Semiconductor Characteristics of Nd Doped PbO-Bi$_2$O$_3$-Ga$_2$O$_3$ Films

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In this work optical and semiconductor characteristics of gallium oxide based thin films are studied. This material has important electro-optic applications and offers possibilities for semiconductor applications in heavy metal oxide semiconductor technology. In this study thin films of PbO-Bi$_2$O$_3$-Ga$_2$O$_3$ were deposited by reactive sputtering. Two targets with different concentrations of Nd$_2$O$_3$ (0.2 and 1.0 wt%) were prepared. Thin films were deposited by pure Ar plasma, at 5 mTorr pressure and RF power of only 20 W. Films were deposited on three inch diameter substrates of (100) silicon wafers. Optical UV-Vis-Nir transmittance and FTIR analyses showed that the films are transparent in the visible and middle infrared region of the electromagnetic spectrum. The refractive index of the films was of about 2.3, as measured by ellipsometry; Rutherford Backscattering Spectroscopy (RBS) analyses were employed for the compositional analysis of the films. For the electrical characterization it was used metallic electrodes, and the final structure obtained is a capacitor structure where the gallium oxide film plays the role of a dielectric. In the current versus voltage (IxV) analyses, the samples with 1.0 wt% of Nd$_2$O$_3$ show semiconductor characteristics similar to the ones obtained for the degenerated transistors. The electric characteristics of these films allow applications with electro-optic devices (phototransistors and photo detectors).

Keywords: PbO-Bi$_2$O$_3$-Ga$_2$O$_3$ films; Optical and semiconductor characteristics; Nd^{3+} doped

I. INTRODUCTION

The study of rare-earth doped glass for lasers and optical amplifiers has become a subject of renewed interest now that high power cw diode lasers are available for use as efficient pump sources. With the development of powerful diode lasers emitting around 800nm studies of laser materials doped with Nd^{3+} were renewed. Most solid state Nd laser systems pumped by high power diode lasers are now standard tools for many applications due to their high efficiencies. This has motivated investigations of Nd^{3+} doped glass thin film waveguides that offer a possible means of incorporating sources and amplifiers into integrated optical circuits. In this work we report studies of sputtered Nd:glass films based on heavy metal oxides (HMO) [1]. The films are produced using PbO-Bi$_2$O$_3$-Ga$_2$O$_3$ glass doped with Nd$_2$O$_3$ for the target. It has been shown recently that heavy metal oxide (HMO) glasses are very attractive hosts for rare-earth ions with applications in photonic and optoelectronic [2,3,4]. PbO and Bi$_2$O$_3$ oxides determine the optical properties and GaO favors the thermo stability and the electrical properties. The motivations for the use of this composition for the thin films are due to the following properties: large thermal expansion coefficient (123x10^{-7}/K), high refractive index (-2.3) with applications in photonics, good physical and chemical stability and large transmission window (550 nm to 8000 nm). We have to remember that wide infrared transmission window normally indicates that the vibrational phonon energy is small and this provides opportunities towards the realization of more efficient lasers. The other motivation for the production and study with these films is based on the previous results obtained with PbO-Bi$_2$O$_3$-Ga$_2$O$_3$ glasses doped with Nd$_2$O$_3$ [5].

II. EXPERIMENTAL

Target manufacturing: The target was manufactured from four 99wt% pure oxides: 12wt%Ga$_2$O$_3$-46wt%PbO-42wt%Bi$_2$O$_3$-(0.2wt% and 1wt%)Nd$_2$O$_3$. The reagents were melted in a platinum crucible at 1000 ^{o}C during 1 hour. Then the melt was poured into a graphite mould and annealed at 300 ^{o}C for 3 hours.

Substrates: 75 mm diameter silicon wafer were used as substrates. The silicon wafers have a resistivity between 1 and 10 Ohm.cm, p type, (100) orientation.

Deposition: The sputtering processes were performed at room temperature, 5mTorr pressure, RF (13.56 MHz) power of (only) 20 W, with pure argon (99.995%). Before deposition the base pressure was as low as 9 x 10^{-7}Torr to minimize the number of impurities.

Analysis: the film thickness, were measured with a Height Step Meter Dektak 3030. The refractive index was determined with an ellipsometer with three wavelengths: 405 nm, 632.8 nm and 830 nm.The chemical composition was measured by RBS (Rutherford Backscattering Spectrometry) using a de He^{++} beam with 2.2 MeV of energy. Optical transmission was measured with a Cary 5200 UV-Vis-NIR spectrometer, in the 220 nm to 2550 nm wavelength range. Transmission in the infrared region was performed in a JASCO FT-IR system. Photoluminescence was determined using an Argon laser at 514 nm. For photonics measurements, contacts were deposited at the front side of the wafer, by aluminium evaporation in order to obtain 300 nm thick layer. At the backside of the wafer, a 500-nm thick aluminium film was evaporated. The dark and light current was measured by HP 4140A picoamperemeter.

III.   RESULTS AND DISCUSSION

The properties of the films were compared with those of the glass target [5] in terms of both physical and chemical composition. The deposition rate is of (1.1 ± 0.1) nm/min as can be observed by the results shown Table 1. The variations of the refractive index are within the experimental error. As the film absorbs light at 405 nm, it was not possible to measure its refractive index at that wavelength.

TABLE I: Thickness and refractive index

Deposition time (min)	Thickness (nm)	Refractive index @ 632.8 nm	Refractive index @ 830 nm
30	29	2.229	2.214
60	71	2.225	2.295
120	123	-	2.284
Target	3 mm	2.251	2.277

The RBS technique confirmed that the atomic composition of the deposited film corresponds to the one of the glass target employed (Figure 1). This may be attributed to the use of pure argon plasmas. The absorption spectrum of the Nd^{3+} is related to the electronic transitions from the ground state $^4I_{9/2}$, to various excited states. Figure 2 presents the absorption spectrum, at room temperature, for the glass doped with 1.0 wt% of Nd_2O_3 (2 mm thickness). In this spectrum we can observe the absorption bands with peaks at 874, 803, 747, 682, 630 and 583 nm related, respectively to the $^4F_{3/2}$, $^4F_{5/2}$ $^4F_{7/2}, F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2}$ and $^4G_{7/2}$ transitions of Nd^{3+}. The location, intensity and breadth of the absorption bands are determined by interaction of Nd^{3+} ion with local crystalline fields. Each absorption band usually consists of a multiplicity of states. Unlike the local crystal field experienced by Nd^{3+} ion in crystalline hosts, the crystal field at sites in glasses varies from site to site. This distribution of crystal fields results in the inhomogeneous broadening of the absorption spectra of rare earth ions in amorphous media. Owing to this inhomogeneous broadening some bands are assumed to be superimposed because they are not resolved. The absorption spectra confirm the incorporation of Nd^{3+} and also indicate that the absorption edge, in the visible region, starts at 550 nm.

Figure 3 presents the transmission in the infrared region of the glass target; we note a large transmission window up to 8 μm. The band around 3 μm is related to the presence of OH^- radicals [5].

In our previous studies [5] we observed, for the emission measurements of the glasses (2 mm thickness), that, at larger neodymium concentrations, quenching by ion-ion or ion-impurities interaction become important. The maximum emission was measured for the sample with 1.0 wt% of Nd_2O_3; a quenching for 2.0 wt% of Nd_2O_3 was observed (Figure 4). These results lead us to use 1.0 wt% Nd_2O_3 as the maximum doping level for the production of the glass target.

Figure 5 presents the emission in the infrared region for the PbO-Bi_2O_3-Ga_2O_3 thin film with 1.0 wt% of Nd_2O_3, with
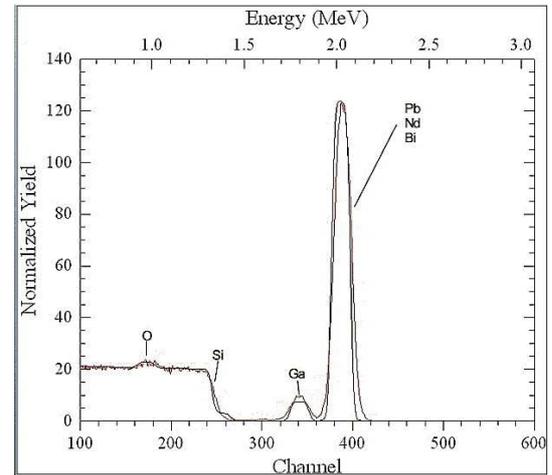
FIG. 1: RBS spectrum of the samples deposited during 2 hours.
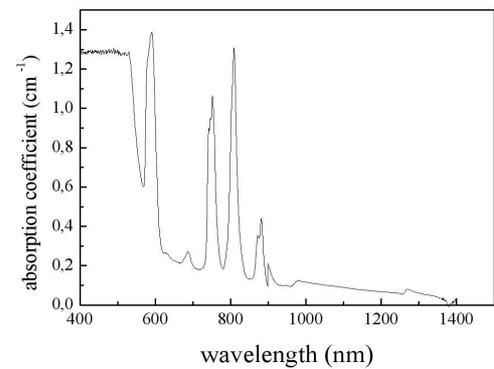
FIG. 2: Absorption spectrum of the PbO-Bi_2O_3-Ga_2O_3 glass doped with Nd_2O_3 (2 mm thickness).

peak at about 1100 nm, related to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+}. This is the most important transition of Nd^{3+} because it is normally the most intense one and with applications in the second telecommunication window. The emission from the films is broadened and shifted to longer wavelength, when compared to the emission of the glass target. This indicates that there is a difference between the neodymium environment in the glass film and in the glass target, as predicted in the literature for films sputtered from phosphate glasses doped with Nd_2O_3 [6]. We remark that the emission of the film with 0.2 wt% was not measure because of the low intensity of the signal.

Figure 6 shows the photoconductivity of the PbO-Bi_2O_3-Ga_2O_3 thin films with 0.2 and 1.0 wt% of Nd_2O_3.

It is observed that the film with higher content of Nd_2O_3 has the current increased when illuminated by white light [7]. This effect is a characteristic of semiconductor materials but the same does not occur for the low doping thin films with 0.2 wt% Nd_2O_3. In this case the main characteristic is its low resistivity. Both effects, semiconductor and low resistivity, can be explained by doping concentration in each side of the
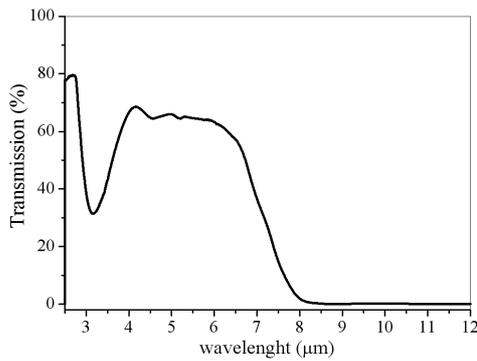
FIG. 3: Infrared transmission spectrum of the Nd_2O_3 doped PbO-Bi_2O_3-Ga_2O_3 glass target (1.0 wt% of Nd_2O_3).
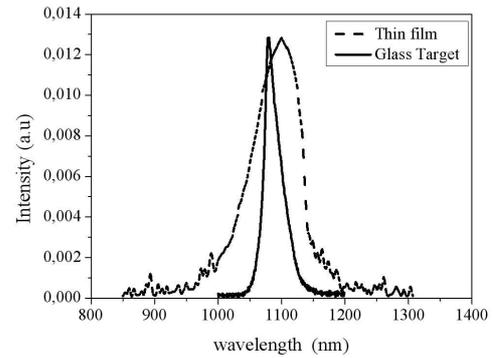
FIG. 5: Emission in the infrared region for the thin film and glass target of PbO-Bi_2O_3-Ga_2O_3 with 1.0 wt% of Nd_2O_3.
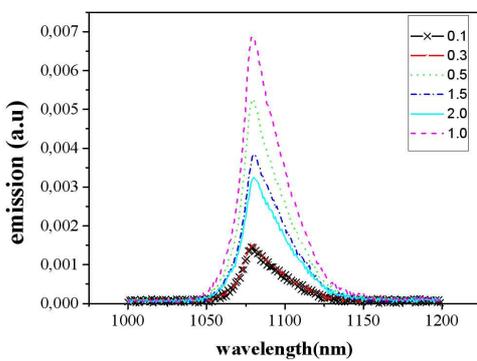
FIG. 4: Emission spectra of PbO-Bi_2O_3-Ga_2O_3 glasses doped with different concentrations of Nd_2O_3 (wt %).
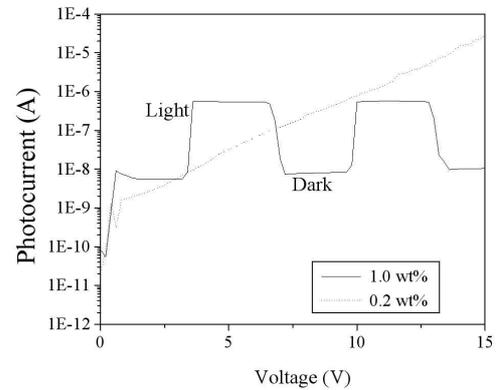
FIG. 6: Light and dark photocurrent of the PbO-Bi_2O_3-Ga_2O_3 with 0.2 and 1.0 wt% of Nd_2O_3 under illumination.

junction Si – GaO. If the junction has one highly doped side (Si) and one lightly doped side (0.2 wt% Nd_2O_3), the lightly doped side determines the properties of the junction and low energy is sufficient to transport the carrier from one side to the other. That is why no difference is observed when the film is illuminated or not. When the junction is formed by two highly doped sides Si and 1.0 wt% Nd_2O_3, higher energy is necessary to transport the carrier from one side to the other. In this situation, light is used in order to give energy to the carrier to pass the one side to the other. Then its movement is observed as high current.

IV. CONCLUSIONS

In this work we present optical and semiconductor characteristics of gallium oxide based thin films. The sputtering deposition technique was an efficient method to obtain amorphous thin films from glass targets. The atomic composition of the deposited film correspond to the one of the glass target used; this may be attributed to the use of pure argon plasmas during the deposition. The deposition rate of 1 nm/min re-

mained constant using 20 W RF power. The film with 1.0wt% of Nd_2O_3 presented emission around 1100 nm originated from Nd^{3+}ions, with applications in the second telecommunication window. The refractive index of the films was of about 2.3, as measured by ellipsometry; Rutherford Backscattering Spectroscopy (RBS) analyses were performed and confirmed that the atomic composition of the deposited film is very similar to the glass target. It is observed that the film with 1.0 wt% of Nd_2O_3 has characteristic of semiconductor materials when illuminated by white light. This effect was not observed for 0.2 wt% of Nd_2O_3. This is the first time that semiconductor characteristics are observed for PbO-Bi_2O_3-Ga_2O_3 thin films with 1.0 wt% of Nd_2O_3. The electric characteristics of these films indicate that they are potential candidates for applications with electro-optic devices (phototransistors and photo detectors).

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