Effects of thermal annealing on structure, morphology and optoelectronic properties of TiOPc ultrathin films

R Ye,†, D Xiong, M Yanagida, K Ohta, T Abe and M Baba

1Faculty of Engineering, Iwate University, Morioka 0208551, Japan
2Graduate School of Engineering, Iwate University, Morioka 0208551, Japan
3Iwate Industrial Research Institute, Morioka 0200852, Japan

E-mail: ye@iwate-u.ac.jp

Abstract. This article reports the effects of thermal annealing on structure, morphology and optoelectronic properties of titanyl phthalocyanine (TiOPc) ultrathin films grown at room temperature. When the thermal annealing temperature (T_α) is over 160 °C, a peak at 2θ = 7.5° with d_{010} = 1.194 nm was observed, which suggests that TiOPc molecules were restructured and crystalline α-form films were formed. By the detailed x-ray diffraction analysis, the optimum thermal annealing conditions are as follows: T_α is 160 °C, and the thermal annealing time is 4 h. The root-mean-square roughness and grain size are also increased due to recrystallization with increasing T_α. Similarly, these absorption spectra of TiOPc ultrathin films reveal the gradual formation of the crystalline α-phase, as evidenced by the development of a red-shifted absorption band, peaking 845 nm, and the corresponding reduction of the 720 nm amorphous phase peak when T_α was increased from 120 °C to 180 °C. Furthermore, device performance of TiOPc thin film transistors could be improved and mobility was enhanced by thermal annealing, which originated from amorphous TiOPc films transformed into crystalline α-TiOPc films and increasing of grain size. At T_α = 160 °C, the device achieved the highest performance with field-effect mobility of 6.34 × 10^{-3} cm²V⁻¹s⁻¹.

1. Introduction

Metal phthalocyanines (MPcs) are organic dye materials, used in printing inks, as colorants for plastics and fibers, and their semiconducting properties are exploited for applications such as thin film transistors (TFTs), light emitting diodes, solar cells and gas sensors.[1-16] Titanyl phthalocyanine (TiOPc), one of non-planar phthalocyanines, has five polymorphs with different preparation and treatment procedures.[8-16] Amorphous or nearly amorphous TiOPc films were obtained for vacuum deposition at substrate temperature below 0 °C while β-form (phase I) or a mixture of α-form (phase II) and β-form polycrystalline films at substrate temperature above 20 °C and crystallinity increased with increasing of substrate temperature, and at substrate temperature of above 170 °C only α-form films were obtained. Moreover, amorphous TiOPc films could be transformed into crystalline α-TiOPc film through thermal annealing or vapor exposure. [13, 15] It has been known that α-TiOPc presents a particularly efficient charge photogeneration and a strong optical absorption in the red and near-IR spectral regions and a very promising organic semiconductor with high mobility due to showing the pi-stacking structure with concave pair and convex pair with significant molecular overlaps and very...

† To whom any correspondence should be addressed.
short intermolecular distance.[16] However, few studies have been carried out on the correlation between structures and optoelectronic properties of TiOPc films. In this study, we report on effects of thermal annealing on structure, morphology and optoelectronic properties of TiOPc ultrathin films.

2. Experimental details
TiOPc thin films of ca. 30 nm were deposited on heavily n-doped Silicon substrates with a 300 nm thermally grown SiO₂ layer ($C_i \approx 10^{10}$ nF/cm²) at room temperature and under a base pressure of less than $1 \times 10^{-3}$ Pa. Film thickness and growth rates were monitored by a thickness and rate monitor (CRTM-6000, ULVAC). Samples were annealed in Ar-ambient and dark conditions at temperatures ranging from 120 °C, 140 °C, 160 °C to 180 °C, respectively. The XRD analysis was performed on a diffractometer (Rint 2200V, RIGAKU Co., Ltd.) with graphite monochromatized CuKα radiation ($\lambda=1.54056$ Å), operating in the Θ-2Θ mode. The morphology of the films was examined using AFM (Nanocute, Seiko Instruments Co., Ltd.); the cantilevers were used in the tapping mode with a length of 90 μm and a force constant of 0.12 N/m. For valuating electronic properties of top-contact TiOPc TFTs, Au source and drain electrodes of ca. 30 nm were vacuum-deposited through a shadow mask with a channel width of 5 mm and length of 70 μm. The electrical characteristics of devices were measured using a two channel voltage current source/monitor system (R6245, Advantest) under ambient laboratory air conditions. Furthermore, TiOPc thin films of ca. 30 nm were also deposited on glass substrates for optical measurements. The absorption spectra were recorded with UV/VIS spectrophotometer (V-550, JASCO) at room temperature.

3. Results and Discussion
Figure 1(a) shows XRD patterns of TiOPc ultrathin films of ca. 30 nm before and after annealed at various temperature for 4 h. The as-deposited film was in amorphous state. When the annealing temperature ($T_A$) is over 160 °C, a peak at $2\theta = 7.5^°$ with $d_{010} = 1.194$ nm was observed, which suggests that TiOPc molecules were restructured and crystalline α-phase films were formed. However, the full width at half maximum (FWHM) of the 010 diffraction line of the films annealed at 160 °C is smaller than that of the films annealed at 180 °C. From the detailed XRD analysis of Figs. 1(a) and (b), the dependence of the ratios of integration intensity (RII) of the (010) peak on $T_A$ and time were shown in Fig. 1(c). Thus the optimum thermal annealing conditions are as follows: $T_A$ is 160 °C and the thermal annealing time is 4 h.

![Figure 1](image-url)
Figure 2 shows the $2 \mu m \times 2 \mu m$ AFM topographic images of TiOPc thin films before and after the thermal annealing for 4 h. In Fig. 2(a), many small projections are observed, and in Fig. 2(b), some adjacent grains are joined together, which suggests that the local recrystallization has occurred due to the thermal annealing. As can be seen in Fig. 2(c), the grain size is increased and the density is decreased with increasing $T_A$. Furthermore, the local reevaporation could be observed in Fig. 2(d).

![Figure 2](image1.png)

**Figure 2.** Topographic AFM Images of TiOPc ultrathin films before and after annealed at various temperatures for 4 h.

![Figure 3](image2.png)

**Figure 3.** The RMS and GS are shown as a function of $T_A$. The inset shows the RMS amplitude ($\sigma$) vs. $1000/T$ with a linear fit yielding the activation barrier of $E_A = 0.220$ eV.
Figure 3 shows the RMS and grain size increase with increasing $T_A$. While $T_A$ is over 180 °C, the grain size was decreased due to reevaporation. The RMS roughness amplitude ($\sigma$) increases closely following an Arrhenius behavior as $\sigma = \sigma_0 \exp(-E_A/k_B T)$ with the activation energy $E_A = 0.220$ eV, and $k_B$ is the Boltzman constant in the inset of Fig. 3. The value of $E_A$ is smaller than that of oligomer thin films grown on the elevated substrates. This suggests that the thermal annealing caused a local aggregation of TiOPc molecules which led to an increase in the RMS, unlike pure thermal diffusion growth on elevated substrates. [17]

Figure 4 shows absorption spectra of TiOPc ultrathin films prepared as-deposited and thermal annealing form 120 °C to 180 °C. The as-deposited film was amorphous and its absorption spectrum consists of the Q-band peaking at 720 nm with a well defined vibronic replica at 653 nm. When $T_A$ was increased from 120 °C to 180 °C, these sequence absorption spectra reveal the gradual formation of the crystalline $\alpha$-phase, as evidenced by the development of a red-shifted absorption band, peaking 845 nm, and the corresponding reduction of the 720 nm amorphous phase peak. The 845 nm peak, which is a spectroscopic signature of $\alpha$-phase, has been attributed either to excitonic delocalization induced by the formation of J aggregates in the crystalline phase or to molecular distortion lifting the degeneracy of the fundamental electronic transition. This result is coincided with that of the XRD data.

Figure 4. Absorption spectra of TiOPc thin films before and after annealed at various temperatures for 4 h.

Figure 5 shows output characteristics of TiOPc TFTs before and after annealed at 160 °C for 4 h. These devices typically work in $p$-channel accumulation mode. Compared with the as-deposited device, the saturated drain current of the annealed device at $V_D=V_G=-60$ V was enhanced up to over 3 times. Figure 6 shows the transfer characteristics of TiOPc TFTs before and after annealed at various temperatures for 4 h. Generally, the device performance of TFTs is evaluated with field-effect mobility ($\mu$) and threshold voltages ($V_T$) extracted using the saturated drain current $I_D$ vs. $V_G$ relation [18]:

$$I_D = \frac{W}{2L} C_i \mu (V_G - V_T)^2,$$

where $W$, $L$ and $C_i$ are channel width, channel length and gate dielectric capacitance per unit area, respectively. From Fig. 6, the dependence of mobility on $T_A$ is shown in the inset of Fig. 6. With increasing $T_A$, the device performance was improved. At $T_A = 160$ °C, the device achieved the highest performance with mobility of $6.34 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. But the device mobility is decreased at $T_A = 180$ °C. The enhancement of mobility originated from the phase transition from amorphous TiOPc to $\alpha$-TiOPc with an ultra closely pi-stacked structure and increasing of grain size.
4. Conclusion
We have investigated the effects of thermal annealing on structure, morphology and optoelectronic properties of TiOPc ultrathin films grown at room temperature. When $T_A$ is over 160 °C, a peak at 2θ = 7.5° with $d_{010} = 1.194$ nm was observed, which suggests that TiOPc molecules were restructured and crystalline $\alpha$-form films were formed. By the detailed XRD analysis, the optimum thermal annealing conditions are as follows: $T_A$ is 160 °C and the thermal annealing time is 4 h. The RMS and grain size are increased due to recrystallization with increasing $T_A$. Similarly, these absorption spectra of TiOPc ultrathin films reveal the gradual formation of the crystalline $\alpha$-phase, as evidenced by the development of a red-shifted absorption band, peaking 845 nm, and the corresponding reduction of the 720 nm amorphous phase peak when $T_A$ was increased from 120 °C to 180 °C. Furthermore, device performance of TiOPc TFTs could be improved and mobility was enhanced by thermal annealing, which originated from amorphous TiOPc films transformed into crystalline $\alpha$-TiOPc film and...
increasing of grain size. At $T_A = 160^\circ C$, the device achieved the highest performance with field-effect mobility of $6.34 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

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