



Electrosynthesis and studies on Cadmium-Iron-Sulphide thin films

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ABSTRACT

Cadmium-Iron-Sulphide (Cd-Fe-S) thin films have prepared on indium doped tin oxide (ITO) coated conducting glass substrates by potentiostatic electrodeposition technique. X-ray diffraction pattern shows that the deposited films exhibit mixture of hexagonal CdS and hexagonal FeS phases. Surface morphology and film composition represent that films with smooth surface and better stoichiometry are obtained at 0.0375 M CdSO₄ concentration. Optical parameters such as band gap, refractive index and extinction coefficient which are evaluated from optical absorption measurements. The experimental observations are discussed in detail.

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1. Introduction

Thin films of transition metal chalcogenides have received much attention due to their wide range of applications in semiconducting devices, photovoltaics, optoelectronic devices, radiation detectors and solar energy converters [1–3]. Among them, cadmium chalcogenides exert a pull on many researchers because they fulfill few of the requirements for several new electronic and optoelectronic devices such as light emitting diodes, photodiodes, blue green lasers etc., [4,5]. Cd_{0.8}Fe_{0.2}S is found to be a direct band gap semiconductor with an energy gap value of 1.93 eV which make them interesting for photoelectrochemical solar cells [5]. Even though several research reports are available concerning the preparation and properties of Zn_{1-x}Cd_xSe [3], Zn_{1-x}Fe_xSe [6] and Zn_{1-x}Fe_xS [7], but very little is available on Cd_{1-x}Fe_xSe [8], Cd_{1-x}Fe_xTe [9] and Cd_{1-x}Fe_xS [5,10,11]. Thin films of Cd-Fe-S are usually crystallized in hexagonal (CdS) and in hexagonal (FeS) phases. Deshmukh et al have prepared Cd_{0.8}Fe_{0.2}S thin films on stainless steel and fluorine doped tin oxide coated conducting (FTO) glass substrates using electrodeposition technique [5]. Preparation of Cd_{1-x}Fe_xS thin films by spray pyrolysis technique and their structural, optical and Raman spectroscopic observations

have been investigated by Nitu Badera et al. [10]. Liu et al have prepared Cd_{1-x}Fe_xS thin films using low pressure metal organic chemical vapor deposition and studied their properties using X-ray diffraction, scanning electron microscopy, energy dispersive analysis by X-rays and optical absorption techniques, respectively [11]. Electrochemical and chemical bath deposition are the alternative methods that are particularly adopted for the preparation of chalcogenide materials [12,13]. The iron chalcogenide compounds have been the objects of numerous studies concerning thin film electrodeposition from an aqueous solution [13]. Electrodeposition technique is widely used for synthesizing semiconducting thin films after the pioneering work by Kröger and Panicker et al. [14,15]. Recently, electrodeposition has emerged as a simple economical and viable technique to get good quality films for device applications. This technique provide many advantages over vacuum and other processes, such as low temperature processing, the possibility to control the film thickness and morphology by readily adjusting the electrical parameters as well as the composition of the electrolytic solution [12,13]. To the best of our knowledge very few research reports are available concerning the growth and characterization of Cd_{1-x}Fe_xS thin films [5,10,11]. Hence, we have planned to carry out electrodeposition of Cd-Fe-S thin films and to study their properties.

In the present work, thin films of Cd-Fe-S are electrodeposited on indium doped tin oxide (ITO) coated conducting glass substrates by potentiostatic electrodeposition technique from an aqueous electrolytic bath consists of CdSO₄, FeSO₄, Na₂S₂O₃ and EDTA. The deposited films are characterized using X-ray diffraction, Scanning

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electron microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques, respectively. The effect of electrolyte (CdSO_4) concentration on structural, morphological, compositional and optical properties of the films are studied and the results are discussed.

2. Experimental Details

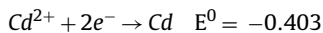
Thin films of Cd-Fe-S were deposited on ITO substrates from an aqueous acidic bath containing (0.0125–0.05) M CdSO_4 , 0.01 M FeSO_4 and 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.05 M EDTA as complexing agent using potentiostatic electrodeposition technique. The chemicals used in this work were of Analar Grade reagents. The pH of the electrolytic bath was adjusted in the range between 2.5 and 5.0 ± 0.1 by adding adjustable amount of dilute H_2SO_4 and NaOH. At lower pH values (below 3.0 ± 0.1) adherence of the film to the substrate was very poor. At higher pH value (above 4.0 ± 0.1) there is precipitation of electrolytic bath occurs, which yields films with poor quality. Hence, an optimum solution pH value of 3.5 ± 0.1 must be fixed in order to get films with good quality. All the depositions were carried out using a PAR scanning potentiostat/galvanostat unit (EG & G, Model 362, Princeton Applied Research, USA) employing three electrode configuration with ITO substrate as cathode, platinum electrode as anode and saturated calomel electrode (SCE) as reference electrode, respectively. The bath temperature, deposition potential and solution pH were fixed as 75°C , -950 mV versus SCE and 3.5 ± 0.1 , respectively.

Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer with $\text{CuK}\alpha$ radiation with wavelength ($\lambda = 1.540\text{ \AA}$) was used to analyze the crystalline nature and phases of the deposited films. The surface morphology and film composition were analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope (JEOL JSM 840). Optical absorption spectrum of the deposited films was recorded using an UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics).

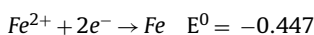
3. Results and Discussion

3.1. Electrochemistry of Cd-Fe-S thin films

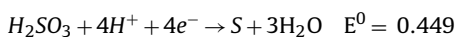
The electrochemical deposition of Cd-Fe-S thin films is carried out potentiostatically from an aqueous acidic bath containing CdSO_4 , FeSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and EDTA as complexing agent. The electrochemical Eq.'s involving the co-deposition of Cd, Fe and S are described as follows:



$$E_{\text{Cd}} = E_{\text{Cd}}^0 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Cd}}^{2+}}{a_{\text{Cd}}} \right] \quad (1)$$



$$E_{\text{Fe}} = E_{\text{Fe}}^0 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Fe}}^{2+}}{a_{\text{Fe}}} \right] \quad (2)$$



$$E_{\text{S}} = E_{\text{S}}^0 + \left[\frac{RT}{4F} \right] \ln \left[\frac{a_{\text{S}_2\text{O}_3}}{a_{\text{S}}} \right] + \left[\frac{RT}{4F} \right] \ln (a_{\text{H}^+})^4 \quad (3)$$

where E_{Cd}^0 , E_{Fe}^0 and E_{S}^0 are the standard electrode potential for Cd, Fe and S respectively, with respect to SCE and a_{Cd}^{2+} , a_{Fe}^{2+} are the activities of Cd and Fe ions in the electrolyte and a_{Cd} and a_{Fe} are the activities

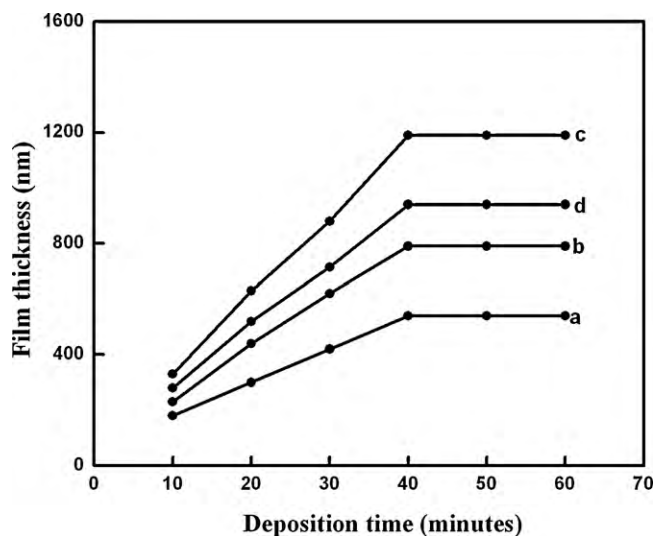


Fig. 1. Variation of film thickness with deposition time for Cd-Fe-S thin films obtained at various CdSO_4 concentrations: (a) 0.0125 M (b) 0.025 M (c) 0.0375 M (d) 0.05 M.

of the respective atoms in the deposited film. The deposition of Cd and Fe occur at potentials more positive than their standard reduction potential by gaining free energy in compound formation [14–16] and ternary alloy films of Cd-Fe-Se are formed via the Eq. (4)



It has been reported by Kröger [15] that under potential deposition of less noble constituent (here Cd) of a compound (Cd-Fe-S) is brought about by the gain of free energy by its formation. Hence, it is essential to obtain the co-deposition of Cd, Fe and S, we used a higher concentration of Cd and lower concentration of noble metal Fe, to bring the electrode potentials of three deposits closer.

3.2. Film thickness

The film thickness is estimated using stylus profilometer. The variation of film thickness with deposition time for Cd-Fe-S thin films prepared at various CdSO_4 concentrations from 0.0125 to 0.05 M is shown in Fig. 1. Fig. 1 (a–d) represent that the value of film thickness increases with deposition time and tend to attain its maximum value at a deposition time of 40 minutes for films obtained at all CdSO_4 concentrations. It is also observed that the value of film thickness increases while increasing the concentration of CdSO_4 from 0.0125 to 0.0375 M (Fig. 1 (a–c)). Further increasing CdSO_4 concentration above 0.0375 M, there is decrease in value of film thickness is obtained which is indicated in Fig. 1d. If the deposition time is increased above 40 minutes thickness of all the deposited films decreases slightly not shown in Fig. 1. Hence, CdSO_4 concentration and deposition time are fixed as 0.0375 M and 40 minutes in order to get good quality films with higher thickness.

3.3. Structural studies

X-ray Diffraction (XRD) analysis is carried out in order to determine the structural properties of the deposited films. From XRD data, the crystalline nature and phases of the deposited films are determined. The temperature of the electrolytic bath plays an important role in obtaining good quality films. If the temperature of the bath is increased, the diffusion coefficient and precursor solubility are increased which in turn increasing the deposition rate [8]. Cd-Fe-S thin films prepared at bath temperature below 50°C are

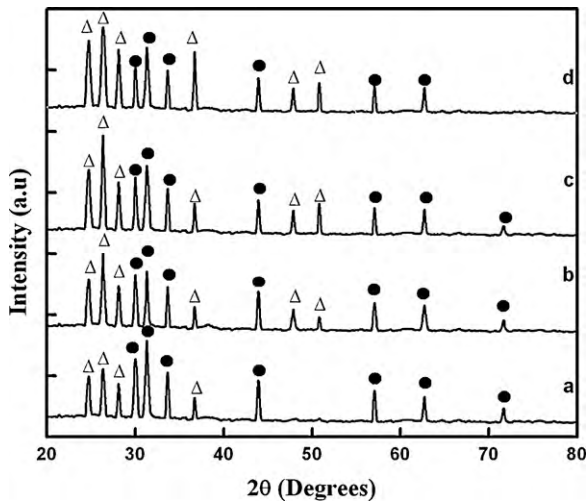


Fig. 2. X-ray diffractions pattern of Cd-Fe-S thin films obtained at various CdSO_4 concentrations: (a) 0.0125 M (b) 0.025 M (c) 0.0375 M (d) 0.05 M.

found to be poorly crystallized, whereas the films deposited at bath temperature above 75°C are found to exhibit well defined peaks in the diffractogram. The electrochemical deposition of Cd-Fe-S thin films are carried out in the solution pH values ranging from 2.5 to 5.5 ± 0.1 . At pH value lower than 3.5 ± 0.1 the formation of films may be hindered due to hydrogen evolution reaction. If the solution pH value is greater than 3.5 ± 0.1 precipitation of electrolytic bath occurs which in turn yield poor quality films. Therefore, the bath temperature and solution pH value are fixed as 75°C and 3.5 ± 0.1 in order to get good quality films for further depositions.

XRD pattern obtained for Cd-Fe-S thin films on ITO substrates at a bath temperature and solution pH value of 75°C and 3.5 ± 0.1 under various CdSO_4 concentrations from 0.0125 to 0.05 M are shown in Fig. 2(a–d). Fig. 2 revealed that the deposited films of Cd-Fe-S exhibit mixture of hexagonal (CdS) and hexagonal (FeS) phases. The observed diffraction peaks of hexagonal (CdS) are found at 2θ values of angles 24.72, 26.33, 28.12, 36.72, 47.87 and 50.82 (marked by Δ) corresponding to the lattice planes (100), (002), (101), (102), (103) and (200), whereas the diffraction peaks of hexagonal (FeS) are observed at 2θ values of angles 30.02, 31.32, 33.67, 43.87, 57.07, 62.72 and 71.40 (marked by \bullet) corresponding to the lattice planes (100), (002), (101), (102), (103), (200) and (202), respectively. The observed 'd' values of semiconducting Cd-Fe-S thin films are found to be in good agreement with standard JCPDS values for hexagonal (CdS) and hexagonal (FeS) phases [17,18]. It is observed from Fig. 2 that, some new peaks of hexagonal (CdS) are begin to appear while increasing the CdSO_4 concentration from 0.0125 to 0.0375 M. It is also observed from Fig. 2 that the intensity of hexagonal (FeS) peaks are found to decrease, whereas the intensity of hexagonal (CdS) peaks are observed to increase if the concentration of CdSO_4 is increased from 0.0125 to 0.0375 M. The crystallite size of Cd-Fe-S thin films is calculated using FWHM data and Debye-Scherrer's formula [12]. The sizes of the crystallites for films prepared at various CdSO_4 concentrations are found to be in the range between 35 and 56 nm.

3.4. Morphological and compositional analyses

The surface morphology of Cd-Fe-S thin films is analyzed using scanning electron microscope. Fig. 3a,b shows the scanning electron microscope image of Cd-Fe-S thin films obtained at 0.0125 and 0.037 M CdSO_4 concentrations. Fig. 3a shows that the film surface is observed to be flat and there is no definite grain structure. Cracks are seen at all places in the surface of the film. It is observed from

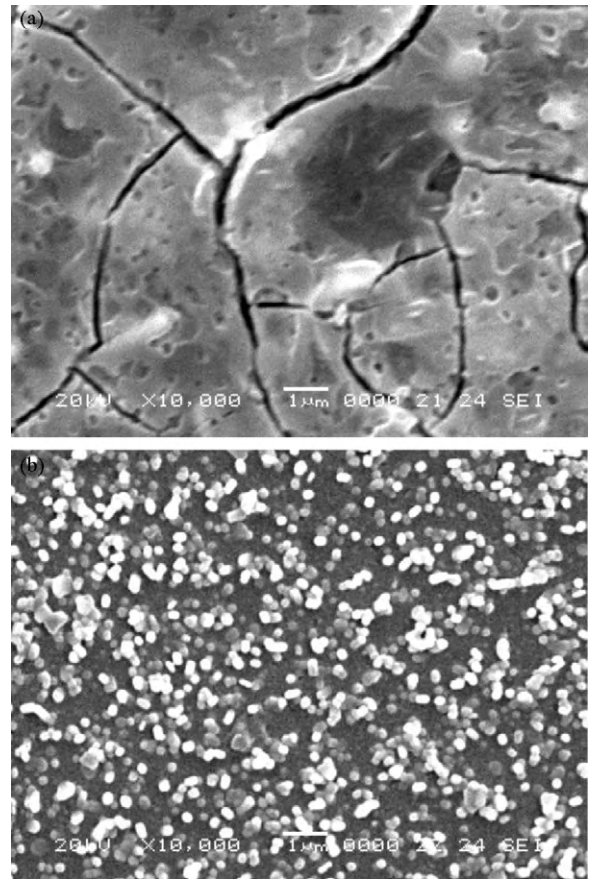


Fig. 3. Scanning electron microscope image of Cd-Fe-S thin film obtained at different CdSO_4 concentrations: (a) 0.0125 M (b) 0.0375 M.

Fig. 3b, that the surface is covered with tiny spherically shaped grains. The grains are evenly distributed over the entire surface of the film. The sizes of the grains are found to be in the range between 0.20 and $0.66 \mu\text{m}$. The average size of the grains is found to be $0.42 \mu\text{m}$. The quantitative determination of Cd-Fe-S thin films is performed with an aim to determine the relationship between film composition and CdSO_4 concentration. Quantitative estimation of Cd-Fe-S thin films are analyzed using an EDX set up attached with scanning electron microscope. Fig. 4 shows the variation of Cd, Fe and S content with CdSO_4 concentration for Cd-Fe-S thin films

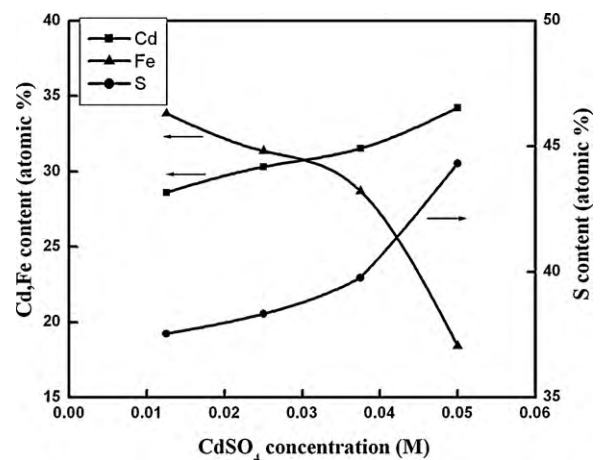


Fig. 4. Variation of Cd, Fe and S content with CdSO_4 concentration for Cd-Fe-S thin films obtained at various CdSO_4 concentrations.

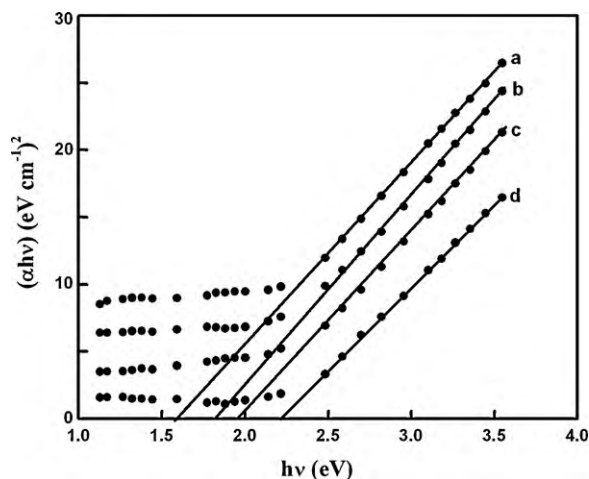


Fig. 5. Plot of $h\nu$ versus $(\alpha h\nu)^2$ for Cd-Fe-S thin films obtained at various CdSO_4 concentrations: (a) 0.0125 M (b) 0.025 M (c) 0.0375 M (d) 0.05 M.

obtained at various CdSO_4 concentrations. It is observed from Fig. 4 that the content of Cd and S increased, whereas the content of Fe decreased if the concentration of CdSO_4 is increased from 0.0125 to 0.05 M. This observation is also evidenced by the improvement of hexagonal (CdS) phase and decrease in hexagonal (FeS) phase which is also evidenced from XRD pattern.

3.5. Optical properties

The optical parameters such as absorption coefficient and bandgap are determined from optical absorption measurements. The value of absorption coefficient for strong absorption region of thin film is calculated using the following Eq. (5) [20]

$$\alpha = \frac{1}{t} \ln \left(\frac{A}{T} \right) \quad (5)$$

where α is the absorption coefficient in cm^{-1} , t is the thickness of the films, A is absorbance and T is transmittance. The nature of transition is determined using the following Eq. (6) [21]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (6)$$

where α is absorption coefficient in cm^{-1} , $h\nu$ is photon energy, E_g is an energy gap, A is energy dependent constant and n is an integer. The value of n determines the type of transition present in the material. In this case, $n = 1/2$ represents that the transition involved in the material is direct allowed. Typical plot of $h\nu$ versus $(\alpha h\nu)^2$ for Cd-Fe-S thin films obtained at various CdSO_4 concentrations from 0.0125 to 0.05 M is shown in Fig. 5 (Tauc's plot). The plot is linear indicates that the transition involved is direct allowed. Extrapolation of linear portion of the graph to energy axis (X-axis) gives the band gap value of the material. The band gap value of Cd-Fe-S thin films obtained in the present work is found to be vary in the range between 1.58 and 2.22 eV. The variation in band gap observed may be due to the following reason. The films prepared at 0.0125 M CdSO_4 concentration, the content of Fe is high which shift the band gap value of the material (1.58 eV) towards (FeS) side. Similarly, the films prepared at 0.05 M CdSO_4 concentration the content of Cd is high which shift the band gap value of material (2.22 eV) towards (CdS) side [5]. The band gap value of films obtained at 0.0375 M CdSO_4 concentration is found to be 1.95 eV which is in close agreement with the value reported earlier for $\text{Cd}_{0.8}\text{Fe}_{0.2}\text{S}$ thin films [5]. The refractive index (n) and extinction coefficient (k) are

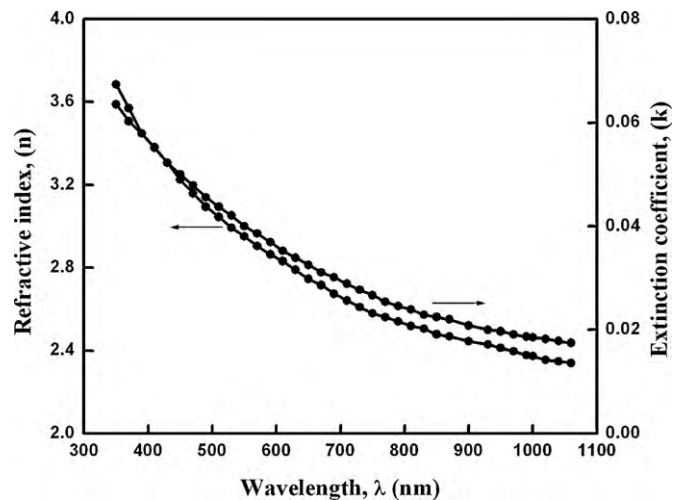


Fig. 6. Variation of refractive index (n) and extinction coefficient (k) with wavelength (λ) for Cd-Fe-S thin films obtained at 0.0375 M CdSO_4 concentration.

determined using the following Eq. (7) and (8) [22]

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (7)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (8)$$

where n is the refractive index of the material and k is extinction coefficient, R is reflectance (%) and λ is wavelength in nm. Fig. 6 shows the variation of refractive index (n) and extinction coefficient (k) with wavelength (λ) for Cd-Fe-S thin films obtained at 0.0375 M CdSO_4 concentration. It is observed that both refractive index and extinction coefficient exhibit decreasing dependence with wavelength which is shown in Fig. 6. The decreasing dependence are associated with an inter band transition for photon energies smaller than the smallest band gap [22]. The value n and k are found to be 2.78 and 0.033 correspond to band gap value of material obtained at 0.0375 M CdSO_4 concentration

4. Conclusions

Thin films of Cd-Fe-S are deposited on ITO substrates using potentiostatic cathodic electrodeposition technique. XRD patterns shows that the deposited films exhibit mixture of hexagonal (CdS) and hexagonal (FeS) phases for films obtained at different CdSO_4 concentrations. The crystallite size of the deposited films are found to increase while increasing the concentration of CdSO_4 from 0.0125 to 0.0375 M, thereafter it decreases slightly. Surface morphology reveals smooth surface with spherically shaped grains for films obtained at 0.0375 M CdSO_4 concentration. EDX analysis represents that the content of Cd and S increases, whereas the content of Fe decreases while increasing CdSO_4 concentration from 0.0125 to 0.05 M. Optical absorption measurements shows that the films obtained at optimized concentration has a direct band gap value 1.95 eV. The value of refractive index and extinction coefficient are found to be 2.78 and 0.033, respectively.

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