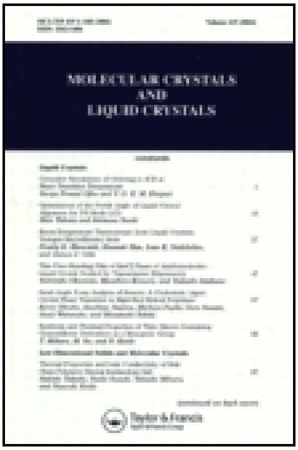

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Post-Deposition-Annealing-Induced Alignment of Copper Phthalocyanine Thin Films under UV Irradiation and Their Electrical Properties

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POST-DEPOSITION-ANNEALING-INDUCED ALIGNMENT OF COPPER PHTHALOCYANINE THIN FILMS UNDER UV IRRADIATION AND THEIR ELECTRICAL PROPERTIES

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Copper phthalocyanine (CuPc), a widely-used semiconducting material, was deposited onto quarts substrates via a vacuum process. SEM and XRD analysis were employed to characterize the structure-controlled CuPc films. As-deposited CuPc thin films were weakly oriented according to the XRD result and were homogeneous. The conductivity of CuPc film was estimated using four-point probe measurement technique and the values of the conductivity were 8.0×10^{-8}–$3.5 \times 10^{-7}\ \Omega^{-1}cm^{-1}$. *It was observed that thermal annealing under UV irradiation could make CuPc film well-aligned since UV irradiation could participate to increase the interaction among the CuPc molecules and between the CuPc molecule and the surface of the substrate leading to closer stacking of CuPc molecules. For well-aligned CuPc thin films, the threshold voltage in I-V characteristics of the ITO/CuPc/Al device was decreased by 20% compared to as-deposited CuPc films.*

Keywords: alignment; conductivity; phthalocyanine; semiconducting material; UV irradiation

INTRODUCTION

Metal-substituted macrocylic materials have recently attracted considerable interests due to their applications such as nanoscale devices, sensors, nonlinear optics, magnetic storage media, organic film transistors, and anisotropic conductors due to their unique properties (e.g., electronic, optical, magnetic) [1,2]. Typically, metallic and inorganic semiconductor thin films or nanostructures can be obtained via simple vacuum process,

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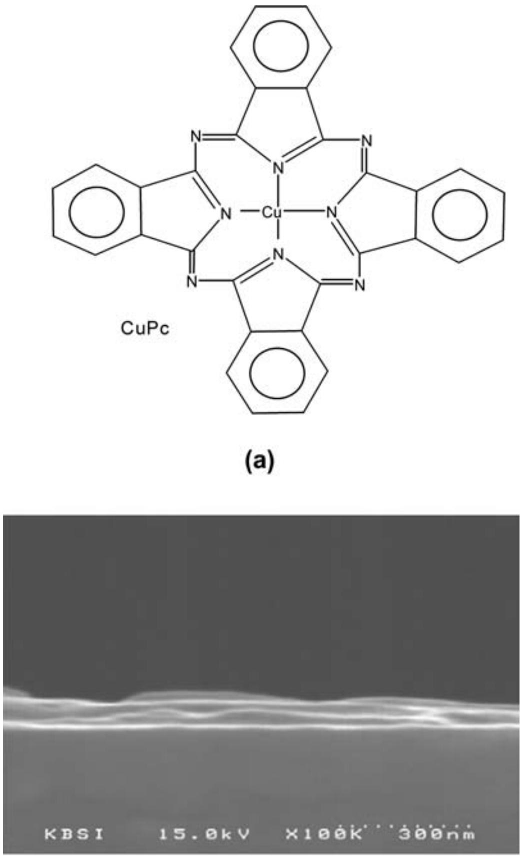
catalyst-assisted electrodeposition and various schemes based on the vapor-liquid-solid (VLS) mechanism under vacuum conditions at high temperature [3]. Alternatively, the growth of metallic dendritic structures can be obtained by heat treatment and plasma-assisted field emission using volatile organometallic compounds. Among volatile organometallic compounds, copper phthalocyanine derivatives were found that the molecules could stack in solution and/or on the liquid phase as Langmuir-Blodgett films giving rise to a number of interesting properties such as semiconductivity or conductivity. Single crystals of copper phthalocyanine (CuPc) derivatives can be grown from the vapor phase in a stream of gas using similar techniques as for other organic semiconductor materials [4,5]. In the present study, copper phthalocyanine was deposited onto quarts substrates via vacuum process and post-deposition annealing was carried out under UV irradiation in air with increasing temperature up to 250°C in order to investigate the effect of post-deposition annealing under UV irradiation on the structural alignment of CuPc thin films.

EXPERIMENTAL

CuPc was sublimed to obtain thin films via vacuum process. This technique participates to obtain homogeneous layers/films with a controlled thickness. The deposition rate was controlled to 0.42 nm/min to obtain 50 nm of thickness of CuPc films. As-deposited CuPc thin films were thermally treated under UV irradiation in a cylindrical furnace in air. Thermal treatment was carried out for 2 hours with increasing temperature up to 250°C. The chemical structure of CuPc is shown in Figure 1(a). SEM and XRD analysis were employed to characterize the structure-controlled CuPc films.

RESULTS AND DISCUSSION

The thickness of vacuum-deposited CuPc thin film was 50 nm as shown in Figure 1(b). High purity and highly homogeneous films were obtained. As-prepared films were weakly oriented according to the XRD result shown in Figure 2(a), in which a weak intensity peak around 7.6 degree is seen. The conductivity of CuPc film was estimated using four-point probe measurement technique and the values of the conductivity were 8.0×10^{-8} –3.5×10^{-7} $\Omega^{-1}cm^{-1}$, which is within the value range of typical metallophthlocyanines (i.e., $1.4-6.0 \times 10^{-7}$ $\Omega^{-1}cm^{-1}$) [2]. Relatively lower values of the conductivity were observed because the CuPc molecules were not preferentially-stacked in the film resulting in poor electron transporting.



(b)

FIGURE 1 Chemical structure of copper phthalocyanine (CuPc)(a) and vacuum deposited CuPc thin film(deposition rate = 0.42 nm/min, film thickness = 50 nm)(b).

Thermal annealing under UV irradiation could make CuPc film well-aligned as shown in Figure 2(b), in which a bigger rise of intensity peak around 7.6 degree was observed. It is known that most of metal-substituted macrocyclic materials possess polar and/or magnetic behavior. UV irradiation participates to increase the polarity of the CuPc molecules and the surface of the substrate leading to closer stacking of CuPc molecules. Thus, CuPc films were to be oriented in the (200) direction according to the XRD result shown in Figure 2(b).

A schematic diagram of the generic device structure of the single layer is shown in Figure 3(a). The organic layer was evaporated to an

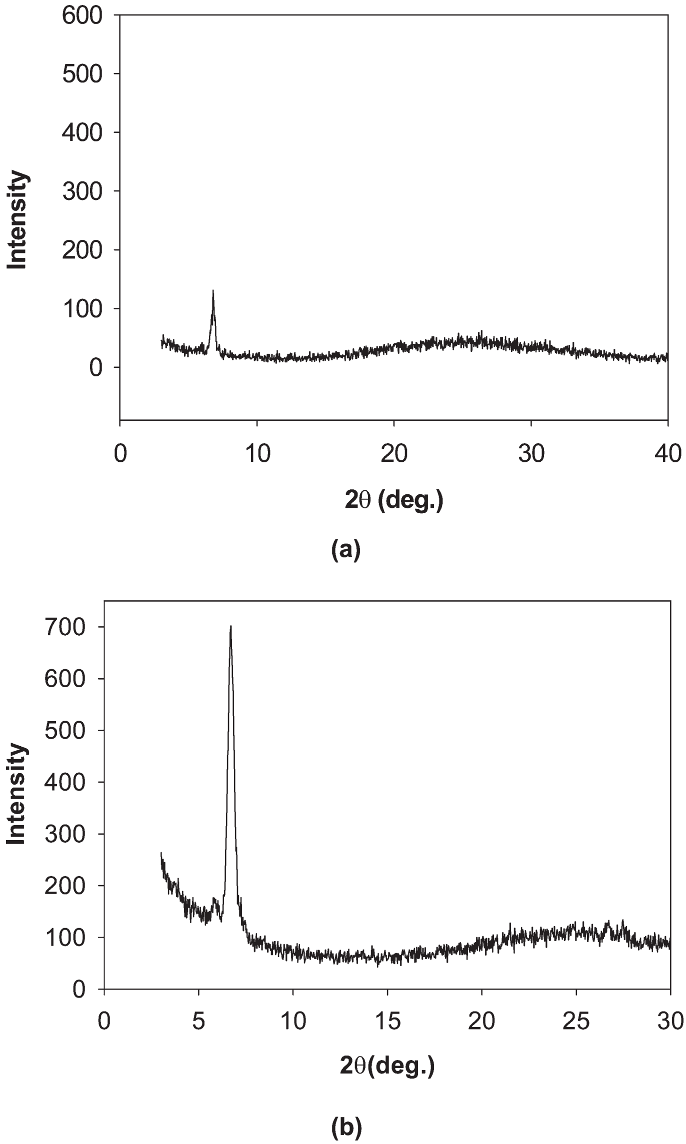


FIGURE 2 X-Ray diffraction patterns of CuPc films: as-deposited film(a) and after thermal treatment of as-deposited CuPc film under UV irradiation in air at 180°C(b).

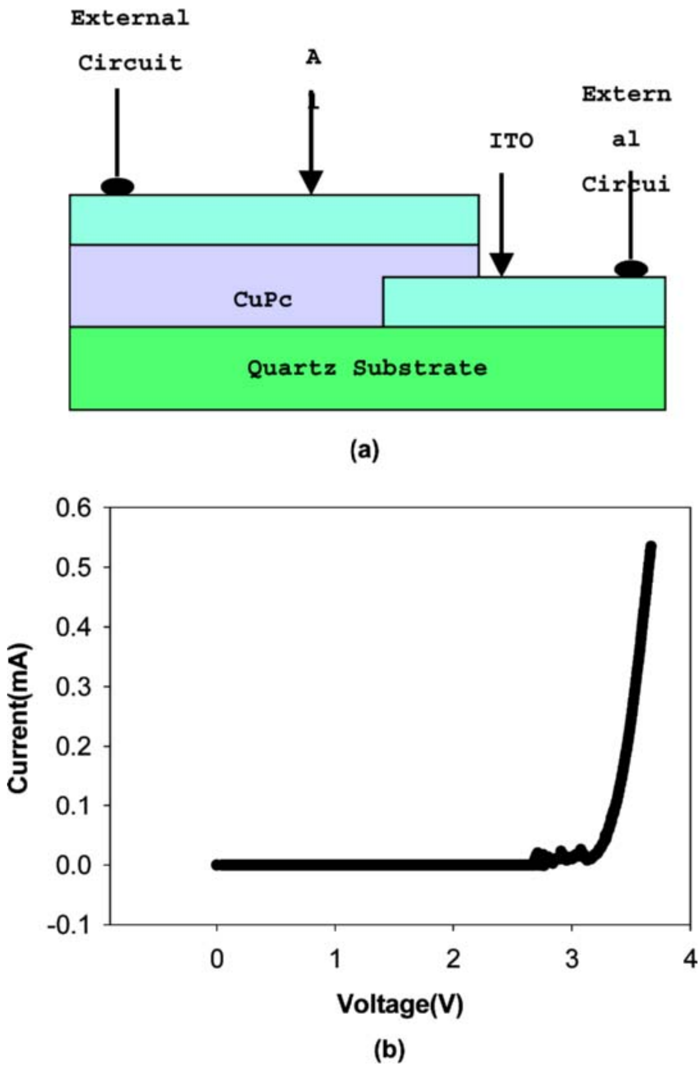


FIGURE 3 Schematic diagram of the generic device structure of the single layer(a) and I-V characteristics of the ITO/CuPc/Al device(threshold voltage = 3.2 V)(b).

overall thickness of 50 nm, while the top electrode was 100 nm. Typical current–voltage(I-V) characteristics of the ITO/CuPc/Al is shown in Figure 3(b), in which the threshold voltage is 3.2 V. For well-aligned CuPc thin films, the threshold voltage was decreased to 2.6 V. This behavior was due to closer stacking of CuPc molecules within CuPc layer. Thus, an increase of the bulk conductivity of the CuPc layer is observed. Above the temperature of 180°C, the CuPc thin films were deformed.

CONCLUSIONS

As-deposited CuPc thin films were weakly oriented according to the XRD result and were homogeneous. As a widely-used semiconducting material, the values of the conductivity of CuPc film was 8.0×10^{-8}–3.5×10^{-7} Ω^{-1}cm^{-1}, which is within the value range of typical conductivity of metallophthlocyanines. It was clearly observed that thermal annealing under UV irradiation could make CuPc film well-aligned since UV irradiation could participate to increase the polarity of the CuPc molecules and the surface of the substrate leading to closer stacking of CuPc molecules. Thus, CuPc films were to be well-aligned. For well-aligned CuPc thin films, the threshold voltage in I-V characteristics of the ITO/CuPc/Al was decreased from 3.2 to 2.6 V.

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