Influence of Substrate Temperature on Structural Properties of Thermally Evaporated Nano CuPc Thin Films

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Abstract:

A 200 nm thickness of Copper Phthalocyanine (CuPc) thin films were thermally evaporated at 10-5 mbar in a PVD device on glass substrate at temperature of 303 and 403 oK. This study focused on the effect of substrate temperature on structural properties of CuPc thin films. X-ray diffraction analysis (XRD) showed that films were deposited at 303 oK represent β-phase and films were deposited at 403 oK represent α-phase, that is in mean phase transition from β-phase to α-phase in CuPc layers. Grain size increased from 30 nm for films deposited at 303 oK to 360 nm for the films deposited at 403 oK. Scanning electron microscope (SEM) and atomic force microscopy (AFM) images showed increasing in CuPc Nano rods sizes , crystallization and surface roughness as substrate temperature increased.

Keywords: Phthalocyanine, Substrate temperature , Grain size, crystalline, Nano rods.

تأثير درجة حرارة الأرضية على الخصائص التركيبية لأغشية نحاس ثالوسيانين النانوية المحضرة بطريقة التبخير الحراري

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الخلاصة:

حضّرت أغشية نحاس ثالوسيانين بسمك ٢٠٠ نانومتر وبطريقة الترسيب الحراري PVDعلى أرضيات من الزجاج عند درجتي حرارة ٣٠٣ و٤٠٣ كلفن وتحت ضغط بحدود ١٠-٥ ملي بار. تم دراسة تأثير درجة حرارة الأرضيات على الخواص التركيبية لأغشية نحاس ثالوسيانين.أظهرتحليل نتائج حيود الأشعة السينية تحول بالطور التركيبي من الطور β للأغشية المرسبة عند درجة حرارة ٣٠٣ كلفن الى الطور التركيبي نوع α للأغشية المرسبة عند درجة حرارة ٤٠٣ كلفن، وزيادة الحجم الحبيبي من ٣٠ nm للأغشية المرسبة عند درجة حرارة ٣٠٣ كلفن الى ٣٦٠ nm للأغشية المرسبة عند درجة حرارة ٤٠٣ كلفن.كما أظهرت صور ال SEM و ال AFM زيادة النمو والتبلور للقضبان النانوية وكذلك خشونة سطح الغشاء بزيادة درجة حرارة الترسيب.

الكلمات المفتاحية: ثالوسيانين، درجة حرارة القاعدة (الأرضية)، الحجم الحبيبي، التبلور، قضبان نانوية.

1. Introduction

Metal-Phthalocyanine find extensive use as a dye pigment in dyeing industry, as charge generating layer for organic xerography, catalysts for redox reactions and recently as p-type in organic electronic devices. Organic semi-conductor materials such CuPc have stimulated interest in recent years for low cost, versatile electronic devices, in organic thin film transistors(OTFTs) and sensors led to extensive investigation on a range of metal substituted Phthalocyanine [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and gas detectors [3-4]. Phthalocyanine has potential applications in optical display devices, electrophotography, electroprinting, gas detectors [5] and solar cells [6,7].

These materials are generally p-type semi-conductors and have an advantage of being sufficiently stable towards chemicals and heat. They can be easily vacuum sublimed, resulting in high purity thin films without decomposition to about 500oC. The physical and chemical properties of phthalocyanine can be altered by changing the central metal ion. Film properties of this proto type organic semi-conductor are dependent on the film thickness, evaporation rate, substrate temperature and post annealing [8, 9].

In this paper, we will investigate the structural properties of CuPc thin films prepared at 303 oK and 403 oK substrate temperature by using thermal evaporation method. The X-ray characteristics conditions were also studied. SEM images show the effect of substrate temperature on grain size and growth rate of Nano rods of CuPc thin films.

2. Experiment

Powder of 99% CuPc heated by controlled DC-current about 50-60 A in a molybdenum boat at 10-5 mbar pressure in a PVD devise. Before the CuPc evaporation, the substrates of glass were pre-cleaned by ion cleaning and the materials were carefully degassed by closed shutter for about 30 minutes under 10-5 mbar pressure at room temperature. Thin films of CuPc were deposited on substrates using a (15F6 HindiVac) coating unit. The evaporation rate of 3-5 Aº /s is controlled with a crystal thickness monitoring during the disposition. The thicknesses of both prepared films were 200 nm. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties. The absorption spectra of the CuPc films were measured at room temperature using a double-beam spectrometer (RAY LIGH, UV– 2100) within the range (200 – 900) nm. X-ray patterns were obtained using X’Pert Pro (PAN Analytical) with Cu Kα radiation (λ = 1.5404Aº) in the range 0-30º.SEM images were obtained with Tescann-VegaII microscope.

3. Result and Discussion:

The optical absorption spectra of thin films deposited at two different substrate temperatures are shown in Fig. 1. These spectra have been characterized by two major bands i.e. B and Q band, both corresponding to $\pi - \pi^*$ Transitions [10].

UV–Vis absorption spectra of both 200 nm thin films which deposited at 303 oK (planar) and at 403 oK (Nano rods) CuPc are showed in Fig1. Interestingly, light absorbed by CuPc Nano rods for all wave lengths has remarkably increased compared to planar CuPc. It means that the

Nano rods can absorb more visible photons and consequently generating more exactions , compared to planar CuPc. Thus, these rods have a good potential for solar cell applications. This increase in the light absorption could be attributed to the light trapping due to the rough structure of the CuPc Nano rods[11].

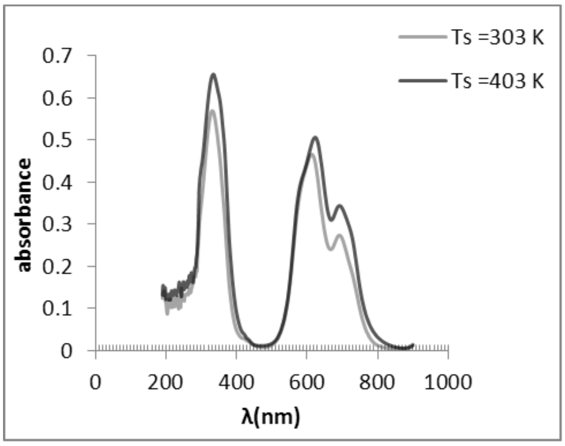


Fig.1. Absorption spectra of CuPc thin films which prepared at both substrate temperatures (303 oK and 403 oK)

Fig. 2(a) shows the SEM images of thin CuPc film grown on glass substrate by thermal evaporation at substrate temperature of 303 oK to create CuPc islands. Fig. 2(b) shows the CuPc Nano rods have been grown

Nano rods is approximately 50 nm and the average length of them is around 150 - 200 nm. The Nano rods are found to be bended over the surface.

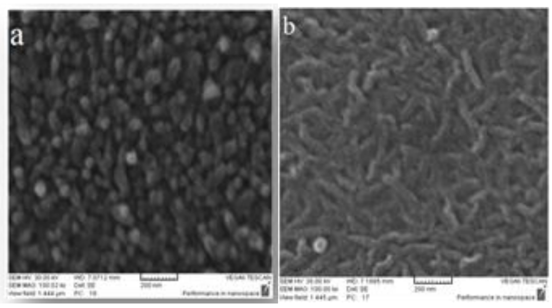


Fig. 2. SEM image of Nano-structure CuPc grown on glass substrate at both substrate temperatures (a) 303 oK (b) 403 oK

Our experiments show that the Nano rods can grow directly on this islands (Fig.2-a) bended over the substrate surface. Nakhaee et.la[11] showed that the existence of these islands is crucial as nucleation centers on substrate surface for Nano rods grow.

Fig. 3. shows the XRD pattern of CuPc thin films which prepared at both substrate temperatures 303 oK and 403 oK. Intensity of diffraction peak increases with the increase of substrate temperature. The diffraction peak at $2\Theta = 6.983^{o}$confirms the existence of the β - phase in CuPc crystalline for the planer thin film with growth temperature 303 oK, whereas for 403 oK substrate temperature the diffraction peak at $2\Theta = 6.736^{o}$confirms the existence of the α –phase in CuPc crystalline for the Nano rods which is similar results that were CuPc rather than the seed type. The crystalline nature of the rods is important for efficient hole transport through the Nano rods and high collection rate for photo-generated holes in the OPV devices. The average grain size (D) has been calculated using the Scherrer formula [17]:

$$D = \lambda/B \cos\theta$$

where λ is wavelength of X-rays , B is FWHM and θ is Bragg's angle. Average grain size is observed to increase with increasing the substrate temperature indicating better crystalline films and crystallization at higher substrate temperature. Crystallization calculated from the ratio between sum of net area under x-ray curve to the total area.

Table 1.Variation in crystalline and grain size for both substrate temperatures CuPc thin films

Substrate Temperature °K	Phase & ASTM Card	2θ° standard	2θ° exp	Crystallization %	Grain Size (A°)
303	β–phase 11-0893	7.066	6.983	49.62	28.9
403	α–phase 36-1883	6.742	6.736	66.72	361.7

shown by other researchers [12–16]. This probably shows that the growth.

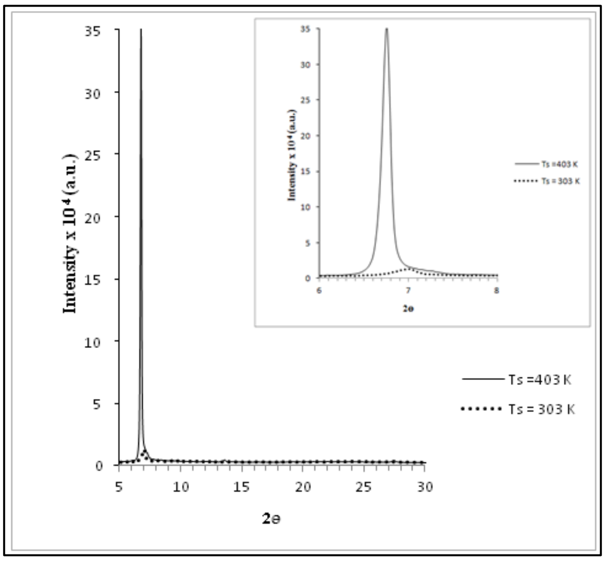
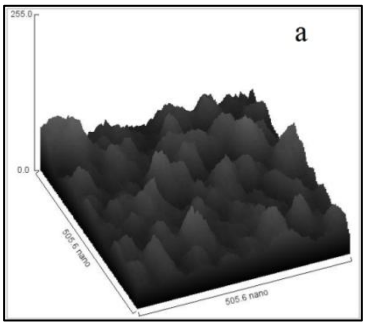


Fig. 3. XRD pattern of CuPc thin films deposited at 303 °K and 403 °K

Fig. 4 show the surface morphology for films deposited at 303 and 403 °K on glass substrate. It is clear that the surface roughness of films deposited at 403 °K is more than surface roughness of films deposited at 303 °K, it was attributed to increasing of crystallization.



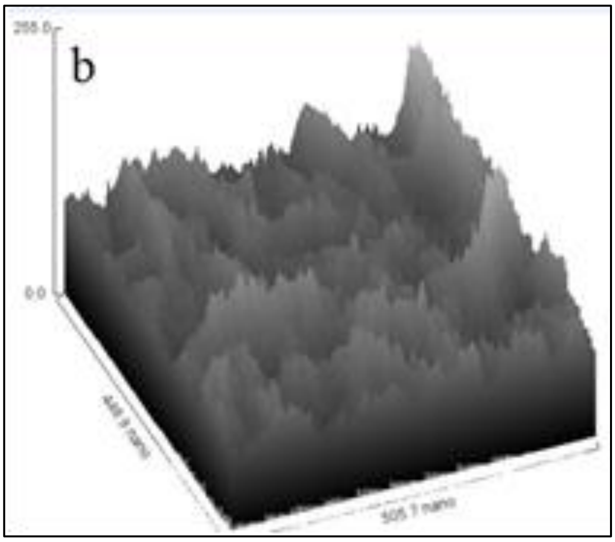


Fig.4.AFM images of CuPc thin films deposited at Ts=303 °K in a) and Ts=403 °K in b)

The structure, morphology, and optical properties of the films are crucial for their technological applications. For example, a high crystallization is known to improve the conducting properties, but smooth amorphous films allow better contacts.

4. Conclusions

Optical absorption vary with light wavelength and increases with increasing substrate temperature. Average grain size increase with increase in substrate temperature indicating better crystallization of films deposited at higher substrate temperature. UV–Vis spectra of CuPc thin films indicate the possible candidature of metal- phthalocyanine (here copper- phthalocyanine) as photovoltaic material. For the growth of CuPc layer by vacuum evaporation, the surface morphology of the thin film is influenced very strongly by the

substrate temperature during film deposition which cause the transition from β-CuPc phase to α-CuPc phase .

Excellent flexibility and easy bending and twisting of CuPc Nano rods upon electron beam exposure indicates that these nanostructures may represent a low-cost and low-temperature alternative to inorganic nanostructures for application purposes. These prepared CuPc thin films were good candidates for use as a base layer material in organic photovoltaic (OPV).

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