entire visible region (exceeding 85%). Figure 5 shows the transmission curves of the three new coatings at comparable thicknesses on quartz substrates. To further determine the internal transmission of these coatings, the transmission curve of OptiNDEX A14 on a sapphire substrate was measured at a thickness of about 0.3 μm, and it shows a substantial improvement over the transmission curves on quartz. The interference peaks and valleys were suppressed; the move towards higher transmission indicates that the film internal transmission is good (Figure 6).

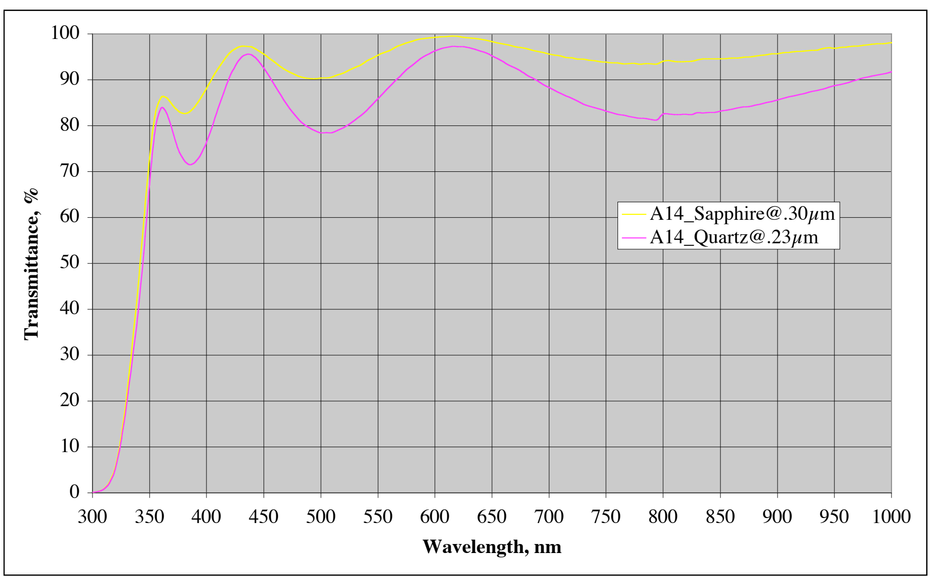

Figure 6. Comparative transmission curves on quartz and sapphire substrates.

The single coating film is well characterized and understood in terms of refractive index and transparency. However, there are some concerns on how well the film made from multiple-coating applications behaves because thicker films (0.5-1.0 μm) are needed for some of the applications. Experiments show that the refractive indices of multi-layer coatings are almost the same as a single layer coating with a slight increase due to the under-layer experiencing a longer cure time. Table 3 lists typical refractive indices at three typical wavelengths.

Table 3. Refractive indices of multi-coatings at selected wavelengths.

	n at 400 nm	n at 633 nm	n at 800 nm
Single layer	2.16	1.99	1.96
Double-layer	2.16	1.99	1.96
Triple-layer	2.17	2.00	1.97

Cross-section SEM images shows no apparent interface between two or three consecutive coatings. (See Figure 7 for details.) The transmission curves of multiple-coatings that are not reported here responded according to thickness and suggest that no interface scattering has occurred.

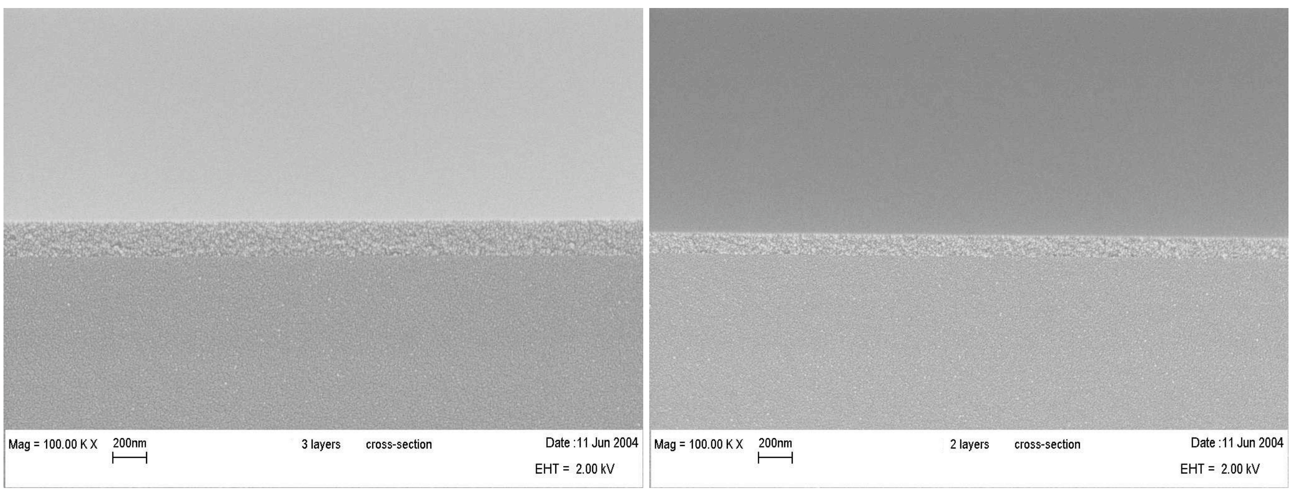

Figure 7. SEM images of two-layer coating (left) and three-layer coating (right).

4. DISCUSSION

Titanium dioxide has long been known as a typical high refractive index material and that a thin layer of TiO_2 over active optical circuitry will improve the overall device performance greatly. Organo-titanium–containing compounds such as titanium (IV) ethoxide, titanium (IV) isopropoxide, and titanium (IV) butoxide are well known precursors to produce titanium dioxide when thermally decomposed at a temperature of 300ºC or higher over a period of time; moreover, their analogous polymers are precursors that do the same. However, a thin film that does not crack prepared by this pure thermal decomposition process is only about 100 nm, which makes it less viable for industry use that normally requires a thickness of 500 nm to 1000 nm. Good progress has been achieved over the titanium dioxide thin film–making process. Thick films (150-200 nm) can be made by a sol-gel method that hydrolyzes *in situ* and condenses the precursor and then thermally decomposes to titanium dioxide, however thicker film preparation is still an issue. The full sol-gel process is often time consuming and may require a higher temperature (greater than 450ºC) bake that will limit its use due to some of the substrates not being high-temperature resistant. Complicated manufacturing schemes, limited storage stability, and reliability are the other factors that indicate that the sol-gel method is not the best titanium dioxide thin film preparation route. Sputtering is the other process that could produce thicker titanium dioxide films, but low throughput and high cost is an issue for device manufacturers. The ability to produce thicker films (~350 nm) without cracking, along with high indices (higher than 1.9) and high transparency over the visible region, makes the new hybrid polymer solutions, OptiNDEX A14, EXP04048, and EXP04054, practical and valuable to the optoelectronic device industry.

The main reason for titanium dioxide film cracking is the film stress caused by large shrinkage during the baking process. A secondary reason is the mismatch of the coefficient of thermal expansion between titanium dioxide and the substrate. Basically, all the current titanium dioxide film preparation methods other than sputtering are either directly or indirectly decomposing organo-titanium polymer precursors at a high temperature (UV cure is a possibility also). Large film shrinkage as a result of precursor decomposition caused by the release of a large amount of volatile organic compounds is to be expected.

The composition of the precursor is very important to produce thicker and high-quality titanium dioxide films. This is evident from the performance leap in going from OptiNDEX A07 to A14. The addition of a chelating compound converts the reactive tetra-coordinate titanium to a less reactive hexa-coordinate species and increases the coating solution stability on one hand. On the other hand, the addition of other functional group containing polymer(s) that may interact with titanium atoms will stabilize the solution further. Both of the chelated hexa-coordinate species and the polymers are decomposed during the thermal curing process, and the ability to form primary or secondary chemical bonding between the polymer and the titanium dioxide phase during the curing process increases film flexibility and effectively reduces its stress to allow thicker film formation. The choice and combination of chelating compounds and polymers partially set how thick the film can be prepared. Our new hybrid coating solutions, OptiNDEX A14, EXP04048, and EXP04054 apparently have good combinations; among them EXP04054 is the best. A study of OptiNDEX A14 and EXP04048 show greater than 6 months' room temperature stability. EXP04054 is expected to have the same stability because it is very close in composition to the other two coating solutions.

One other important factor to produce a thin film is how the coatings are processed (bake schedule). A three-stage bake is recommended to avoid film smoking, though an immediate 300ºC hard bake after the soft bake is applicable with a slight change in refractive index and thickness. The less heat-treated film may have enough time to dissipate the stress build up before it is too rigid. Experiments show that most of the volatiles are lost at the very beginning during the high temperature bake; successive curing had only a small effect on the refractive index and optical clarity. Therefore the high index hybrid coatings are respond well to multiple-coating applications as a means for increasing film thickness.

Evidence of a slight increase in refractive index after multiple-coating applications and no interface between successive layers (Table 3 and Figure 7) suggests that the organic and inorganic polymers are very compatible and promote a high degree of dispersion. Small domain size (Figure 7 SEM cross-section) keeps the light scattering to a minimum and will not cause film transmission loss after multiple-coatings.

5. CONCLUSION

Spin-on applicable inoganic-organic hybrid high refractive index polymer solutions that yield relatively thicker crack-free titanium dioxide films have been prepared. The organic-inorganic hybrid polymer solution is prepared by first reacting the titanium alkoxide (oligomers) with a chelating agent to convert the highly reactive tetra-coordinate titanium nucleus to a less reactive hexa-coordinate species. Then other components were added to the stabilized solution to further increase stability and boost film thickness when the solution was coated and cured.

The coating systems are prepared such a way that avoids the problems associated with nano-particle dispersions and sol-gel techniques. The solutions are stable up to 6 months at room temperature storage conditions and can be easily processed by a spin coat application onto a desired substrate. When the coatings were cured at an elevated temperature, the hybrid polymer coatings decompose to form a metal oxide–rich film that has a high refractive index. The films have refractive indices higher than 1.90 over the entire visible light region and thickness of about 350 nm resulting from a single coating application. Thicker films were achievable with multi-coating applications. Transmission spectra indicate that the films have greater than 90% internal transmission in the visible wavelengths, and SEM cross-section images show no apparent interface between layers in two or three consecutive coatings. The hybrid high refractive index coatings are stable upon exposure to both thermal and radiation.

6. REFERENCES

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