Thick Film Gamma Radiation Sensors with Sensitive Layers of NiO and La_2O_3–Fe_2O_3 Mixture

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Abstract

Thick films of Nickel oxide (NiO) and mixture of Lanthanum oxide (La_2O_3) and Iron oxide (Fe_2O_3) were investigated for γ-radiation dosimetry purposes. Samples having a metal-semiconductor-metal sandwich structure were fabricated using the thick film screen printing technique. These films were exposed to a ^{60}Co γ-radiation source with a dose rate of 6 Gy/min. The effects of γ-radiation on the electrical properties of NiO and La_2O_3-Fe_2O_3 thick films were studied.

1. Introduction

The need for appropriate dosimetry was recognized soon after the discovery of ionising radiation, as it has a deleterious effect on the human body. It was not only the radiation hazard involved in the use of ionising radiation, but its controlled use in biology, industry, medicine, research, and military applications that required measurement of the radiation energy absorbed. The remarkable progress in the technology associated with devices and systems operating at room temperature has resulted in the occurrence of various semiconductor radiation dosimeters.

Electrochromic materials, for example Nickel oxide, are used in applications such as energy efficient "smart windows", glare-free and variable reflectance mirrors, high-contrast non-emissive information displays, switchable displays, devices for thermal control, semiconductor-based sensors, etc. [1-4]. Mixtures of oxide materials, such as La_2O_3 and Fe_2O_3, are mainly used in gas sensing applications [5-9]. Mixing the different oxides in various proportions can control the properties of the semiconductor films [10, 11].

The aim of this paper is to document the use of NiO and La_2O_3-Fe_2O_3 thick films in radiation dosimetry. The influence of ionising radiation on Nickel oxide and its mixture with other oxides prepared by various techniques has been explored [12, 13]. Nickel oxide is a typical binary transition metal oxide with a rock salt structure and antiferromagnetic properties below a temperature of 523 K. There were no information found up to date about the use of La_2O_3 and Fe_2O_3 oxides mixture for dosimetry purposes.

2. Experimental procedure

Throughout the experimental procedure two types of thick films were used. The first is a polymer paste made of 92 wt.% of NiO and 8 wt.% of $C_8H_{18}O_3$ with Diethylenglycolmonobutylether as a solvent. The starting materials for the second type of the paste were La_2O_3 (50 wt.%) and Fe_2O_3 (50 wt.%). The weighed fractions of the starting materials were mixed and wet-ball milled in alcohol for 24 hours, then dried. The resulting powder mixture was fired at 1473 K for 1 hour. After this procedure, a solid amount of the functional material was obtained. This solid lump was broken up and ground down to a powder using mortar and pestle. Further preparation procedure for this type of polymer paste was the same as for the NiO material. Polymer pastes and commercial DuPont 4929 silver paste were used to fabricate the radiation sensitive layers and contacts respectively. Pastes were printed on glass substrates using a DEK RS 1202 automatic screen printer to form a sandwich Metal-Semiconductor-Metal (MSM) structure with an active area of $1cm^2$. As a result, samples having a layout, as shown in Figure 1, were fabricated.

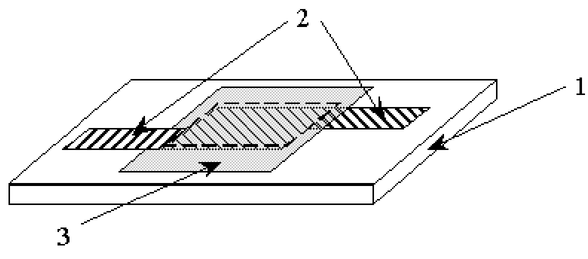

Figure 1. Sandwich MSM structure, where 1 is a glass substrate, 2 – silver paste layers used as electrodes, 3 – layer of radiation-sensitive material.

A ^{60}Co radiation source with a dose rate of 6 Gy/min was used for exposing all the samples to γ-radiation. Series of irradiations were performed by changing the exposure time and hence the dose. The current-voltage characteristics for as-printed and γ-irradiated specimens were recorded after each exposed dose. A Hewlett Packard impedance analyser (HP 4277A LCZ-meter) was used for pertinent AC electrical measurements of the thick film samples.

3. Results and discussion

3.1. NiO thick film structure

Current-voltage characteristics for NiO thick film samples were measured after each exposure dose, which was increased in steps of 180 Gy. Figure 2 shows plots of the I-V characteristics that were recorded for as-printed and γ-irradiated Ag-NiO-Ag thick film sandwich structures. Figure 3 shows a linear response of the normalized current $(I-I_0)/I_o$ with radiation dose up to 720 Gy under an applied voltage of 3V.

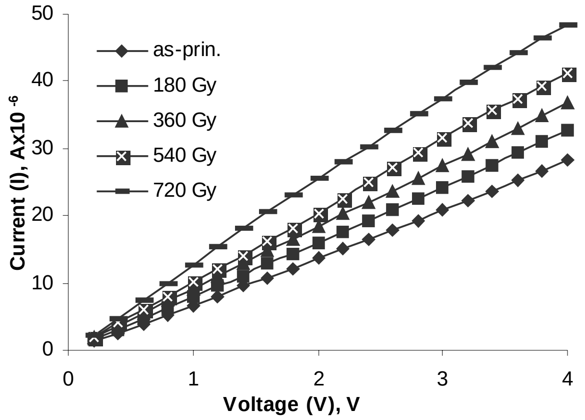

Figure 2. Plots of current-voltage characteristics that were recorded for as-printed and irradiated Ag-NiO-Ag thick film sandwich type structures.

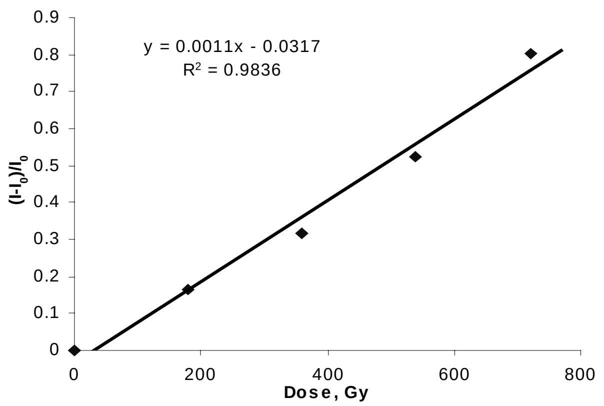

Figure 3. Dependence of normalized current $(I-I_0)/I_0$ with radiation dose under an applied voltage of 3V.

Figure 4 shows the plots of log (I) versus $V^{1/2}$ for as-printed and gamma irradiated NiO thick film samples. This relation is indicative of either Schottky emission or the Poole-Frenkel effect. Both phenomena are described by Eq. 1:

$$I_c \propto \exp\left[\frac{\beta E^{1/2}}{kT}\right] \tag{1}$$

where I_c is the circulating current, E is the electric field gradient ($E=V_b/d$, V_b being the applied voltage and d is the film thickness), k is Boltzmann's constant, T the absolute temperature in Kelvin and β is the field lowering coefficient given by Eq.2:

$$\beta = \left(\frac{e^3}{n\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \tag{2}$$

where e is the electronic charge, ε_0 is the permittivity of free space and ε_r is the relative permittivity of the dielectric. The difference between these two effects is expressed by $n = 1$ for the Poole-Frenkel effect and $n = 4$ for Schottky emission. In the Schottky emission process, the electrons are emitted from the metal electrode into the conduction band of the insulator over the potential barriers between the electrons at Fermi levels of the electrode and of the conduction band of the insulator [14]. Poole-Frenkel conduction occurs as a field emission of electrons from localized donors located at an energy level below the insulator conduction band.

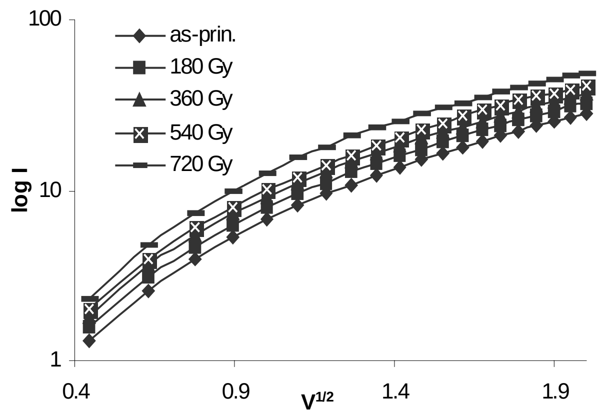

Figure 4. Plots of log (I) vs. $V^{1/2}$ for as-printed and irradiated NiO thick film samples.

To distinguish the predominant conduction mechanism, theoretical values of β coefficient had to be calculated and consequently, it was necessary to measure the capacitance. Related measurements were performed using an impedance analyser (HP 4277A LCZ-meter) at frequency of 1 kHz. Theoretical permittivity was calculated using the Eq.3:

$$\varepsilon_r = Cd/\varepsilon_0 A \tag{3}$$

where C is the measured capacitance and A is the effective area. For comparison, the measured and calculated permittivity values of as-printed and γ-irradiated samples are given in Table 1.

Table 1. Comparison of the measured and calculated permittivity values to reveal the conduction mechanism

Radiation dose, Gy	Capacitance C, x 10^{-11} F	Permittivity ε_r		
		Measured by LCZ-meter	Poole-Frenkel effect	Schottky emission
0	14.0	9.49	9.5	23.9
120	11.8	8.00	7.4	18.6
360	9.7	6.57	6.1	15.4
540	8.0	5.42	4.6	11.6
720	6.2	4.20	3.9	9.9

The experimental values of ε_r for the samples under investigation lay close to the calculated values for n = 1. One may therefore regard the high-field conduction mechanism as being predominantly of the Poole-Frenkel type. The decrease in the measured dielectric constant values with an increase in radiation dose is shown in Figure 5.

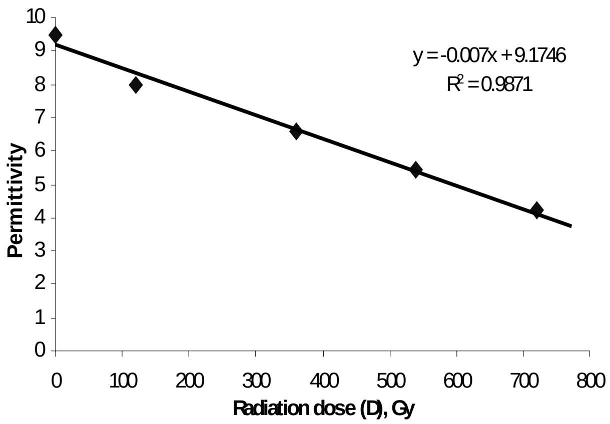

Figure 5. Linear decrease in measured permittivity values ε_r with the increase in radiation dose.

The values of ε_r for as-printed samples were found to be 9.5. In contrast, the dielectric constant for Nickel oxide has been found to decrease with the increase of frequency and to reach a constant value of 11.9 at a frequency of 10^5 Hz and at a temperature of 298 K [15]. This discrepancy may be attributed to the different film fabrication techniques used.

Figure 6 shows typical plot of the conductance vs. frequency dependence, recorded for as-deposited Ag – NiO – Ag samples using impedance analyser. Figure 7 shows dependence of the conductance on radiation dose at a frequency of 224 kHz for NiO thick film samples. At lower frequencies radiation-induced changes in value of conductance were less pronounced.

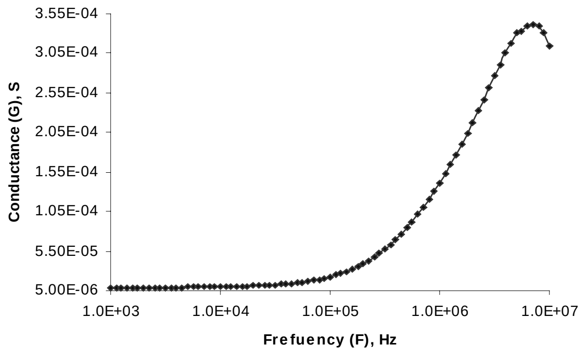

Figure 6. Typical plot of conduction vs. frequency dependence for NiO thick film samples.

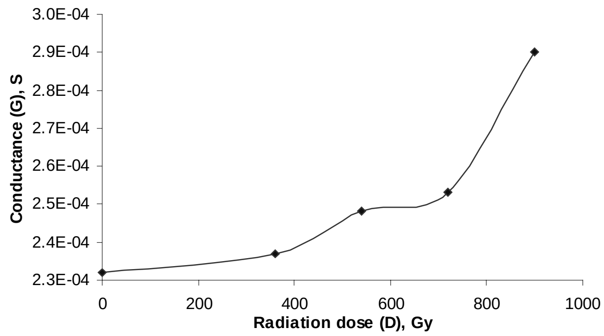

Figure 7. Dependence of conductance on radiation dose at a frequency of 224 kHz for NiO thick films.

3.2. La_2O_3 – Fe_2O_3 thick film structure

Figure 8 shows dependence of the conductance on radiation dose that was measured using HP 4277A LCZ-meter at frequencies of 2.8, 6.3 and 7.1 MHz for thick film samples made with La_2O_3-Fe_2O_3 polymer paste. The radiation-induced changes in values of conductance are more pronounced at higher frequencies, whereas at frequencies below 2 MHz the changes were not measurable.

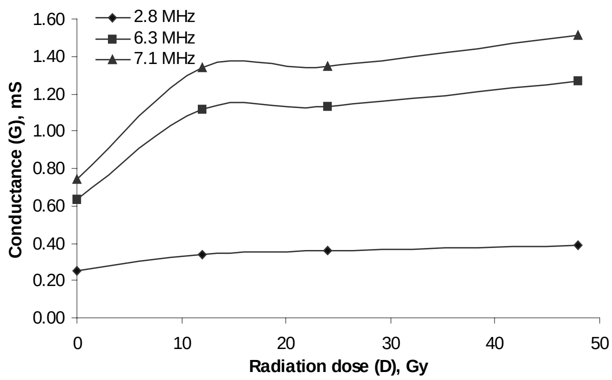

Figure 8: Dependence of the conductance G on radiation dose at a frequency of f = 6 MHz for La_2O_3-Fe_2O_3 thick film samples

Figure 9 shows dependence of the capacitance versus radiation dose at a frequency of 10 kHz for La_2O_3-Fe_2O_3 thick film samples.

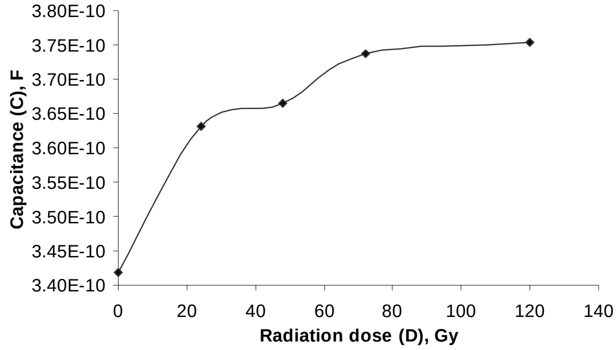

Figure 9. Dependence of capacitance vs. radiation dose at frequency of 10 kHz for La_2O_3-Fe_2O_3 thick film samples.

Both NiO and La_2O_3-Fe_2O_3 films exhibited a p-type semiconductor behaviour. The behaviour of the electrical properties for both types of the specimens under the influence of γ-radiation was found to be similar to the dose response of most materials used in thermoluminescence dosimetry [16]. They usually show a linear, then supralinear, followed by saturating response and further increase in dose leads to their damage.

All exposed samples were annealed in a Thelco Model 6 laboratory oven for 12 hours at 388 K to restore their initial electrical properties. A higher annealing temperature was not recommended as a diffusion of the material could occur. Irradiation of the samples and subsequent annealing was continuously repeated to ensure repeatability of the results.

Up to a certain level of radiation dose, the samples showed an increase in the values of current. The regions of linear response may be considered as a working region for dosimetry purposes as usually radiation sensors have linear dose-response characteristics in certain region of doses. However, the samples are susceptible to the environmental conditions, such as temperature, humidity, electromagnetic field, etc. This may result in under- or overestimation of the absorbed dose. To eliminate such effects, there is a need for corresponding signal conditioning.

4. Conclusion

NiO and La_2O_3-Fe_2O_3 thick film structures can be considered as effective materials for room temperature real time γ-radiation dosimetry due to the linear response in their electrical properties with radiation dose.

4. Acknowledgments

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5. References

[1] D. D. Ragan, P. Svedlindh, and C. G. Granqvist, "Electrochromic Ni oxide films studied by magnetic measurements", *Solar Energy Materials and Solar Cells*, 1998, vol. 54, pp. 247-254.

[2] A. Neubecker, T. Pompl, T. Doll, W. Hansch, and I. Eisele, "Ozone-enhanced molecular beam deposition of Nickel oxide (NiO) for sensor applications", *Thin solid films*, 1997, vol. 310, pp. 19-23.

[3] R. Lechner and L. K. Thomas, "All solid state electrochromic devices on glass and polymeric foils", *Solar Energy Materials and Solar Cells*, 1998, vol. 54, pp. 139-146.

[4] G.G. Gilmore, *Handbook of Inorganic Electrohromic Materials*, Amsterdam, Elsevier, 1995.

[5] X. Ge, Y. Liu, and X. Liu, "Preparation and gas-sensitive properties of $LaFe_{1-y}Co_yO_3$ semiconducting materials", *Sen. & Act. B: Chem.*, 2001, vol. 79, pp. 171-174.

[6] K. Li, F. Wu, D. Wang, T. Xie, and T. Li, "Electron behavior and photoelectric gas-sensitive characters of nanocrystalline $La_{1-x}Sr_xFeO_3$", *Materials Chemistry and Physics*, 2001, vol. 71, pp. 34-39.

[7] S. Zhao, J.K.O. Sin, B. Xu, M. Zhao, Z. Peng, and H. Cai, "A high performance ethanol sensor based on field-effect transistor using a $LaFeO_3$ nano-crystalline thin-film as a gate electrode", *Sen. & Act. B: Chemical*, 2000, vol. 64, pp. 83-87.

[8] K. Li, D. Wang, F. Wu, T. Xie, and T. Li, "Studies on photoelectric gas-sensitive characters of nanocrystalline $LaFeO_3$", *Materials Chemistry and Physics*, 1999, vol. 60, pp. 226-230.

[9] G. Martinelli, M.C. Carotta, M. Ferroni, Y. Sadaoka, and E. Traversa, "Screen-printed perovskite-type thick films as gas sensors for environmental monitoring", *Sensors and Actuators B: Chemical*, 1999, vol. 55, pp. 99-110.

[10] K. Arshak, C.A. Hogarth, and M. Ilyas, "A study of electron spin resonance and optical absorption edge in amorphous mixed films of SiO and In_2O_3", *Journal of material science letters*, 1984, vol. 3, pp. 1035-1038.

[11] K. Tominaga, T. Murayama, I. Mori, T. Okamoto, K. Hiruta, T. Moriga, and I. Nakabayashi, "Conductive transparent films deposited by simultaneous sputtering of zinc-oxide and indium-oxide targets", *Vacuum*, 2000, vol. 59, pp. 546-552.

[12] V. Múcka, J. Podlaha, and R. Silber, "NiO–ThO_2 mixed catalysts in hydrogen peroxide decomposition and influence of ionizing radiation", *Radiation Physics and Chemistry*, 2000, vol. 59, pp. 467-475.

[13] V. Múcka and E. Baburek, "Catalytic properties of nickel-yttrium mixed oxides and the influence of ionizing radiation", *Radiation Physics and Chemistry*, 1998, vol. 53, pp. 483-489.

[14] D. Basak and S. K. Sen, "Electrical, dielectric and optical properties of M/Y_2O_3/M devices", *Thin Solid Films*, 1995, vol. 254, pp. 181-186.

[15] V.V. Volkov, Z. L. Wang, and B. S. Zou, "Carrier recombination in clusters of NiO", *Chemical Physics Letters*, 2001, vol. 337, pp. 117-124.

[16] Y.S. Horowitz, "Theory of thermo-luminescence gamma dose response: The unified interaction model", *Nuclear Instruments and Methods in Physics Research Section B*, 2001, vol. 184, pp. 68-84.