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The analysis of thermoluminescent glow peaks of copper doped ZnS thin films after β-irradiation

A.Necmeddin Yazici*, Mustafa Öztaş, V.Emir Kafadar, Metin Bedir, Hüseyin Toktamış

Department of Engineering Physics, University of Gaziantep, 27310, Gaziantep, Turkey

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Abstract

In the given study, the thermoluminescence (TL) properties of copper (Cu)-doped ZnS thin films were investigated after β-irradiation at room temperature (RT). It was observed that the glow curve of this material has two broad TL peaks, in which one of them was centered at about 110 °C and the other at about 170 °C for a heating rate of 1 °C s^{-1} in the temperature range from RT to 350 °C. The additive dose (AD), $T_m(E_a)-T_{stop}$, repeated initial rise (RIR), variable heating rate (VHR) and computerized glow curve deconvolution (CGCD) methods were used to analyze its glow curves. These methods indicated that the glow curve of this material is the superposition of a number of first- and general-order glow peaks, or at least due to the distribution of traps. The dose responses and fading process of both peaks were also examined, and it was observed that the dose responses of both peaks have similar pattern. First they follow a good linearity with different slopes and then saturate at approximately same dose level (2 kGy). The low-temperature broad peak nearly disappeared after 1 week storage in the dark at RT. On the other hand, the intensity of the high-temperature broad peak was approximately reduced to 50% of its original value. The TL emission spectrum of this material has two main emission bands, namely, the blue and green bands. The first glow peak emits predominantly in blue region, whereas the second glow peak in the green region.

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Keywords: Thermoluminescence; ZnS:Cu; Thin film; Spray pyrolysis

1. Introduction

ZnS is one of the well known II–VI compound semiconductors suitable to be used as host matrix for large variety of dopants because of its wide direct energy band gap (≈3.7 eV). It is known that ZnS phosphors have a broad-band luminescence from the near ultraviolet (UV) to the near infrared (IR). Therefore, it has been often used in the field of optoelectronic devices, such as for light-emitting diodes and flat-panel displays [1]. Especially, when ZnS is doped with a small amount of metallic ions, it emits a light in the visible region which is characteristic for the incorporated impurity. Therefore, it forms a very important class of phosphors for the fabrication of thin film electroluminescent devices. In addition, the density of ZnS (4.09 g/cm^3) could be considered adequate, radiation detection being higher than that of many currently used phosphors-scintillators such as NaI [2]. Silver-activated ZnS has been previously used in nuclear radiation detection instruments. Because of their low effective atomic number, ZnS phosphors could be suitable for use with low-energy X-rays, which, however, are employed in many radiographic examinations. Therefore, many properties of ZnS phosphors doped with metallic ions have been discussed extensively in the literature [3].

The thermoluminescence (TL) properties of pure and doped ZnS below room temperature (RT) have been extensively studied over 60 yr [4–9]. Garlick and Gibson discussed the TL of ZnS in terms of the models of Randall and Wilkins [4]. Hoogenstrateen systematized the many effects of sample preparation of dopants on the glow curves of ZnS phosphors [5]. However, all the past works have been carried out on powders prepared under a variety of

*Corresponding author.
E-mail address: yazici@gantep.edu.tr (A.N. Yazici).

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conditions for the temperature region below RT. Moreover, there has not been sufficient work on the TL properties of both bulk and thin film materials above RT up to now [6–8]. Materials in thin film form have great attention mainly because of their singular properties, which may differ significantly from their bulk attributes making them attractive for a wide variety of applications [9]. In particular, TL properties of thin films have a wide spectrum of potential applications in dosimetry for non-ionizing radiation [10,11]. The interest to study the TL response of thin films has been motivated for their importance in the measurements of absorbed doses from weakly penetrating radiation to highly energetic radiation. In the previous papers [12,13], we have studied the TL properties of undoped ZnS thin films above RT and it was shown that the thin film production techniques such as substrate temperature, ratio of starting material and heat treatments before the irradiations are highly effective on the TL intensity and emission spectra of pure ZnS samples that were grown by spray pyrolysis method. The thermoluminescent characteristics of Cu-doped ZnS have never been studied above RT up to now. Therefore, in the given present study, the TL properties of Cu-doped hexagonal ZnS thin films deposited by spray pyrolysis method are discussed in detail.

2. Experimental procedure

In the given study, ZnS:Cu thin films were obtained by spray pyrolysis in air atmosphere. The experimental set-up used for the preparation of pyrolytically spray-deposited films was described in our previous papers [12,13]. The initial solution is prepared from zinc chloride ($ZnCl_2$) at 0.5 M concentration and 0.5 M thiourea ($(SC(NH)_2)_2$) in deionized water. The Cu dopant is added to spray solution in the form of $CuSO_4$ (0.05 M). The prepared solution is sprayed (5 ml/min) onto the clean glass substrates, heated at 400 °C. The crystallinity of the films were characterized by X-ray diffraction using a Philips X-ray powder diffractometer provided with a Cu tube with K_α radiation at $\lambda = 0.154$ nm at an interval 20° to 50° [12,13]. It was observed that all ZnS films grown by spray-pyrolysis method were polycrystalline with hexagonal wurtzite crystal structure with preferred orientation in $\langle 0\,0\,2 \rangle$ direction using the XRD patterns of ZnS/glass structures. The glow curves of ZnS thin films were measured using a Harshaw QS 3500 manual type TL reader at a linear heating rate of 1 °C/s under a continuous flux of nitrogen. All the films were irradiated using a $^{90}Sr/^{90}Y$ β-source (2.27 MeV) at a dose rate of approximately 0.015 Gy/s at RT. An Aminco-Bowman Series 2 Luminescence Spectrometer was used to measure the TL emission spectra between 300 and 750 nm using a linear heating rate 20 °C/min and a scan rate of 30 nm/s. The recorded spectra have been corrected for the photomultiplier response. The emission spectrum of TL peaks is analyzed by curve fitting program [13]. The recorded glow curves were analyzed using computer glow curve deconvolution (CGCD) program, initial rise and heating rate methods [12,13].

3. Results and discussions

As mentioned in our previously published study [14], it is essential to find the kinetic order (b) and exact number of the glow peaks in each glow curve before the evaluating of trap depth (activation energy E_a) and frequency factor (s). Therefore, to find the b-values of each individual glow peak, the additive dose method was firstly used. Some of the selected glow curves after different dose levels are shown in Fig. 1. As shown in this figure, the TL glow curves of ZnS:Cu thin films exhibit two main peaks, where one of them is centered at about 110 °C and the other is at about 170 °C. In TL theory, for slow retrapping ($b \approx 1$), it is expected that the peak temperatures of the glow peaks are only changed with the heating rate (β). However, in the case of fast retrapping ($b \neq 1$), it was observed that the peak temperatures are shifted to the lower temperature side with increasing dose levels. It is seen from Fig. 1 that the structures of the TSL glow curves remains constant without any observable change in the structure of the glow curves for different periods of irradiation time. However, for longer times (>24 h) the intensity of high-temperature peak (I_{m2}) at 170 °C becomes more than the low-temperature peak (I_{m1}) at 110 °C because of the high thermal fading of peak at 100 °C than the peak at 170 °C during the irradiation process. In addition, the peak temperature of low-temperature peak (T_{m1}) was firstly shifted to the low-temperature side for the irradiation time between 1 and 180 s and then started to shift to the high-temperature side with increasing irradiation time (see Fig. 2). On the other hand, the peak temperature of high-temperature peak (T_{m2}) in the glow curve of ZnS:Cu is within the experimental error ± 2 °C for the irradiation time between 1 s and 1.5 h. As similar to the first peak, if the irradiation time is increased above 1.5 h, the peak temperature of this peak is also started to shift to the higher-temperature sides. Although the peak temperatures of both peaks shift to the high-temperature sides with increasing dose levels, these results indicate that the observed low-temperature peak might be considered under the general-order kinetics, whereas the high-temperature peak is the first-order kinetics.

The CGCD is another powerful technique in the study of TL and it is frequently used to determine the trapping parameters and in the study of thermoluminescent dosimeters. The application of the CGCD technique for the decomposition of a composite TL glow curve into its individual glow peaks is widely applied since 1978 [15]. A typical analyzed TL glow curve from 1 h irradiated ($\approx$20 Gy) ZnS:Cu thin film is shown in Fig. 3 along with the components obtained from CGCD. It is obvious that only two TL peaks are insufficient to analyze the glow curve of the ZnS:Cu. In this case, it was obtained that the best-fit curve differs substantially from the experimental