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Structural, optical and electrical properties of indium nitride polycrystalline films

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ABSTRACT

The structural, optical and electrical properties of InN polycrystalline films on glass substrate are investigated by means of X-ray photoelectron spectroscopy, Raman scattering measurements, X-ray diffraction analysis, optical spectroscopy, and electrical measurements as a function of the inverse of temperature. The absorption edge for the films is most likely due to an impurity band formed by the presence of defects in the material. Such an impurity band, located at 1.6 eV extends itself to about 1.8 eV above the Fermi level, and it is attributed to nitrogen vacancies present in the material. The Raman scattering data also reveal the incorporation of oxygen in the InN films, leading to the formation of the In_2O_3 amorphous phase during the process of sputtering. Additionally, the X-ray photoelectron spectroscopy of the valence band, which is highly desirable to the determination of the Fermi level, confirms the optical gap energy. Furthermore, the X-ray diffraction patterns of the thinner films present broader peaks, indicating high values for the strain between the film lattice and the glass substrate. Finally, first principles calculations are used to investigate the optical properties of InN and also to support the experimental findings.

1. Introduction

Indium nitride (InN) is a promising material for optoelectronic devices, such as low cost solar cells with high efficiency and various types of sensors. Recent progress in InN growth techniques, such as molecular beam epitaxy (MBE), metalorganic chemical vapor deposition and metalorganic vapor phase epitaxy, has resulted in good structural quality layers [1–3] and extremely pure samples. The difference between the band gap values of 1.8 eV, in this work, and 0.7 eV attributed to pure material, is by hypothesis due to the presence of the impurity band, at 1.6 eV above Fermi level, filled up to 1.8 eV. This band is caused by nitrogen vacancies present in the material, thus allowing indium to provide electrons for the crystal. This impurity band explains the samples conductivity as well as the appearance of an absorption band at 0.6 eV [4]. In pure samples, grown by the MBE technique, the band gap is strongly dependent on the carrier concentration, where the band gap varies from 0.7 to 2.2 eV (with carrier concentrations from 10^{17-18} to 10^{20} cm^{-3}, respectively) [5–7].

In the present work, a systematic study of InN polycrystalline films deposited on glass substrates, with thicknesses varying from 95 nm to 520 nm, is presented. Raman scattering, transmission, reflection and absorption spectroscopy, X-ray diffraction measurements, and X-ray photoelectron spectroscopy were used to support the explanation of the aforementioned properties. Theoretical calculations within the framework of density functional theory using the local density approximation plus the onsite Coulomb interaction and employing the full potential plane augmented wave method are used to model the electronic structure and the optical properties of InN. The comparison between theoretical results and experimental data for the electronic structure, the dielectric function, and the absorption is in good agreement.

2. Samples preparation and experimental measurements

Indium nitride films were deposited by reactive d.c. magnetron sputtering in an atmosphere of argon and nitrogen, using an indium target. The sputtering chamber was evacuated to a pressure of 3×10^{-5} Pa before introducing argon and nitrogen (purity 99.998%) [8]. The deposition took place under oblique angle conditions with 50° between the normal to the substrate's surface and the mean direction of the sputtered flux, and at a target-to-substrate distance of 13 cm [9]. The target total accumulated sputtering time, in this study, never exceeded 20 h. The indium nitride films were deposited on soda lime glass (standard microscope slides). The film thickness was determined by profilometry (Tencor Alpha Step). The conditions are summarized in Table 1.

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The optical transmission and reflection measurements were performed at room temperature using a Czerny-Turner visible/near-infrared Spectrometer. Unpolarized light micro-Raman measurements were made (at room temperature) in the backscattering configuration, using ~1.5×10^4 W/cm^2 of the 514.5 nm line of an Ar laser as the exciting source. Scattered light was analyzed with a triple Jobin-Yvon T-4000 XY spectrometer equipped with a multi-channel charge-coupled device. For X-ray measurements, an X-Pert MRD Philips system, with either a curved pyrolytic graphite as the diffracted beam monochromator for Cu Kα_1 radiation ($\lambda=1.54056$ Å), for focusing the beam, or a parallel plate collimator, with a flat pyrolytic graphite monochromator for the parallel beam, was used. Two geometries were used in the measurements: Bragg-Brentano (θ–2θ scan) and grazing incidence (incident fixed angle $\omega=5°$). From these measurements, a determination of the lattice spacing, crystalline size, and film quality was obtained. X-ray photoelectron spectroscopy analysis was performed on a VG MKII ESCALAB device using non-monochromatic Kα Mg (1253.6 eV) radiation. The elastic line at C 1 s, of 284.8 eV, was used as a reference. The SPECTRA software was used for data acquisition and processing.

3. Results and discussions

The structural properties of the InN polycrystalline films were studied by X-ray diffraction measurements. The polycrystalline structure of these films can be clearly observed in the grazing X-ray patterns. The exhibited patterns appear indexed by using the hexagonal crystal system, as shown in Fig. 1. One can observe that just a few peaks could be detected for thinner films while the lattice contributions of the hexagonal lattice could be better observed for thicknesses above 310 nm. The strongest peak, representing the (101) reflection in the range of these measurements, is analyzed in detail in order to illustrate the thickness effect (inset in Fig. 1). Thinner films, in agreement with observed Raman data, present broader peaks, indicating higher strain between the films and the glass substrate. Despite the contamination by oxygen in the formation of In_2O_3, no peak corresponding to the presence of this element is observed in the X-ray patterns.

From the X-ray measurements, it was also possible to obtain the crystallite sizes as a function of the film thickness, as shown in Fig. 2. The patterns were analyzed by means of the widely used Warren's method [10]. It was used for instrumental calibration purposes, the peak corresponding to the (104) reflection of the standard Al2O3 powder which appears just in the standard pattern, at 2θ–35.1°. It clearly shows the crystallite size increase for thicker films, however, a saturation crystallite size value of approximately 23 nm is likely to be reached by 500 nm film thickness, confirming the formation of the hexagonal crystalline structure, as mentioned above. In Fig. 2 it should be noticed the obtained crystallite size values are of the order of the literature ones [11,12].

The Raman spectra for different film thickness in the 95–520 nm range, (Fig. 3), present additional structures around 300 and 380 cm^{-1}, besides the phonon structures A_1 (transversal optical — TO), E_2 (high), A_1(longitudinal optical — LO) and B_2(low) related to InN. By comparing these additional structures with the Raman spectrum of In_2O_3, as in the inset of Fig. 3 [13–15], where the two lines appear very close to additional structures (300 and 380 cm^{-1}). This suggests incorporation of oxygen into the InN structure during the sputtering process, although the occurrence of this possible contamination by oxygen and the formation of In_2O_3. These lines have not been clearly detected in the X-ray patterns since, the contamination is very low. Thus, we can attribute to the In_2O_3 phase to these new structures.

Table 1
The deposition conditions used during d.c. magnetron sputtering of indium nitride films.

Deposition conditions	
Base pressure	3×10^{-5} Pa
d.c. Power	100 W
Target	99.999% In
Gas pressure	8.8 Pa
Gas flux	12 ml/min
Nitrogen/Argon	83%/17%
Deposition rate	0.26 μm/h

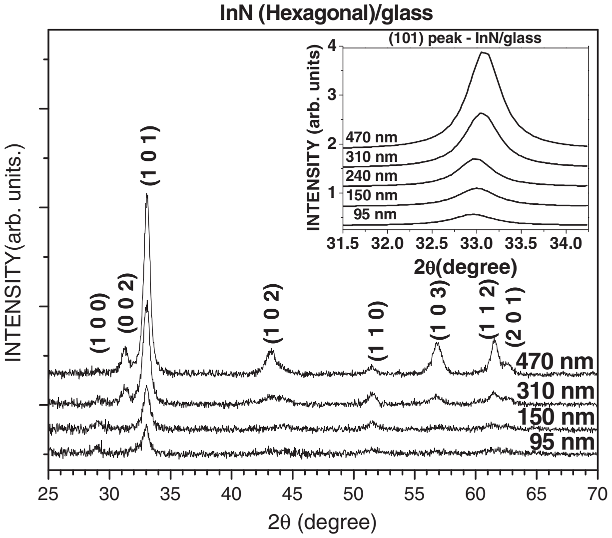

Fig. 1. X-ray diffraction grazing incidence patterns of the InN films with different thicknesses grown on glass substrate. Inset shows the detail of the (101) peak of the InN films with different thicknesses used in the crystallite size determination.

Fig. 4 also shows the thickness film effect evidenced on the plot of the normalized intensity of the E_1 (LO) versus the thickness of the films - thinner films present broader lines indicating a poor interface condition between film and glass.

In order to determine the resistivities of the InN samples an AC bridge was used to measure the resistance of the devices in a He-4 cryostat, in which sample temperature was controlled to within 0.5% between 1.7 and 300 K. As seen in Fig. 5, the samples resistivities show a typical behavior of a semiconductor: that is, an increase of the resistivity with decreasing temperature, due to the decrease of carriers in the conduction band, leading to electrical conduction. This behavior is observed in all the range of temperature variation. Similarly, the values of the resistivities, ranging from 0.1 to 100 Ω-cm, in the region of lower temperature, confirm the semiconducting character of the samples.

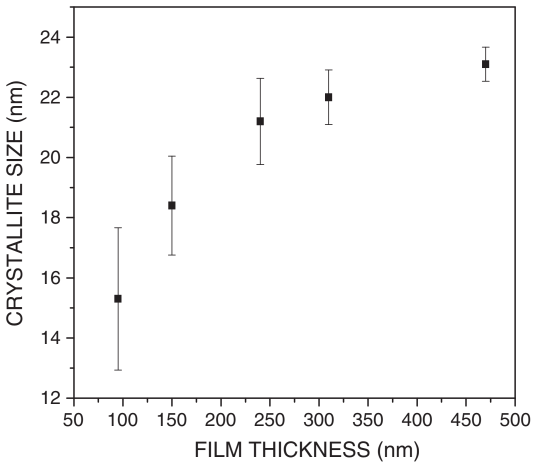

Fig. 2. Crystallite size of the InN films obtained from the peaks of the X-ray patterns.