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Optical and electrical properties of sputtered InNO thin films

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In this work we study the deposition of indium oxynitride prepared by reactive RF magnetron sputtering. This material shows multi-functionality in electrical and photonic applications. It shows transparence in visible range, wide band gap, high resistivity, low linkage current and response for light. The deposition processes were performed in a home build magnetron sputtering system, using a four-inch pure In (99.999%) target, nitrogen and oxygen as process gases. The pressure was kept constant in 1.33 Pa and the RF power (13.56 MHz) was constant 250 W. The optical band gap was estimated for samples deposited with 0%, 10%, 20%, 50%, 80% and 85% of oxygen concentration in the gas mixture and the band gap values obtained were 1.32 eV, 2.47 eV, 2.65 eV, 2.50 eV, 3.04 eV and 3.00 eV, respectively. The IxV analysis shows a low leakage current (~10^{-8} A). The increase in the oxygen concentration in the plasma promotes change in the character of these thin films from conductor to semiconductor material.

1 Introduction

Transparent oxides are the master piece in the photovoltaic devices and displays fabrication. Many studies of this conductive oxides are focused in the material synthesis and fabrication. Among these materials there is indium oxide, an n-type semiconductor with a wide band gap (~3.6 eV) and it has been widely employed in the microelectronics area. Due to the wide range of applications, many researches are under development for various devices [3].

On the other hand, for nitride semiconductors, there is the indium nitride (InN) that has been the subject of intensive research in the past few years due to its potential applications in optoelectronic area. The narrow indium nitride band gap has generated great interest in InN for applications such as high-efficiency solar cells, light-emitting diodes, laser diodes, and high-frequency transistors [1,2].

Recently, it was obtained a new oxide type that combines oxygen, nitrogen and indium: the indium oxynitride [3]. The indium oxynitride is a new class of materials with optical, mechanical and electrical properties potentially interesting for industrial applications [4]. Some properties of the InNO, e.g., index of refraction and intensity of the photoelectric effect, vary according to the proportion of oxygen and nitrogen contained in the deposited film [5]. Because InN has a small bandgap 0.7 eV and In_2O_3 has a large optical gap 3.6 eV, the band gap of indium oxynitride can potentially be engineered in a very wide range [3,4].

It is visible that there is influence of oxygen incorporation in the film: the pure InN has a dark brown coloration, it is not transparent, with low resistivity (this material is almost a conductor), high carrier density around 10^{21} cm^{-3} and with photoelectric effect lower than the seen for indium oxynitride. The InNO is transparent, it has a wider band gap (around 3.4 eV) and nearest indium oxide, which makes it an excellent candidate to be employed in sensors in the ultraviolet region.

In the present work, a study of the relationship between optical and electrical characteristics of InNO grown using RF magnetron sputtering is reported.

2 Experimental

Initially, a cleaning process, denominated “Piranha” clean ($4H_2SO_4$ + $1H_2O_2$) followed by HF dipping (2%), was performed. In Table 1 is shown the deposition parameters of InNO thin films. The deposition processes were performed in a home build magnetron sputtering system, using a four-inch 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 250 W. The substrate was silicon (75 mm, p-type, 1-10 W.cm). Six different oxygen gas concentrations were used in deposition processes (Table 1). The thickness, RMS roughness and deposition rate of the InN thin films were obtained by Profilometer (Sloan DEKTAK 3030).

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%, 10%, 20%, 50%, 80%, 85%.
Deposition time	1 hour

To obtain the band gap Tauc analysis was used, a method based in UV-Vis Reflectance spectra. Room temperature Reflectance measurements were performed with a near-infrared-visible-UV spectrometer (scanning spectral range between 250 nm and 2500 nm). Emission from a halogen light source was used to provide the spectral range for the measurements in glass samples. The reflected light from the UV to near infrared spectral region was collected using different detectors.

The XRD patterns of the InN and InNO films deposited at room temperature for various hydrogen gas concentrations were measured. The electrical properties of the films (resistivity, mobility, carrier concentration and type) were determined by Hall-effect measurements using silver contacts by Van der Pauw technique.

The photocurrent was obtained by I x V curves using a HP 4140A picoamperemeter. Aluminum circle contacts were deposited at the front side of the wafer by evaporation in order to obtain 300 nm thick layer. At the backside of the wafer, a 500 nm thick aluminum film was evaporated.

Rutherford Backscattering Spectrometry (RBS) was used to estimate the estequiometry of the films. The percenteage of each element, oxygen, nitrogen and indium was determined by the SIMNRA [6] program.

3 Results

The O, N and In relative quantities obtained from RBS spectra analysis are summarized in Table 2.

Table 2 RBS analysis results.

Sample	O (%)	N (%)	In (%)
10% O_2	44	16	40
20% O_2	40	22	38
50% O_2	48	12	40
80% O_2	50	12	38
85% O_2	52	10	38

Figure 1 shows the XRD diffractograms for films produced at various oxygen concentration. It should be noted that the intensity scale is different for each XRD diffractogram.

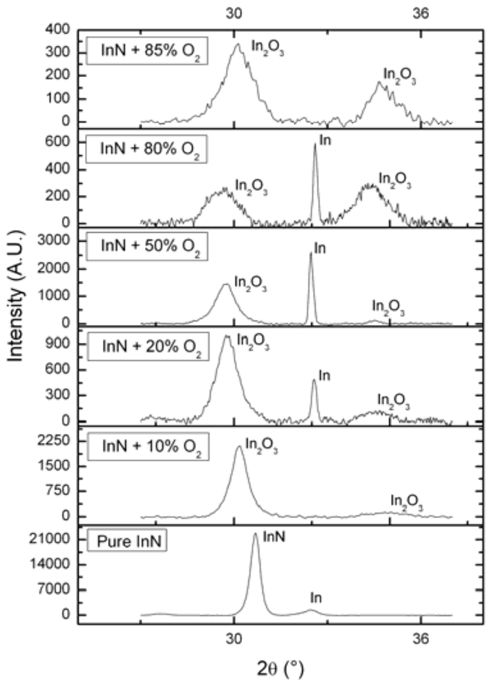

Figure 1 XRD diffractograms of the films produced with different oxygen concentrations.

Table 2 and Fig. 1 shows oxygen dependence in InNO deposited with different oxygen concentration, because the N concentration is too low to form InN or InNO crystals of enough size to be detected in the x-ray diffractometer. In these conditions, the oxygen reactivity is higher than the nitrogen with indium. It is possible to note that the oxygen incorporation changes completely the film cristallinity, because the InN peak at 31° (002) disappeared and a new one oxygen based at 29.5° appeared (222). The samples that were deposited with a high oxygen concentration (range 80% and 85%) also showed another peak at ~ 35° position on the cubic structure (400) of indium oxide [5]. Besides these characteristics, it is also possible to observe the presence of unreacted metallic In (position 33°) in the InN and InNO thin films.

The InN and InNO band gap was estimated for each sample from their reflectance spectra. Figure 2 shows a typical curve used to obtain the band gap, see also Table 3.

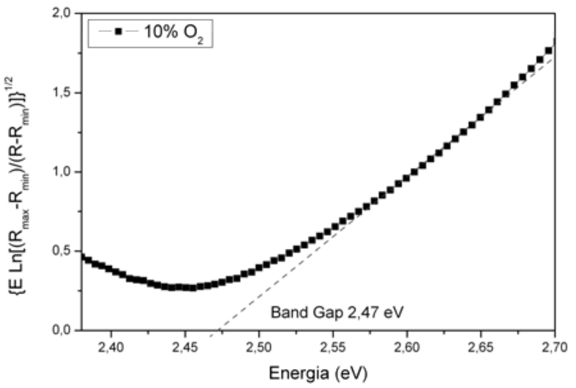

Figure 2 Application of Tauc's method to obtain the optical band-gap of the sample produced with 10% of oxygen in the gas mixture.

Table 3 Thickness and estimated band gap values.

Sample	Thickness (nm)	Band Gap (eV)
InN Reference	825.2	1.32
O_2 20%	222.5	2.65
O_2 10%	220.0	2.47
O_2 50%	226.9	2.50
O_2 80%	93.7	3.04
O_2 85%	117.0	3.00

The oxygen concentration in the deposited films affects directly the optical band gap energy of the films: it can be observed through these results that increasing the concentration of oxygen cause an increase in the value of the band gap. This is consistent with the work of Limpijumnong et al. [7] that reported 2.4 eV band gap value for film with 20% of oxygen concentration.

The results obtained from the Hall effect measurements (Table 4) show that, in general, the resitivity of the InNO films deposited on Si is very high (using InN as reference). It can be associated with the IxV analysis that shows a low leakage current (Table 5). Goldys et al. [5] reported values within the range 1.6 to 4 mW.cm for InN [3] and Sungthong et al. observed 100 W.cm for InNO with 30% oxygen [5].

The carrier density, Fig. 3, decreases exponentially as a function of mobility and carrier density, which means that oxygen, when incorporated, decreases the amount of donors.

Table 4 Electrical measurements results of the films.

Sample	Resistivity (Ω cm)	Mobility (cm²/Vs)	Density (cm^{-3})	Sheet Resistance (Ω/sq)	Type
InN	$8.8x10^{-3}$	1.1	$7.7x10^{20}$	$1.1x10^{2}$	N
O_2 20%	0.2	$1.7x10^{4}$	$1.9x10^{15}$	$9.0x10^{3}$	N
O_2 10%	$1.2x10^{2}$	$1.5 x10^{3}$	$3.6x10^{13}$	$5.4x10^{6}$	N
O_2 50%	0.8	$2.0x10^{4}$	$3.9x10^{14}$	$3.5x10^{4}$	N
O_2 80%	$1.0x10^{-2}$	$1.0x10^{4}$	$5.9x10^{16}$	$1.1x10^{3}$	N
O_2 85%	0.6	$1.5x10^{4}$	$6.5x10^{14}$	$5.5x10^{4}$	N

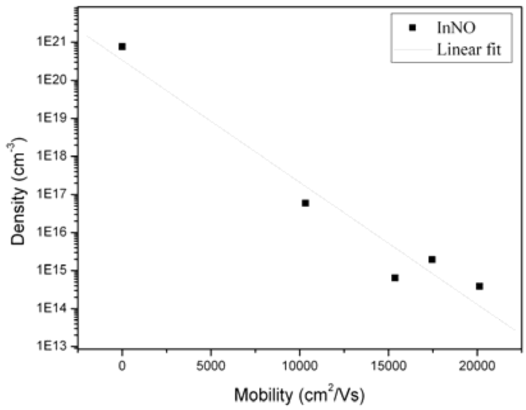

Figure 3 Carrier density in function of carrier mobility.

In Hall effect analisys, it can be observed that the oxygen incorporation modify the semiconductor electric properties. The presence of oxygen reduces the structural defects because the oxygen fill existing vacancies and bind to In atoms that form the metallic contamination responsible for the material low resistivity. There is a higher probability to form bonds with oxygen, because the enthalpy energy of binding In-O (320.1 kJ mol^{-1}) is greater than the binding In-N (282.2 kJ mol^{-1}), being stable. The confirmation of the presence of a large percentage of oxygen in the samples can be verified through analysis by RBS technique (Table 2).

The intensity of the photoelectric effect was verified from the difference of the light and dark current values, Fig. 4.

The InNO carrier mobility is high if compared with InN that interferes in the photoelectric effect response: the difference between light and dark current for these materials is more evident.

The deposition condition that showed the best results in function of electric analysis (IxV) and photoelectric effect was the InNO film deposited with 20% of oxygen.

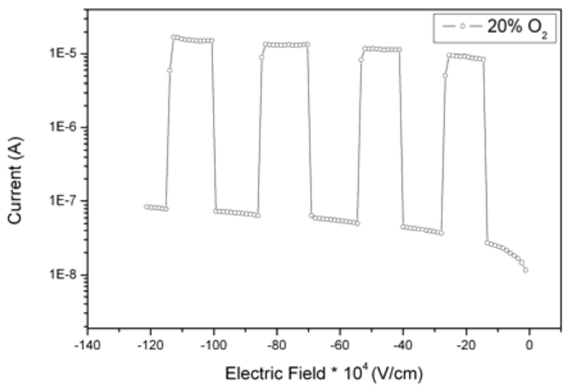

Figure 4 Light effect on IxV measurement of the film produced with 20% of oxygen in the gas mixture.

When these values are compared with the InN films photoelectric effect results (Table 5), it becomes evident that InNO shows a better response for the light influence.

Table 5 Current values obtained from the IxV measurements of the films.

Sample	Light current (A)	Dark current (A)	Increase (times)	Position (V/cm)
0% O_2	$4.28x10^{-5}$	$2.68x10^{-5}$	1.60	$-5.5x10^5$
10% O_2	$2.40\ x10^{-5}$	$1.47\ x10^{-7}$	163.27	$-5.5x10^5$
20% O_2	$1.19x10^{-5}$	$5.01x10^{-8}$	237.53	$-5.5x10^5$
50% O_2	$7.72x10^{-6}$	$7.17\ x10^{-8}$	107.67	$-5.5x10^5$
80% O_2	$3.07x10^{-6}$	$3.29\ x10^{-8}$	93.31	$-5.5x10^5$
85% O_2	$1.95x10^{-6}$	$4.69\ x10^{-8}$	41.58	$-5.5x10^5$

In this study, there are evidences that the oxygen incorporation in the film reduces the conductivity, which means that there was a decrease of material defects. The InN has a percentage of metallic indium, which increases the concentration of free electrons in the structure, making it a low resistivity semiconductor. When the oxygen is added, it establishes bonds with this metallic indium, decreasing the carrier concentration and leakage current (dark current), which promotes the increase of the photoelectric effect.

4 Conclusions

This material shows multi-functionality in electrical and photonic applications. The influence of oxygen is very important; the increase in the oxygen added in the plasma, promotes the change in the character of these thin films from conductor to semiconductor material. The change of film composition by varying the oxygen concentration causes significant change in the crystalline structure, optical bandgap and sheet resistance. Oxygen causes mobility increase, and also as a dopant decreasing the electron concentration. The potential application of this material is in photonic devices as active material in photo-sensors. Other applications were the nocturne vision visors and dielectric in electronic devices, transparent electrodes in solar cells.

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