



Structural comparison studies of PbPc and CuPc thin films

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ABSTRACT

The thin film of Lead Phthalocyanine (PbPc) and Copper Phthalocyanine (CuPc) on glass are prepared by Vacuum deposition method. Deposition of PbPc and CuPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr are achieved by slowly varying the current. The rate of evaporation is properly controlled and maintained constant during all the evaporations. The thicknesses of the films are 150 nm, 300 nm and 450 nm on glass substrate. The thickness of sample 450 nm annealed at 323 K and 373 K temperature. Diffraction is one of the most powerful methods of the study and structure of materials, which may involve X-rays, electrons. The relative ease and convenience, large diffraction angle, representation of the average crystalline lattice throughout the film and simultaneous display of diffraction pattern from the film make the XRD method a successful analytical technique for the study of thin films. The sample has been analysed by X-ray diffraction (XRD) to get structural analysis of the PbPc and CuPc thin films.

Keywords: Phthalocyanine, X ray diffraction, monoclinic, triclinic and dislocation density.

INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors[OTFTs] and sensors has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities[13].

Phthalocyanines have potential applications in optical logic display devices, electrophotography, security printing, gas detectors [14], solar cells [15, 16], sensitizers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

This paper deals with the structural studies of lead phthalocyanine (PbPc) and copper phthalocyanine thin films prepared by vacuum evaporation technique. The materials are an organic semiconducting material which has various functional groups.

MATERIALS AND METHODS

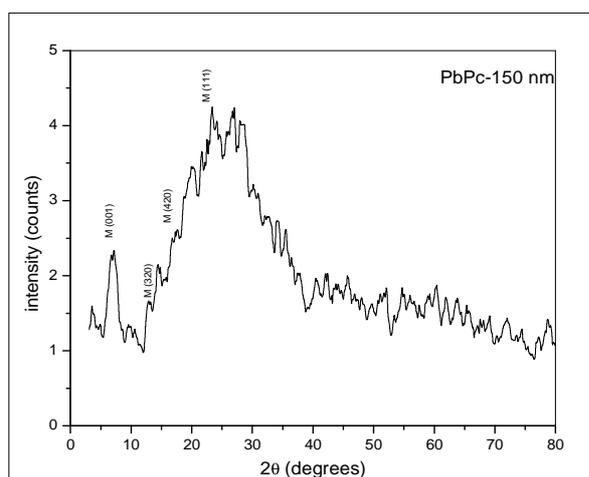
The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of 10^{-6} Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. This procedure is used for preparing PbPc and CuPc thin film on pre-cleaned glass substrate. 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 structures of the films were examined by θ -2 θ X-ray diffraction using a Cu K α source.

RESULTS AND DISCUSSION

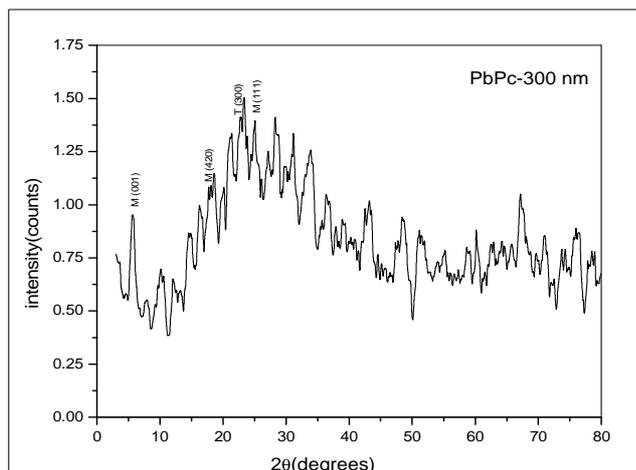
Effect of thickness

The X-ray diffraction patterns of thermally evaporated PbPc and CuPc films of thicknesses 150, 300 and 450 nm prepared at room temperature are shown in Figure 1 & 2 (a, b and c). The PbPc patterns at lower thickness (150 nm) shows peaks at 2 θ values 6.85°, 14.16° and 24.55° that were assigned to monoclinic (001), (320) and (111) lines respectively. The patterns at thickness (300 nm) shows an extra peak at 2 θ value 17.49° and is assigned to the monoclinic (420) line. A peak at 2 θ value 30.26° coinciding with the triclinic (400) line is seen for higher thicknesses (300 and 450 nm). The CuPc patterns at lower thickness (150 nm) shows peaks at 2 θ values 8.69°, 12.98° and 25.18° that were assigned to monoclinic (001), (320) and (111) lines respectively. The patterns at thickness (300 nm) shows an extra peak at 2 θ value 31.58° and is assigned to the monoclinic (400) line. A peak at 2 θ value 26.78° coinciding with the triclinic (420) line is seen for higher thicknesses (450 nm). The peak values are in good agreement with the previous literature works [21, 22].

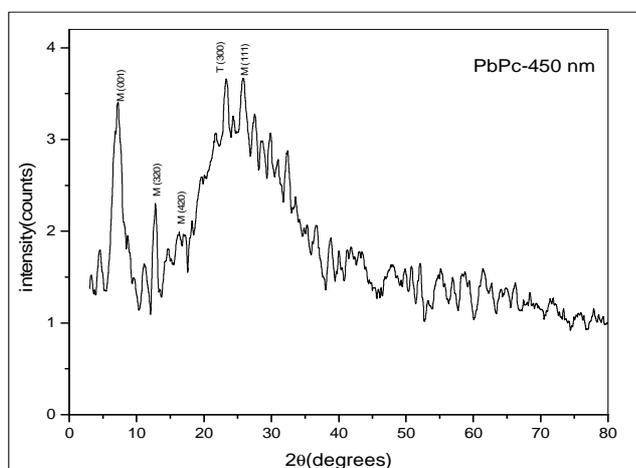
From the XRD patterns of PbPc and CuPc films of different thicknesses, it is clear that as thickness increases, triclinic grains (T) are seen along with monoclinic (M) forms. Thus evaporated films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher thicknesses [24, 25]. These evaporated films are polycrystalline in nature.



(a) 150 nm

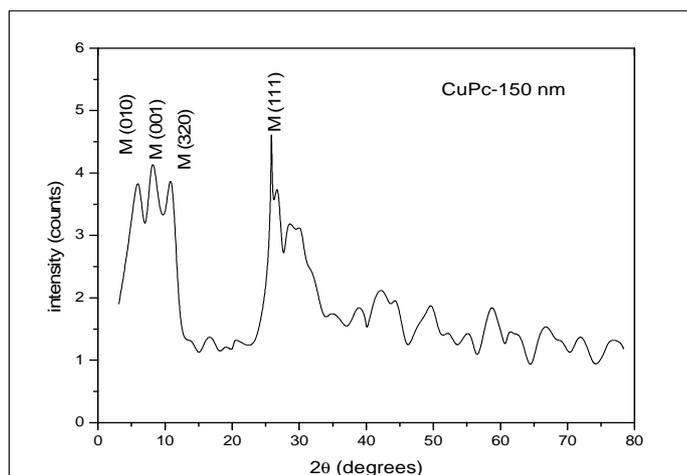


(b) 300 nm

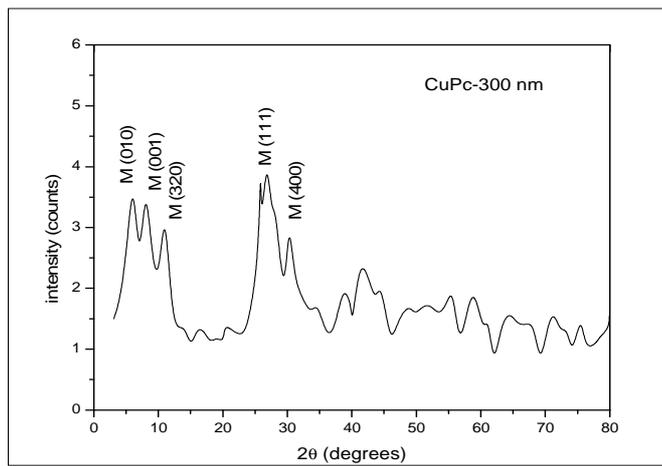


(c) 450 nm

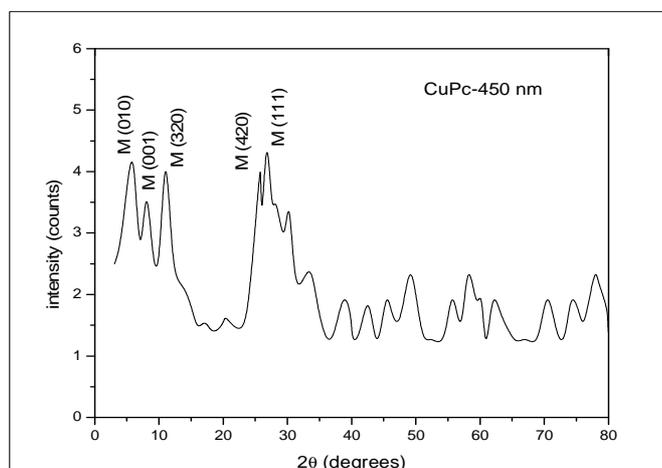
Figure 1 XRD patterns of PbPc films for thicknesses on glass substrate



(a) 150 nm



(b) 300 nm



(c) 450 nm

Figure 2 XRD patterns of CuPc films for thicknesses on glass substrate

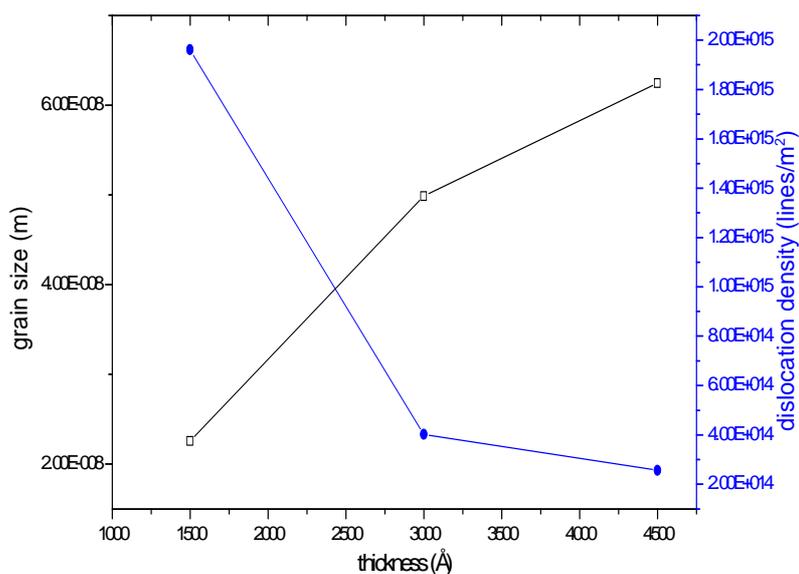


Figure 3 Variation in grain size (D) and dislocation density (δ) as a function of thickness of PbPc

A weak intensity of (320) reflection and absence of (h00) reflections in all thicknesses implies a low degree of crystallinity of the monoclinic film compared with the triclinic film. The XRD patterns shows weak diffraction peaks for (320) and (420) monoclinic lines of PbPc and (320) and (400) of CuPc. PbPc and CuPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. Such a structure explains the weak diffraction peaks of monoclinic crystals [22, 25, 26 and 27]. In this phase, the molecules stack linearly to form a molecular column parallel to the c axis [28].

Table 1 and 2 shows the structural parameters of PbPc & CuPc films for different thicknesses. From the table it is clear that full width half maximum (FWHM) decreases with the film thickness. Such a decrease reflects the decrease in internal microstrain within the films and an increase in grain size.

Figure 3 & 4 shows the variation in grain size and dislocation density as a function of thickness. From this we conclude that as thickness increases, grain size increases and defects like dislocation density and strain decreases. This may be due to the improvement in crystallinity in the films [29].

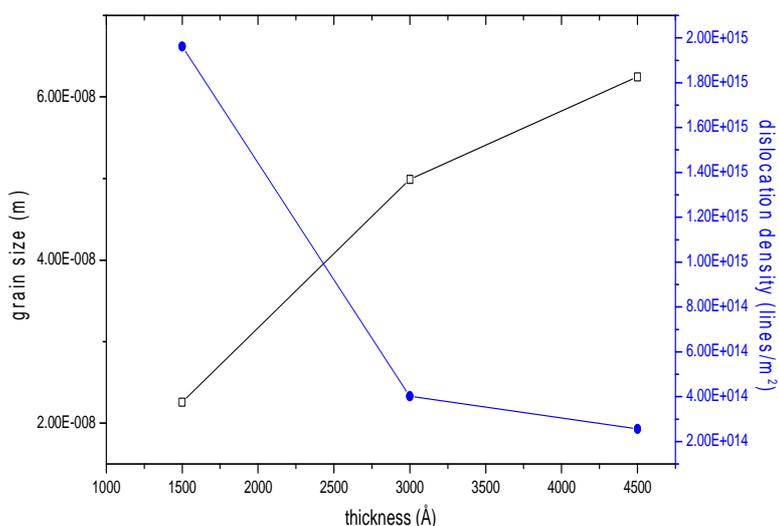
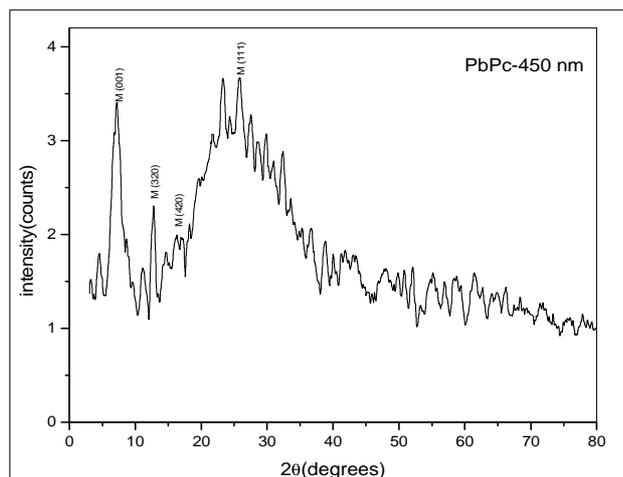


Figure 4 Variation in grain size (D) and dislocation density (δ) as a function of thickness of CuPc

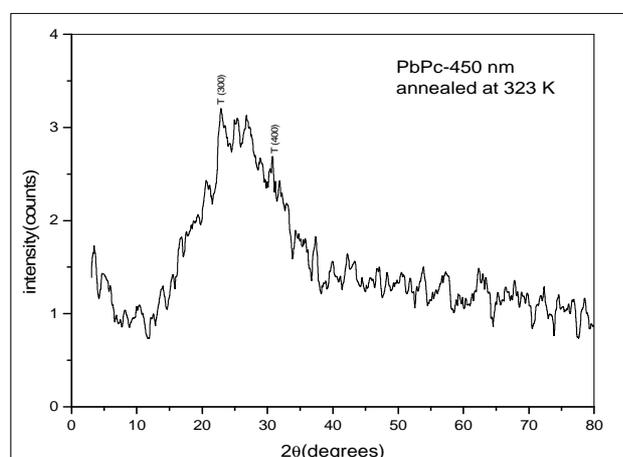
Effect of temperature

The XRD patterns of PbPc and CuPc films for thickness 450 nm at different annealed temperatures are shown in Figure 5 & 6 (a, b and c). The peaks obtained at 303 K are assigned to the monoclinic phase films with some triclinic grains, and is already mentioned.

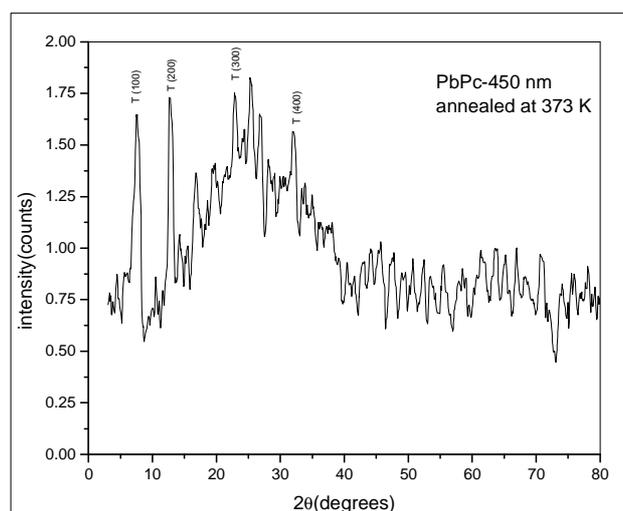
The XRD graph of PbPc at 323 K shows peaks at 2θ values 14.9° , 22.4° and 30.3° assigned to the triclinic (200), (300) and (400) lines respectively. Here all peaks are of small range. When temperature is increased to 373 K one more peak at 2θ value 7.43° arise which gets assigned to the (100) reflection of triclinic phase. The results are consistent with the previous literature works [21,22]. The XRD of CuPc at 323 K shows peaks at 2θ values 26.12° , 27.63° and 34.21° assigned to the triclinic (300), (200) and (400) lines respectively. Here all peaks are of small range. When temperature is increased to 373 K one more peak at 2θ value 26.83° arise which gets assigned to the (100) reflection of triclinic phase. The results are consistent with the previous literature works [30, 31].



(a) 303 K

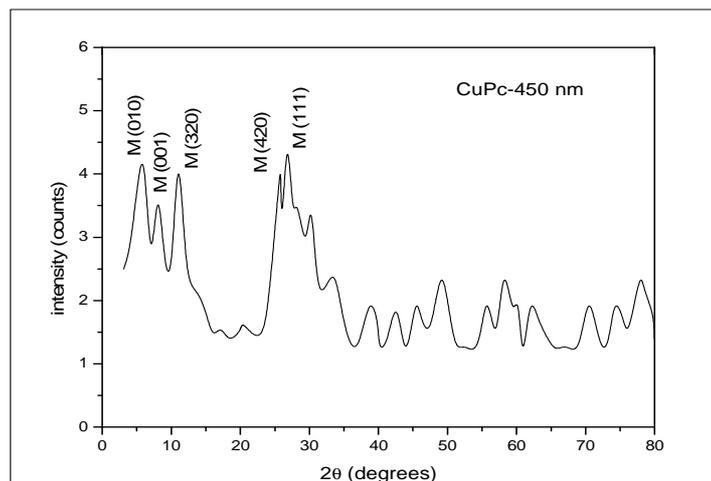


(b) 323 K

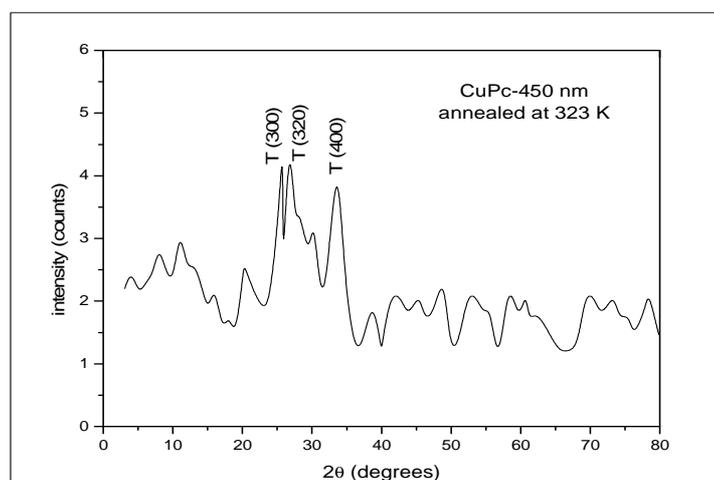


(c) 373 K

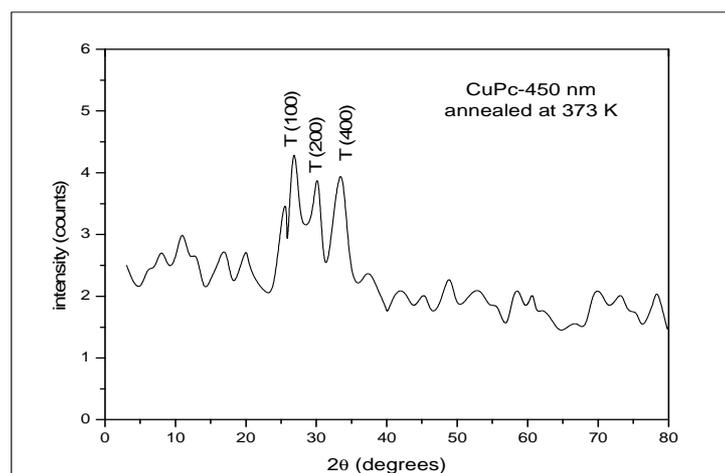
Figure 5 XRD patterns of PbPc films for thickness 450 nm at annealed temperatures



(a) 303 K



(b) 323 K



(c) 373 K

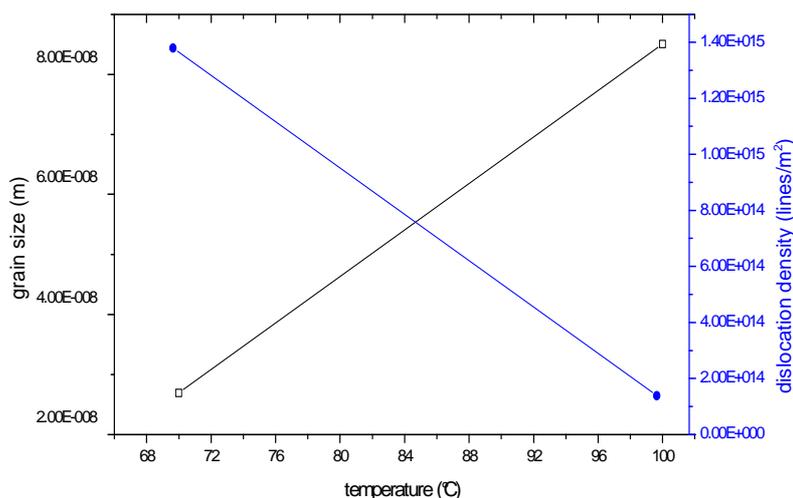
Figure 6 XRD patterns of CuPc films for thickness 450 nm at annealed temperatures

Table 1. Structural parameters of thermally evaporated PbPc films for different thicknesses

Thickness (nm)	(hkl)	2 θ (degrees)		Interplanar Spacing d (Å)	FWHM $\beta \times 10^{-3}$ (radians)	Grain size D (nm)	Dislocation density $\delta \times 10^{15}$ (lines/m ²)	Strain $\epsilon \times 10^{-4}$
		Observed	Previous literature values					
150	(001)	6.851	6.89	12.89	11.560	12.544	6.3549	28.8481
	(320)	14.156	12.59	6.25	5.160	28.269	1.2513	12.8027
	(111)	24.553	24.155	3.62	6.5617	22.577	1.9617	16.0208
300	(001)	6.9	6.89	12.75	8.648	16.760	3.5560	21.1583
	(420)	17.492	16.58	5.06	16.232	44.350	0.5083	8.1600
	(111)	25.438	24.155	3.49	2.975	49.874	0.4020	7.2559
450	(001)	6.981	6.89	12.65	5.8855	24.641	1.6469	14.6860
	(320)	12.718	12.59	6.95	4.9594	29.369	1.1593	12.3222
	(111)	25.706	24.155	3.46	2.3769	62.465	0.2562	5.7935

Table 2. Structural parameters of thermally evaporated CuPc films for different thicknesses

Thickness (nm)	(hkl)	2 θ (degrees)		Interplanar Spacing d (Å)	FWHM $\beta \times 10^{-3}$ (radians)	Grain size D (nm)	Dislocation density $\delta \times 10^{15}$ (lines/m ²)	Strain $\epsilon \times 10^{-4}$
		Observed	Previous literature values					
150	(001)	8.516	8.69	13.25	12.621	12.454	3.5426	18.7884
	(320)	12.436	12.98	7.64	5.857	26.125	1.4516	16.8452
	(111)	26.354	25.18	5.42	6.436	22.714	1.4521	14.5247
300	(001)	8.97	8.94	13.12	8.895	16.451	2.5756	17.5583
	(320)	11.924	11.24	5.46	15.245	34.945	0.8253	8.4516
	(111)	27.382	29.97	4.58	22.475	48.415	0.8220	7.5651
450	(001)	8.891	8.89	13.18	6.215	22.859	1.8459	14.4265
	(320)	11.876	11.48	7.54	5.689	23.989	1.2546	11.6451
	(111)	26.854	26.54	4.49	3.954	61.452	0.8457	5.9854

Figure 7 Variation in grain size (D) and dislocation density (δ) as a function of temperature of PbPc

From the XRD patterns at different annealed temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. In the triclinic structure, the molecular stack along the α -axis orienting their convex and concave sides alternatively. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant. The annealed films are also polycrystalline in nature.

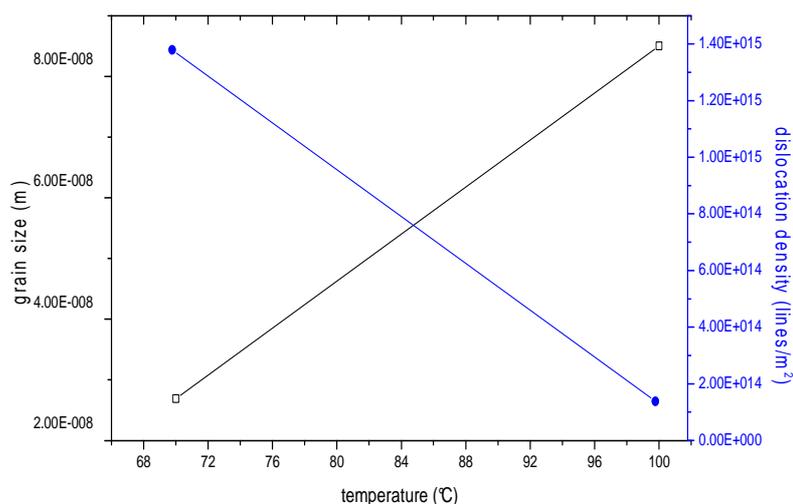


Figure 8 Variation in grain size (D) and dislocation density (δ) as a function of temperature of CuPc

Table 3 Structural parameters of thermally evaporated PbPc films of thickness 450 nm at different annealed temperatures

Thickness (nm)	Temperature (K)	(hkl)	2θ (degrees)		Interplanar spacing d (Å)	FWHM (β) $\times 10^{-3}$ (radians)	Grain size D (nm)	Dislocation density (δ) $\times 10^{15}$ (lines/m ²)	Strain (ϵ) $\times 10^{-4}$
			Observed	Previous literature values					
450	323	(200)	13.775	14.94	5.86	4.555	32.008	0.9760	11.3058
		(300)	22.76	22.46	3.86	3.1281	47.204	0.4487	7.6665
		(400)	30.589	30.26	2.92	5.5736	26.925	1.3793	13.4072
	373	(100)	7.775	7.437	11.36	3.9058	37.148	0.7246	9.7420
		(200)	15.315	14.94	5.70	2.0321	71.876	0.1935	5.0349
		(300)	22.770	22.46	3.90	2.9317	50.368	0.3948	7.1850
		(400)	32.221	30.26	2.77	1.7722	85.023	0.1383	4.2564

Table 4. Structural parameters of thermally evaporated CuPc films of thickness 450 nm at different annealed temperatures

Thickness (nm)	Temperature (K)	(hkl)	2θ (degrees)		Interplanar spacing d (Å)	FWHM (β) $\times 10^{-3}$ (radians)	Grain size D (nm)	Dislocation density (δ) $\times 10^{15}$ (lines/m ²)	Strain (ϵ) $\times 10^{-4}$
			Observed	Previous literature values					
450	323	(300)	26.638	25.96	8.548	6.4155	39.658	1.5426	12.2544
		(200)	27.638	28.88	4.254	4.1235	42.415	0.8457	7.5612
		(400)	34.213	35.12	3.587	3.9854	26.546	1.8489	11.6541
	373	(100)	26.832	26.74	8.452	3.8451	39.814	1.1245	9.5485
		(200)	30.437	30.01	5.542	2.8345	68.425	0.9545	5.3443
		(400)	34.431	35.94	2.874	1.9859	62.543	0.8153	4.8757

Table 3 & 4 shows the structural parameters of PbPc and CuPc films of thickness 450 nm at annealed temperatures (323 K and 373 K). Figure 7 & 8 shows the variation in grain size and dislocation density as a function of temperature PbPc and CuPc films. From these we conclude that as temperature increases, grain size increases.

CONCLUSION

XRD analysis confirmed that thermally evaporated PbPc and CuPc films at room temperature are of monoclinic nature at lower thickness and a mixture of monoclinic and triclinic nature at higher thicknesses. These evaporated films are polycrystalline in nature. Thickness increases, grain size increases and defects like dislocation density and strain decreases due to the improvement in crystallinity in the films. From the XRD patterns at different annealed temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant. The annealed films are also polycrystalline in nature. Various structural parameters such as grain size, dislocation density and strain have been estimated, reported and conclude that as temperature increases, grain size increases.

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