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Growth and transport properties of nanocrystalline CdS thin film

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Cadmium Sulphide (CdS) nanoparticles were synthesized by a chemical route using organic substance as the desired matrix at room temperature 300K. The crystallite sizes of the films are determined from X-ray diffraction lines. The optical band gap 'E_g'of the CdS films are determined from the UV absorption spectroscopy and are found to be 2.9 eV. The current-voltage curve of the films are drawn and temperature-dependent conductivity (300-523K) are found out to be of the order of 10^{-5} – 10^{-6} ohm^{-1} cm^{-1}. The "as deposited" films are annealed in air at 523K for 2 h and the effect of annealing on structural, morphological, optical and electrical properties are studied. The annealed films show a 'redshift" of 0.6 eV in their optical band gap 'E_g'. After annealing, the diffraction peaks in the XRD pattern become sharp with high intensity and the crystallites' size increases from 10 – 39 nm, which results in a increase in electrical conductivity. From the conductivity measurement at different temperatures, for fresh and annealed films, the activation energy of the films were calculated and found to be between 0.30 - 0.57 eV for low temperature regions and between 1.24 - 1.34 eV for high temperature regions.

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1. Introduction

In recent years, much attention has been paid to studies of composite organic-inorganic materials. Nanocomposites consisting of organic polymers and semiconductor nanocrystals often exhibit a host of mechanical, electrical, optical and magnetic properties, which are far superior to those of the indivisual components [1,2]. The preparation of nanostructured semiconductor-polymer composites has been extensively studied [3,4,5]. CdS is a typical wide direct band gap II-VI semiconductor having a bandgap 2.42 eV at room temperature. Specifically, this material has immense potential applications in lasers, light-emiting diodes, solar cells, and luminescence devices [6,7,8]. It has been shown that the simple way of synthesizing CdS nanoclusters is through an arrested precipitation reaction of Cd^{2+} and S^{2-} in an aqueous solution with the presence of a stabilizing agent, such as polymers[9], zeolites[10], or porous glass[11].

Out of several methods for deposition of nanocrystallites, chemical bath deposition (CBD) technique in polymer matrix is relatively simple, cost effective and suitable for deposition of films on large area substrates. Our approach in this study is to find out the properties of nanocrystalline CdS films deposited at room temperature 300K as well as annealed at 523K, and to synthesize a high quality CdS nanocrystallites with good luminescence for device making.

2. Experimental

2.1 Substrate cleaning

Substrate cleaning plays an important role in the deposition of thin films. Commercially available glass microslides of dimensions 26mm×76mm×2mm were first washed with mild liquid soap, then boiled in chromic acid and kept in it for 24hrs, rinsed in acetone and finally ultrasonically cleaned with double distilled water and dried before use.

2.2 CdS film preparation

In the present work, cadmium sulphate ($CdSO_4$) and thiourea (CN_2H_4S), dissolved in an alkaline medium, were taken as the source of cadmium and sulphur respectively and polyvinyl alchohol (PVA) as the capping agent. The nanocrystalline CdS thin films were deposited on glass substrates at room temperature 300K. The matrix solution was prepared by adding cadmium sulphate (0.5M) to an aqueous solution (2%) of polyvinyl alchohol (PVA) with constant stirring at constant temperature (70°C) maintained for 90 minutes. The pH of the solutions were maintained at around 11, by slowly adding NH_4OH solution. Then the equimolar solutions of thiourea were added to the mixture solution. Within a few minutes colour of the solution changes to yellow. The substrates were kept in the solution for16 - 20 hrs. for deposition of films. After deposition the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air.

The reaction mechanism for the CdS film formation is given below [12]

$$\text{(i)} CdSO_4 + 4NH_3 \rightarrow Cd[(NH_3)_4]SO_4$$

$$\text{(ii)} CN_2H_4S + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$\text{(iii)} HS^- + OH^- \rightarrow S^{2-} + H_2O$$

$$\text{(iv)} Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS + 4NH_3$$

Aluminium electrodes are then deposited on the dried films by thermal vacuum evaporation technique at vacuum better than 10^{-5} torr. A gap type electrode film geometry with a gap of 3 mm is taken for electrical study. The "as deposited" films are then annealed in air at 523K for 2 h and the effect of annealing on structural, morphological, optical and electrical properties are studied.

2.3 Characterization of CdS thin films

All the measurements were done at room temperature for the films. Grain sizes of the films were then measured by X-ray diffractometer (Philips X-pert Pro diffractometer (PW 1830)) at room temperature with CuK_α radiation in the 2θ range of 20º- 80º. Surface morphological study of the CdS thin films were done using the Scanning Electron Microscope (SEM) (LEO 1430 VP) operating with an accelerating voltage 20 kV, with an attached energy dispersive x-ray analysis (EDAX) analyzer to qualitatively measure the sample stoichiometry.. Optical absorption spectra at 300 K were obtained using a UV visible spectrophotometer (VARIAN CARY 300 Scan) in the wavelength range 300 nm to 700nm. For conductivity studies the current measurement is done with the help of a high impedence ($\sim 10^{14}\Omega$) ECIL (electrometer amplifier (EA815)) with an accuracy of ± 3%. A series of highly stable dry cells each of emf 9V was used for providing the applied bias. A copper-constantan thermocouple was placed behind the glass substrate for the measurement of ambient temperature in conjunction with a d.c. microvoltmeter (Sys 412,Sr.No.403).

3. Results and discussion

3.1 X-ray diffraction

The X-ray diffractogram of the CdS films show broadened diffraction profiles and the XRD patterns show a preferred orientation along (002) plane. The "as deposited" CdS films grew with nanocrystalline hexagonal phase along with some amorphous phase [Figure 1(a)]. After annealing, the diffraction peaks in the XRD pattern become sharp with high intensity indicating the significant increase in crystallite size [Figure 1(b)]. The crystallites' size increases from 10 – 39 nm The crystallite size of the nanocrystalline films is estimated using Scherrer formula

$$D = K\lambda/\beta_{2\theta}\cos\theta \quad (1)$$

where K is a constant taken to be 0.94, λ the wave length of X-ray used (λ=1.54Å) and $\beta_{2\theta}$ the full width at half maximum of (002) peak of XRD pattern, Bragg angle 2θ is around 26.5°.

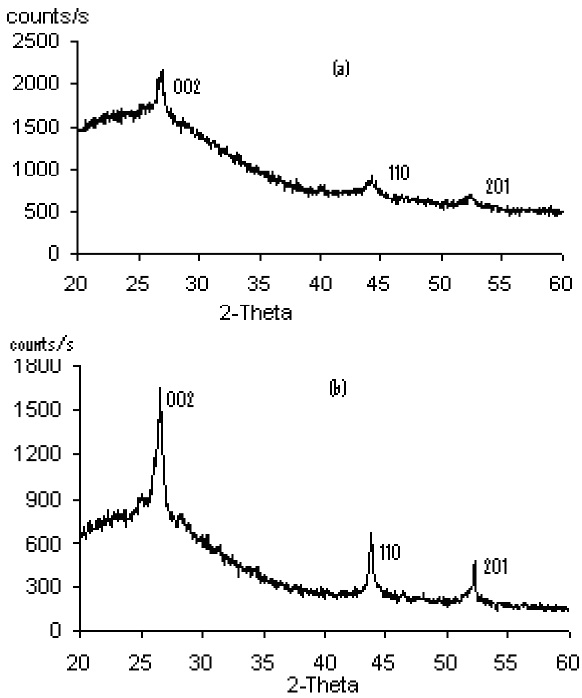
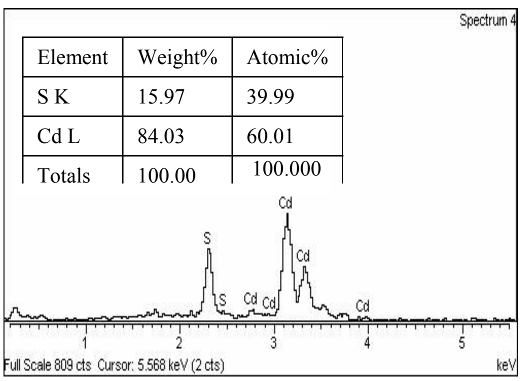


Fig. 1. XRD spectra of CdS films (a) as deposited at 300 K and (b) annealed at 523 K.

3.2 Composition analysis

The quantitative analysis of the film was carried out by using the EDAX technique for "as deposited" CdS thin films deposited on a glass substrate at 300 K, at different points to study the stoichiometry of the film.



Element	Weight%	Atomic%
S K	15.97	39.99
Cd L	84.03	60.01
Totals	100.00	100.000

Fig.2. Typical EDAX spectrum and compositional data of 'as-deposited' CdS film at 300 K.

Fig. 2 shows a typical EDAX pattern and details of relative analysis for "as deposited" CdS film. The elemental analysis was carried out only for Cd and S; the average atomic percentage of Cd **:** S was 60 **:** 40, (i.e.1.5 **:** 1 ratio), showing that the sample was slightly S^-deficient.

3.3 SEM analysis

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Figure 3(a) shows the surface morphology of the CdS thin films deposited at room temperature. From the micrographs, it is observed that in the "as-deposited" films, the distribution of grains are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the substrates well. We clearly observe the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdS thin films.

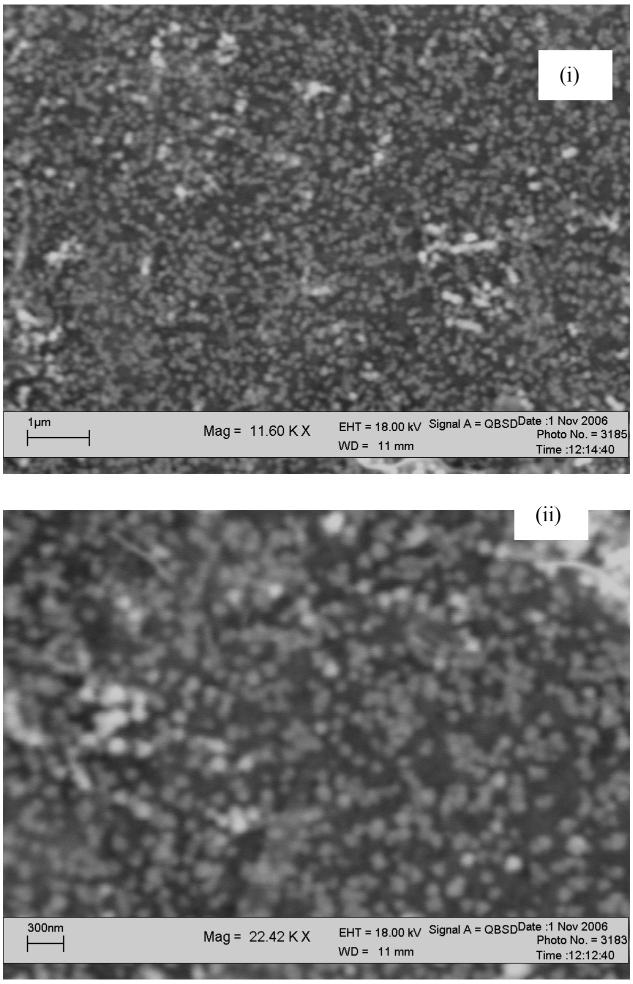


Fig. 3(a). SEM photograph of CdS film as deposited at 300 K: (i) 11.6KX and (ii) 22.4KX

The SEM of an annealed film in air at 523 K, Fig. 3(b) clearly shows the conversion of nanograins into larger grains, i.e. an increase in crystallinity after air annealing[13]. From these images, it can be seen that the grain sizes of the films are not uniform Therefore average grain sizes were estimated from different grains within the film and found to be about 39.5 nm for as deposited films and 139.8 nm for annealed films. It is quite clear from the results that the crystallite sizes revealed from SEM pictures are higher than the crystallite size values calculated from the XRD peaks. Such a difference might be due to the presence of some amorphous phase in the films along with their predominant crystalline phase[14].

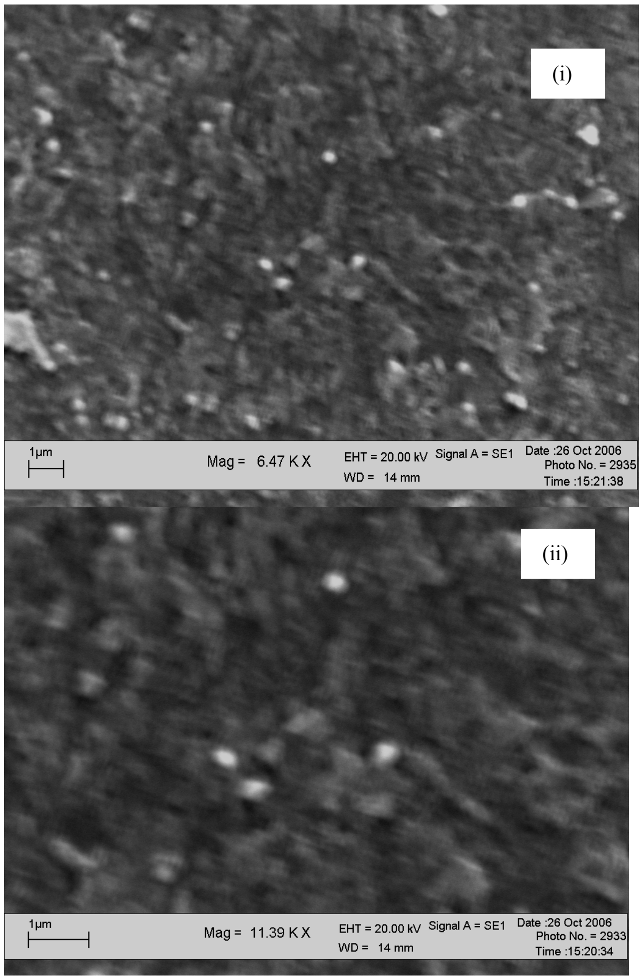


Fig. 3(b).SEM photograph of CdS film annealed at 523K: (i) 6.5 KX and (ii) 11.4 KX

3.4 Absorption studies

The optical absorption spectra of the CdS films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 300-700 nm. Figs. 4 and 5 show the variation of optical absorbance(αt)

and percentage transmission (%T) with wavelength (λ), respectively. They show an increase in optical absorption and a decrease in transmission after annealing the film. This is possibly due to the increase in grain size and the decrease in the number of defects after annealing.

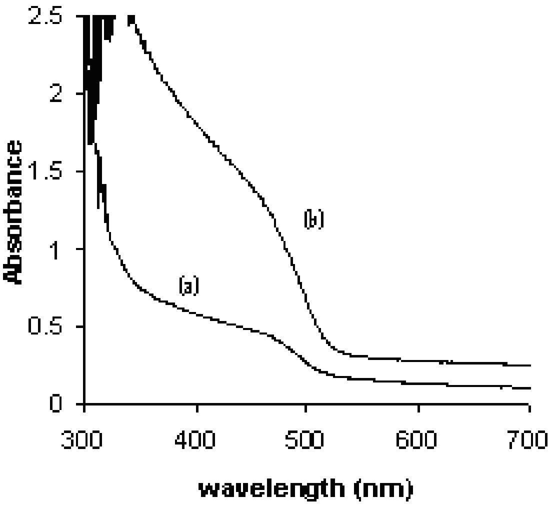


Fig. 4. Plot of optical absorbance (αt) versuswavelength (λ) of CdS films (a) as deposited at 300 K and (b) annealed at 523 K.

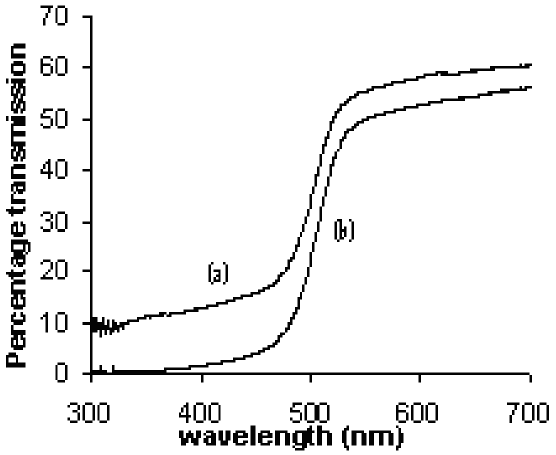


Fig. 5. Plot of optical transmissions (%T) versus wavelength (λ) of CdS films (a) as deposited at 300 K and (b) annealed at 523 K.

From the spectrograph, it is clearly seen that the absorption and transmission edge shifts towards a longer wavelength for annealed films. This shifts indicates a decrease of the optical band gap 'E_g'. CdS is a typical direct band gap semiconductor. According to Tauc relation, the absorption coefficient for direct band material is given by,

$$\alpha = c(h\nu - E_g)^{1/2}/h\nu \qquad (2)$$

where α is the absorption coefficient, c is a constant, hν the photon energy and E_g the band gap. The spectrographs were studied using the standard relation (2).

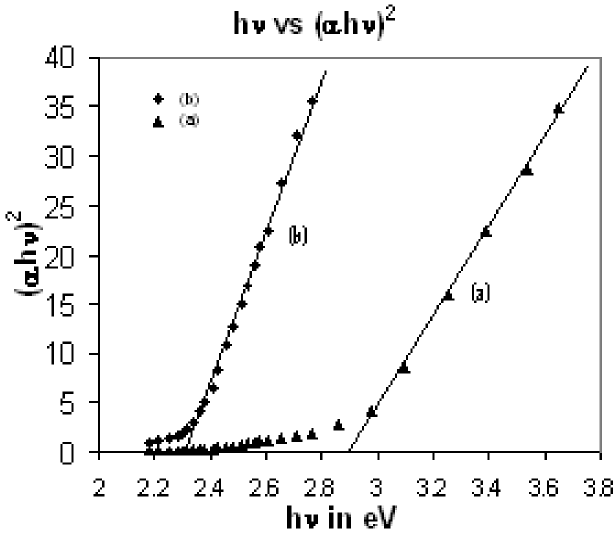


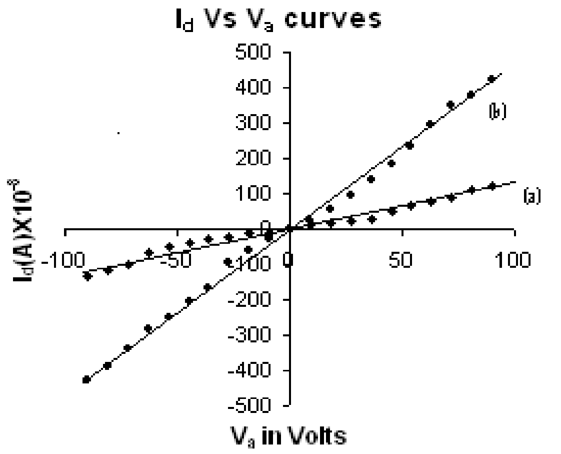
Fig. 6. Plot of $(\alpha h\nu)^2$ versus hν of CdS films (a) as deposited at 300 K & (b) annealed at 523 K.

A graph between hν Vs $(\alpha h\nu)^2$ is plotted for (a)'as-deposited'and (b)annealed film and shown in Fig. 6. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap of film materials.

It was found to be 2.9 eV for as-deposited and 2.3 eV for annealed films.The increase in band gap for as-deposited CdS films (2.9eV) from the bulk value(2.4eV) is due to the nanocrystalline nature of CdS thin films, where charges are localized in indivisual nanocrystals. This observation of increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation [15]. The decrease in band gap from 2.9 eV to 2.3 eV shows that annealing the film causes a strong 'redshift' of 0.6 eV in the optical spectra ,due to sintering of the nanocrystallites into larger crystallites [16].

3.5 Electrical conductivity

The dark current (I_d) Vs applied bias (V_a) characteristics of the CdS thin films are found to be ohmic within the range of the applied bias –90volt - 0 - (+90volt) which also indicates that the electrode contact is ohmic for dark conductivity (Figure7). For both the positive and negative bias condition the dark current I_d Vs applied bias V_a characteristics are found to be linear (approx.)



(a)

Fig.7. I_d versus V_a characteristics of CdS films (a) as deposited at 300 K & (b) annealed at 523 K.

The dark electrical conductivity of 'as-deposited' and annealed CdS films was measured at room temperature. It was found that the room temperature electrical conductivity of the film is 0.24 $X10^{-6}$ Ω^{-1} cm^{-1} which then increases to 0.36 $X10^{-5}$ Ω^{-1} cm^{-1} after annealing the film at 523 K.

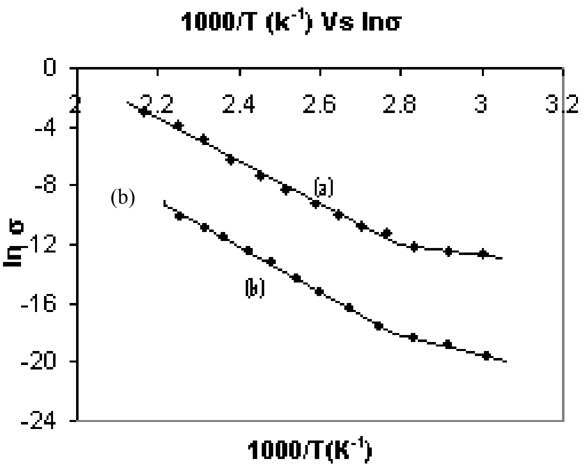


Fig. 8. Plot of lnσ versus 1000/T of CdS films (a) as deposited at 300 K & (b) annealed at 523K.

Table 1. Representation of various results of CdS thin films as deposited at 300 K and annealed at 523 K

Thin films	Crystallite size (nm) from XRD	Band gap E_g (eV)	Conductivity σ (Ω^{-1} cm^{-1})	Temp[r]. range in K	Activation energies (eV)
Deposited at 300K	10	2.9	0.24$X10^{-6}$	(300K-353K) (363K-463K)	0.30 1.24
Annealed at 523 K	39	2.3	0.36$X10^{-5}$	(300K-353K) (363K-473K)	0.57 1.34

It is well known that [17] electronic transport properties of thin polycrystalline semiconductor films are strongly influenced by their structural characteristics and purity.

The variation of electrical conductivity of the CdS measured in the 300 - 473 K temperature range are shown in figure 8.

The temperature dependence of dark conductivity are studied by raising the temperature of the films from room temperature to 523 K. The rise of dark conductivity (σ) is found to be exponential in nature which is usually expressed as -

$$\sigma = \sigma_o \exp(-E/KT) \quad (3)$$

where σ_o is the parameter depending on the sample characteristics, K is the Boltzmann constant and E is the activation energy measured from the bottom of the conduction band and T is absolute temperature. It can be observed that (figure 8) the plot of ln σ versus 1000/T for as-deposited and annealed samples clearly show two conduction regions.

The first is at a lower temperature range (T = 300-353K) characterized by a smaller slope. In the higher temperature range the curves are characterized by a higher slope. From the slopes the activation energies are calculated and varies as 0.3 – 0.57 eV for the lower temperature portion and 1.24 – 1.34 eV for the higher temperature portion. Table 1 depicts the various results obtained in the present investigation.

4. Conclusions

From the studies, it is concluded that the CdS thin films deposited by an aqueous alkaline medium at room temperature grow with nanocrystalline hexagonal phase, with band gap 2.9 eV and electrical conductivity of the order of 10^{-6} Ω^{-1} cm^{-1}. Thermal annealing was found to increase the crystallinity of films. Due to air annealing, the crystallite size of particle increases from 10 nm – 39 nm that results in increase of electrical conductivity. Activation energy increases after annealing as shown. Optical absorption spectra reveals the crystallite size-dependent properties of the energy band gap and the the film shows a 'redshift' of 0.6 eV in its optical spectra, i.e band gap changes from 2.9 eV to 2.3 eV.These changes have been attributed to the crystallite size dependent properties of CdS semiconductor thin films. From this study, it is understood that annealing is not preferable to achieve nanocrystalline structures.

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