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Abstract

In this study, the thermoluminescence (TL) glow curves of ZnS thin films developed using chemical spraying technique were carefully investigated and its kinetic parameters were determined with a specially developed computer program. The results of investigations have shown that the trapping states of ZnS thin films could not be analysed by a well-known Randall-Wilkins (RW) or General-Order (GO) models. A detailed investigation of experimental results has indicated that the trapping states have a form that is best described by a distribution of energies. After the comparison of the experimental glow curves of ZnS thin films with theoretically generated glow curves, it was found that the distribution of traps is of an exponential type distribution.

Key Words: Thermoluminescence, Trapping Parameters, ZnS

1. Introduction

ZnS crystals are known as a material having high photoluminescence and thermoluminescence properties above room temperature and are widely used in opto-electronic devices for their photoluminescence properties [1]. ZnS crystals produced using vacuum evaporation or chemical spraying techniques have a highly defective polycrystalline structure [2].

Materials having the thermoluminescence property emit light that can be best described by a "glow curve", which may present several glow peaks during a heating process. The positions and shapes of the glow curves are related to the various parameters of the trapping states. These parameters are namely: the trapping depth (activation energy) below the conduction band E (eV); frequency factor (pre-exponential factor) s_0 (s^{-1}) which has lattice vibrations on the order of 10^8-10^{15} s^{-1} in crystalline solid; kinetic order b; and the number of trapped electrons in traps n_0 (cm^{-3}) [3]. For example, when E increases, the peak temperature T_m of the glow peak shifts to higher temperatures, along with a decrease in the height and an increase in the width (but with the area remaining constant). The effect of frequency factor is inversely related with trap depth E. And also, it is to be noted that the peak position stays fixed, while the height of the peak is directly proportional to the number of trapped electrons n_0. Thus, the mathematical analysis of glow curves gives the possibility to determine the aforementioned parameters. There are various methods to obtain the numerical values of these parameters from TL glow curves [4]. However, the mathematical equations used for these kinds of analysis have been derived assuming that there is a single electron trap and a single recombination center corresponding to single energy level in the band gap of the material (as they do in the RW or GO models). This assumption may be true for high quality single crystals, but it can't be true for most of the TL materials such as amorphous or vitreous materials. The energy levels associated with

particular defect in these materials will be spread over a range of values rather than being a uniquely defined level. Evidence of this energy distribution comes from a variety of experimental techniques, for example from SPLC (space charge limited current) and TSC (thermally stimulated conductivity) experiments. In addition, the $T_m - T_{stop}$ experimental method can also be employed to extract the distribution of energy states from TL glow curves [5]. However, the glow curves of TL materials, which have a continuous trap distribution, are more difficult than the RW and GO models [6-7].

In this study, it was shown that the energy levels associated with a particular type defect in ZnS thin films produced via chemical spraying technique are distributed over a range of values rather than being uniquely defined level. To demonstrate this distribution, the glow curves of ZnS thin films were first obtained. Then, the form of the energy level distributions was evaluated by means of the $T_m - T_{stop}$ experimental method. As a result, it was found that the distribution of traps in ZnS crystals is an exponential type of trap distribution. This result was also confirmed by comparing the experimental glow curves with the theoretically generated glow curves. The fitting results, which have been obtained by specially developed computer program, also indicated that the best-fit results are always obtained when using an exponential type of trap distribution.

2. Theory

It is well known that trapping states always exist in the band gap of amorphous semiconducting materials. These states do not have only one energy level, but have energy distributions. Moreover, their distributions may have various forms. In general, there are three types of trap distributions in crystals; linear, exponential and gaussian type distributions [3-4].

The equations giving the number of trapping states according to the energy for linear, exponential and gaussian types of distributions are as follows:

1. Uniform (linear) distribution of trapping states between E_A and E_B in the energy gap:

$$N(E) = N_m(\frac{E - E_A}{E_B - E_A}), \tag{1}$$

where $N(E < E_A) = N(E > E_B) = 0$ and $N(E_A < E < E_B) = N_t$ is the uniform trap density between E_A and E_B.

2. Exponential distributions from E_A to E_B:

$$N(E) = N_m \exp(-\frac{E}{kT_c}), \tag{2}$$

where N_m is a constant ($\mathrm{m^3eV^{-1}}$) and T_c *is* a characteristic temperature for the distribution.

3. Gaussian distribution of trapping states between E_A and E_B:

$$N(E) = N_m \exp(-d(E - E_m)^2), \tag{3}$$

where N_m is the maximum density at energy E_m and d is a constant.

Assuming negligible retrapping, the TL glow curve for a first-order (b=1) process involving a distribution of energies $N(E)$ can be rewritten as

$$I(T) = \int_{E_A}^{E_B} \{N(E)s_0 \exp(-\frac{E}{kT}) \exp[-\frac{s_0}{\beta}\int_{T_0}^{T} \exp(-\frac{E}{T'})dT']\}dE, \tag{4}$$

where s_0 is the frequency factor, β is the heating rate (°C/sec), $E$is the trap depth (eV), T_0 is the room temperature (K or °C), and k is the universal Boltzmann's constant.

The analytical solution of Eq. 4 is not possible. Therefore, this equation involving the double integral was solved by a specially developed computer program under MATHAMATICA and employees numerical solution techniques.

3. Experimental Procedure

ZnS thin film samples were first produced via chemical spraying technique under normal atmospheric condition. The detail of thin film preparation technique has been given in our previous studies [8-9]. All films that were investigated are polycrystalline with a wurtzite (hexagonal) structure [9]. The prepared samples were irradiated at room temperature with beta rays emitted from a ^{90}Sr-^{90}Y source for 1 hour. The glow curves were immediately recorded at the end of the irradiation, so that there was no significant fading of the TL peaks at room temperature. All TL glow curves were measured with a low heating rate of 2°C/sec using a standard TL reader (Harshaw QS 3500 Manual Model) interfaced to a PC where TL signals were analysed.

In the investigation of kinetic analyses, $T_m - T_{stop}$ experiment was employed to extract and to understand the type of the distribution of trapping states [3-4]. Therefore, the following procedures were employed:

The ZnS thin films are irradiated at room temperature.

The irradiated samples are heated up to the desired temperature and then cooled in air at approximately 75°C/min to room temperature.

The glow curves of the samples are measured between room temperature and 250°C.

4. Results

The theoretically computed glow curves using the computer program composed under MATHAMATICA for discrete (according to RW model), uniform (linear), exponential and Gaussian type of trapping distributions are shown in Fig. 1. In these calculations, the following values for the trapping parameters were used: s_0=1x10^{11} sec^{-1}, E_A=0.96 eV, E_B=1.04 eV and β=1°C/sec. As seen from this figure, the shapes of TL glow curves differ from each other and their shapes highly depend on the type of the distribution functions $N(E)$. For example, the peak temperature T_m, and the rising and falling parts of the glow curves are highly different from each other although the assumed trapping parameters were the same. Additionally, the calculated geometric shape factors $\{\mu_g = (T_2 - T_m)/(T_2 - T_1)\}$, where μ_g is the geometric shape factor, T_m is the peak temperature and T_1 and T_2 are the low- and high-temperatures at the half-heights of the glow peaks, are well differentiated from each other.

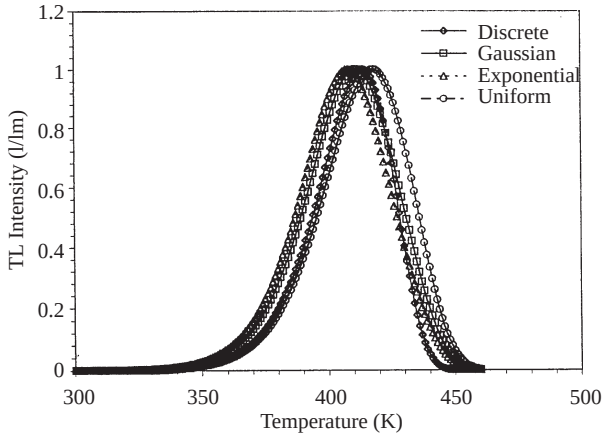

Figure 1. Theoretically computed glow curves obtained by using computer program MATHAMATICA for single energy level traps (discrete) and linear, exponential, gaussian types of trapping distribution.

Determination of the form of energy state distribution from a thermoluminescence glow-curve is crucial and several authors have worked on this subject using different methods [3-4]. One of these methods is suggested by S. W. S. McKeever [5], and is known as the experimental $T_m - T_{stop}$ method. This method indicates the presence of a trap distribution in a crystal and is also used to obtain the kinetic order b of glow peaks.

Glow curves obtained for various stopping temperatures T_{stop} are shown in Fig. 2. It can be seen from this figure that the peak temperatures are shifting with increasing stopping temperature. The plot of $T_m$versus T_{stop} obtained by using the data in Fig. 2 is shown in Fig. 3. Theoretically, a linear continuous distribution of traps will produce a straight line in a $T_m - T_{stop}$ experiment [10]. As strongly suggested by Fig. 3, the graph of shifting of peak temperature T_m versus T_{stop} is similar to an exponential curve. On the other hand, this curve can be considered as being a composite of two different straight lines each having different slopes. The slope of the first straight part of the curve "A" increases slowly until approaching near the peak temperature of ZnS thin film glow curves ($T_m = 118$°C). However, the second part of curve, denoted "B" increases very rapidly after the peak temperature ($T > 120$°C) with a much larger slope than A. Therefore, it can be considered that the ZnS thin films have a distribution of traps. Furthermore, there is no any experimental method to understand the form of trap distribution from experimental glow curves. In general, the form of the trap distribution can be understood by using the shape of the TL glow curves. This can be easily understood using theoretical approximations.

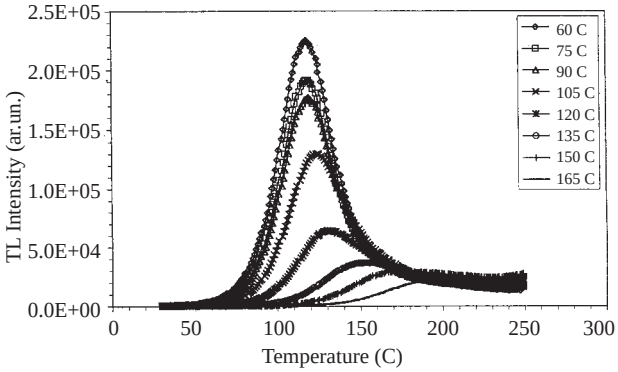

Figure 2. Measured glow curves of ZnS thin films obtained after different stopping temperatures.

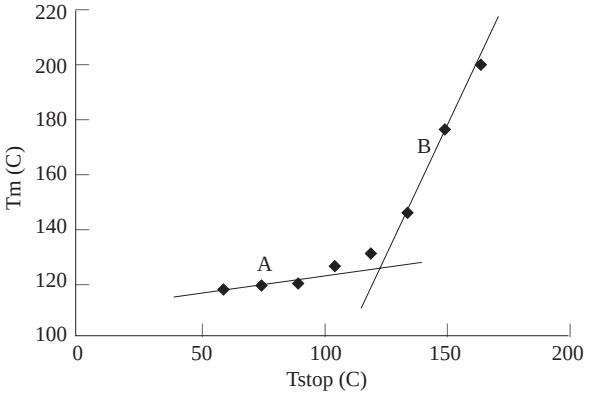

Figure 3. Graph of T_m versus T_{stop} obtained by using the data in Fig. 2.

So, to further the understanding of the trap distribution, two computer programs were written to solve Equation (3) while another, computer program, known as the Computer Glow Curve Deconvolution Program (CGCD), was specially developed in Fortran to compare experimental data with the numerically computed glow peaks. Results from CGCD indicated that the best fit was always obtained when an exponential distribution is used to model the ZnS glow curves. Figure 4a and b shows a best-fit plot against the ZnS thin film data as produced by the CGCD program. As seen from this figure, there is good agreement between the experimental and theoretically computed glow curve when the exponential distribution of Energy is used in Equation 4.

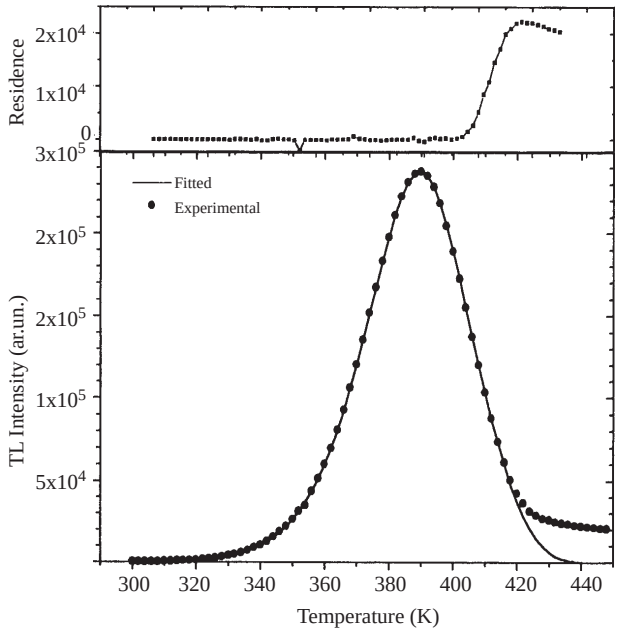

Figure 4. Comparison of analysed glow curve obtained from the program CGCD and the experimental glow curves of ZnS thin films.

5. Discussion and Conclusion

The exponential model presented here is certainly not unique and any model based on the distribution of energies would probably describe adequately the experimental data. Nevertheless, there is a physical basis for using the exponential model; one can assume that localised distortions due to vacancies, impurities and/or dislocations give rise to trapping centers, which are exponentially distributed throughout the crystal [11].

Additionally, curve fitting of the glow curve alone does not produce a unique set of s_0 and $N(E)$ parameters; several s_0, $N(E)$ combinations can yield a good fit, but when this method is combined with other methods (i.e. initial rise, peak-shape, etc.) [3-4] it would give good results.

In summary, the experimental TL glow curves of ZnS thin films which are developed under different conditions [12] can be described by the distribution of energies which most probably have exponential distribution with the evaluated trapping parameters given in Table 1.

Table 1. The evaluated trapping parameters of ZnS thin films using the program CGCD.

E_A	E_B	s_0	T_c	N_m
0.938 eV	1.02 eV	4.02E+11 sec^{-1}	790 K	8.28E+13 eVm^{-3}

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