Thermoluminescence properties of hausmannite Mn$_3$O$_4$ thin films induced by UV light

H Hristov$^1$, R Mateva$^1$, N Arhangelova$^1$, V Velev$^1$, Y Baneva$^2$, K Boubaker$^3$, T Larbi$^4$, G Moschini$^5$ and N M Uzunov$^{1,5}$

$^1$ Faculty of Natural Sciences, Shumen University “K. Preslavsky”, 115 Universitetska str., 9712 Shumen, Bulgaria
$^2$ Dept. of Physics and Biophysics, Medical University, 150 Tzar Liberator str., 9000 Varna, Bulgaria
$^3$ Higher School of Sciences and Techniques of Tunis, University of Tunis, 63 Rue Sidi Jabeur, 5100, Mahdia, Tunisia
$^4$ Physics of Semiconductor Devices Unit, Faculty of Sciences of Tunis, Tunis El Manar University, 2092 Tunis, Tunisia
$^5$ National Laboratories of Legnaro, INFN, Viale dell’Universita 2, 35020 Legnaro (PD), Italy

E-mail: nikolay.uzunov@lnl.infn.it

Abstract. Thermoluminescence (TL) properties of Hausmannite thin films deposited onto glass substrates have been studied. The thin Mn$^{2+}$Mn$^{3+}$O$_4$ films were grown at 350°C on 1×2 cm$^2$ glass substrate by a spray pyrolysis technique. UV light from a XBO lamp was used to induce thermoluminescence in the film and the thermoluminescence properties of the Hausmannite layer were studied measuring the intensities of the TL peaks from the glow-curve deconvolution. The TL kinetic parameters of the Hausmannite were obtained from the TL glow curves analysis. The spectral emission of the Mn$^{2+}$Mn$^{3+}$O$_4$ layer has been studied using interference filters. The TL peak-fading assessment of the Hausmannite layer revealed that the peaks at 110°C, at 142°C and 194°C have relatively long fading. The analysis of the thermoluminescence properties of the Hausmannite thin films deposited onto glass substrates shows that they possess very good sensitivity for UV emission and could be used for quantitative measurements of UV light.

1. Introduction

The development of thin metal-oxide layers in recent years receives an outstanding boost. On the one hand they are very interesting in terms of their fundamental physical properties, and on the other they have a wide range of applications. In particular manganese oxide thin films have attracted a great deal of attention because of their large variety of practical exploitation such as electrochemical applications, magnetic sensors and data storage based on their magnetic properties [1 – 3], catalysis of a number of processes [2, 4], supercapacitive media in electronics and microelectronics [2, 5, 6], etc. However, despite the large spectrum of studies on the properties of manganese oxide thin films, available data concerning their thermoluminescence (TL) properties are still very scarce or absent.

Spinel Mn$_3$O$_4$ (also indicated as Mn$^{2+}$Mn$^{3+}$O$_4$) is a kind of manganese oxide naturally existing as a mineral Hausmannite. It is often obtained in a simple way by applying chemical spray pyrolysis...
In this work we present the first hand results from the study on the TL emission of Hausmannite $\text{Mn}_3\text{O}_4$ thin film deposited onto a glass substrate using chemical spray pyrolysis technique. The TL properties of the Hausmannite thin films have been studied after irradiation with ultraviolet (UV) light. We discuss the opportunity such material to be exploited as a potential quantitative indicator, sensible to the ultraviolet light in the range of 290nm — 340nm.

2. Materials and methods

Manganese oxide $\text{Mn}_3\text{O}_4$ layers were prepared at the Unit of Physics of Semiconductor Devices (UDPS), Tunisia. The thin films were grown at a temperature of 350°C on $1\times2$ cm$^2$ glass substrate by the spray pyrolysis technique. A schematic presentation of the process is presented in figure 1. A filtered compressed nitrogen gas was used as a gas carrier at a flow of 4 l/min. The sprayed aqueous solution, containing manganese chloride ($\text{MnCl}_2\cdot6\text{H}_2\text{O}$) 0.1 M as precursor, was inserted at a constant flow of about 4 ml/min. The substrate temperature was fixed using a digital temperature controller with a k-type thermocouple. The distance between the nozzle and the substrate was about 27 cm. The total deposition time was maintained at 20 min. After the deposition, the coated substrates were allowed to cool down naturally to room temperature.

![Figure 1. A schematic presentation of $\text{Mn}_3\text{O}_4$ thin-film deposition using spray pyrolysis technique.](image)

To obtain the glow curves from the TL emission of the Hausmannite thin films we used a TL setup developed in the Laboratory for nuclear physics and radioecology (LNPR) at the University of Shumen [9]. The system is composed of a module for sample heating, a TL measuring module on the basis of photomultiplier tube, and a setup for sample irradiation with high-intensity large-band ultraviolet (UV) light. The TL measuring module is realized on the basis of PIC16F876 microcontroller as well as on original forward/backward feedback method, based on the so-called model predictive controllers to achieve higher temperature stability and repeatability of the analyses conducted.

The TL properties of the Hausmannite thin films have been studied after initial irradiation with a xenon short-arc lamp type XBO 75 W/2 (OSRAM), emitting light with a wavelength in the range of 250 nm $\leq \lambda \leq$ 1200 nm. The crystals have been placed at a distance of 20 cm and the time of irradiation (exposition time) was determined after studying the Hausmannite saturation curve.

The TL glow curves (GC), representing the intensity of the TL emission as a function of the linear
increase of the temperature, were analyzed using glow curve decomposition analysis. Each of the peaks in the GC was treated as a composition of several glow peaks and the fitting procedure consisted in minimization of the $\chi^2$ function varying the three parameters of each peak: the temperature, corresponding to the maximum of the peak intensity $T_m$; the activation energy $E$, and the so-called kinetic order parameter [10].

Glow curves, obtained with the TL reader were smoothed using a Savitzky-Golay filter after transferring to a personal computer. The GC data have been analyzed using a developed in the LNPR computer program implementing a minimization procedure based on conjugated gradients method.

In order to measure the fading of the GC peaks as a function of the storage time the Hausmannite thin films were irradiated with the XBO lamp for exposure time big enough to ensure full TL saturation. The irradiated samples were kept for a certain time after the irradiation in a dark storage at a temperature of 20°C. The intensity of the TL emission was measured as the net peak area of the GC peaks and the fading was presented as the peak intensity versus the storage time.

3. Experimental results

A glow curve of Mn$_3$O$_4$ thin films obtained at a heating rate of 0.16°Cs$^{-1}$ immediately after 5 minutes of irradiation with UV light is presented with thicker black line in figure 2. Three peaks, shown with a thinner line in figure 2, have been revealed by the decomposition analysis of the glow curves: peak 1 at 110°C, peak 2 at 142°C and peak 3 at 194°C, indicated in the figure as 1, 2 and 3 respectively. Another peak with higher value of the maximum temperature position 347°C, indicated as 4 in figure 2, has also been detected. In the same figure the residual is presented with a broken line and the resulting fit, which is a sum of all peaks, is presented with white line. The calculated kinetic parameters for the peaks appearing in the TL glow curves, calculated using the GC decomposition analysis, are shown in table 1.

A plot of the calculated peak intensities (the integrated counts in the corresponding peak areas from figure 2) as a function of the time of irradiation of the Hausmannite with the XBO lamp at a distance of 20 cm is shown in figure 3. From the figure it is clearly seen that a full saturation of the Mn$_3$O$_4$ film begins after 40 minutes of irradiation.

![Figure 2. Glow curve of Mn$_3$O$_4$ thin film, obtained after 5 minutes irradiation with UV light.](image-url)
The dependence of the TL emission on the wavelength of the irradiating light (the spectral sensitivity) has been studied measuring the intensity of the TL glow curves for Hausmannite thin film. Interference optical filters for different wavelength were placed consecutively between the XBO lamp and the crystals during each irradiation. The Hausmannite film was exposed to irradiation from the XBO lamp for time ensuring the full saturation of the states. The calculated intensities for peak 1, peak 2 and peak 3 from the measured TL glow curves versus the wavelength of the irradiating light are shown in figure 4. The obtained thus spectral sensitivity of the material reveals a maximum at 290 nm and a wavelength limit of around 340 nm.

Measurements to determine the fading of the peaks observed in fig 1 have been conducted for a maximum time period of 168 hours. To perform this kind of measurements each time the Hausmannite film was irradiated with an equal amount of light from the XBO lamp for exposure time ensuring the full saturation of the states. After the irradiation the Hausmannite film was kept for certain time period in dark place at a temperature of 20°C. A plot of the areas of the three peaks, calculated from the fits of the TL glow curves versus the storage time of the phosphors is shown in figure 5.

### Table 1. Calculated kinetic parameters of the peaks in the TL glow curve of Mn$_3$O$_4$ thin film.

| Peak reference | Maximum temperature position (°C) | Activation energy (eV) | Kinetic order |
|----------------|-----------------------------------|------------------------|---------------|
| Peak 1         | 110 ± 2                           | 1.2 ± 0.2              | 2.0 – 0.1     |
| Peak 2         | 142 ± 1.8                         | 0.84 ± 0.09            | 2.0 – 0.1     |
| Peak 3         | 194 ± 1.3                         | 0.62 ± 0.08            | 2.0 – 0.1     |

**Figure 3.** A plot of the peak intensities of the GC peaks of of Mn$_3$O$_4$ thin film as a function of the time of irradiation with UV light.

4. Conclusion
The quantitative assessment of the fading of Peak 1, Peak 2 and Peak 3 from fig. 2 reveals that the peaks possess low degree of fading, allowing thus stable quantitative TL measurements within a couple of weeks. The three peaks have relatively low activation energies and good count-rate statistics.
In this connection a good reason would be the determination of dipole moment of manganese electron transitions from a metastable to the ground state as it is shown in [11] for the electrons of cobalt in the doped oxide glasses.

The assessment of the spectral sensitivity of the Hausmannite Mn$_3$O$_4$ thin film shows that the material is suitable for qualitative and quantitative measurements of UV light with a wavelength up to 350nm. Furthermore, a comparison of the intensity of the TL emission of the Mn$_3$O$_4$ thin film with other UV sensitive materials previously studied by our group [12,13] shows on the superior qualities of the Hausmannite as a UV detector. The physical characteristics of the Hausmannite studied so far suggest a reasonable opportunity to exploit such a material as an excellent media for UV measurements.
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