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A quality photocatalytic activity of an amorphous titanium oxide film achieved using the selectively photochemical etching and its application for the organic light emitting diode encapsulation

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ABSTRACT

In this study, a rapid, cost-effective, and room-temperature achieved selectively photochemical etching (SPCE) process was developed to improve the photocatalytic activity of a PECVD-deposited amorphous titanium oxide (a-TiO_x) film. The a-TiO_x film treated by the SPCE process showed a photocatalytic activity comparable to that of a high-temperature prepared TiO_x film. As examined from the surface roughness and morphologies, optical transmittance, and chemical bond configurations, the mechanism responsible for the significant enhancement on the photocatalytic activity was ascribed to the formation of the nano-textures with the increase in the surface acidity due to the incorporating of fluorine ions. The SPCE-treated a-TiO_x film with the quality photocatalytic activity was then applied to encapsulate the blue organic light emitting diode (OLED) to result in the surface with self-cleaning function. A super-hydrophilic surface was available using the internal light irradiation. In addition, the OLED encapsulated by the SPCE-treated a-TiO_x film also was beneficial for enhancing the light-extraction efficiency as a consequence of its notably nano-textured surface.

1. Introduction

Transparent titanium oxide (TiO_x) film possesses a high refractive index has been comprehensively used as an optical coating for several decades. Its excellent photocatalytic activity also has attracted significant attention as specific function, such as anti-bacterial, anti-pollution, decolourization, and deodorization, for the environmental purification, dye-sensitization, surface self-cleaning/antifogging, and biomedical engineering applications [1–4]. Since the TiO_x film with anatase phase is the known structure that exhibited the best photocatalytic activity, most researchers are devoted to enhance its efficiency via increasing the film's specific surface area and/or retarding the recombination of the photo-generation electro-hole pair [5–9]. Unfortunately, the prepared temperature required for the crystallization of the TiO_x film with anatase phase typical was too high to apply as a modification coating on the temperature-sensitive substrate or device packaging. Accordingly, low-temperature prepared hydro-oxygenated amorphous TiO_x (a-TiO_x) film abundant in OH groups using plasma-enhanced chemical vapor deposition (PECVD) has became a promising candidate in substitution for the high-temperature obtained crystal-TiO_x film. However, the photocatalytic activity of the PECVD-deposited a-TiO_x film still was a grade inferior to that of the anatase TiO_x film [10,11], revealing that more effort to enrich the surface activation of the PECVD-deposited a-TiO_x film is needed. As quoted from the previous reports to modify the surface property of the a-TiO_x film [12–14], we developed a room-temperature achieved two step process consisted of the selective pre-irradiation and the following fluorination etching to improve the film's photocatalytic activity [15]. Though the results demonstrated that the a-TiO_x film modified by this two step process exhibited a quality photocatalytic activity comparable to the anatase-TiO_x film, the selective pre-irradiation on the film for the sequential fluorination etching was too long (5 h) to realize the applications on the substrate modification or device packaging.

With the aim to simplify and shorten the above-mentioned two step process to realize its application on substrate modification and device packaging, a selectively photochemical etching (SPCE) process combined with the selective UV light irradiation and fluorination etching simultaneously was presented in this work. Such room-temperature, cost-effective, and rapid achieved process on the a-TiO_x film to result in the nano-textured surface with the fluorination ions incorporation was then practically applied to the OLED device encapsulation. In addition to investigate the enhancement on the photocatalytic activity of the SPCE-treated a-TiO_x film, the improvement on the photo-induced surface wettability using the external UV and internal blue light irradiation as well as the light extraction efficiency for the OLED device encapsulated by the SPCE-treated a-TiO_x film also was measured and discussed.

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2. Experimental

Hydro-oxygenated a-TiO_x films with thickness of 200 nm were deposited onto silicon and glass substrates by PECVD using titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, TTIP) and oxygen gas mixture. The titanium precursor was reservoired in a bubbling cylinder heated at 70 °C with the nitrogen carrier gas, and the gas line was heated to 100 °C to prevent condensation. The TTIP-oxygen gas mixture was sprayed through a showerhead array at the upper electrode, which was 50 mm away from the substrates' holder. The deposition pressure, rf power, and gas flow rate of TTIP/O_2 gas mixture were controlled at 40 Pa, 100 W, and 120/20 sccm, respectively. Then, the SPCE process was treated on these a-TiO_x films by immersing these samples in a 0.5 vol.% dilute hydrofluoric acid (HF) solution and selectively irradiating by an UV lamp (TLD 10 W/08, Philips; centered at 365 nm with the intensity of 3 mW/cm^2) through a porous alumina anodic membrane (AAM) mask simultaneously. The UV light intensity and the acid concentration for achieving the SPCE process were designed to effectively activate the surface property to resist the concurrent etching process and thus result in the optimal selective fluorination etching. Fig. 1 illustrates a schematic configuration of this SPCE process. Another set of the as-deposited a-TiO_x films were annealed at 500 °C for 30 min under oxygen ambient (hereafter denoted as annealed TiO_x) to cause the structural crystallization with anatase phase for comparing their photocatalytic activity. Eventually, the a-TiO_x films with and without the SPCE treatment were respectively deposited onto the top-emission OLED devices which had been passivate by a 300 nm-thick SiON barrier film.

Film thickness of these fluorinated samples with and without the UV light irradiation was measured using a surface profile system. The surface roughness and morphologies were observed using the atomic force microscopy (AFM, DI-3100, Veeco) and a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL), respectively. Optical transmittance was measured using an UV–Vis-NIR spectrophotometer (UVD 3500, Labomed, Inc.). The chemical bond states of these samples were examined by a Fourier transform infrared (FTIR) spectrometry (FT/IR-4100, JASCO). Photocatalytic activity of the a-TiO_x films as well as the annealed TiO_x film was determined from the decolorization of a methylene blue (MB) solution by an UV light irradiation at a constant intensity of 1 mW/cm^2. In addition, the associated photo-induced surface wettability to water drop also was conducted by the water contact angle meter. The current density–voltage (J–V) and luminance–current density (L–J) properties of the OLED devices encapsulated by these a-TiO_x films were measured using a semiconductor parameter analyzer and an integrated sphere detector.

3. Results and discussion

Fig. 2 shows the etching thickness for the a-TiO_x films immersed in the dilute HF solution with and without the UV light irradiation

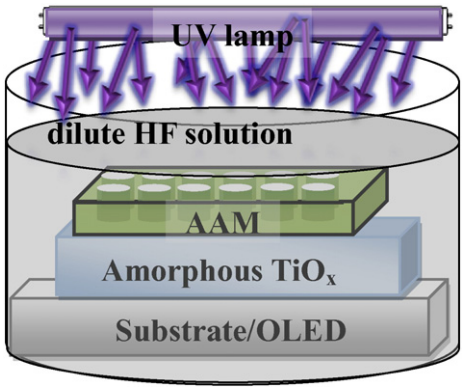

Fig. 1. Schematic configuration of the selectively photochemical etching process.

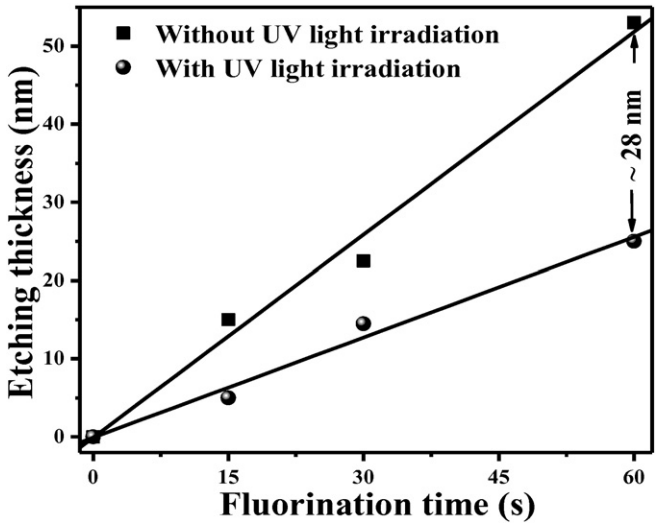

Fig. 2. Etching thickness for the a-TiO_x films immersed in the dilute HF solution with and without simultaneously irradiating the UV light.

simultaneously. Since the electrons generated on the a-TiO_x film by the UV light irradiation was prone to transform the surface Ti(IV) cation to Ti(III) state, as expressed in Eq. (1) [16], and thereby reduce the acidity of the etching solution [17,18], the etching thickness of the fluorinated a-TiO_x film combined with the UV light irradiation thus was lower than that of the film only etched by the dilute HF solution.

$$e^- + \mathrm{Ti(IV)}{-}\mathrm{OH} \rightarrow \mathrm{Ti(III)}{-}\mathrm{OH}^- \quad (1)$$

Accordingly, the difference in the etching thickness between the fluorinated a-TiO_x films with and without the UV light irradiation etched for 60 s was about 28 nm as indicated in Fig. 2. As the etching thickness on the a-TiO_x film was apparently alleviated by incorporating with the UV light irradiation, a SPCE process combined with the selectively photocatalytic activation through a AAM mask with nano-sized porous (~20 nm) and the fluorination etching was carried out to roughen the film surface to enlarge its specific surface area. Fig. 3(a) and (b), respectively, illustrate the surface roughness of the as-deposited a-TiO_x film and the SPCE-treated a-TiO_x film for 60 s. It can be seen that large amounts of white and sharp protrusions distributed over the SPCE-treated a-TiO_x film, resulting in its root–mean–square surface roughness, R_q, was significantly increased to 5.53 nm as compared to that of the as-deposited TiO_x film (~1.35 nm). Fig. 3(c) and (d) further highlight the surface morphologies of the as-deposited and SPCE-treated a-TiO_x films conducted from FE-SEM observations. The surface morphology of the as-deposited a-TiO_x film exhibited densely and abnormally distributed particles with visible boundaries, while those particles distributed over the SPCE-treated a-TiO_x film surface became separated with significant grooves. In addition, due to the fluorination etching on the areas of the a-TiO_x film surface without the UV light irradiation were more drastic than the areas irradiated by UV light, the particles distributed over the SPCE-treated a-TiO_x film almost had the same diameter of about 20 nm, a value very close to the porous size of the AAM mask. The optical transmittances of the as-deposited and SPCE-treated a-TiO_x films are given in Fig. 4. The average transmittances in the visible wavelengths ranged from 400–700 nm for the as-deposited and SPCE-treated a-TiO_x films were 88 and 96%, respectively. The increase in the average optical transmittance for the a-TiO_x film treated by the SPCE process was both attributed to the thinner thickness as compared to the as-deposited a-TiO_x film and the reduction in the reflectance due to its rougher surface [19]. In addition, the absorption onset of the SPCE-treated film also markedly shifted toward a shorter wavelength as compared to the untreated film. Accordingly, The