Optical absorption studies on 1,4-/1,8-dihydroxy-9,10-anthraquinone films

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1,4-Dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films have been grown by thermal evaporation technique onto the glass substrate kept at different temperatures in a vacuum of 10^{-5} \text{torr}. The experimental conditions are optimised to obtain better crystallinity of the films. The films so prepared have been studied for their optical properties in the wavelength range 300-800 nm. Observations reveal that the optical band gap of the films increases with increase in substrate temperature and lie in range of 1.6-2.36 eV. The extinction coefficient ($k$) and refractive index ($n$) of films have also been calculated.

Anthraquinone compounds have attracted a lot of attention due to their potential applications as they exhibit optical and photosemiconducting properties in addition to third harmonic generation\textsuperscript{1-3}. Anthraquinone films have been used as reversible optical recording material\textsuperscript{4-5}. Wahed \textit{et al.}\textsuperscript{6} have reported the electrical conductivity of some anthraquinone complexes. The electrical and optical properties of 9,10-anthraquinone films deposited on the glass substrate have been studied by Latef \textit{et al.}\textsuperscript{7,8} Pohl and Opp\textsuperscript{9} have investigated the resistivity and activation energy of some polyacene quinone radical polymers.

In this paper, the optical band gap, extinction coefficient and refractive index of 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films prepared by thermal evaporation technique onto the glass substrate kept at different temperatures in vacuum are reported.

Experimental Procedure

Films were prepared by evaporating 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone material (of high purity) from tantalum boat enclosed in the vacuum chamber of Hind High Vacuum coating unit 12A4H with pressure less than 10^{-5} \text{torr} onto the glass substrate kept at different temperatures. The glass slides having dimensions 75x25x1 mm\textsuperscript{3} were used as substrate. The slides were chemically washed and then, ultrasonically cleaned in isopropyl alcohol using ultrasonic cleaner VS-120 obtained from Vibronics (India). The films thus deposited were annealed at 353 K for 36 h and kept in a dessicator to prevent direct contact from the atmosphere.

The transmittance spectra of films were recorded at room temperature in the wavelength range from 300 to 800 nm using UV-1601PC (Shimadzu, Japan) spectrophotometer. The absorption coefficient and the optical constants of films were determined as a function of photon energy.

Results and Discussion

The optical transmittance spectra for 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films deposited onto the glass substrate are shown in Fig. 1. A prominent absorption peak at 392 nm and 353 nm has been observed for 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films, respectively. 1,8-Dihydroxy-9,10-anthraquinone films indicate a steep rise in the trans-
mittance within the wavelength range 500-591 nm, before showing a gradual increase, while 1,4-dihydroxy-9,10-anthraquinone films exhibit two absorption humps in the photon energy range $2.53 < \text{hv} < 2.34$ eV and $2.34 < \text{hv} < 2.15$ eV.

The absorption coefficient, $\alpha$, was determined from the transmittance $T$. On neglecting the multiple reflections, $T$ is determined as:

$$T = (1-R)^2\left(\frac{1+K^2}{n^2}\right) / \left(\exp(\alpha d) - R^2\exp(-\alpha d)\right)$$

where $d$ is the thickness of film, and $R$ is the reflectivity described by:

$$R = \left(\frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}\right)$$

where $n$ and $K$ are the refractive index and extinction coefficients, respectively. The transmittance in case of semiconductor ($K^2 << n^2$) is given as:

$$T = (1-R)^2\exp(-\alpha d)$$

The absorption coefficients of 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films have been determined over the energy range $1.55-2.14$ eV and $1.55-2.6$ eV, respectively, which correspond to absorption hump in the lower energy region. These absorption humps are examined in terms of interband transition. In the case of direct interband transition, the dependence of absorption coefficient, $\alpha$, upon energy $\text{hv}$ of the incident photon is given as:

$$\alpha \text{hv} = B(\text{hv} - E_g)^{1/2}$$

where $B$ is the constant, $E_g$ is the band gap and $\nu$ is the frequency of the incident light. Figs 2a and 2b show the spectral variation of $\alpha$, for 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films, respectively. The extrapolation of the straight line to $\alpha \text{hv} = 0$ gives the value of optical band gap. It is observed that the optical direct transitions lie in the range $2.075-2.1$ eV and $2.3-2.36$ eV for 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films respectively deposited at different temperatures.

Since, indirect interband transitions are associated with phonon assistance, the absorption coefficient, $\alpha$, has following dependence on the photon energy $\text{hv}$:

$$\alpha \text{hv} = C(\text{hv} - E_g + E_p)^2$$

where $C$ is a constant and $E_p$ the energy of the phonon associated with the transition. The plot of the square root of the absorption coefficient versus photon energy of the films prepared at different temperatures is shown in Figs 3a and 3b. Extrapolation of the line for

Fig. 2—Spectral variation of absorption coefficient under direct interband transition for: (a) 1,4-dihydroxy-9,10-anthraquinone; (b) 1,8-dihydroxy-9,10-anthraquinone films
Fig. 3—Spectral variation of absorption coefficient under indirect transition for: (a) 1,4-dihydroxy-9,10-anthraquinone; (b) 1,8-dihydroxy-9,10-anthraquinone films

Fig. 4—Spectral variation of extinction coefficient for: (a) 1,4-dihydroxy-9,10-anthraquinone; (b) 1,8-dihydroxy-9,10-anthraquinone films
Fig. 5—Spectral variation of refractive index for: (a) 1,4-dihydroxy-9,10-anthraquinone; (b) 1,8-dihydroxy-9,10-anthraquinone films.

$\alpha dhv = 0$ gives an intercept in the range 1.6-1.65 and 1.71-1.98 respectively for 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films. These intercepts give band gap plus or minus the energy of the assisting phonon for indirect transitions. It has been observed that band gap energy of the 1,4-/1,8-dihydroxy-9,10-anthraquinone films increases with the increase in the substrate temperature, under both direct and indirect transitions. This may be attributed to the fact that in case of films deposited at low temperatures, grain boundaries are highly disordered, which give a marked contribution to the absorption for films with low grain sizes, whereas the films deposited at higher substrate temperatures favour the growth of larger grain sizes and stronger orientation of crystallites,

The extinction coefficient ($k$) and refractive index ($n$) of 1,4-/1,8-dihydroxy-9,10-anthraquinone films has been determined from absorption coefficient$^{13}$ and refractivity$^{10}$ of material respectively, using the relation:

$$\alpha = 4 \pi k / \lambda,$$

$$T = (1-R) / (1+R) = 2n / (1+n^2)$$

Figs 4a-4b and 5a-5b show the spectral variation of the extinction coefficient ($k$) and refractive index ($n$) respectively for 1,4-/1,8-dihydroxy-9,10-anthraquinone films. It is noticed that extinction coefficient and refractive index of 1,8-dihydroxy-9,10-anthraquinone films is higher than 1,4-dihydroxy-9,10-anthraquinone in the photon energy range from 1.55-2.7 eV. It is also observed that extinction coefficient ($k$) and refractive index ($n$) of films show an increasing dependence on photon energy. Films deposited at higher substrate temperature show a decrease in extinction coefficient and refractive index, which is in accordance with optical band gap data.

**Conclusions**

The optical band gap energy of 1,4-dihydroxy-9,10-anthraquinone and 1,8-dihydroxy-9,10-anthraquinone films deposited on the glass substrate kept at different temperature lie in the range 1.6-2.1 eV and 1.7-2.36 eV, respectively. The substrate temperature appears to influence the optical parameters of films. The optical band gap of the films increases with increase in substrate temperature while the extinction coefficient and refractive index decrease.
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References
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