

# Packaging organic Light Emitting Diode with surface self-cleaning using a highly active amorphous titanium oxide photocatalytic thin film

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## 1. Introduction

High efficient and functional lighting provides energy saving and environmental benefit. In an attempt to strengthen the lighting with self-cleaning surface, one potential coating is titanium oxide ( $\text{TiO}_x$ ) material due to its excellent photocatalytic activity [1-2]. The photocatalytic activity of the  $\text{TiO}_x$  film is determined by the crystalline structure, specific surface area, and functional group incorporations [3]. Since it is impossible for the application of the anatase  $\text{TiO}_x$  film with an excellent photocatalytic activity on the heat-sensitive device packaging, the research on the amorphous  $\text{TiO}_x$  films having sufficient photocatalytic activity is thus indispensable. In this work, a selectively photochemical etching (SPCE) process was developed to strengthen the photocatalytic activity of the amorphous  $\text{TiO}_x$  film and employed for device encapsulation with surface self-cleaning application.

## 2. Experimental procedure

Hydro-oxygenated amorphous  $\text{TiO}_x$  films were prepared by plasma-enhanced chemical vapor deposition using titanium tetraisopropoxide (TTIP) and oxygen gas mixture. These films were then fluoridized in a 0.5 vol.% dilute HF solution while simultaneously irradiated by an UV lamp ( $3 \text{ mW/cm}^2$  at 365 nm) through a porous alumina anodic membrane (AAM) mask. Figure 1(a) illustrates a schematic configuration of the SPCE process.

Film thickness was measured using a surface profile system. The optical transmittance was measured using an UV-Vis-NIR spectrophotometer. The surface roughness and morphologies were observed using an atomic force microscopy and a field emission scanning electron microscope. The film and surface chemical bond states were examined by a Fourier transform infrared spectrometry and an X-ray photoelectron spectroscopy. The photocatalytic activity was determined from the decolorization of a methylene blue (MB) solution. The current-voltage ( $I$ - $V$ ) and the luminance-current ( $L$ - $I$ ) properties of these amorphous  $\text{TiO}_x$  films encapsulated OLED devices were measured using a semiconductor parameter analyzer and an integrated sphere detector. Photo-induced surface wettability was conducted by the water contact angle meter.

## 3. Results and discussions

Figure 1(b) shows the etching thickness for the  $\text{TiO}_x$  films with and without UV light irradiation. Due to the accumulation of the photogenerated electrons tend to reduce  $\text{Ti(IV)}$  cation to  $\text{Ti(III)}$  state on the film surface, as

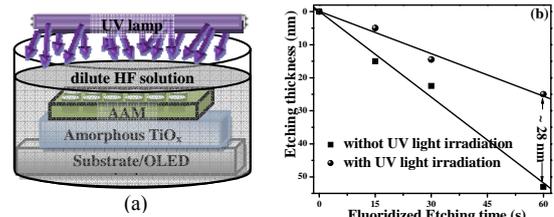
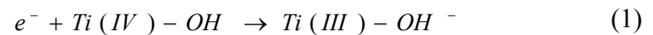


Fig. 1 (a) A schematic configuration of the SPCE process and (b) etching thickness of the  $\text{TiO}_x$  film as a function of the etching time, with and without the UV light irradiation.

expressed in Eq. (1), the etching thickness of the amorphous  $\text{TiO}_x$  film with the UV light irradiation was significantly lower than that of the film directly etched by the dilute HF solution.



The difference on the etching thickness was about 28 nm for these  $\text{TiO}_x$  films etched for 60s as indicated in Fig. 1(b). Figures 2(a) and (b) show the surface morphologies of the as-deposited  $\text{TiO}_x$  film and SPCE-treated  $\text{TiO}_x$  film for 60s, respectively. The Densely and uniformly round-shaped grains are distributed over the as-deposited  $\text{TiO}_x$  film surface with well-distributed columnar structures as shown in the cross-sectional micrographs inset in Fig. 2(a). By contrast, the grooves and pores are observed on the SPCE-treated  $\text{TiO}_x$  film surface as a consequence of the grains nano-sizing. In addition, the columnar structures, as

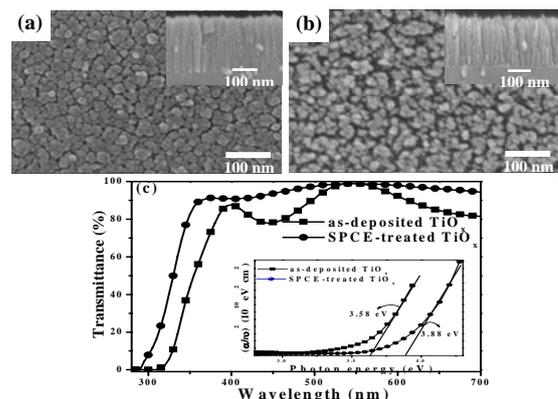


Fig. 2 Surface morphologies of (a) as-deposited and SPCE-treated  $\text{TiO}_x$  films (cross-sectional micrographs are shown in inset figures), and (c) optical transmittances of these two samples (the inset figure show the  $(ahv)^2$  versus the photon energy ( $eV$ )).

shown in inset figure of Fig. 2(b), are highly irregular with sharp and separated pinnacle, suggesting that the specific surface area featured as such nano-textured structures is enhanced apparently. The optical transmittances of these

two samples are given in Fig. 2(c). The average optical transmittance in the visible wavelengths for SPCE-treated  $\text{TiO}_x$  film was higher than that of the as-deposited  $\text{TiO}_x$  film. The onset of the absorption edge also shifted toward short wavelength due to the nano-sized effect [4], thereby resulting in the markedly increase in the optical energy bandgap ( $\sim 3.88$  eV) as determined in the inset figure.

FTIR spectra of the as-deposited and SPCE-treated  $\text{TiO}_x$  films are shown in Fig. 3(a). Two broad peaks appeared within  $400\text{--}800\text{ cm}^{-1}$  and  $2800\text{--}3700\text{ cm}^{-1}$  are observed in these FTIR spectra, which is in turn assigned to the Ti–O bond and hydroxyl (O–H) groups [5]. Another peak approximately at  $840\text{--}900\text{ cm}^{-1}$  only appeared in the SPCE-treated film was attributed to Ti–F bond as a consequence of the surface fluorination [6]. In addition, since the fluoridized etching resulted in the increase of the surface acidity, in agreement with the report [7], the O–H groups in the SPCE-treated film thus was enhanced and the wavenumber was lower than that of the as- $\text{TiO}_x$  film by about  $100\text{ cm}^{-1}$  [8]. The inset figure also shows a fluorine single ( $\sim 684.3$  eV), corresponds to F<sup>-</sup> physically adsorption [9], in the SPCE-treated  $\text{TiO}_x$  film surface. Figure 3(b) illustrates the photocatalytic degradation of MB solution over the as-deposited, SPCE-treated, and annealed  $\text{TiO}_x$  films with anatase crystallinity. Clearly, the decomposition to the MB solution by the SPCE-treated film is comparable to that by the annealed film. The rate constant,  $k$ , related to the degree of the photocatalytic activity using the apparent first-order rate equation as well as the surface roughness,  $R_q$ , for these films are summarized in Table 1. The rate constant of the SPCE-treated  $\text{TiO}_x$  film surface fluoridized

Table 1 Rate constant and surface roughness of the as-deposited, SPCE-treated, and annealed  $\text{TiO}_x$  films.

Sample	as-deposited	SPCE-treated	annealed- $\text{TiO}_x$
$k$ ( $\text{min}^{-1}$ )	0.0078	0.0204	0.0258
$R_q$ (nm)	1.35	5.53	4.78

with nano-texture is significant increased to  $0.0204\text{ min}^{-1}$ . Accordingly, the irradiation time required for the surface exhibiting self-cleaning effect (i.e. water contact angle below  $5^\circ$ ), as shown in the inset figure, is markedly shortened ( $\sim 4$ hrs).

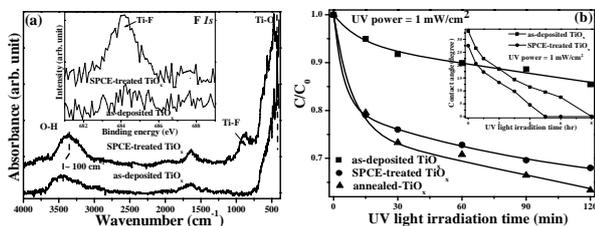


Fig. 3 (a) FTIR spectra of the as-deposited and SPCE-treated  $\text{TiO}_x$  films (F  $1s$  core level is given in inset figure) and (b) degradation of MB solution for the as-deposited, SPCE-treated, and annealed films (photo-induced surface wettability is given in inset figure).

$I$ - $V$  curves of the OLED encapsulated by the PET plate coated with and without an amorphous  $\text{TiO}_x$  surface modification layer are given in Fig. 4(a). All the turn-on voltages and dominated emission peak at an injection current  $12\text{ mA/cm}^2$  ( $\sim 488\text{ nm}$  as shown in inset figure) of these devices were identical except for a high current

density and EL intensity obtained from the  $\text{TiO}_x$  encapsulated devices. The photo-induced surface wettability of the SPCE-treated  $\text{TiO}_x$  packaging OLED device became super-hydrophilicity when the internal light irradiation ( $\sim 0.3\text{ mW/cm}^2$ ) for 5 hr is highlighted in Fig. 4(b). In addition, due to the reduction of the Fresnel loss contributed by the surface nano-textured structures [1], the luminance efficiency of the SPCE-treated  $\text{TiO}_x$  packaging OLED (as shown in the inset figure) was approximate 1.25 times higher than that of the conventional OLED.

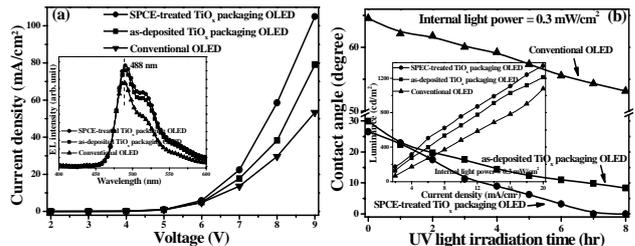


Fig. 4 (a)  $I$ - $V$  curves of the OLED encapsulated with and without an amorphous  $\text{TiO}_x$  coating and (b) photo-induced surface wettability of these OLED devices (the associated EL spectra and  $I$ - $L$  curves of these samples are also given in inset figures).

#### 4. Conclusions

A SPCE method was developed to enhance the photocatalytic activity of an amorphous  $\text{TiO}_x$  film. Due to the significant increase in the specific surface area and the surface fluorination, the rate constant was significantly increased to  $0.0204\text{ min}^{-1}$ , a value being comparable to that of an anatase  $\text{TiO}_x$  film. By applying such coating on the OLED packaging, the self-cleaning effect was achievable for the device lighting for 5 hr ( $\sim 0.3\text{ mW/cm}^2$ ). In addition, such an amorphous  $\text{TiO}_x$  film with nano-textured surface also was beneficial for enhancing the light-extraction efficiency by a factor of 25%.

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#### References

- [1] D. S. Liu, T. W. Lin, B. W. Huang, F. S. Juang, P. H. Lei, and C. Z. Hu, *Appl. Phys. Lett.* **94** (2009) 143502.
- [2] A. N. Noemaun, F. W. Mont, G. B. Lin, J. Cho, E. F. Schubert, G. B. Kim, C. Sone, and J. K. Kim, *J. Appl. Phys.* **110** (2011) 054510.
- [3] G. Tian, H. Fu, L. Jing, and C. Tian, *J. Hazard. Mater.* **161** (2009) 1122.
- [4] K. Lv, X. Li, K. Deng, J. Sun, X. Li, and M. Li, *Appl. Catal. B* **95**, 383 (2010).
- [5] J. G. Yu, J. F. Xiong, B. Cheng, and S. W. Liu, *Appl. Catal. B* **60**, 211 (2005).
- [6] C. Y. Wu, B. S. Chiang, S. Chang, and D. S. Liu, *Appl. Surf. Sci.* **257**, 1893 (2011).
- [7] A. Vijayabalan, K. Selvam, R. Velmurugan, and M. Swaminathan, *J. Hazard. Mater.* **172**, 914 (2009).
- [8] D. Li, H. Haneda, S. Hishita, N. Ohashi, and N. K. Labhsetwar, *J. Fluorine. Chem.* **126**, 69 (2005).
- [9] J. Yu, W. Wang, B. Cheng, and B. L. Su, *J. Phys. Chem. C* **113**, 6743 (2009).