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Highly smooth and refractive films fabricated from titanium oxide hydrate solution

Seung Koo Park*, Chul Woong Joo, Joo Yeon Kim, Byoung-Hwa Kwon, Jin-Wook Shin, Doo-Hee Cho, Jaehyun Moon, Jeong-Ik Lee

Soft I/O Interface Research Section, Smart I/O Platform Research Department, Information & Communications Core Technology Research Laboratory, Electronics and Telecommunications Research Institute, 218 Gajeongno, Yuseong-gu, Daejeon 305-700, South Korea

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ABSTRACT

Highly smooth, refractive, and transparent films have recently received attention in the fields of lighting and display applications for being used as energy saving devices via light extraction. Here, we have prepared a titanium oxide hydrate solution from titanium (IV) butoxide in N, N-dimethyl acetamide (DMAc) and evaluated inorganic films fabricated from the solution. The solution was transparent and homogenous mainly due to the complexation of titanium oxide hydrate with DMAc. The solution was spin-coated on a silicon wafer or a glass plate and dried under nitrogen to create a transparent film. The refractive index of the film was ca.1.97 at a wavelength of 550 nm, even when it was annealed at a low temperature of 150 °C. Atomic force microscope (AFM) results showed that the films were highly smooth and that the root-mean-square (R_a) values of the film's surface roughness were sub-nm scale, irrespective of the film drying condition. We identified our titanium oxide hydrate solution in DMAc as a possible good candidate material for films with a high refractive index and surface evenness.

1. Introduction

Organic light emitting diode (OLED) displays, OLED and LED lighting, antireflective coatings, and microlens component industries have focused on high refractive index (n) materials and their films for the effective use of optical sources [1–6]. In particular, transparent films with a high refractive index as well as surface evenness are essential to effectively extract light in OLED lighting and display applications [6–9]. These films should completely cover a corrugated substrate, from which light is scattered, for the flat deposition of anode. It is desirable that the refractive index of the films is higher than that of indium tin oxide (ITO), which is the most widely used anode in transparent devices. It is also beneficial that the films are transparent in a visible region such as ITO in order to obtain high light extraction efficiency. In addition, the high refractive index films have to be flat in order to obtain a high quality ITO layer when it is deposited on the films [10,11].

A titanium dioxide (TiO_2) nano powder-dispersed solution has been generally used to prepare high refractive index films because TiO_2 is simply synthesized from its precursors such as titanium (IV) ethoxide, titanium (IV) butoxide, and titamium (IV) chloride in aqueous and alcoholic media. TiO_2 films are obtained by spin- or dip-coating the TiO_2 dispersed solution, followed by sintering the TiO_2 particles at high temperature. The film is generally very thin (<100 nm) and uneven because the solid content of TiO_2 in the media is low (<10–20 wt%) and the TiO_2 film is crystallized during sintering. The sintering process has been carried out at very high temperatures (>500 °C) [12,13].

In our study, we prepared a titanium oxide hydrate solution via the sol–gel reaction of titanium (IV) butoxide in N, N-dimethyl acetamide (DMAc). It is expected that the titanium oxide hydrate would be soluble in DMAc because of the hydrogen bonding between the carbonyl groups of DMAc and the hydroxyl groups of titanium oxide hydrate [14,15]. This soluble preoperty would be advantageous for us to obtain highly flat films. The DMAc hydrogen-bonded with the titanium oxide hydrates hinders the progress of crystallization of the TiO_2 films when they are annealed. Therefore, in our system, amorphous TiO_2 films with high refractive index and surface evenness can be obtained from the titanium oxide hydrate soiution in DMAc even at low annealing temperature. Also, we discuss the possibility of using the solution as a candidate material for high refractive and smooth films.

2. Material and methods

Materials: Titanium (IV) butoxide were purchased from Tokyo Chemical Industry Co., Ltd. N, N-dimethyl acetamide (DMAc), a 37% hydrochloric acid solution in water, and 1-methyl-2-pyrrolidinone

* Corresponding author.
E-mail address: skpark@etri.re.kr (S.K. Park).

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(NMP) were purchased from Aldrich Chemical Co., Inc. All reagents were used as received.

Preparation of titanium oxide hydrate solution and its film: After 0.87 mL of 37% hydrochloric acid solution in water was added carefully in 3.2 mL of DMAc under nitrogen, 2.0 g of titanium (IV) butoxide was added dropwise into the DMAc solution with stirring. The reaction was carried out for 1 day at room temperature. Several hours after the 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 solution layer was thermally annealed at each temperature under nitrogen for 1 h.

Fabrication of OLED device with a nano-structured scarttering layer: A glass with randomly nano-structured scattering layer was prepared with a silver dewetting mask. After a TiO_2 colloidal polyvinylpyrrolidone (PVP, M_n=40,000) solution layer coated on the nano-structured glass was annelaed, the titanium oxide hydrate solution was coated on the TiO_2/PVP layer and annealed at 250 °C. Indium tin oxide and aluminum as an anode and a cathode, respectively, and various organic materials for hole transport, electron transport, and emitting layers were vacuum-deposited. Details on the preparation of TiO_2 colloidal PVP solution, materials, and the above fabriction processes have been reported elsewhere [6–9].

Measurements: Infrared (IR) and UV–vis spectra were recorded with a Nicolet 6700 FT-IR spectrophotometer and a PerkinElmer Lambda 750 UV/VIS/NIR spectrophotometer, respectively. The solution viscosity was measured at 25 °C by an AND SV-1A viscometer. Atomic force and scanning electron micrographs were obtained on a PSIA XE-100 atomic force microscope and an FEI Sirion scanning electron microscope, respectively. The film's crystal structure was examined with a Rigaku RU-200BH X-ray diffraction analyzer. The refractive indices of the films were measured using a J.A. Woollam M-2000V and a EC-400 spectroscopic ellipsometer. The Cauchy dispersion relation was applied to a three-layer model consisting of air, film, and a silicone substrate. WVASE32® software was used for data analyses.

3. Results and discussion

A titanium oxide hydrate solution was prepared by using titanium (IV) butoxide in DMAc, as shown in Fig. 1a. Titanium (IV) butoxide is hydrolyzed by water. Titanium oxide hydrate is obtained by the condensation reaction between the hydroxyl groups of hydrolyzed titanium (IV) butoxide. The condensation reaction (sol–gel reaction) was carried out under acidic condition. Under this condition, the condensation reaction between the hydroxide groups of hydrolyzed titanium (IV) butoxide is slow, even though the hydrolysis reaction of the alkoxide group in titanium (IV) butoxide is fast [16]. A 37% hydrochloric acid solution

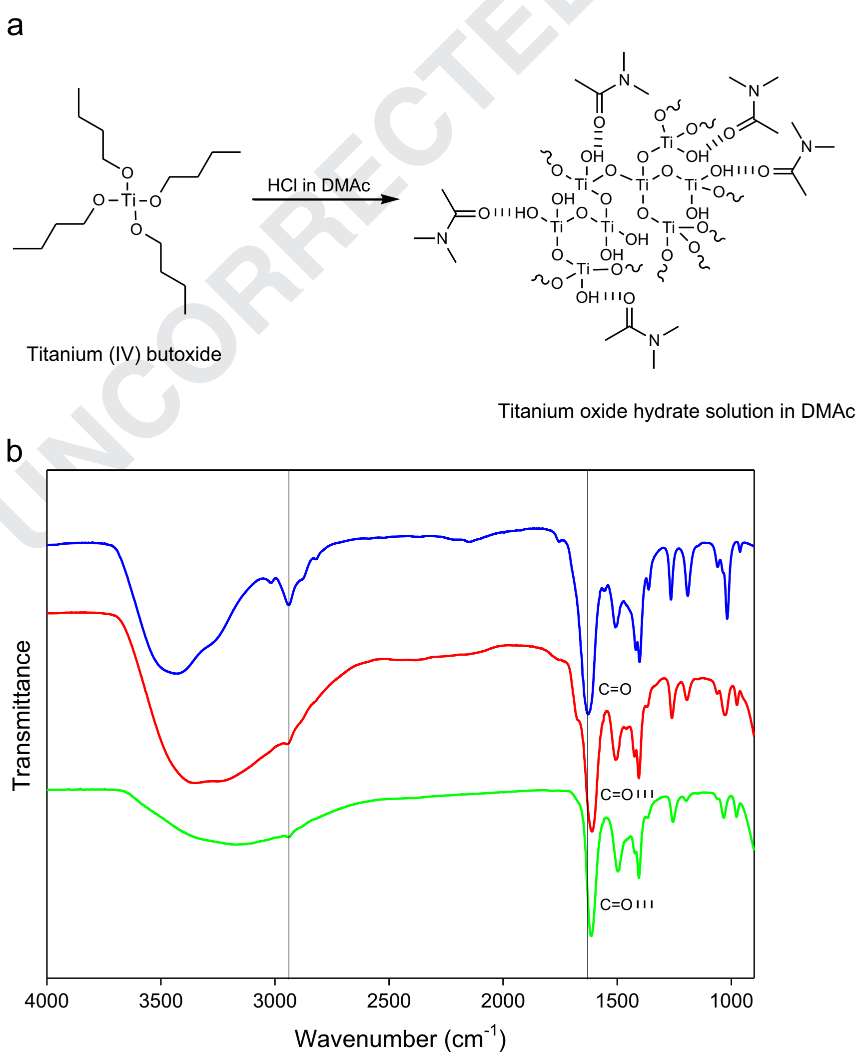

Fig. 1. An idealized reaction for preparing titanium oxide hydrate solution in DMAc (a) and IR spectra of DMAc (▬), titanium oxide hydrate solution in DMAc (▬), and the titanium oxide hydrate film (▬) annealed at 150 °C for 1 h under nitrogen (b).