

Sulfur-Rich Polyimide/TiO₂ Hybrid Materials with a Tunable Refractive Index

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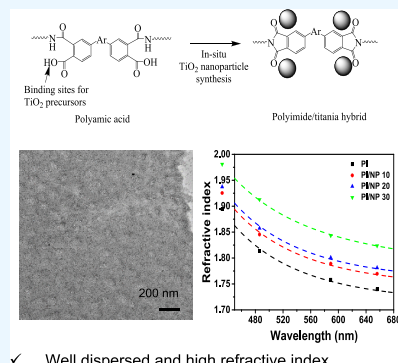
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ABSTRACT: High refractive index (RI) polyimide/titania nanoparticle hybrid materials were synthesized and characterized in this study. The polyimide synthesis took place via the conventional polycondensation process following the preparation of poly(amic acid), and the nanoparticles were incorporated using an *in situ* sol–gel process. Thin films of the polyimide/titania nanoparticle hybrids were prepared by optimizing the coating conditions using a spin coater. Thermal imidization of the nanoparticle containing poly(amic acid) films on Si wafers was completed in a temperature-controlled drying oven under a N₂ atmosphere. Fourier transform infrared spectroscopy revealed the successful formation of inorganic bonds as well as imide linkages, and transmission electron microscopy results show well-dispersed nanocrystalline TiO₂ nanoparticles of around 5 nm in the polymer matrix. Thorough optimization of the reaction time and concentration of TiO₂ precursors enabled to achieve a titania content as high as 30% (wt). The RI of the resultant hybrid materials was found to be tunable according to the titania content, while the RI increased linearly with increasing titania content. A homogeneous hybrid material with a very high RI of 1.84 at 589 nm was achieved in this work for 30% (wt) TiO₂.



INTRODUCTION

The study of organic/inorganic hybrid systems has been actively pursued for several decades and is an important research field as it results in the production of versatile materials with advanced features.^{1,2} Organic/inorganic hybrid materials are capable of exhibiting very high refractive indices, e.g., polyimide/silica hybrid films exhibit refractive indices in the range of 1.5–1.6 at 1319 nm,^{3–5} and polyimide/titania hybrid films exhibit refractive indices in the range of 1.5–1.9 at 633 nm.⁶ These typically find applications in image sensors, antireflective coatings, waveguides, etc. In optical applications, this strategy of incorporating nanoparticles into the polymer matrix is well-studied. The focus for the scientific community is to achieve higher refractive indices in organic–inorganic hybrid systems as compared to pristine polymers.^{7–10} For example, a study by Wang and co-workers showed that pristine PEK (poly(arylene ether ketone)) and PSF (poly(arylene ether sulfone)) exhibited a refractive index in the range of 1.60–1.62 whereas their hybrids with titania nanoparticles (70% by weight) showed an RI higher than 1.75.¹¹ Furthermore, to prepare applicable hybrid systems, there is a constant need for the optimization of several production parameters. For example, in optical applications, the nanoparticles must have a size with less than 40 nm diameter to avoid loss due to scattering from particles while maintaining the material's optical transparency.¹²

A number of polymer matrices are reported in the literature, which can be used to prepare polymer/TiO₂ hybrids, e.g.,

polysilsesquioxanes,^{13,14} polyimides,^{6,15} poly(methyl methacrylate), and poly(bisphenol A carbonate).¹⁶ These polymer–titania systems have been extensively studied with a focus on the influence of nanoparticles on various polymer properties. For example, incorporation of titania nanoparticles via *ex-situ* sol–gel synthesis and then using melt-compounding along with the PMMA matrix were found to enhance the thermal and mechanical properties of PMMA/titania hybrids.^{17,18} Another work demonstrated the use of 2-hydroxyethyl methacrylate as a coupling agent in the synthesis of sol–gel-derived organic–inorganic hybrid materials consisting of organic poly(methyl methacrylate) (PMMA) and inorganic titania. The refractive index in this case was found to increase from 1.515 to 1.550, measured at 633 nm, with increase in titania content from 20 to 60 wt %.¹⁹

Polyimides fall in the class of high-performance polymers and are associated with excellent thermal and mechanical properties.^{20–22} High refractive index organic pristine polymers are of special interest owing to their ease of processability and wide area coverage feature. Furthermore, pristine polymers

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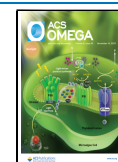


exhibit excellent transparency; however, their refractive indices are often inadequate. In this context, the incorporation of nanoparticles helps to enhance their optical properties.^{23,24}

TiO₂ nanoparticles are of special interest in optical applications by virtue of their high refractive index and very low absorption coefficient. TiO₂ exists predominantly in two different crystal structures, rutile and anatase, with refractive indices of 2.70 and 2.45, respectively, at 589 nm.²⁵ Therefore, the preparation of a hybrid system with TiO₂ nanoparticles is of special focus. There are different methodologies to incorporate nanoparticles in a polymer matrix, e.g., sol–gel pathways, use of bridged precursors, and hydrothermal synthesis.²⁶ Synthesis of hybrids using the *in situ* preparation of nanoparticles allows better dispersion and control of the nanoparticle size, as compared to physically blending the organic polymer and the inorganic nanoparticle, which depends on the extent of compatibility between the organic and inorganic phases.^{27–29}

The emphasis of this work is placed on the synthesis, structure–property relationship, and potential applications of the prepared organic/inorganic hybrid materials. The polyimide of choice is a novel sulfur containing high refractive index polyimide (PI) developed by our group, and it exhibited an RI more than 1.75 at 589 nm. The preparation of the nanoparticles followed *in situ* sol–gel formation of the inorganic titania nanoparticles in a polyimide matrix, which has the advantage of formation of extremely homogeneous particle size. The titania loading is maintained between 10 and 30 wt %, leading to the preparation of samples named PI/NP 10, PI/NP 20, and PI/NP 30. Furthermore, the refractive indices and optical dispersity achieved in this work are significantly higher than those of polyimide/titania nanoparticle hybrids reported in the literature at similar titania content.^{30,31}

EXPERIMENTAL SECTION

Materials. 4,4'-Oxydiphthalic dianhydride (ODPA) was bought from Aldrich, Germany, recrystallized from acetic acid, and heated at 150 °C before use. 4,4'-Thiodianiline, HCl (37%), titanium(IV) butoxide (Ti(OBu)₄), and butanol were purchased from Aldrich, Germany, and used as received. **DAm** (4,4'-((thiophene-2,5-diylbis(2-(trifluoromethyl)4,1-phenylene))bis(sulfanediy))dianiline) was prepared previously by our group using nucleophilic substitution reactions between 2,5-bis(4-fluoro-3-(trifluoromethyl)phenyl)-thiophene and 4-aminothiophenol using methodologies from the literature.³²

Instruments. A Vertex 80v (Bruker) instrument was used to measure Fourier-transform infrared (FTIR) spectra for the polyimide/hybrids with a Golden Gate Diamond ATR (attenuated total reflection) unit. Thermogravimetric analysis (TGA) of the polymers was carried out using a Thermobalance Q5000 (TA Instruments). A heating rate of 10 K/min was followed, and all of the experiments were performed under a N₂ atm with a mass flow of 50 mL/min. Differential scanning calorimetry (DSC) analysis for the polymers was carried out using a dynamic differential calorimeter Discovery DSC 2500 (TA Instruments). The heating rate was 10 K/min, and the experiments were performed in a nitrogen environment. AFM measurements of the hybrid films were done using a Dimension 3100 Nanoscopic IV (Digital Instruments Inc.) instrument in tapping mode. A Zeiss LSM 780 NLO microscope was used to take the light microscope images. For the preparation of homogeneous polyimide/hybrid films

on interference-enhanced Si substrates (IES) (1000 nm SiO₂ on Si, IHM TU Dresden) for ellipsometry,³³ a Polos wafer spinner was used with the following parameters: 3000 rotations for 1 min at an acceleration of 1000 rotations/min², for each sample. Ellipsometry data of spin-coated polyimide/hybrid films were recorded using a rotating compensator multi-wavelength ellipsometer M2000-UI (J.A. Woollam Co. Inc.) with a spectral range of 245–1690 nm at incidence angles of 65, 70, and 75°. For optical modeling, a box model of silicon, SiO₂, and polymer film with sharp interfaces was applied, using optical dispersions from the database for silicon and SiO₂ (CompleteEASE, J. A. Woollam Co., Inc.). The optical dispersion of the polymer films was modeled by one Tauc–Lorentz and one to two Gaussian oscillators with an isotropic model. Transmission electron microscopy (TEM) was performed in a Libra 120 microscope (Zeiss Microscopy Deutschland GmbH, Oberkochen, Germany). For plan view, the thin film of PI/NP 10 on silicon wafer was coated by 20 nm amorphous carbon film in an SDC500 coater (Leica Microsystems GmbH, Wetzlar, Germany) and floated off the silicon wafer in 1 M NaOH, transferred to a TEM grid, and washed for 10 s in deionized water. The cross section of the PI/NP 10 thin film on a silicon wafer was prepared by *in situ* lift-out microsampling using a NEON40 (Zeiss Microscopy Deutschland GmbH, Oberkochen, Germany) scanning electron microscope with integrated focused ion beam (SEM/FIB).

Synthesis of Polyimide/TiO₂ Hybrids and Thin-Film Preparation. A typical synthesis procedure for PI/NP 10 is explained as follows: 0.380 g **DAm** (0.92 mmol), 0.200 g 4,4'-thiodianiline (0.61 mmol), and 0.476 g ODPa (1.54 mmol) were taken together in a round-bottom flask, to which 30 mL of DMF was added and the reaction was left to stir at room temperature. After 0.5 h, there was a significant increase in the viscosity of the reaction mixture, indicating the formation of poly(amic acid) (PAA). The stirring was continued for another 3 h, after which 0.190 mL of HCl was added dropwise to the PAA. This was then left to stir for another 0.5 h under the same conditions. Then, a mixture of 0.474 mL Ti(OBu)₄ and 0.412 mL butanol was added dropwise to the reaction mixture and allowed to stir for an additional 0.5 h. Finally, a fraction of the resulting precursor solution for PI/NP 10 was passed through a 0.45 μm PTFE filter to a clean and dried Petri dish at 80 °C to prepare a bulk hybrid sample. For thermal imidization, the following temperature protocol was maintained: the Petri dish was at first held at 80 °C overnight, followed by maintaining it at 100, 120, 150, 180, 200, 220, and 250 °C for 1 h each in air. The temperature of the oven was then adjusted to 150 °C overnight under vacuum. After this curing process, all the polyimide/TiO₂ hybrid samples were obtained as brittle films, in contrast to the pristine polyimide, PI, which could be lifted off from the Petri dish and was obtained as a free-standing polymer film.³⁴ To prepare thin films, the precursor was diluted with DMF to make the resulting concentration of 20% (w/v). It was then passed through a 0.45 μm PTFE filter, spin-coated on IES wafers, and then subjected to thermal curing via the same temperature protocol as detailed above. The reaction composition of all the samples is summarized in Table 1, and the synthesis scheme is shown in Scheme 1.

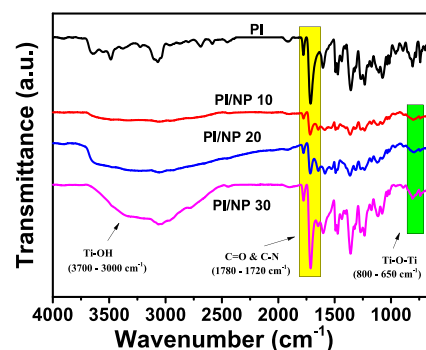
Table 1. Reaction Composition of the Pristine Polyimide and Polyimide/Titania Hybrid Samples

Entry	reactant composition (wt %)		TiO ₂ content (wt %)
	PI	Ti(OBu) ₄	
PI	100	0	0
PI/NP 10	67.8	32.2	10
PI/NP 20	48.4	51.6	20
PI/NP 30	37.4	64.6	30

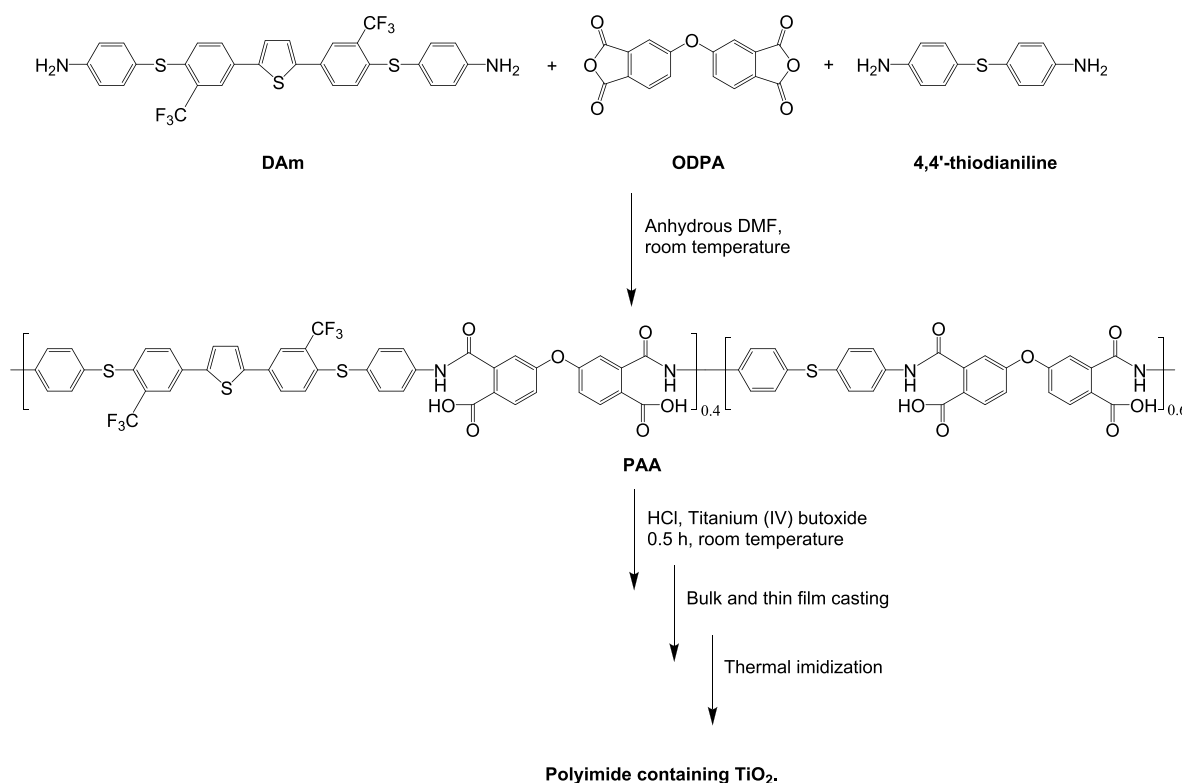
RESULTS AND DISCUSSION

Synthesis of the Pristine Polyimide and Polyimide/TiO₂ Hybrids. To ensure the preparation of well-dispersed nanoparticles, an *in situ* sol-gel synthesis of nanoparticles was performed. First, polyamic acid (PAA) was prepared as described before,³⁴ and then Ti(OBu)₄ a TiO₂ precursor was added to the PAA solution and stirred for 0.5 h at room temperature (Scheme 1). To prepare TiO₂ particles with a rutile crystal structure, HCl was used with Ti(OBu)₄ as the nanoparticle precursor. This work reports the preparation of a polyimide/TiO₂ hybrid without the use of a coupling agent. This limited the dispersion of titania to 30% (wt). On further increasing the titania content, gelation could be seen in the precursor formulation. This is attributed to the formation of cross-linking between PAA and titanium butoxide. The carboxylic acids in the PAA probably serve as binding sites for the titania precursor,³⁵ leading to the formation of a homogeneous hybrid material after thermal imidization of the PAA. The incorporation of the TiO₂ nanoparticles in the polyimide resulted in an insoluble, brittle hybrid material, which could not be prepared as a free-standing film, in contrast to the pristine polyimide PI.

The resulting polyimide/TiO₂ hybrids were characterized with the help of FTIR spectra (Figure 1). The presence of

**Figure 1.** FTIR spectra of pristine polyimide, PI, and polyimide/TiO₂ hybrids.

typical peaks at 1780 cm⁻¹ (asym. C=O str.), 1720 cm⁻¹ (sym. C=O str.), 1385 cm⁻¹ (C-N), and 1253 cm⁻¹ (C-F) demonstrates the formation of the imide linkages during thermal imidization.²¹ Also, the characteristic bands at 800–650 cm⁻¹ indicate the presence of the Ti–O–Ti band for the polyimide/titania hybrids.⁶ Additionally, the absorption peaks around 3700–3000 cm⁻¹ correspond to the hydroxyl groups of TiO₂ crystalline, which is not present in the pristine PI film. The intensity of the bands at 3400 cm⁻¹ increases with an increase in the titania content. This is attributed to the hydrolysis of Ti(OBu)₄. This broad absorption band could also be a result of the incomplete imidization in the presence of titania, which induces a competition between ring closure to form imide and chelation between COO groups and Ti atoms. However, the chelating ligands can be removed if the

Scheme 1. Steps Involved in the Synthesis of Polyimide/TiO₂ Hybrids

imidization process is carried out above 350 °C in the presence of titania nanoparticles. The presence of less intense peaks at 1530 cm^{-1} in case of the nano hybrids probably hints toward the presence of COO (asymmetric) bidentate chelation.³⁶

Thermal Properties of the Pristine Polyimide and Polyimide/TiO₂ Hybrids. The TGA curves of the pristine polyimide and organic/TiO₂ hybrid samples are shown in Figure 2a. A heating rate of 10 °C/min until 800 °C was

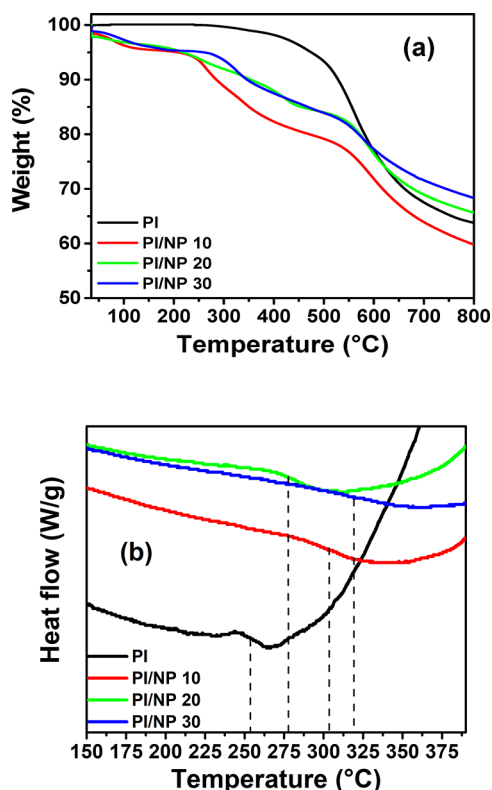


Figure 2. (a) TGA thermograms and (b) DSC plots of pristine polyimide and polyimide/TiO₂ hybrids.

maintained under a nitrogen atmosphere. The weight loss followed three stages, at temperatures below 150 °C, between 150 and 400 °C, and between 400 and 800 °C. The initial weight loss in case of the hybrids is attributed to a loss of water and remaining solvent in the hybrid films, followed by elimination of carbon, hydrogen, and oxygen in the polyimide, and beyond 400 °C, the loss is attributed to the further combustion of the remaining organic residues.³⁷ The char yields were found to increase with an increase in the filler loading with the highest char yield of 68% (wt) obtained for PI/NP 30. The samples containing titania nanoparticles show a much lower decomposition temperature as compared to the pristine polymer. This decrease in thermal stability on the incorporation of titania nanoparticles may be attributed to the incomplete imidization and subsequent chelation of carboxylic groups with titanium moieties.³⁵ The 5% degradation temperature and glass transition temperatures are recorded in Table 2. Figure 2b shows the DSC plots of the pristine polyimide and prepared hybrids. As compared with the pristine polymer, the hybrid samples show a higher glass transition temperature (T_g), indicating an increased chain stiffness in the samples with an increasing titania content. This is attributed to the increased cross-linking arising from the titanium oxide.^{38–40}

Table 2. Refractive Indices, Roughness Data, and Abbe Number of PI/NP X Hybrids

Entry	TiO ₂ wt %	$T_{45\%}$ (°C)	T_g (°C)	T_{589}^a (%)	RI	Abbe number	reference
PI	0	480	260	81	1.757	10	³⁴
PI/NP 10	10	210	300	100	1.785	12	this study
PI/NP 20	20	220	275	99	1.801	11	this study
PI/NP 30	30	260	305	99	1.843	12	this study

^aRefractive index measured at 589 nm with a maximum error of ± 0.002 .

Morphology of the Pristine Polyimide and Polyimide/TiO₂ Hybrid Thin Films. The formation of homogeneous thin films that are free of cracks and pinholes is of utmost importance for a material to be applied in the field of flexible electronics, such as LEDs, solar cells, and printed biosensors. The preparation of polyimide/TiO₂ thin films on silicon wafers required special optimization of spin-coating protocols, for example, concentration of the PAA with titania, the rpm of the Si wafers, and the temperature protocol for completion of imidization. The thickness of the thin films was maintained between 30 and 50 nm. The morphology of hybrid thin films was investigated using AFM. The AFM height images for PI and the hybrids are given in Figure 3. For PI, PI/NP 10, and PI/NP 20, the surface roughness (R_a) was found to be 0.32, 0.64, 2.66, and 5.89 nm, respectively, and the root-mean-square roughness (R_q) was found to be 0.41, 0.91, 3.24, and 7.23 nm. The variation of R_a and R_q with titania content is shown in Figure 4. As the wt % of the nanoparticles in the polymer matrix was increased, the homogeneity of the film surface decreased with a possibility of agglomeration; however, because of *in situ* preparation of the nanoparticles, a well-dispersed hybrid material was obtained without large agglomeration of TiO₂. Furthermore, the roughness values of the hybrid sample PI/NP 10 are within the acceptable range for applications in optoelectronic devices.^{41,42}

Figure 5 shows the TEM image of the hybrid material PI/NP 10 (plane view and cross-sectional view). The images show that the TiO₂ nanoparticles are well dispersed within the polymer matrix, forming an island structure with approximately 100 nm large islands. The average nanoparticle size is around 5 nm. Although the nanoparticles are hardly visible in the cross-sectional view (in the cross-sectional measurement, the electron beam crosses about ~ 150 nm of the sample coming from the side compared to ~ 35 nm thickness of the plan view specimen), the lack of any profound contrast hints to the fact that the nanoparticles are uniformly distributed in the vertical direction. We could not detect the island structure in the cross section, which we attribute to the projection effect (3D distribution of nanoparticles in ~ 150 nm thick FIB lamella is projected into a 2D image).

Optical Properties of the Pristine Polyimide and Polyimide/TiO₂ Hybrid Thin Films. It was found that the incorporation of the nanoparticles in the polyimide matrix led to an increase in the refractive index of the PI/NP thin films as compared with the pristine polymer because of the high molar refraction of titania (Figure 6). As the filler loading increased, likewise the refractive index also increased.

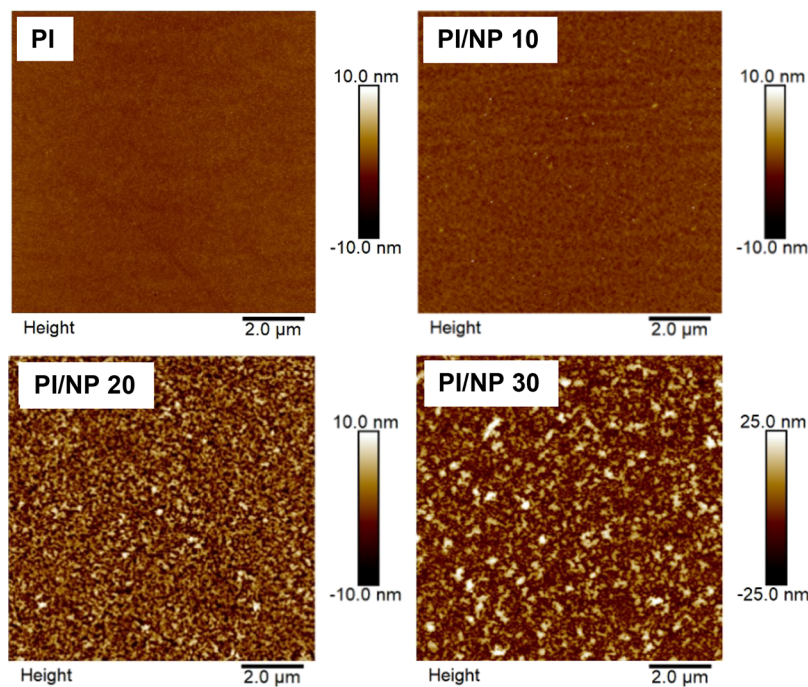


Figure 3. AFM height images of pristine polyimide and polyimide/TiO₂ hybrids.

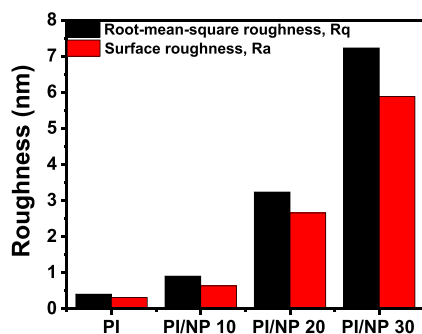


Figure 4. Plot of thin-film roughness versus titania content.

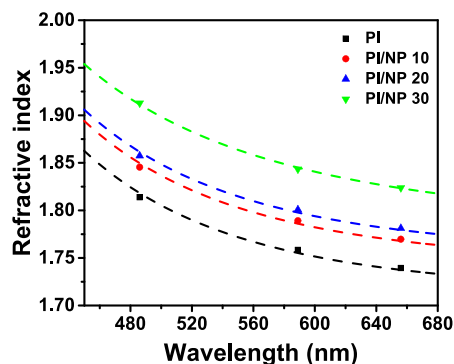


Figure 6. Wavelength-dependent refractive index of PI films and PI/NP X hybrid films modeled from ellipsometry data. Refractive indices used for calculation of the Abbe numbers are shown individually.

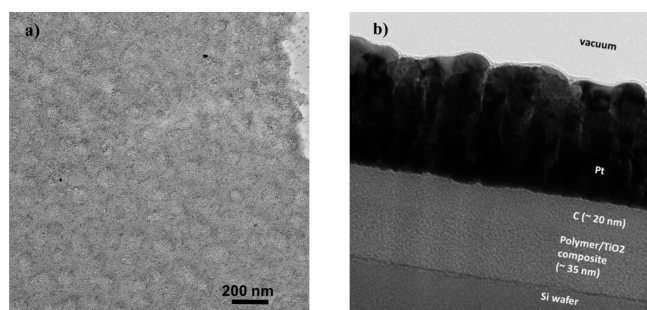


Figure 5. TEM image of PI/NP 10, (a) plan view and (b) cross-sectional view (image intentionally defocused).

The refractive index values are reported in Table 2 for the polymer/TiO₂ nanoparticle hybrids coated on IES wafers. At approximately 20 wt % of nanoparticles, previously reported polyimide/nanoparticle hybrid exhibited RI in the range of 1.68 and 1.75 at 589 nm; however, in this work, we were able to achieve RI of around 1.80 at similar titania contents.^{30,31} The hybrid films were found to exhibit Abbe numbers (ν_D) slightly higher than ν_D of pristine polyimide, PI, and significantly higher than ν_D of the other pristine polymers

previously synthesized.⁴³ The Abbe number was calculated as $\nu_D = (n_D - 1)/(n_F - n_C)$, where n_C , n_D , and n_F are the respective RI of any material at 656.3, 589.3, and 486.1 nm (Fraunhofer C, D, and F spectral lines, respectively). The Abbe number quantifies the degree of dispersion of the material and is an important property in optical applications. However, due to the trade-off tendency between ν_D and n_D , achieving materials with high RI as well as high Abbe number is often a challenge. The hybrid samples prepared in this work exhibited ν_D values in a range similar to those of previously reported polyimide/nanocrystalline-titania hybrid optical materials.⁴⁴

Figure 7 shows the variation of refractive index, RI, and extinction coefficient, k , as obtained from the average of the model fits of ellipsometric data of three thin-film samples on silicon wafer for the nanohybrid named PI/NP 30 with 30 wt % of TiO₂. A near-zero k value denotes that the material shows little to no absorbance in the particular wavelength region (420–1700 nm). This can be quantified using the following

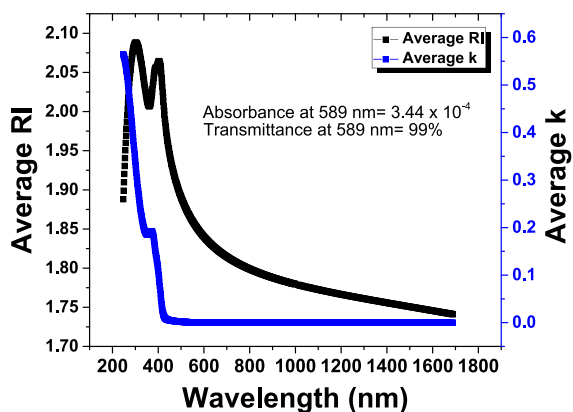


Figure 7. Plot of average of refractive index RI and extinction coefficient k vs wavelength for PI/NP 30.

equation from the theory of absorption and extinction coefficients,

Absorbance, $A = \frac{4 \times \pi \times k}{\lambda} \times z$, where z and λ are thickness and wavelength in nm, respectively.

Using the above equation, the transmittance (T%) for a 45 nm PI/NP30 film is 99.9% at 589 nm. The value of transmittance as obtained for a free-standing film of pristine polymer PI with $\sim 10 \mu\text{m}$ thickness, as reported previously, was 81% at 589 nm.³⁴ A conversion of the calculated absorbance of the nm thin film in this study to the μm range would indicate a theoretical transmittance of 92% of a $10 \mu\text{m}$ -thick PI/NP 30 film. Thus, it can be concluded that the incorporation of titania nanoparticles does not affect the transmittance of the final hybrid polymer film. Please note that it was not possible to measure transmittance directly by UV-vis spectroscopy of the in situ formed thin hybrid films prepared for ellipsometry on silicon wafers.

CONCLUSIONS

This work demonstrated the successful preparation of organic/titania hybrids, with loading different weight percents of TiO_2 nanoparticles by an *in situ* sol-gel process. The use of a novel polyimide with inherent high RI as the polymer matrix is demonstrated. The TiO_2 nanoparticles were formed during the preparation of PAA from its precursor. The *in situ* preparation resulted in avoiding agglomeration at a higher titania content. AFM and TEM results concluded that the nanoparticles were well dispersed in the polyimide matrix. Also, the filler loading had a positive influence on the thermal stability of the hybrids. Optimizing conditions, the polyimide/ TiO_2 samples were successfully coated as thin films over Si wafers with uniform thickness and homogeneity. By ellipsometry, it was found that the refractive index of the thin films was increased with increasing titania content; i.e., the hybrid with the highest filler loading was found to exhibit the highest RI of 1.84 at 589 nm. The hybrid samples had better optical dispersion than that of the pristine polyimide and comparable to previously reported values, and the samples retained high transparency in the visible range. For instance, the sample labeled PI/NP 10 exhibited an RI more than 1.79 at 589 nm, an Abbe number of about 12, and a thin-film surface roughness within 1 nm. These values make it a potential candidate for a number of optical applications, such as the application of OLED encapsulants and antireflective coatings.

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Author Contributions

K.M., S.B., and B.V. contributed to the design and implementation of the research. E.B. contributed data and analysis tools for ellipsometry. K.M. collected the data, performed the analysis, and wrote the paper with inputs from all authors.

Notes

The authors declare no competing financial interest.

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