Effect of Substrate Temperature on Optical Properties of Thermally Evaporated CuPc Thin Films.

تأثير درجة حرارة الأرضية على الخصائص البصرية لأغشية نحاس ثالوسيانين الرقيقةالمحضرة بطريقة التبخير الحراري

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Abstract:

Thin films of Copper Phthalocyanine (CuPc) of about 200 nm thicknesses have been deposited by thermal evaporation method on glass substrate at 303 °K and 403 °K substrate temperature (T_s) and under pressure better than10^{-5} mbar. This study concentrated on the effect of substrate temperature on some physical properties of CuPc thin films such as optical properties within the visible range. Optical characterization has been carried out at room temperature using the absorption spectra, at normal incidence, in range 200-900 nm. Absorption and extinction coefficients of the films so obtained have been evaluated. Both of these have been observed to vary with wavelength. The values of refractive index have been found to increase with increasing substrate temperature whereas decrease in optical band gap energy, for direct allowed transitions, with increasing substrate temperature has been noticed. It was attributed to the increasing of defects a round Grain boundaries due the phase transition from β –phase to α –phase and .

Keywords: Absorption, Extinction Coefficients, Refractive Index ,Energy Band Gap.

الخلاصة:

حضّرت أغشية نحاس ثالوسيانين بسمك 200 نانومتر وبطريقة الترسيب الحراري على أرضيات من الزجاج عند درجتي حرارة 303 و403 كلفن وتحت ضغط أعلى من 10^{-5} ملي بار. تم دراسة تأثير درجة حرارة الأرضيات على الخواص البصرية لأغشية نحاس ثالوسيانين ضمن الجزء المرئي من الطيف البصري خلال المدى 200-900 نانومتربالأستفادة من طيف الامتصاص لمعرفة كيفية تغير معاملي الامتصاص و الخمود مع الطول ألموجي. لوحظ زيادة قيم معامل الانكسار بزيادة درجة حرارة الأرضيات عند الترسيب بينما نقصت فجوة الطاقة البصرية وقد عُزيَ ذلك إلى زيادة العيوب حول الحدود الحبيبية و التحوّل من الطور- β الى الطور- α .

INTRODUCTION:

Semiconducting properties of organic semiconductors are due to the presence of conjugated double bonds in their molecular structure. Π orbitals are the most relevant orbitals for optoelectronic properties of organic semiconductors [1]. The flexibility of synthesizing new molecules by changing either the functional groups or atomic arrangement, which in turn induces a change in the electronic properties of new molecules, and hence makes these organic semiconductors attractive candidates for opto-electronic applications[2].

Metal Phthalocyanines are an important class of materials for opto-electronic device applications. Many metal phthalocyanines have been investigated for different applications such as thin film transistors, photovoltaics and gas sensors [3].

Copperpthalocyanine is an p -type, air stable, organic semiconductor with applications in field effect devices and photovoltaics. Optical absorption properties in thin film form are important parameters for the suitability for a material for opto-electronic device applications. In the present work the effect of substrate temperature on optical properties of Copperthalocyanine (CuPc) have been studied.

In the near UV region the B-band or Soret band [4,5], representing the $\pi \rightarrow \pi^*$ transition appear with peak position in the range about 329– 333 nm depending on the nature of substrate used. The absorption band in the visible region for each sample film known as the Q-band representing the $\pi \rightarrow \pi^*$ transition [5] has a doublet due to Davydov splitting [6].

EXPERIMENT:

Powder of CuPc 99% (Sigma Aldrich company, Germany) is kept in a molybdenum boat (50-60 A current rating) heated with high Dc current controlled by a transformer. The transformer is capable 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 room temperature for about 30 minutes with the closed shutter. Thin films of CuPc are deposited at room temperature on pre-cleaned glass substrates under pressure better than 10^{-5} mbar using a (15F6 Hind Hivac, Bangalore -India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations . The thicknesses of the films are 200 nm. The thickness of the films is measured by Quartz crystal monitor. This procedure is used for preparing 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 thin film was evaporated from a molybdenum boat and deposited at a rate of 3-5 A° /s. The absorption spectra of the CuPc films were measured at room temperature using a double-beam spectrometer (RAY LIGH, UV – 2100).

RESULTS AND DISCUSSION:

The optical absorption spectra of thin films deposited at different substrate temperatures have been shown in Fig. 1.These spectra have been characterized by two major bands i.e. B and Q band, both corresponding to $\pi \rightarrow \pi^*$ transitions. Absorption coefficient α was calculated from the relation[7] ; $\alpha = 2.303 * A/\mathbf{t}$ where A is the absorbance and **t** is the film thickness, the absorption coefficient spectra of thin films deposited at different substrate temperatures have been shown fig.2 . The optical transmittance spectra of thin films deposited at different substrate temperatures have been shown in fig. 3. Band gap was calculated using Tauc's relation [8] ; $\alpha h\nu = \mathbf{B}(h\nu - E_g)^n$, where **B** is band edge parameter and value of n determines the nature of optical transition (n = ½ indicates direct transition and n = 2 indicates indirect transition). Variation between $(\alpha h\nu)^2$ and hν has been recorded in Fig. 4. Linearity of the dependence indicates direct transitions. Extrapolating the linear regions to αhν = 0 gives the value of band gap. Values of band gap calculated for films deposited at different substrate temperatures are listed in table 1. It is found that the optical band gap decreases from 3.29 eV for the film deposited at 303 °K to 3.23 eV for film deposited at 403 °K. This can be attributed to the increasing of localized states in the forbidden gap which is due to increasing of the films defects (such as voids)between grain boundaries with increasing substrate temperature or due the phase transition from β –phase to α –phase . Optical properties of a material depend upon the interaction of the material with electric field of the electromagnetic wave. The extinction coefficient is a measure of damping of the incident wave in the material [9]. The extinction coefficients has been calculated using the relation $k = \alpha\lambda/4\pi$.

Both the absorption and extinction coefficients are found to vary with incident energy. The extinction coefficient depends directly on absorption coefficient. Variation of extinction coefficients with wavelength for films at different substrate temperatures is shown in Fig. 5. Refractive index of CuPc was estimated from the reflectance R data using the relation [10]:

$$n = \sqrt{\frac{4R}{(1-R)^2} - k^2} - \frac{R+1}{R-1}$$

The variation of the refractive index versus wavelength in the range 375 – 425 nm have been shown in Fig.6. It is clear from this figure that the refractive index in general increases with increasing of substrate temperature.

The real and imaginary parts of dielectric constant were evaluated using the formulas: $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$ [10]which were shows that the variation of the dielectric constants depend on the value of the refractive index and also the dielectric loss depend mainly on the extinction coefficient values which are related to the variation of absorption. The variation of the real and imaginary parts of dielectric constants values versus wavelength have been shown in Figures 7 and 8.

Table 1.Variation in optical energy gap, Crystallinety percentage with substrate temperature for CuPc thin films.

Substrate Temperature °K	Phase	E_g (eV)	Crystallinety %
303	β –phase	3.29	49.62
403	α –phase	3.23	66.72

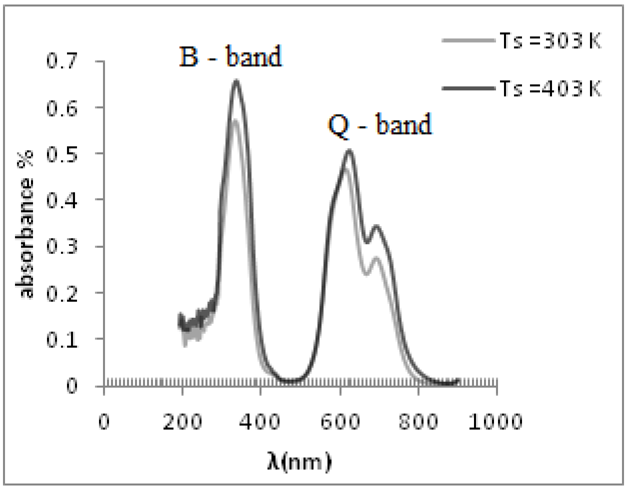

Fig. 1. Absorbance vs wavelength for CuPc films deposited at 303 °K and 403 °K.

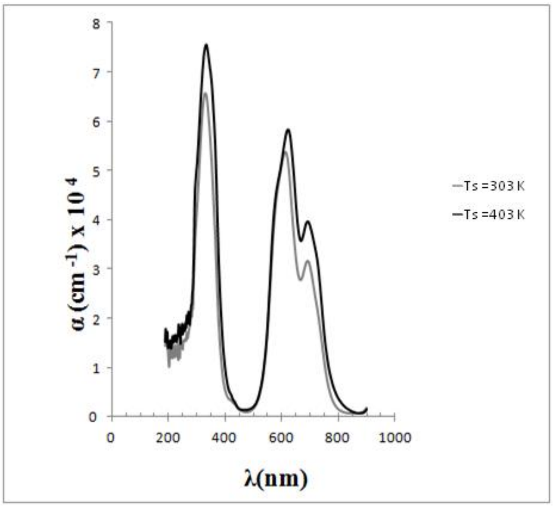

Fig. 2. Variation of absorption coefficient with energy for CuPc films deposited at 303 °K and 403 °K.

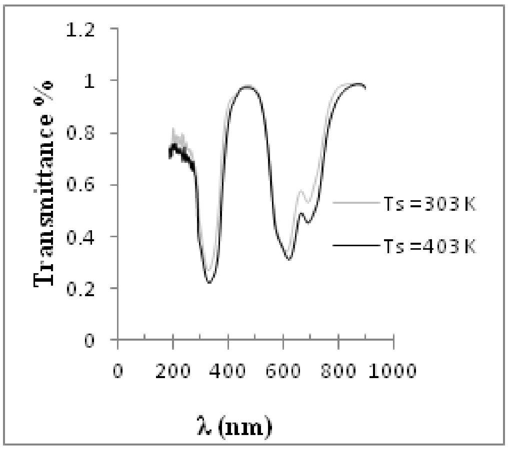

Fig.3 . Transmittance vs wavelength for CuPc films deposited at 303 °K and 403 °K

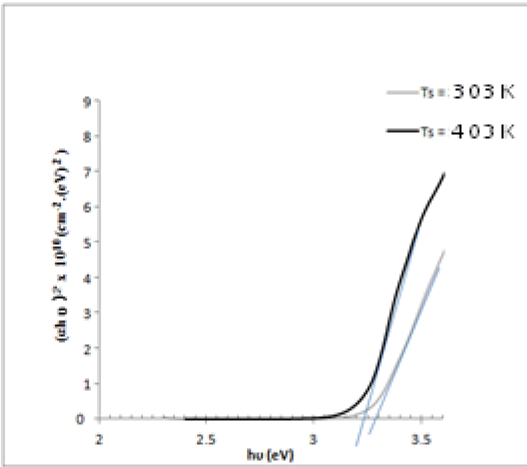

Fig. 4. Variation of $(\alpha h\nu)^2$ with hν for films deposited at 303 °K and 403 °K

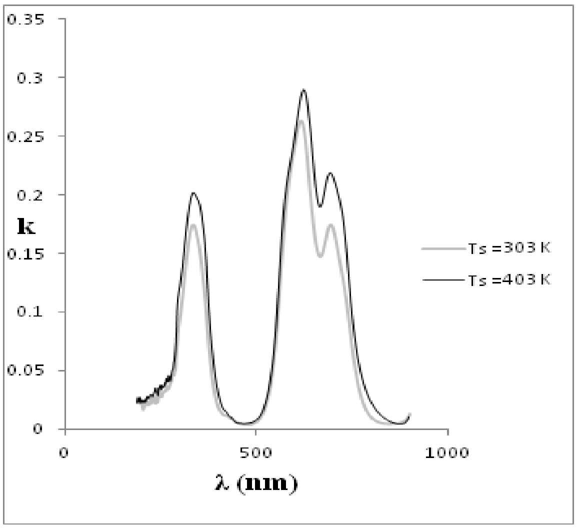

Fig.5 . Variation of extinction coefficient with wavelength for CuPc films deposited at 303 °K and 403 °K.

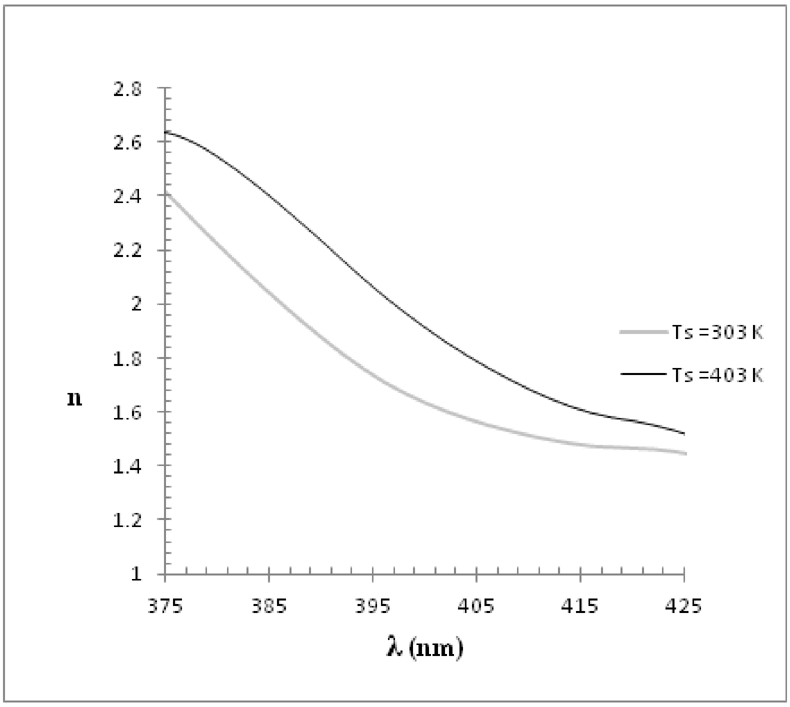

Fig.6 . Variation of refractive index with wavelength for CuPc films deposited at 303 °K and 403 °K.

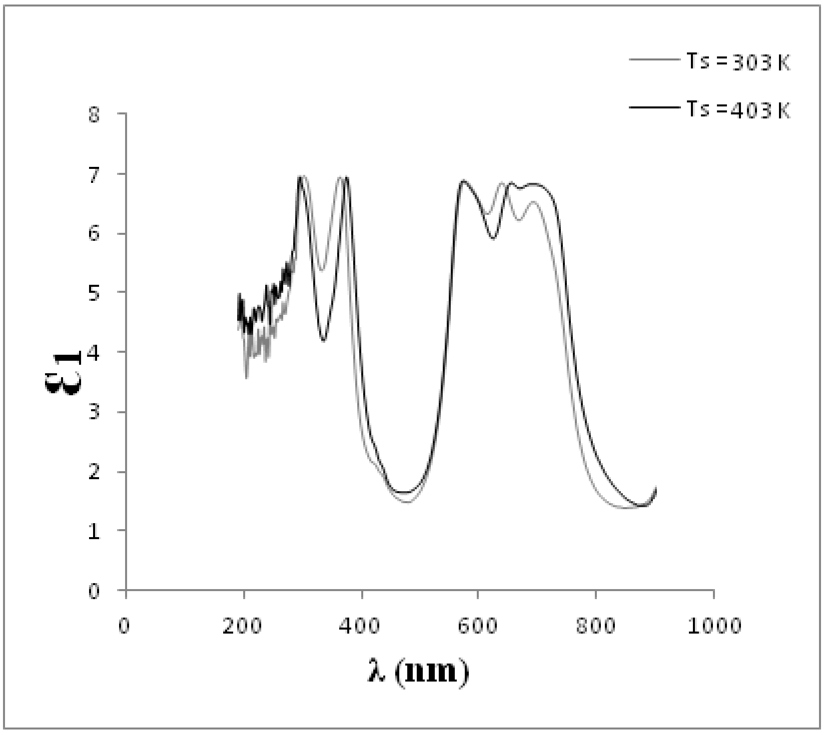

Fig.7. The variation of real part of dielectric constant with wave length for CuPc thin films deposited at 303 °K and 403 °K.

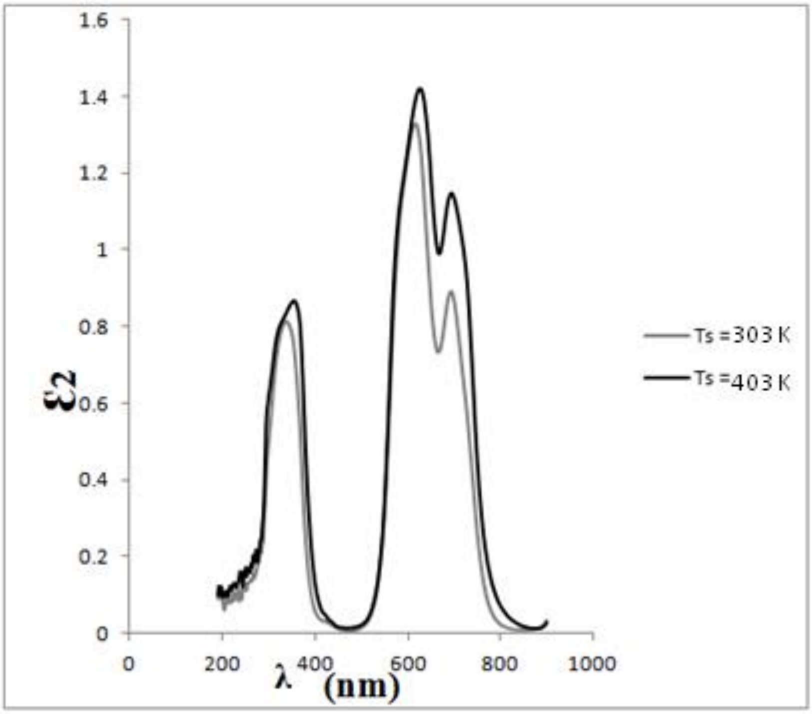

Fig.8. The variation of imaginary part of dielectric constant with wave length for CuPc thin films deposited at 303 °K and 403 °K.

CONCLUSION:

Optical band gap decreases with the increasing substrate temperature. Absorption and extinction coefficients vary with wavelength and they increase with increasing of substrate temperature. Refractive index in the range 325 – 425 nm increase with increasing substrate temperature. Increase in substrate temperature indicating better crystallinity of films deposited at higher substrate temperature. The optical properties indicate the possible candidature of copper phthalocyanine as photovoltaic material.

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