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Study of Indium Nitride and Indium Oxynitride Band Gaps

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This work shows the study of the optical band gap of indium oxynitride (InNO) and indium nitride (InN) deposited by magnetron reactive sputtering. InNO shows multi-functionality in electrical and photonic applications, transparency in visible range, wide band gap, high resistivity and low leakage current. The deposition processes were performed in a magnetron sputtering system using a four-inches pure In (99.999%) target and nitrogen and oxygen as plasma gases. The pressure was kept constant at 1.33 Pa and the RF power (13.56 MHz) constant at 250 W. Three-inches diameter silicon wafer with 370 micrometer thickness and resistivity in the range of 10 ohm-centimeter was used as substrate. The thin films were analyzed by UV-Vis-NIR reflectance, photoluminescence (PL) and Hall Effect. The band gap was obtained from Tauc analysis of the reflectance spectra and photoluminescence. The band gap was evaluated for both films: for InNO the value was 2.48 eV and for InN, 1.52 eV. The relative quantities obtained from RBS spectra analysis in InNO sample are 48% O, 12% N, 40% In and in InN sample are 8% O, 65% N, 27% In.

Keywords: *indium oxynitride, sputtering, band gap, semiconductor*

1. Introduction

Indium nitride (InN) and alloys are materials with high potential for applications in optoelectronic devices due to their optical and electronic properties. InN has a calculated band gap around 1.9 eV, however, in literature, it appears frequently between 0.7 and 0.9 eV[1] for films deposited by MBE (molecular beam epitaxy). Thin films deposited by sputtering show a band gap around 1.4 eV. The narrow indium nitride (InN) band gap has generated great interest for applications such as high-efficiency solar cells, light-emitting diodes, laser diodes, and high-frequency transistors.

When oxygen is added in InN thin film deposition, indium oxynitride thin film (InNO) is formed. This ternary alloy belongs to a new class of materials with optical, mechanical and electrical properties potentially interesting for industrial applications.

Sungthong et al.[2] reported that numerous properties of InNO, such as the refractive index and the photoelectric effect intensity, vary according to the proportion of oxygen and nitrogen contained in the formed film.

InN has a narrow band gap and In_2O_3 has a wide optical gap (3.6 eV)[3]. It means that the band gap of indium oxynitride can potentially be engineered in a very wide range[4,5]. In fact, InNO has a band gap value between indium oxide and indium nitride band gaps.

In the present work, a study of the relationship between optical and electrical characteristics of InNO and InN grown using RF magnetron sputtering is reported. The main objectives of this work were to calculate the influence of temperature in carrier density of indium oxynitride and to estimate the A_0 constant for both semiconductors.

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2. Material and Methods

2.1. *Deposition process*

Initially, a cleaning process ($4H_2SO_4 + 1H_2O_2$), followed by HF dipping (2%), was performed. Table I shows the deposition parameters of InNO thin films. The deposition processes were performed in a magnetron sputtering system, using a four-inches diameter pure In target (99.999 %), nitrogen (99.995 %) and oxygen (99.998 %) as plasma precursors. The pressure was kept constant in 1.33 Pa and the RF power (13.56 MHz) was constant at 250 W. The substrate was silicon (75 mm, p type, 1-10 W.cm). Two different oxygen gas concentrations were used in deposition processes (Table 1).

2.2. *Band Gap*

Tauc analysis was used (a method based in UV-Vis Reflectance spectra) to obtain the optical band gap of InN and InNO. Room temperature Reflectance measurements were performed with a near-infrared-visible-UV spectrometer (scanning spectral range between 250 nm and 2500 nm). The A_0 constant was calculated using the band gap values obtained by the Tauc's analysis.

For the photoluminescence (PL) analysis, an experimental arrangement (set-up) with helium–cadmium (He–Cd) laser, with 325 nm wavelength as an excitation source was used. A mirror directed the laser beam to the sample. The analysis temperature was between 14 K and 250 K. The photoluminescence signal was collected by lens and redirected to spectrometer input. A photo multiplier cell detected the photoluminescence intensity. A software was responsible for data treatment. It was shown

in microcomputer monitor the PL amplitude in function of wave-length[6].

2.3. *Hall effect measurements*

This technique enables to obtain the values of charge density, resistivity, sheet resistance, mobility and carrier type (n-type or p-type). The measurements in this study were made at the Instituto de Física da Universidade de São Paulo with a equipment from MMR technologies (Hall Van de Pauw Controller H50).

2.4. *RBS measurements*

Rutherford Backscattering Spectrometry (RBS) was used to estimate the stoichiometry of the films. The percenteage of each element, oxygen, nitrogen and indium was determined by the SIMNRA program.

3. Results and Discussion

The spectrum in Figure 1 was obtained by UV/Visible analysis to calculate the Band Gap with Tauc method.

The InN and InNO band gaps were estimated for each sample from their reflectance spectra.

$$(\alpha E)^{1/2} = \{ELn[(R_{max}-R_{min})/(R-R_{min})]\}^{1/2} \quad (1)$$

Using Tauc method (Equation 1), the Reflectance axis was converted. A tangent straight line was plotted in the generated curve, and in the point where this line crosses the graph energy axis the gap value is obtained[7].

The band gap was calculated for both deposited films: for InNO the estimated value was 2.48 eV and for InN, 1.52 eV. This analysis was performed at room temperature (300 K).

Using the band gap value obtained by Tauc's analysis, we could calculate the A_0 constant for InNO and InN by the following formula:

$$n_i^2 = A_0 T^3 e^{-Eg/kT} \quad (2)$$

The carrier density n_i was obtained from Hall Effect analysis. The result for InN, 7.70×10^{20} cm^{-3}, was higher than for oxynitride indium, 3.89×10^{14} cm^{-3}. Therefore, the A_0 for InN was 6.98×10^{56} and for InNO was 2.69×10^{63}, with $k = 8.62 \times 10^{-5}$ eV/K $= 1.38 \times 10^{-23}$ Joules/K.

Rutherford Backscattering Spectrometry (RBS) was used to estimate the stoichiometry of the InNO film. The percentage of each element, oxygen, nitrogen and indium was determined by the SIMNRA program. The relative quantities obtained from RBS spectra analysis in InNO sample are 48% O, 12% N and 40% In[8]; in InN sample are 8% O, 65% N and 27% In due to contamination by oxygen in deposition process. The increase in the oxygen added to the plasma promoted the change in the characteristics of these thin films. The band gap values increased when the oxygen percentage increased.

The photoluminescence spectra showed emission band for InNO sample deposited with 50% oxygen (Figure 2). This analysis was performed at six different temperatures.

The PL spectra at 14 K, 50 K, 100 K, 150 K, 200K and 250 K temperatures for InNO film grown on Si substrates are shown in Figure 2.

It is possible to observe that all samples showed an emission peak around 2.5 eV. The peak intensity decreased in function of temperature as shown in Table 2.

Table 1. Deposition parameters.

Target	99.999% Indium, 4 in. diameter
Substrate	Silicon p-type
Substrate distance	6 cm
Base pressure	1.33 Pa
RF Power	250 W
O_2 gas concentrations	0% and 50%.

Table 2. Photoluminescence results.

Temperature (K)	Intensity (A.U.)	Peak (nm)	Band gap (eV)
14	36322	489.70	2.53
50	32531	492.20	2.52
100	18883	497.00	2.49
150	19641	500.00	2.48
200	20855	502.00	2.47
250	10619	503.00	2.46

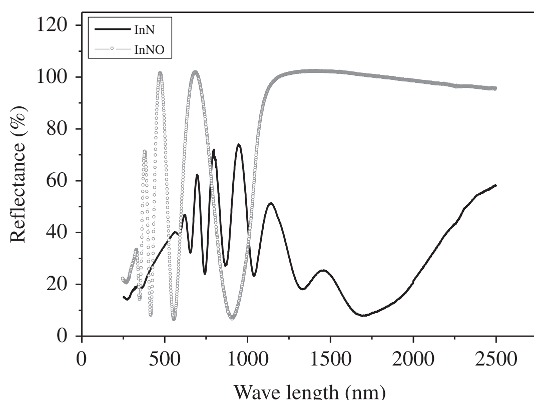

Figure 1. Reflectance spectra for indium nitride and indium oxynitride thin films.

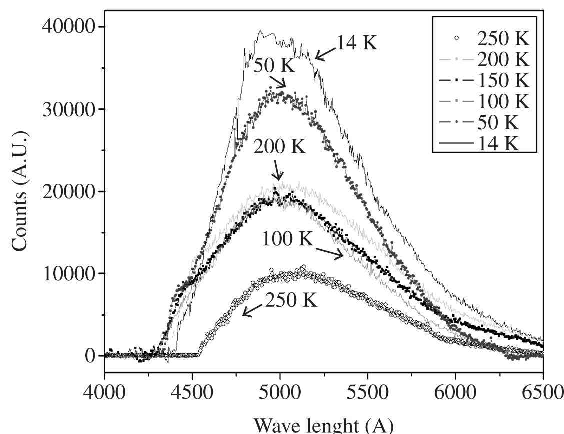

Figure 2. Photoluminescence spectra of InNO film.

Table 3. Temperature dependence of carrier density.

Temperature (K)	Density (cm^{-3})
14	0
50	0
100	0
150	2.91×10^{-8}
200	1.91×10^{3}
250	6.34×10^{9}

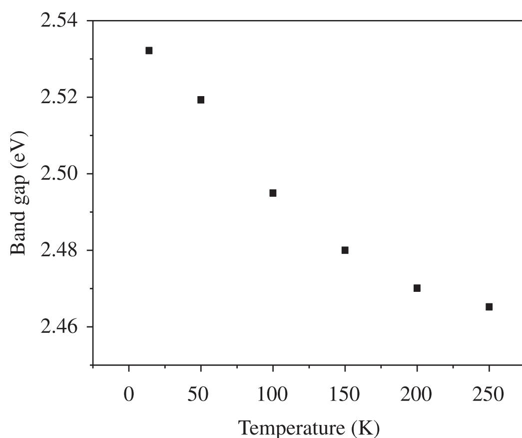

Figure 3. Temperature dependence of the intrinsic band gap of InNO.

One of the basic characteristics of the band gap is its temperature dependence behavior[9] as plotted in Figure 3.

The temperature dependence of the PL peak energy can be also seen in the figure. The PL peak energy decreases from 250 K to 14 K. The band gap shifts to lower energy by ~60 meV as temperature increases from 14 K to 250 K.

Using Equation 2 and obtained A_0 for InNO, it was calculated the carrier density of indium oxynitride for each temperature (Table 3).

4. Conclusions

The band gap of InN and InNO samples, grown by RF sputtering on silicon, has been measured using UV-Vis Reflectance and PL analysis.

The calculated A_0 constant was 6.98×10^{56} for InN and 2.69×10^{63} for InNO.

One of the basic characteristics of the band gap is its temperature dependence behavior. The band gap shifts to lower energy by ~60 meV as temperature increases from 14 K to 250 K. In fact, the oxygen was incorporated in InNO matrix and changed its electrical and optical characteristics.

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