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Improved photoreceptor decay characteristics of vanadyl-phthalocyanine films annealed under magnetic field

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Abstract

Magnetic field was applied during the annealing of vanadyl-phthalocyanine films prepared by vacuum vapor deposition. It was observed that the Q-band absorption peak position in the UV–vis absorption spectra of the films shifted to longer wavelength, and the X-ray diffraction intensity of the films was enhanced for the film annealed under magnetic field. Remarkable improvements in the photoreceptor decay characteristics of the films were also found for the films annealed under magnetic field. It is suggested that molecular orientation during annealing under magnetic field is responsible for the above phenomena.

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Keywords: Phthalocyanine; Photoreceptor; Magnetic field; Molecular orientation

1. Introduction

Metallophthalocynines (MPc) have been widely used in gas sensors [1–3] and organic photoreceptors [4–6]. Recent studies of MPc films are focused on their applications in data storage devices [7], photovoltaic cells [8–11], non-linear optics [12], organic light emitting devices [13], and organic transistors [14,15], etc. It is known that molecule stacking in the MPc films strongly influences the properties of the MPc films, so it is important to control the stacking and orientation of the MPc films. MPc films deposited under external field such as magnetic field and electric field were reported [16–18]. In a recent paper, molecule orientation of the phthalocyanine films (H_2Pc) annealed under magnetic field was reported by the author of this paper, but no corresponding photoreceptor results were described there since H_2Pc is not a good photoreceptor [19].

In this paper, a good photoreceptor material, vanadyl-phthalocyanine (VOPc) films deposited by vacuum vapor deposition were annealed under magnetic field, shifts of the bands in the UV–vis absorption spectra and improvements in photoreceptor decay characteristics were observed. XRD results demonstrated improved crystalline quality and molecular orientation of the films after annealing under magnetic field.

2. Experimental

VOPc films were deposited on fused quartz (2 cm × 2 cm) in a vacuum chamber with the base pressure of about 1×10^{-3} Pa. Before deposition, the substrates were cleaned in nitric acid first, and then rinsed in deionized water ultrasonically. The detailed structure of the deposition system and procedure were described elsewhere [3]. The substrates were not heated intentionally during deposition.

Annealing of the VOPc films was performed in a tiny heater taken from a soldering iron, and the magnetic field was applied outside the heater by using a pair of Nb–Fe–B permanent magnets (~1.0 T), as shown in Fig. 1. The annealing temperature was 80 °C, and the duration of the annealing was 90 min.

The crystalline structure of the VOPc film was characterized by X-ray diffraction (XRD) using a Rigaku Rotaflex D/max-rA X-ray diffractometer with Cu Kα as the X-ray source, the UV–vis absorption spectra were measured on a Lambda20

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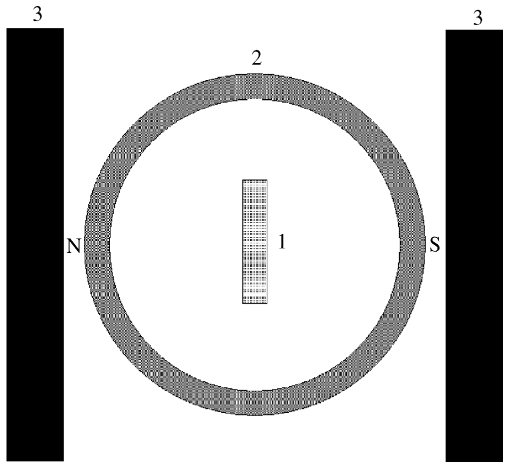

Fig. 1. Schematic diagram of the annealing system. (1) VOPc film, (2) heater and (3) magnets.

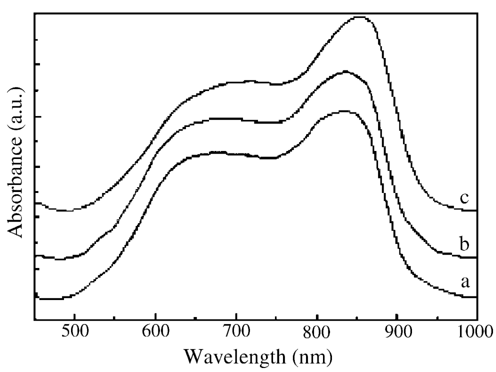

Fig. 2. UV–vis absorption of VOPc. (a) Film A, (b) Film B and (c) film C.

UV–vis absorption spectrophotometer of Perkin-Elmer, and the photoreceptor decay characteristics were measured by a home-made photoreceptor decay curve measuring system.

Three VOPc films were prepared, one is the as-deposited film (film A), the second one is the film annealed without magnets applied (film B), and the third one is the film annealed with magnets applied, i.e., under magnetic field (film C).

3. Results

3.1. UV–vis absorption

The UV–vis absorption spectra and the peak positions of the above films were shown in Fig. 2 and Table 1. Since only the Q-band was responsible for the photoreceptor characteristics of the VOPc, only Q-band absorption was plotted here. It is clear from the UV–vis absorption spectra that the peak position of the Q-band absorption showed red-shifted for film B (curve b, 7 nm), but a much more pronounced shift was found for film C (curve c, 26 nm). Noticing that the only difference between film B and film C is the magnetic field, this difference in absorption spectra must be caused by the application of the magnetic field during annealing.

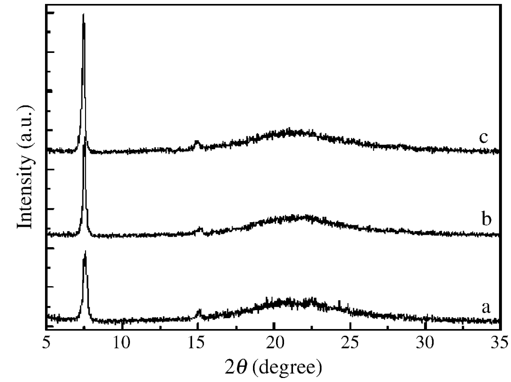

Fig. 3. XRD curves of VOPc films. (a) Film A, (b) film B and (c) film C.

3.2. X-ray diffraction

The XRD results were shown in Fig. 3 and Table 2, which indicate that all three VOPc films were in α-type phase, with two peaks at $2\theta = 7.51°$ and $2\theta = 15.02°$, corresponding to two and one times of the spacing of the ring–ring separation between the π-electron conjugating MPc macrocycles, respectively [20,21]. Peak intensity enhancement and peak width decrease were observed for the annealed film B, and film C, but film C showed a much more stronger peak, which implies that crystalline grains in film C were oriented in the same direction since the peak width of film B and film C is almost the same value. In general, annealing will results in the improvements of the crystalline quality of the films, as compared to film A, but the different intensity of film B and film C indicates that the effect of the magnetic field seems to have something new, since for film B and film C, the only difference is the magnetic field. In a previous paper, we found very similar results for the H_2Pc film annealed under magnetic field, and suggested that molecular orientation occurred during the annealing process of the H_2Pc film under magnetic field is the origin of such improvements [19].

3.3. Photoreceptor decay characteristics

A simple photoreceptor structure was designed and fabricated to measure the photoreceptor decay characteristics of the VOPc films, as shown in Fig. 4, in which VOPc film was deposited

Table 1
Positions and shift of the Q-band from UV–vis absorption measurement

Temperature (K)	Magnetic field (T)	Position (nm)	Shift (nm)
298	0	832.5	0
353	0	839.5	7
353	∼1	858.5	16

Table 2
Results of XRD measurement

Temperature (K)	Magnetic field (T)	Peak width (°)	Peak height (a.u.)
298	0	0.258	1603
353	0	0.182	2190
353	∼1	0.176	3169

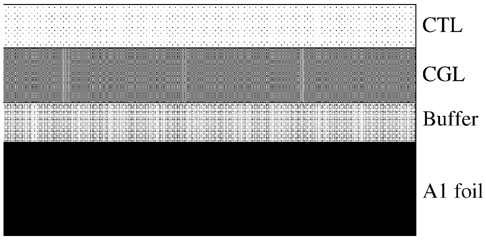

Fig. 4. Schematic diagram of the device structure used to measure the decay curve.

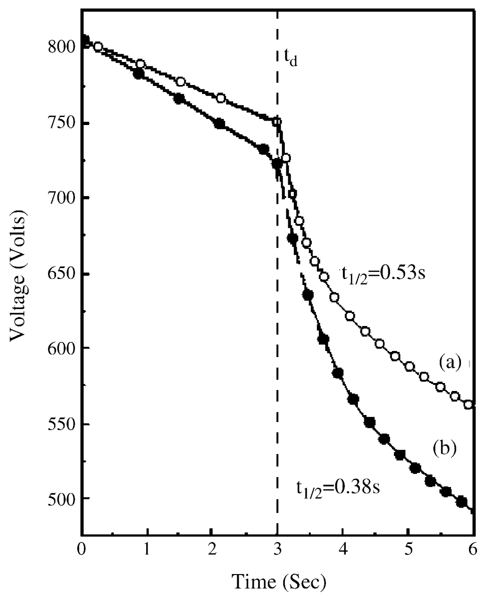

Fig. 5. Decay curves of the photoreceptors. (a) Annealed without magnetic field and (b) annealed under magnetic field.

as the charge generate layer (CGL). Before the deposition of the CGL layer (VOPc), a thin buffer layer of PPMA was dip-coated on the aluminum foil. At the top of the device, a thin charge translation layer (CTL) of 4-diethyl-aminobenzadehyde-α-naphthalenylpenylhydrazone (DENH) was dip-coated.

To measure the decay curves, devices were charged to −800 V, and then kept in darkness for 3 s (i.e., t_d). Finally, the devices were discharged by espousing the devices to the white light emitted from a bulb. The decay curves are shown in Fig. 5. It is found that the device made from film C had a shorter decay time and a lower residual voltage than the device made from film B, indicating of better photoreceptor characteristics. Data fitting of the curves in Fig. 5 gives a decay time $t_{1/2}$ of 0.38 s and a residual voltage of 490 V for the first device (film C), compared to a $t_{1/2}$ of 0.53 s and a residual voltage of 561 V for the second device (film B).

It is known that vanayl-phthalocyanines is a organic molecule materials with almost planar structures, in which π electrons are shared in a porphrin-like rings [20,21]. It is quite possible that such molecule with π electrons will interact with external magnetic field because of the induced magnetic momentum in the ring by strong magnetic filed. A simplified picture of molecular orientation is suggested here. During the annealing of the VOPc films under magnetic field, the magnetic moment of the VOPc molecule normal to the ring is parallel to the external magnetic field to reduce the total energy. Such molecule-oriented film can effectively increase the mobility of the generated charge carrier in the film, and thus enhance the velocity of the carrier in the film, which results the improvements of photoreceptor characteristics of the device made from vanayl-phthalocyanines film annealed under magnetic field.

4. Conclusion

In summary, magnetic field was applied during the annealing process of the VOPc films. Experimental results demonstrated that annealing under magnetic field resulted in a red-shift of Q-band in UV–vis absorption spectra, better crystalline quality and molecular orientation, and improved photoreceptor decay characteristics of the device made from vanayl-phthalocyanines films. It is suggested that molecular orientation of the VOPc molecule under magnetic field was responsible for the above improvements.

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