

Short Communication

Phase modification of copper phthalocyanine semiconductor by converting powder to thin film

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ABSTRACT

Thin films of copper phthalocyanine (CuPc) semiconductor were deposited on glass substrates by a thermal evaporation system using the CuPc powder in a high vacuum. The crystal structures of both the films and the powder were measured by the X-ray diffraction spectroscopy technique. It is observed that CuPc films only show one peak at 6.84° , indicating a high texture of α phase along (200) orientation. In comparison, CuPc powder shows a series of peaks, which are confirmed from the mixture of both α and β phases. The effects of substrate anneal temperature on the film structure, grain size and optical absorption property of CuPc films were also investigated. All the films are of α phase and the full width of half maximum for (200) diffraction peak becomes narrow with increasing the substrate temperatures. The average grain size calculated by the Scherrer's formula is 33.63 nm for the film without anneal, which is increased up to 58.29 nm for the film annealed at 200°C . Scanning electron microscope was further measured to prove the growth of crystalline grain and to characterize the morphologies of CuPc films. Ultraviolet-visible absorption spectra were employed to study the structure effect on the optical properties of both CuPc films and powder. Fourier Transform infrared spectroscopy was used to identify the crystalline nature of both CuPc powder and film.

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1. Introduction

Recently, the metallophthalocyanines have gained huge attention because of their widely application in electronic devices, such as solar cells, gas sensors, organic spin devices and so on [1–15]. Phthalocyanines (Pcs) are two dimension heterocyclic conjugated molecules, which can self-assemble into stacks through π – π molecular interaction [16–20]. The crystalline quality and molecular orientation are important because grain and/or domain boundaries can give rise to carrier scattering [21]. Copper phthalocyanine (CuPc) is one of the most interesting metallophthalocyanine semiconductors because it has not only a high mobility but also excellent optical and electronic properties [22–24]. However, CuPc have several crystal structures, mainly including α and β phases [25–29]. The crystal phases of metallophthalocyanines significantly affect their physical properties, including carrier mobility, anisotropy, magnetism and non-linear

optics [2,16,23,25–30]. α -CuPc has attracted enormous interest for potential use in organic electronics compared to that of β -CuPc. It was reported that the ferromagnetic property of α -CuPc films can be obtained near room temperature [2]. A field-effect transistor prepared using α -CuPc nanowire shows excellent performance with a high carrier mobility of $0.4\text{ cm}^2/\text{V}$ [16]. Enhancement of nonlinear optical susceptibility in α -CuPc films was also observed [23]. In addition, Popielarski et al. further demonstrated that the high-frequency capacitance and conductance of CuPc-Si and CoPc-Si hetero-structures strongly relied on the crystal structure (α or β phase) of metallophthalocyanines [31].

The phase transformation temperature of CuPc from α phase to β phase has been studied by post annealing in literatures [25,26,31–34]. But the results are somewhat conflicting. Assour had determined the transition temperature is 300°C for bulk CuPc crystals [26]. Hassan and Gould have identified the transition temperature to be 240°C for CuPc thin films [25]. Meanwhile, the phase transition at 210°C can also be found in literature [32]. Very recently, Chattopadhyay et al. observed that the transition temperature could be 183°C for CuPc nanorods owing to an enhancement of surface energy for the nanocrystal system [33]. The

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investigations performed by Szybowicz and the co-workers further demonstrated that the phase transformation phenomenon by post annealing exist not only in CuPc but also in other metallophthalocyanines (CoPc, ZnPc and MgPc) [34]. In contrast, it is very rare about the study for an *in-situ* growth of α -CuPc film with annealing in vacuum, and their related structure analysis for α -CuPc film with a high texture. The small grain boundary and low film roughness by this growth technique are more suitable to fabricate advanced organic devices. Moreover, the post annealing of CuPc in air likely absorbs oxygen in CuPc, which may lead to extrinsic results [35].

In this work, CuPc semiconductor thin films were fabricated by a thermal evaporation method using the CuPc powder in a high vacuum. The substrates were heated at different temperatures during the growth of CuPc film. Both the films and the powder were investigated by the X-ray diffraction spectroscopy (XRD), scanning electron microscope, Ultraviolet–visible (UV–vis) spectra and Fourier Transform infrared (FTIR) spectroscopy. It is observed that CuPc films show a high texture of α phase with only one diffraction peak at 6.84° . In comparison, CuPc powder is the mixture of both α and β phases. UV–vis spectra indicate an obviously different property for CuPc films compared to that of powder.

2. Experimental methods

2.1. Preparation of CuPc thin film

The CuPc powder used in this study was synthesized by a solvothermal method. Our initial aim is to prepare α -CuPc powder to grow α -CuPc film because the structure of most commercial CuPc powder is β phase [3,25,36]. Cupric Acetate Monohydrate

and 1, 2-Dicyanobenzene with the mole ratio of 1:4 were mixed in an ethyl alcohol solvent. The solution was transferred into closed Teflon-lined autoclaves of 50 mL capacity, which were filled 80% of the total volume. The tank was heated and kept at 180°C in a furnace for 8 h. After cooling down to the room temperature, the product was dried at 65°C . And then the CuPc powder was collected. The CuPc films were prepared on the glass substrates using the powder by a thermal evaporation technique with a base pressure of 10^{-6} Pa. The vacuum for film growth is $2\text{--}4 \times 10^{-4}$ Pa and the deposition rate is 0.8 nm/min. The present results have a good reproducibility unless the vacuum for film growth is poor. The powder was heated to 350°C and kept for 1.5 h to grow the films. The substrate was rotated using a mechanical motor during the CuPc deposition to homogenize the film. The film thicknesses were measured with a quartz crystal resonator. The substrates were kept to 25°C , or *in situ* annealed and kept at different temperatures (50°C , 100°C , 150°C and 200°C) during CuPc films deposition.

2.2. Characterization

The crystal structures of both CuPc powder and films were measured using a powder X-ray diffractometer (Japan Rigaku X-ray) of Cu $K\alpha$ radiation in the range of $5\text{--}40^\circ$. The surface morphologies of powder and films were analyzed using a field emission scanning electron microscope (FE-SEM, JEOL JEM-7001F). The measurement of absorption spectra of the powder and films were performed on a UV–vis spectrophotometer (Lambda 750S) at room temperature and a Fourier Transform infrared spectrophotometer (Bruker IFS 66 V/S) in the infrared spectral range of $4000\text{--}600\text{ cm}^{-1}$.

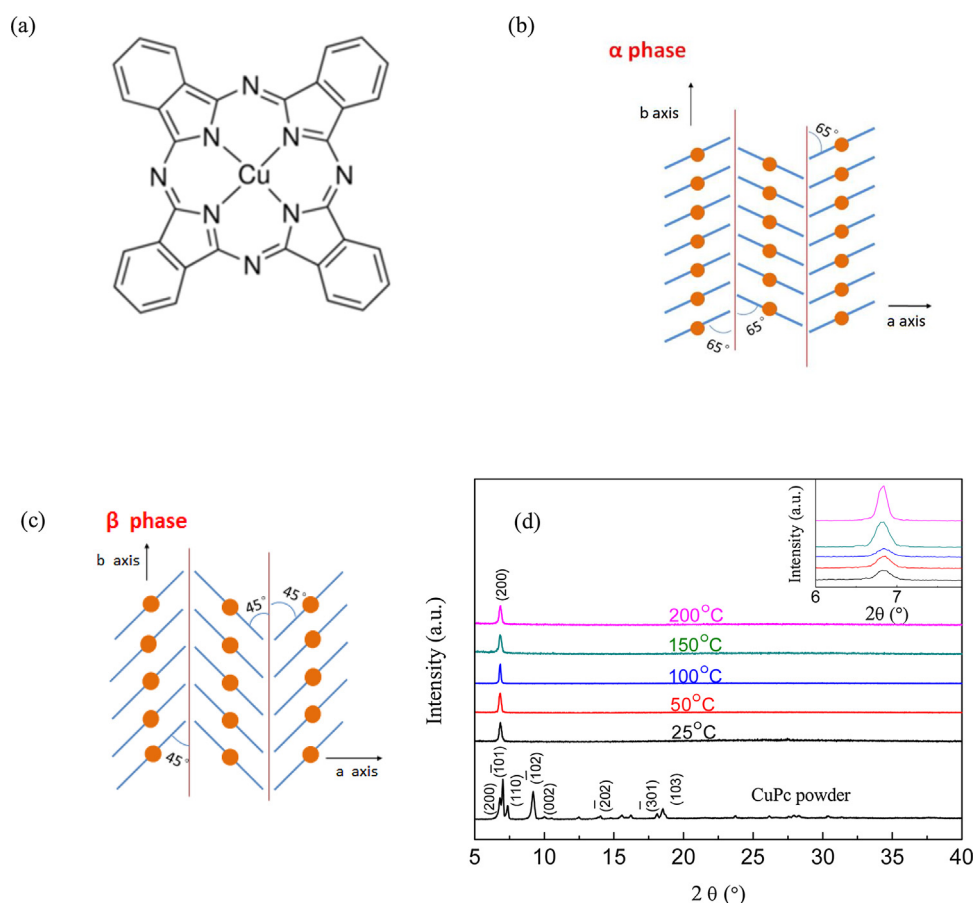


Fig. 1. The structure of the CuPc molecule (a). The stacked structures of α -phase (b) and β -phase (c) of CuPc. XRD patterns of both CuPc powders and films deposited on different substrate temperatures (d).

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