The Effect of Bath Temperature on the Chemical Bath Deposition of Copper Sulphide Thin Films

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Abstract

Copper sulphide thin films were deposited onto indium tin oxide glass substrates by chemical bath deposition technique. The chemical bath contained copper chloride and sodium thiosulfate acted as Cu^{2+} and S^{2-} ion sources, respectively. The influence of bath temperature towards the properties of copper sulphide films was investigated. The deposited films were characterized with X-ray diffraction, atomic force microscopy and UV-Vis spectrophotometer. XRD studies demonstrated that the thin films had hexagonal structure and confirmed the improvement of crystallinity of the films by increasing the bath temperature. Meanwhile, the surface roughness, film thickness and grain size were also increased with increasing of bath temperature from 25 to 45 °C. However, the films deposited at 25 °C showed homogeneous and uniform structure according to AFM images. Optical absorption analysis indicated that the band gap values were increased from 2.5 to 2.7 eV as the bath temperature was decreased from 45 to 25 °C. The XRD, AFM and optical absorption analysis results suggested that the influence of bath temperature on the CuS thin films properties was significant. Therefore, the bath temperature was one of the main deposition parameters that control the properties of semiconductor thin films.

Keywords: Chemical bath deposition; Thin films; X-ray diffraction; Atomic force microscopy; Copper sulphide.

Introduction

Copper sulphide is an important semiconductor material because of its interesting properties, such as direct band gap, abundance in nature and absence of toxicity. Thus, copper sulphide thin films have been widely used in a variety of applications such as solar cells, photothermal conversion, electroconductive electrodes, microwave shielding coatings and solar control coatings. Several techniques have been applied to obtain copper sulphide thin films such as spray pyrolysis[1], SILAR[2], photochemical deposition[3], electrodeposition[4] and chemical bath deposition[5]. Chemical bath deposition technique is simple, low cost and can operate at low processing temperature to produce large deposition area. The chemical

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bath deposition process is a slow process, which requires a source of chalcogen ions and metal ions to deposit on the substrates. The preparations of various thin films using chemical bath deposition technique such as CdS[6], MnS[7], SnSe[8], PbS[9], $Cd_{1-x}Zn_xS$[10], CdSSe[11] and Cu_4SnS_4[12] have been reported by several researchers. Gadave and Lokhande[5] prepared the CuS thin films using copper sulphate as copper source by chemical bath deposition method. The deposition process was carried out at 60 °C at pH 0.5. They found that as deposition time was increased up to 40 min, film thickness also increased and attained maximum value (0.37 μm). When the deposition time was further increased to 60 min, the films were powdery and films thickness decreased.

In this paper, we report on the deposition of copper sulphide thin films for the first time using copper chloride and sodium thiosulfate solutions in acidic medium (pH 3). The deposition was carried out under different bath temperatures in order to investigate the structural, morphological and optical characteristics of the films.

Materials and Methods

Preparation of thin films

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionised water (Alpha-Q Millipore). The copper sulphide thin films were prepared from an acidic bath using aqueous solutions of copper chloride ($CuCl_2.2H_2O$) and sodium thiosulfate ($Na_2S_2O_3.5H_2O$) acted as a source of Cu^{2+} and S^{2-} ions, respectively. The indium tin oxide (ITO) glass was used as the substrate for the chemical bath deposition of CuS thin film. Before deposition, the glass substrates were degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and dried in desiccators. Deposition of CuS thin films was carried out by using following procedure: 25 mL of $CuCl_2$ (0.05 M) was taken in a 100 mL beaker and 25 mL of $Na_2S_2O_3$ (0.05 M) was mixed with it. By adding drop-wise hydrochloric acid, the pH of resultant solution was adjusted to 3. The cleaned ITO glass substrate was immersed vertically into beaker which placed inside a water bath. The deposition process was carried out for 12 hours by varying bath temperatures (25, 35 and 45 °C). After the completion of deposition, the films were washed with distilled water and kept for analysis.

Characterization of thin films

The structure of the film was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a CuK_α (λ=0.15418 nm) radiation source. Data were collected by step scanning from 25° to 60° with a step size of 0.05° (2θ). The surface morphology, thickness and roughness were examined by recording atomic force microscopy (AFM) images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software. The optical properties of the films were measured with a Perkin

Elmer UV/Vis Lambda 20 Spectrophotometer in the wavelength range of 300 to 800 nm. The film-coated indium tin oxide glass was placed across the sample radiation pathway while the uncoated indium tin oxide glass was put across the reference path. From the analyses of absorption spectra, the band gap energy (E_g) was determined.

Results and Discussion

Figure 1 shows the XRD patterns of CuS thin films deposited under various bath temperatures. The chemical bath deposited CuS thin films are found to be polycrystalline in nature. The XRD patterns for all the samples indicate presence of six peaks with different widths and intensities. These peaks are correspond to orientation along (102), (104), (105), (106), (107) and (110) planes of hexagonal phase of CuS[13]. These peaks are well match with the standard JCPDS (Reference code: 00-065-3928) data. The lattice parameter values are a=b=3.768 Å, c=16.27Å, α=β=90°, γ=120°. In figure 1, as the bath temperature increases from 25 (Figure 1 curve a) to 45 °C (Figure 1 curve c), all the diffraction peaks become narrower and intensities of peaks increase indicating an improvement of crystallinity. This means that the grain size increases with increase in the bath temperature. On the other hand, as the bath temperature was increased from 25 to 45 °C, the intensity of the peak corresponding to (102) plane increased. This plane seems dominant at this stage of experiment. From the intensity of the peak, it can be seen that the film crystallinity is mainly affected by bath temperature. For instance, for the films grown at 25, 35 and 45 °C, the intensity of (102) plane of CuS peak reaches maximum 918, 812 and 2006 counts, respectively. Overall, from the XRD patterns, this peak (102) is considered as major peak with higher intensity as compared to others. In our case, the (104), (105), (106), (107) and (110) planes are weak peaks and have lower intensity values. However, the intensity of reflection (104) in figure 1 curve a is greater than that figure 1 curve b for the films deposited at 35 °C. The films deposited at 35 °C have different islands with different sizes, shapes and their distributions on the surface are not homogeneous. These could be the result of the chemical reaction during the deposition.

On the other hand, the presence of the indium tin oxide[14] (JCPDS reference No.: 01-089-4597) peaks in the XRD patterns is due to the ITO glass substrate used during deposition. Two peaks occurred at 2θ values of 30.5° and 50.8° corresponding to (222) and (440) planes were detected as shown in figure 1. At lower temperature (25 °C), the intensities of the CuS peaks [(102), (104), (105), (106), (107) and (110)] are rather low compared to the substrate peaks [(222) and (440)] indicating formation of very thin layer of films. However, as the bath temperature was increased to 45° C, the (102) peak attributable to CuS was of higher intensity compared to the substrate peaks [(222) and (440)], indicating more materials to be deposited on substrates. These results are consistent with the observations from the AFM images.

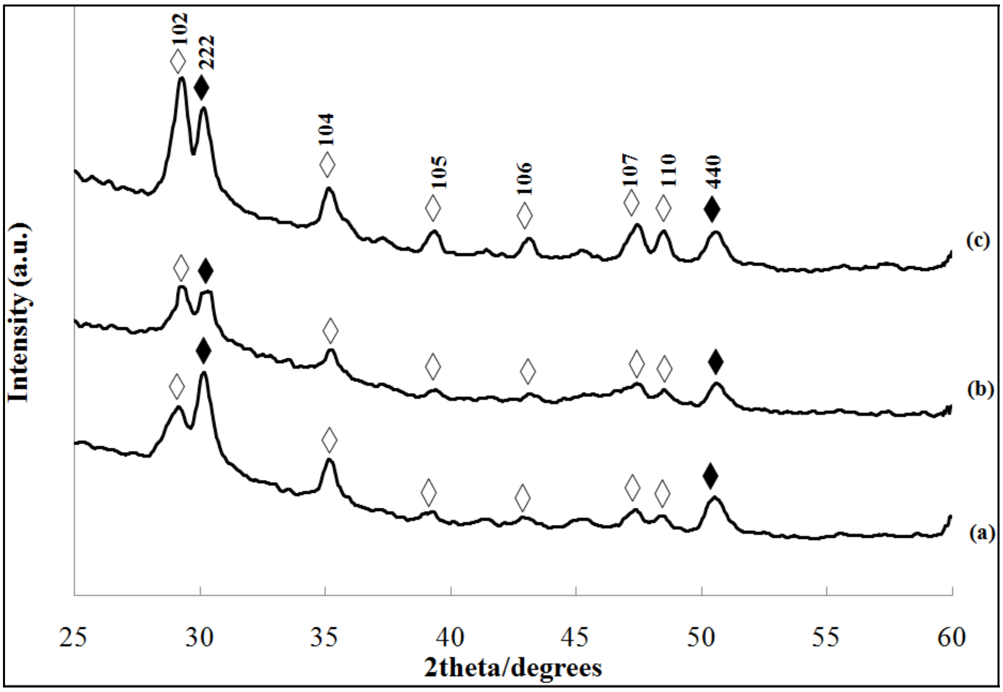

Figure 1: X-ray diffraction patterns of CuS thin films deposited at different bath temperatures. (a) 25 °C (b) 35 °C (c) 45 °C (◇ CuS; ◆ $In_{1.875}O_3Sn_{0.125}$)

The atomic force microscope (AFM) is an instrument that can analyze and characterize samples at the microscope level. This means we can look at surface characteristics with very accurate resolution ranging from 100 µm to less than 1µm. Figure 2 shows the AFM images of CuS thin films deposited under various bath temperatures and the scan size is 5x5 µm. The AFM image indicates that the films deposited at 25 °C are uniform (Figure 2 curve a), smaller grain size (0.5 µm) and the substrate surfaces are well covered with spherical grains. As the bath temperature is increased to 35 °C, the growth is found to be irregular. The grains consist of different sizes varying from 0.3 to 0.8 µm (Figure 2 curve b). When the bath temperature is further extended to 45 °C (Figure 2 curve c), the grain formation is observed as irregular agglomeration with the grain sizes different from one another (0.5 to 1.0 µm). These results show that the size of CuS depends mainly on the bath temperature and it increases with increasing bath temperature. This temperature dependence of size may be explained on thermodynamical grounds of larger grains being more stable than the smaller grains which are more favoured kinetically at lower bath temperature.

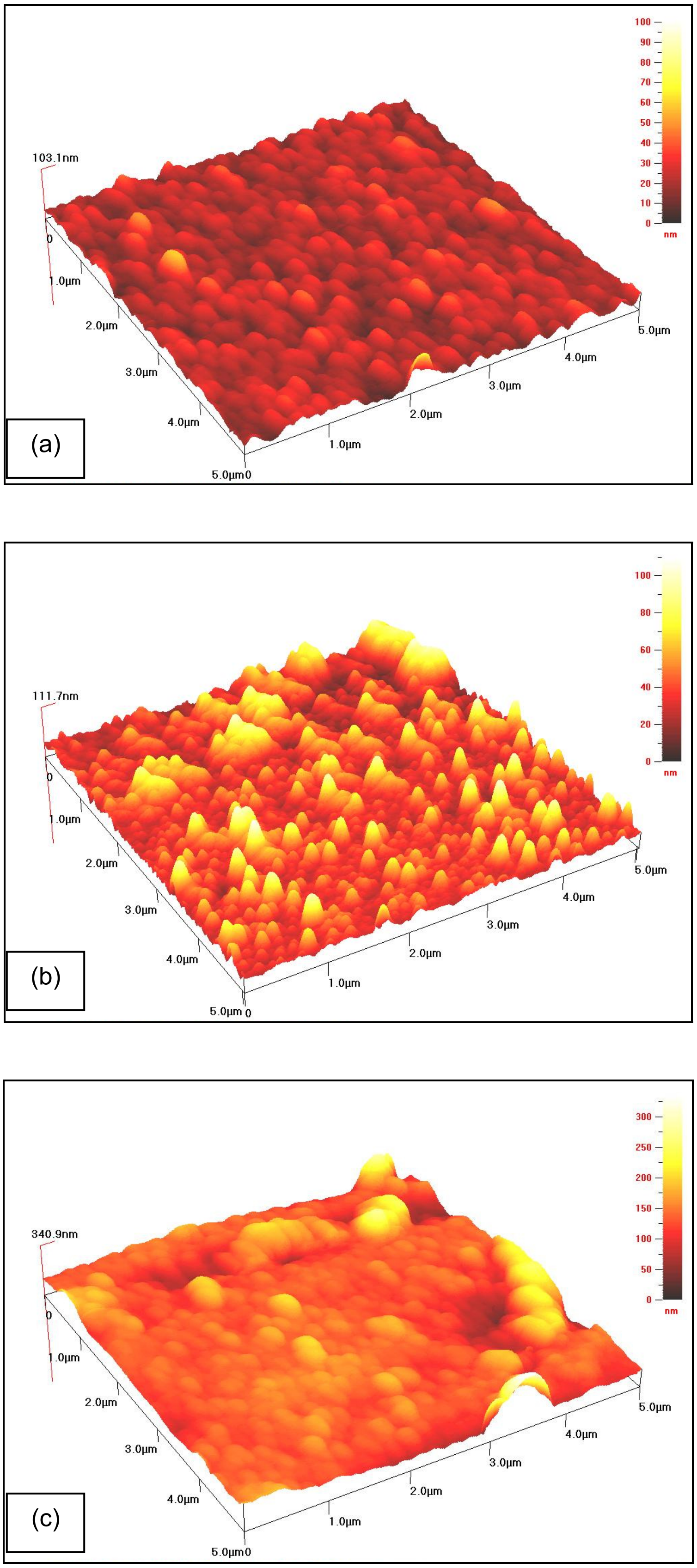

Figure 2: Atomic force microscopy images of CuS thin films deposited at different bath temperatures. (a) 25 °C (b) 35 °C (c) 45 °C

The root mean square (RMS) roughness and thickness of the films were investigated using atomic force microscopy technique. Root mean square roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness[15]. The roughness values of 7, 15 and 31 nm have been observed for the samples prepared at 25, 35 and 45 °C, respectively. With the decrease of bath temperature, the roughness value decreases, which means that the uniformity of the films become better. The surface roughness of the film is unavoidable since grains were grown with different sizes and spherical in shapes. There are many researchers have investigated the film thickness using AFM images[16-18]. At the right side of the images, an intensity strip is shown, which indicates the depth and height along the *z*-axis. The thickness values of 103, 112 and 341 nm have been observed for samples deposited for 25, 35 and 45 °C, respectively. These results indicate that an increase in bath temperature allows more materials to be deposited onto indium tin oxide substrate and thicker CuS films to be formed.

In this experiment, an aqueous medium $Na_2S_2O_3$ dissociates, in which sulfur and electrons are released which then combine to form S^{2-} ions. Following that, these sulphide ions react with Cu^{2+} ions to form copper sulphide thin films. In order to obtain information about growth rate, we have performed different experiments to determine the film thickness under various bath temperatures for 12 hours. The growth rate obtained was 8.6, 9.3 and 28.4 nm/h for the films deposited at 25, 35 and 45 °C, respectively. It is found that the films have smaller thickness for lower bath temperature (25 °C). This has been attributed to the decrease in releasing rates of Cu^{2+} and S^{2-} ions in the solution. In chemical bath deposition process, the rate of formation free ions at fixed ion concentration is dependent on bath temperature. If deposition temperature is higher (45 °C), the rate of formation of free ions is also higher. Therefore, more free ions deposit on the glass surface[19] and caused thicker films obtained. When the bath temperature increases, large number of Cu and S ions gets adsorbed on the substrate which leads to crystallization. This effect is more predominant at higher bath temperature, which leads to a maximum value of crystallite size for films deposited at 45 °C. The bath temperature is expected to influence the deposition arte by increasing the diffusion coefficient of the species and precursor solubility. CuS films deposited at 25 °C and 35 °C are found to be poorly crystallized.

The optical absorbance versus wavelength of the CuS thin films prepared at different bath temperatures is shown in figure 3. The spectra clearly indicate that shorter wavelengths correspond to maximum absorption compared to longer wavelengths. The films produced an absorbance value in the visible region of the solar spectrum indicating possibility of these materials to be used in a photoelectrochemical cells. The films deposited at 45 °C show a higher absorption value as compared with other samples. This response associated with the formation of larger grain size[11] when the films are prepared at higher bath temperature. For larger grain size, the film obtained reduces the number of grain boundaries, which are known to act as recombination centers for minority carriers and trapping centers for majority carriers, thereby reducing the carrier lifetime of a semiconductor. Therefore, high absorption value could be observed. Also, it is clear that the thicker films posses higher absorption nature compared to the other. This phenomenon could be due to more CuS materials are deposited onto the surface of the substrate at this bath temperature.

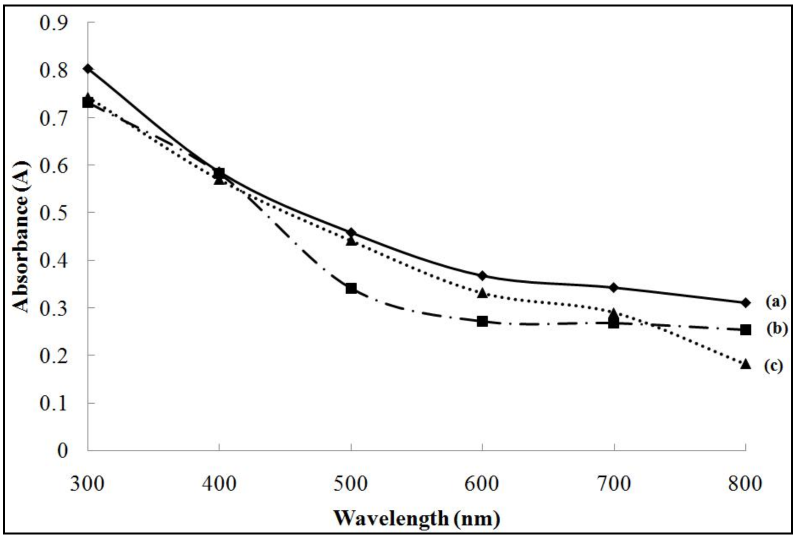

Figure 3: Absorbance versus wavelength spectra of CuS thin films deposited at various bath temperatures. (a) 45 °C (b) 35 °C (c) 25 °C

In order to determine the band gap of thin films, the equation of Stern[20] was used.

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu} \quad \text{...(1)}$$

where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The n value is 1 for a direct gap material and 4 for indirect gap material. Figure 4 shows $(Ahv)^2$ versus hv for the copper sulphide thin films deposited under various bath temperatures. It is expected that the copper sulphide thin films are direct band gap semiconductor when $(Ahv)^2$ is the linear function of photon energy (hv). The band gap values are obtained by extrapolating the linear portion of the plots of $(Ahv)^2$ versus hv to $(Ahv)^2$ =0. The band gap values for the films deposited at 25, 35 and 45 °C are 2.7, 2.6 and 2.5 eV, respectively. These results show that, with a decrease in the bath temperature, the band gap energy increases but the grain size decreases. This increase in band gap energy for the films deposited at lower bath temperature can be assigned to the quantum size effect as expected from the nature of thin films. These band gap values are in good agreement with the band gap values obtained by other researchers [2, 5].

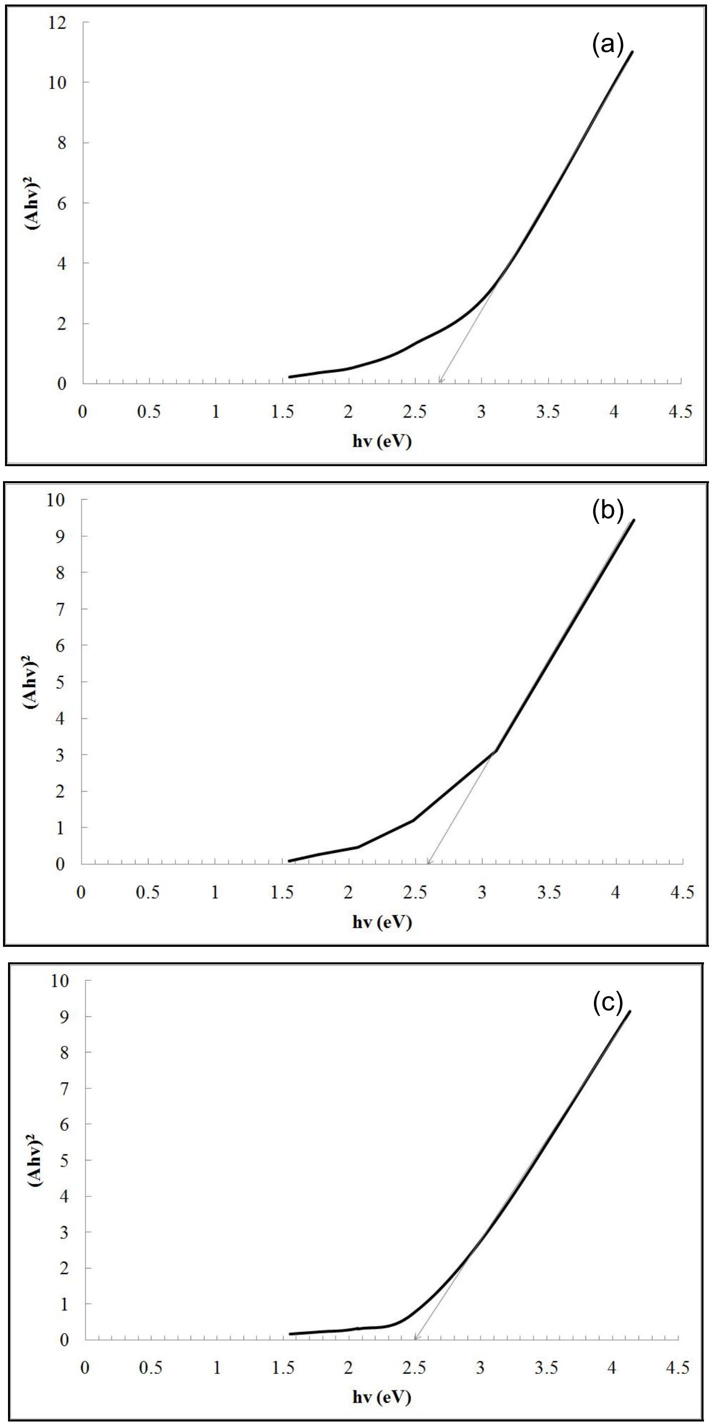

Figure 4: Plot of $(Ahv)^2$ versus *hv* of CuS thin films deposited at various bath temperatures. (a) 25 °C (b) 35 °C (c) 45 °C

Conclusion

The CuS thin films were successfully prepared onto indium tin oxide glass substrates by using simple and cost-effective chemical bath deposition method. The thin films were deposited from solutions of copper chloride and sodium thiosulfate. XRD studies demonstrated that the thin films had hexagonal structure and confirmed the improvement of crystallinity of the films by increasing the bath temperature.

Meanwhile, the surface roughness, film thickness and grain size were also increased with increasing of bath temperature from 25 to 45 °C. However, the films deposited at 25 °C showed homogeneous and uniform structure according to AFM images. Optical absorption analysis indicated that the band gap values were increased from 2.5 to 2.7 eV as the bath temperature was decreased from 45 to 25 °C. Therefore, the bath temperature was one of the main deposition parameters that control the properties of chemical bath deposited CuS thin films based on mentioned results in this study.

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