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Triethylene glycol-titanium oxide hydrate hybrid films with high refractive index and surface evenness

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We have evaluated high refractive organic-inorganic hybrid films fabricated from a solution prepared from triethylene glycol and titanium (IV) butoxide in N, N-dimethyl acetamide (DMAC). The organic-inorganic hybrid solution in DMAC is homogenous and stable. The solution was spin-coated on a silicon wafer and a glass plate and dried under nitrogen to give a transparent film. The refractive index (n), transparency, and thickness of the hybrid films fabricated from the solution was varied with the film drying condition and feeding mole ratio between the organic and inorganic compounds. The film drying condition was observed to have strong influence on the surface evenness of the films. The refractive indices of the films were between 1.62 and 2.16 at a wavelength of ca. 600 nm. Scanning electron microscope (SEM) and atomic force microscope (AFM) results showed that the films were very smooth and that the root-mean-square values (R_a) of the surface roughness of the films were between 0.25 and 2.37 nm depending on the film drying condition. n and R_a of the hybrid film were 2.06 and 0.25 nm, respectively, when it was annealed at 250 °C. The film transparency and thickness increased with decreasing the annealing temperature. We identify our organic-inorganic hybrid solutions as possible good candidate materials for the films with high refractive index and surface evenness.

Introduction

High refractive index (n) materials and their films have been recently spotlighted due to their potential applications for organic light emitting diode (OLED) display, OLED and LED lightings, antireflective coatings, and microlens components.¹ For example, a transparent film with higher refractive index than that of indium tin oxide (ITO) is essential to effectively extract light in OLED lighting and display applications. ITO is transparent in a visible region and dominantly used for an anode of the OLED devices. The planarization films have been used for covering a corrugation structure which is between glass and ITO layers. The corrugation structure is a scattering source with which the confined light can be extracted from the ITO layer to the glass substrate, leading to improved efficiency.² In order to facilitate the light toward the corrugated structure, it is desirable to have a film which bear higher refractive index than that of ITO. If the refractive index of the film is lower than that of ITO, the generated light is more trapped between the ITO and electro-luminescent layers.^{2a,3} The light extraction technology for the OLED lighting and display

panels contributes not only to enhanced luminance but also to energy saving.

The high refractive index films have to be transparent in a visible region and to be flat. Additionally, they have to be fabricated under a mild annealing condition (< 250 °C) for flexible light and display applications. Organic polymer films are somewhat suitable for the purpose. Polymer films are generally transparent, smooth, and thermo-stable, as well. However, the refractive index of general-purpose polymer films is around 1.5 in a visible region, which is much lower than that of the ITO ($n \sim 1.9$). It is well known that the refractive indices of aromatic, halogen, and sulfur-rich polymers increase over ca. 1.7 due to high electron density of the moieties.⁴ It is not easy to obtain the organic polymer films over 1.80 of a refractive index because of their large free volume in comparison of inorganic films.⁵ Only in terms of the refractive index, inorganic materials such as titanium dioxide (TiO_2 , $n \sim 2.6$), zirconium dioxide (ZrO_2 , $n \sim 2.0$), zinc sulfide (ZnS , $n \sim 2.4$), and zinc oxide (ZnO , $n \sim 2.0$) are much better than the organic polymers.⁶ However, since the inorganic films can be obtained by chemical vacuum deposition at extremely high temperature

or by coating an inorganic nano powder-dispersed solution in water or alcohol, the film thickness is several tens of nanometers.⁷ Inorganic nano particles may be mechanically introduced into the polymers to increase the refractive index of the films. However, the feeding content of the nano particles are low because the particles are easily aggregated together in the polymer matrix, calling for special surface modification to achieve dispersion.⁸ Therefore, the refractive index of the composite films prepared by mechanical mixing is usually rather lower than expected. In addition, the polymer must be soluble in water and alcohol because the nano particles are dispersed in those media. To overcome this limitation, the inorganic particles are tried to be complexed with organic compounds. The inorganic materials have transition metals with inorganic or organic ligands which can covalently and coordinatively be linked to various anchors such as hydroxyl and carboxylic acid groups.⁹ The content of the inorganic compound largely increase in the composites due to the covalent and coordinative bond which resulted in a good miscibility between the organic and inorganic compounds.

TiO₂ has been generally used as a filler material to increase thermal stability or refractive index of polymers.¹⁰ TiO₂ particles have been generally produced from the related titanium oxide hydrates as precursors by a condensation reaction between hydroxyl groups of a hydrolyzed titanium precursor. Titanium oxide hydrates have partially hydroxyl groups and the condensation reaction occurs by addition of base or heat treatment.^{6b,11} Water is released in the reaction process. Also, the titanium oxide hydrates are soluble in acidic solvent media due to the hydroxyl groups. Titanium oxide hydrates can be synthesized from their precursors such as titanium (IV) ethoxide, titanium (IV) propoxide, titanium (IV) butoxide, and titanium (IV) chloride, *etc.* in aqueous and alcoholic media. In this case, nano-sized titanium oxide hydrates are dispersed in the media and the solution is slightly opaque. TiO₂ films are obtained from the titanium oxide hydrate dispersed solution by spin-coating or solvent-casting the solution and sintering the titanium oxide hydrate particle layer at high temperature.¹² The film is very thin, uneven, and brittle because a solid content of titanium oxide hydrate in the media is low (< 10~20 w.t. %) and the film is crystallized during sintering.¹³ The sintering process has been carried out at very high temperature (> 400 °C).

It has been reported that the titanium oxide hydrates are synthesized in a polymer solution by introducing the precursors into the solution, which results in an organic-inorganic hybridization.¹⁴ The polymer-titanium oxide hydrate hybrid films fabricated from the hybrid solution show comparatively high refractive indices. However, colour of the films changes to yellow because the polymer of the hybrid films is thermally degraded during annealing at high temperature. Also, the refractive indices of the hybrid films are lower than those of TiO₂ films due to the organic polymer remaining in the films. On the other hand, M. Russo et al. reported that poly (vinyl alcohol) (PVA)-titanium oxide hydrate hybrid films showed high refractive index over 2.0 at a wavelength of 550 nm even

when they were annealed below 250 °C.^{14e} The hybrid films were transparent in a visible region, as well. In this case, the hydroxyl groups in PVA were acted as functional groups which can be reacted with the titanium oxide hydrates. It is expected that low molecular weight multiol compounds would be reacted with titanium oxide hydrates as PVA was done. If the small molecules are liquid and remain unreacted in the hybrid solution, they could be easily eliminated during drying and annealing the hybrid films. Then, the content of unreacted hydroxyl groups in the hybrid films could be substantially decreased and the side effect of unreacted organic compound on mechanical, thermal, and optical properties of the hybrid films might be lessened.

In our study, a liquid type of organic compound which can be easily evaporated around annealing temperature is used for preparing organic-inorganic hybrid films with high refractive index and transparency in the visible region. The organic-inorganic hybrid solution was prepared from triethylene glycol and titanium (IV) butoxide in N, N-dimethyl acetamide (DMAc). It is anticipated that the reaction between hydroxyl groups of triethylene glycol and of the hydrolyzed titanium (IV) butoxide in DMAc occurs, resulting in an organic-inorganic hybrid solution. The unreacted triethylene glycol can be easily removed even at comparatively low annealing temperature. The flexible diol compound chemically connected to the titanium oxide hydrates hinders the progress of crystallization of the hybrid films when they are annealed. It is also expected that the titanium oxide hydrates are more soluble and stable in DMAc because of the hydrogen bonding between the carbonyl groups of DMAc and the hydroxyl groups of titanium oxide hydrates. Therefore, in our system, organic-inorganic hybrid films with high refractive index and surface evenness can be obtained from the stable titanium oxide hydrates hybrid solution even at low annealing temperature. We discussed the possibility of using the hybrid solution as candidate materials for a high refractive index films. The optical and physical properties of the hybrid films prepared from the solution were also studied.

Experimental

Materials

Diol compounds such as diethylene glycol, triethylene glycol (1), and tetraethylene glycol and titanium (IV) butoxide (2) were purchased from Tokyo Chemical Industry Co., Ltd. N, N-dimethyl acetamide (DMAc) and a 37 % hydrochloric acid solution in water were purchased from Aldrich Chemical Co., Inc. All reagents were used as received.

Synthesis of triethylene glycol-titanium oxide hydrate hybrid solution and film preparation from the solution

After triethylene glycol and titanium (IV) butoxide were dissolved in DMAc under nitrogen, a 37 % hydrochloric acid (HCl) solution in water was dropwise added into the DMAc solution with stirring. Total concentration of triethylene glycol and titanium (IV) butoxide was always adjusted to 40 w.t. %

and mole ratio between $[H^+]$ and $[Ti]$ was 1.5. Feeding mole ratio between triethylene glycol and titanium (IV) butoxide was intentionally changed to 2/1, 1/2, and 1/4, respectively. For example, 0.22 g of triethylene glycol, 2.0 g of titanium (IV) butoxide, 0.87 mL of 37 % HCl solution, and 3.6 mL of DMAc were used respectively for preparation of the hybrid solution from triethylene glycol and titanium (IV) butoxide with 1/4 of the feeding mole ratio. The reaction was carried out for 1 day at room temperature. Several hours after the hybrid solution was filtered with a 0.2 μm Teflon filter, it was spin-coated on a silicon wafer or a glass plate at ca. 3000 rpm for 30 s. The films were thermally annealed at various temperatures under nitrogen for 2 h. The film thickness was ca. 90–290 nm depending on the annealing temperature and feeding mole ratio between triethylene glycol and titanium (IV) butoxide.

Measurements

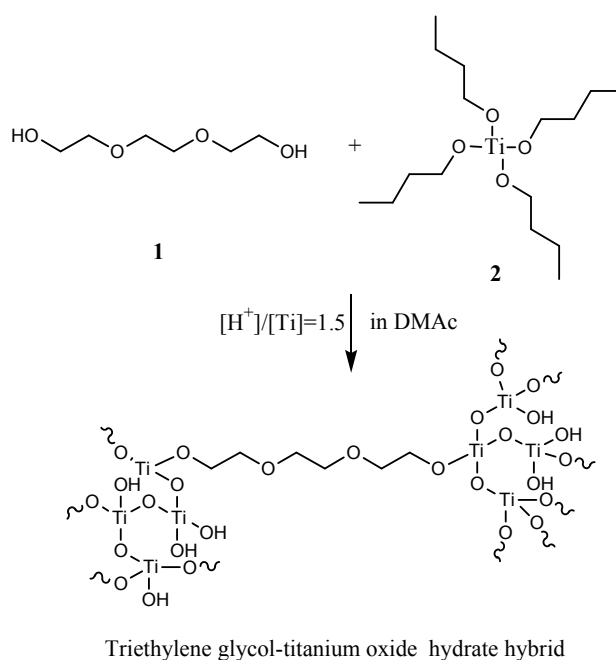
Infrared (IR) and UV-vis spectra were recorded with a Nicolet 6700 FT-IR spectrometer and a Hitachi U-3501 spectrometer, respectively. The isothermal behaviour of diol compounds was monitored by thermogravimetry (TG) using a TA Instruments TGA Q50 under nitrogen at 150 $^{\circ}C$. The hybrid solution viscosity was measured at 25 $^{\circ}C$ by an AND SV-1A viscometer. Scanning electron and atomic force micrographs were obtained on an FEI Sirion scanning electron microscope and a PSIA XE-100 atomic force microscope, respectively. The film crystal structure was examined with a Rigaku RU-200BH X-ray diffraction analyser. The hybrid film surface was atomically analyzed with a Kratos Axis Nova XPS analyzer. The refractive indices and thicknesses of the films were measured using a J. A. Woollam M-2000V and EC-400 spectroscopic ellipsometer. Cauchy dispersion relation was applied to three layer model consisting of air, film, and silicon substrate. *WVASE32*[®] software was used for data analyses.

Results and discussion

Synthesis of triethylene glycol-titanium oxide hydrate hybrid solution and film preparation from the solution

We prepared the organic-inorganic hybrid solution by using triethylene glycol and titanium (IV) butoxide in DMAc. Titanium oxide hydrates as precursors of TiO_2 are prepared from titanium (IV) butoxide and diol compounds can be reacted with the titanium oxide hydrates. The condensation reaction between hydroxyl groups of the diol compounds and of the titanium oxide hydrates during the sol-gel reaction gives the organic-inorganic hybrid solution. It is desirable to remove the unreacted diol compounds to increase the refractive index of the film. Also, introduction of several ether linkages into the titanium oxide hydrate can relieve brittleness of the film and suppress crystallization of the film. From this view, a liquid type of diol compound containing the ether linkage is more suitable for those purposes. Triethylene glycol was used as the diol compound for preparing the hybrid solution because it has comparatively low boiling temperature and multiple ether

linkages. The unreacted organic compounds in the fabricated film can be easily removed during annealing the film at comparatively low temperature. Diethylene glycol has lower boiling point, but one less ether linkage than triethylene glycol. Tetraethylene glycol has one more ether linkage than triethylene glycol, but higher boiling point. Even though diethylene glycol and triethylene glycol are completely removed within 1 h at 150 $^{\circ}C$ under nitrogen, tetraethylene glycol still remains even after 2 h (Fig. S1, ESI[†]). Titanium oxide hydrates have been conventionally synthesized in water or alcohol under acidic or basic condition. Nano-sized titanium oxide hydrates dispersed in basic media can be precipitated due to their condensation reaction. In acidic media, due to the formation of the hydrogen bonding between the carbonyl groups of DMAc and the hydroxyl groups of titanium oxide hydrates, the titanium oxide hydrates are more soluble and stable in DMAc than in water or alcohol.^{9,15}



Scheme 1 An Idealized reaction for preparation of triethylene glycol-titanium oxide hydrate hybrid solution.

As shown in Scheme 1, the sol-gel reaction of triethylene glycol with titanium (IV) butoxide was carried out under acidic condition. It shows an idealized reaction. Actually, the hybrid solution contains water, triethylene glycol, partially hydrolyzed titanium (IV) butoxide, titanium oxide hydrate, and 1-butanol, a side product of the sol-gel reaction, *etc.* in addition to the triethylene glycol-titanium oxide hydrate hybrid material. Under this acidic condition, condensation reaction between hydroxyl groups in the partially hydrolyzed titanium (IV) butoxide is slow, but hydrolysis reaction of alkoxide groups in the precursor is fast.¹⁶ 37 % Hydrochloric acid solution in water was used as a catalyst. Water is necessary for the hydrolysis reaction of alkoxide groups. If mole ratio between $[H^+]$ and $[Ti]$ is set at 1.5 by using 37 % hydrochloric acid solution in water,

mole ratio between [H₂O] and [Ti] is ca. 5.2. Therefore, in this case, extra addition of water is not needed for completeness of the hydrolysis reaction of butoxide group in the precursor. The solutions prepared from triethylene glycol and titanium (IV) butoxide are homogenous, transparent, and slightly greenish (Fig. S2, ESI†). The solution was more colourless with introducing more triethylene glycol. Viscosity of the solution slightly increased from 11.5 to 12.6 cP with changing the feeding mole ratio between the diol compound and the precursor from 2/1 to 1/4.

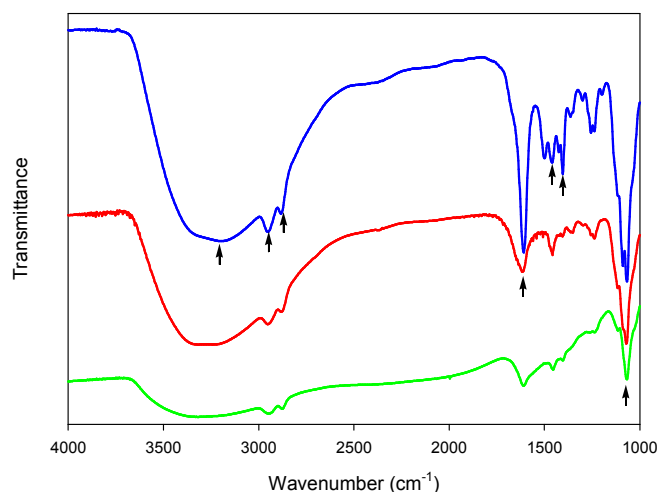


Fig. 1 IR spectra of the organic-inorganic hybrid films fabricated from the hybrid solution prepared from triethylene glycol and titanium (IV) butoxide with 1/2 of the feeding mole ratio and annealed at various temperatures for 2h: 150 °C (—); 200 °C (—); 250 °C (—).

The hybrid solution was spin-coated at a speed of 3000 rpm. The spin-coated film was annealed over 150 °C. IR spectra of the organic-inorganic hybrid films fabricated from the solution prepared from triethylene glycol and titanium (IV) butoxide with 1/2 of the feeding mole ratio and annealed at various temperatures are shown in Fig. 1. The film was spin cast on a NaCl window with the hybrid solution and annealed at various temperatures for 2 h under nitrogen. The NaCl window has almost no absorption between 1000 and 4000 cm⁻¹ (Fig. S3, ESI†). IR spectra of DMAc and triethylene glycol coated on the window were also obtained for reference as shown in Fig. S3, ESI†. Because DMAc is inherently hygroscopic, the characteristic absorption near 3470 cm⁻¹ is due to O-H stretching vibration of water in DMAc. The absorption peak of hydrogen bonded O-H is broader and shifted to lower frequency than that of free O-H.¹⁷ The absorption peak at 1633 cm⁻¹ is due to the carbonyl groups in the IR spectrum of DMAc. The absorption peak of carbonyl group is also shifted to lower frequency when it is hydrogen bonded because the C=O bond is weakened. Triethylene glycol has two absorption peaks at 2920 and 2875 cm⁻¹ due to two methylene groups chemically connected to hydroxyl and ether groups, respectively.

As shown in Fig. 1, the characteristic broad absorption near 3200 cm⁻¹ is due to the unreacted hydroxyl groups of water, triethylene glycol, the hydrolyzed titanium (IV) butoxide, titanium oxide hydrate, the sol-gel hybrid material, and 1-butanol, *etc.* The absorption peak at ca. 1609 cm⁻¹ is due to the carbonyl groups of DMAc. The peak may come from TiO₂, as well.¹⁸ The intensity of absorption peak at 1609 cm⁻¹ decreased with an increase in temperature over 150 °C due to removal of DMAc. Since DMAc cannot be easily eliminated even over the boiling temperature (ca. 165 °C at the pressure of the atmosphere) under the strongly hydrogen-bonded complexation condition,¹⁹ the absorption peak of the film annealed at 200 °C is mainly due to the complexed DMAc and titanium oxide hydrate. The free DMAc would be completely removed at this temperature. The peak at near 1609 cm⁻¹ of the film annealed at 250 °C mainly comes from titanium oxide hydrate.¹⁸ The complexed DMAc would be removed at this temperature. The hydroxyl groups still remained when the film was annealed at 250 °C. It is mainly due to hydroxyl groups of titanium oxide hydrates. The absorption peaks at 2951 and 2883 cm⁻¹ are due to the C-H stretching vibration of methyl and methylene groups of the triethylene glycol, unhydrolyzed butoxide groups of titanium oxide hydrates, the sol-gel hybrid materials, 1-butanol, and DMAc. The absorption peaks at 1459 and 1404 cm⁻¹ are assigned to the C-H bending vibration of the methylene and methyl groups, respectively. The absorption peaks at 2951, 2883, 1459, and 1404 cm⁻¹ slightly remained when the film was annealed at 250 °C, meaning that the absorption peaks were mainly due to the methylene and methyl groups of the reacted triethylene glycol, unhydrolyzed butoxide groups of titanium oxide hydrates, and the sol-gel hybrid materials. The unreacted triethylene glycol, 1-Butanol, DMAc are evaporated at that temperature. The absorption peak at 1068 cm⁻¹ is due to the C-O stretching vibration of the triethylene glycol and unhydrolyzed butoxide groups of the titanium oxide hydrates and the sol-gel hybrid materials.

Optical properties of the hybrid films

Variation of refractive indices and transmittances of the films on the feeding mole ratio between triethylene glycol and titanium (IV) butoxide and on annealing temperature is shown in Fig. 2. Refractive indices of the films increased with increasing the content of titanium (IV) butoxide and annealing temperature. Similar results have been observed in the previous report on hybrid materials of PVA and titanium oxide hydrates.^{14e} Since titanium (IV) butoxide is a precursor which can be chemically converted to titanium oxide hydrate after the sol-gel reaction, an increase in the content of titanium (IV) butoxide corresponds to an increase in the refractive index of the films. At low annealing temperature the refractive indices of hybrid films were relatively low. This is attributed to the low degree of densification and residual unreacted triethylene glycol. The refractive indices of the films remarkably increased when the films was annealed at 250 °C because the unreacted triethylene glycol and DMAc were completely removed near this temperature. In addition, a TiO₂ domain can grow at this

temperature because titanium oxide hydrate can convert to the related TiO_2 by thermal treatment. The domain can be effectively contributed to an increase in the refractive index of the films. The more triethylene glycol is introduced in the reaction, the more triethylene glycol is reacted with the hydroxyl groups of titanium oxide hydrate and hydrolyzed titanium (IV) butoxide. Therefore, the refractive indices of the films were not quite high when the triethylene glycol-rich film was annealed at 250 °C.

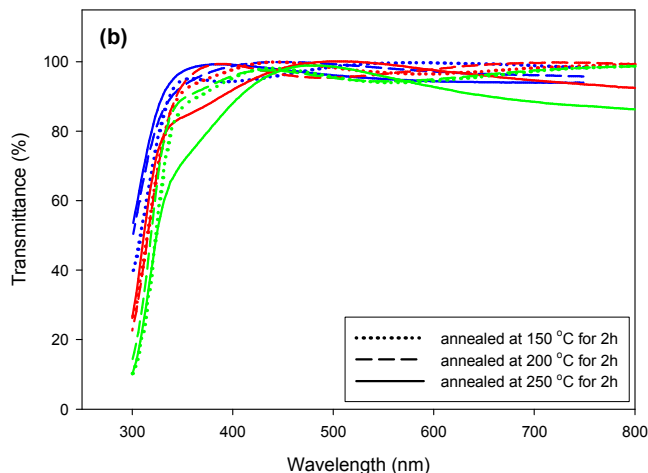
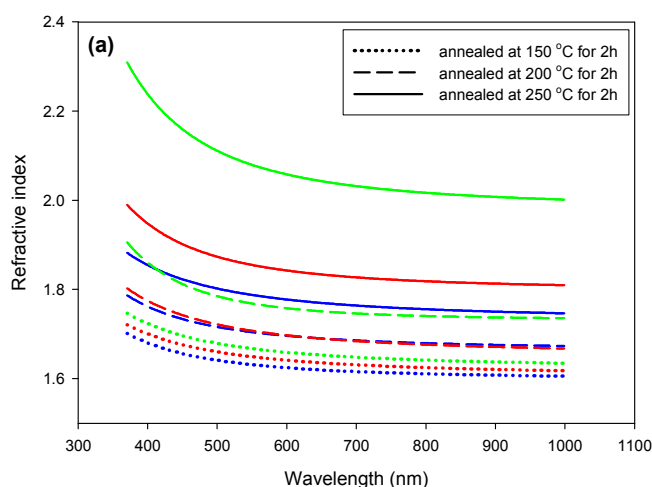


Fig. 2 Refractive indices (a) and transmittances (b) of the organic-inorganic hybrid films fabricated from the hybrid solutions prepared from triethylene glycol and titanium (IV) butoxide according to the annealing temperature and the feeding mole ratio: triethylene glycol/titanium (IV) butoxide=2/1 (—); 1/2 (---); 1/4 (·····).

The refractive index of the film with 1/4 of the feeding mole ratio between triethylene glycol and titanium (IV) butoxide reached 2.06 at a wavelength of 600 nm when it was annealed at 250 °C. But, it decreased to 1.78 when the feeding mole ratio was changed to 2/1. The relative content of Ti increased on the film surface with increasing the feeding mole ratio of titanium (IV) butoxide, which resulted in the increase in the refractive index. (Table S1, ESI†). Thickness of the films increased with

increasing the content of titanium (IV) butoxide and decreasing the annealing temperature (Table S2, ESI†). The viscosity of the hybrid solutions increased with increasing the content of titanium (IV) butoxide due to partly gelation of titanium (IV) butoxide during the sol-gel reaction. The films can be densified when they are annealed at high temperature because the unreacted triethylene glycol is completely removed and titanium oxide hydrate converts to the related TiO_2 . In short, the refractive indices of films increase as the film density increases. These are reasons why the film thickness lessens and the refractive index of the film increases, as well. Thus, in order to obtain films with high refractive indices, it is desirable to increase the annealing temperature and the content of titanium (IV) butoxide.

The transmittances of hybrid films were higher than 85 % in a visible region. At an annealing temperature below 200 °C, the transmittances of the films were not a strong function of the feeding mole ratio between triethylene glycol and titanium (IV) butoxide. Colour of the films gradually became yellowish as the annealing temperature increased to 250 °C. Due to the yellowing, the transmittance decreases in the wavelength range of 350~400 nm. By increasing the content of triethylene glycol and decreasing the annealing temperature, it was possible to suppress the yellowing. This result strongly indicates that the yellowing is due to the presence of the unhydrolyzed butoxide group of the sol-gel hybrid materials and titanium (IV) butoxide.

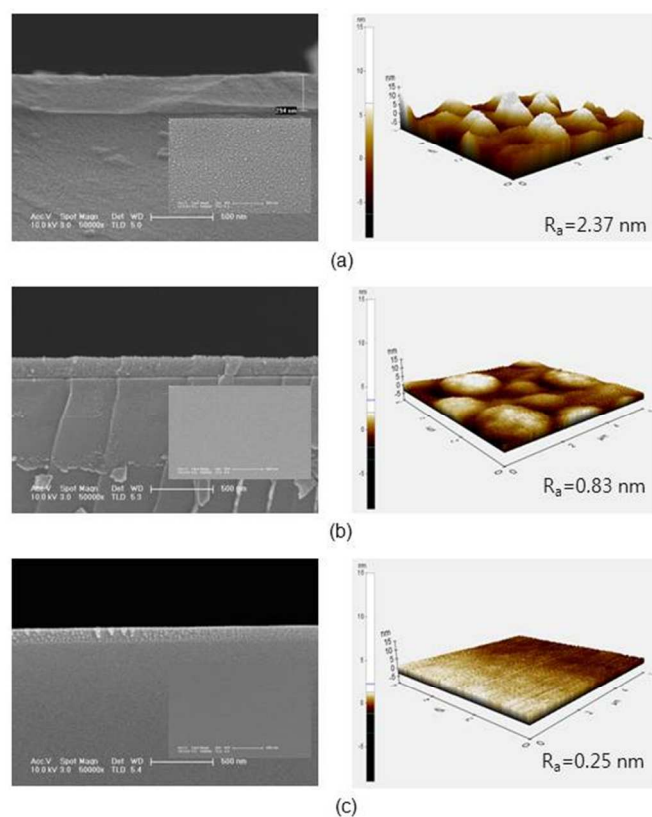


Fig. 3 SEM (a small top view inside a cross-sectional view) and AFM images of the hybrid films fabricated from the hybrid solution prepared from triethylene glycol

and titanium (IV) butoxide with 1/4 of the feeding mole ratio and annealed at the various temperatures: 150 °C (a); 200 °C (b); 250 °C (c).

Morphology of the hybrid films

Fig. 3 shows scanning electron microscope (SEM) and atomic force microscope (AFM) images of the organic-inorganic hybrid films fabricated from the hybrid solution prepared from triethylene glycol and titanium (IV) butoxide (1/4, feeding mole ratio) as a function of the annealing temperature. The film surface became smoother as the annealing temperature increased. TiO_2 domains would be more developed in the film because a condensation reaction between the hydroxyl groups of titanium oxide hydrates occurs when the films were annealed, resulting in conversion of titanium oxide hydrate to the related TiO_2 .¹¹ The root-mean-square values (R_a) of the surface roughness of the hybrid films decreased from 2.37 to 0.25 nm when the films were annealed from 150 to 250 °C. The variation of the film roughness was also found from the top viewed SEM images. Decrease in the surface roughness can be clearly seen in the cross-sectional SEM images. The TiO_2 domains were developed overall on the surface when the film was annealed at 250 °C, which results in the film with high refractive index and surface evenness. The film thickness also decreased with increasing the annealing temperature as explained in Table S2, ESI†. The film thickness shown in the cross-sectional SEM image is almost the same as that measured with the ellipsometer.

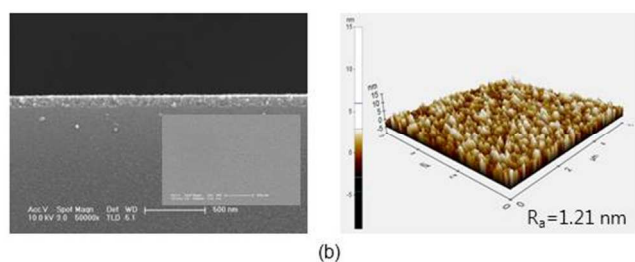
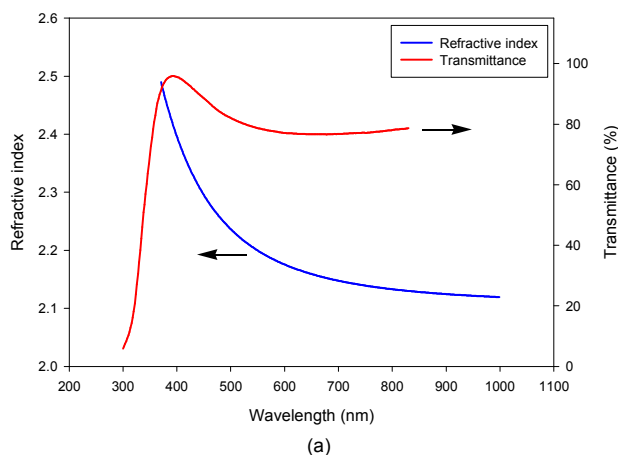


Fig. 4 Refractive index and transparency (a), SEM (a small top view inside a cross-sectional view) and AFM images (b) of the hybrid film fabricated from the hybrid solution prepared from triethylene glycol and titanium (IV) butoxide with 1/4 of the feeding mole ratio and annealed at 400 °C.

High temperature annealing of the hybrid films

In order to obtain more optical and morphological information about the organic-inorganic hybrid film annealed near TiO_2 sintering temperature, the hybrid solution prepared from triethylene glycol and titanium (IV) butoxide (1/4, feeding mole ratio) was annealed at 400 °C. As shown in Fig. 4, the refractive index of the film reached 2.16 at a wavelength of 600 nm and yellow colour of the film completely disappeared. It is because the unreacted butoxide groups are reacted each other to convert to TiO_2 at this temperature, which results in growth of TiO_2 structure. The increase in the refractive index of the film was not considerable compared with the result from annealing at 250 °C as shown in Fig. 2. The film surface evenness was deteriorated. The film thickness decreased to 90 nm. SEM and AFM scans reveal that random growth of TiO_2 occurs, which results in an increase in the film roughness. R_a value of the film increased from 0.25 to 1.21 nm when the annealing temperature increased from 250 to 400 °C.

Effect of annealing temperature on crystallization of the hybrid films

Fig. 5 shows X-ray diffraction (XRD) patterns of the organic-inorganic hybrid films prepared from the hybrid solution synthesized from triethylene glycol and titanium (IV) butoxide (1/4, feeding mole ratio) according to the annealing temperature. The films were almost amorphous when they were annealed below 250 °C. Three peaks were newly observed in the XRD pattern of the film when it was annealed at 400 °C. The observed 2θ values are assigned to 25.2°, 38.3°, 48.3°, which are corresponding to (101), (112), and (200) crystalline planes of an anatase TiO_2 .²⁰ Only TiO_2 domain was developed without crystallization when the films were annealed below 250 °C and the domain was crystallized with annealing at the higher temperature. As shown in previous results, the crystallization does not largely affect the refractive index of the hybrid film. On the contrary, this crystallization deteriorates the film surface morphology. Therefore, in this case, the organic-inorganic hybrid films are needed to be annealed near 250 °C for the refractive index as well as surface evenness.

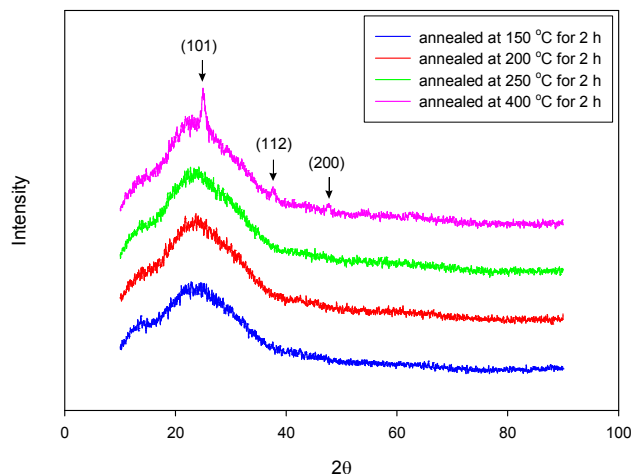


Fig. 5 XRD patterns of the hybrid films fabricated from the hybrid solution prepared from triethylene glycol and titanium (IV) butoxide with 1/4 of the feeding mole ratio and annealed at various temperatures.

Conclusions

We prepared an organic-inorganic hybrid solution by using triethylene glycol and titanium (IV) butoxide as an organic compound and an inorganic precursor, respectively. Triethylene glycol and titanium (IV) butoxide were well reacted in DMAc via a sol-gel reaction. The triethylene glycol-titanium oxide hydrate hybrid materials and titanium oxide hydrates are soluble and stable in DMAc due to hydrogen bonding between the titanium oxide hydrates and DMAc. The refractive index, surface evenness, transparency, and thickness of the hybrid films fabricated from the solutions were varied with the film drying condition and feeding mole ratio between the organic and inorganic compounds. The refractive index and root-mean-square value of the surface roughness of the film were 2.06 and 0.25 nm, respectively, even when it was annealed at 250 °C due to completely removal of the unreacted diol compound. This is much lower temperature than the sintering temperature of TiO₂. Triethylene glycol is more suitable than any other diol compounds for that purpose. The roughness of the film increased when it was annealed near the sintering temperature of TiO₂ because of the film crystallization. The hybrid films were transparent in a visible region. However, the film thickness was still several hundreds of nanometers. Above various results indicate that the organic-inorganic hybrid films can potentially provide possible good candidate materials for the optical films with high refractive index, transparency, and surface evenness.

Future studies will focus on further increasing the film thickness to μm-order as well as on assessing the potential of the solutions for practical applications in light extraction of OLED lighting or display.

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† Electronic Supplementary Information (ESI) available: Isothermal TGA thermograms of three diol compounds, photographs of organic-inorganic hybrid solutions, IR spectra of DMAc, triethylene glycol, and NaCl window, atomic concentration of the hybrid film surface, and thickness of