CHARACTERIZATION OF INDIUM NITRIDE AND ZINC OXIDE THIN FILMS BY AFM AND RBS

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Indium nitride (InN) and zinc oxide (ZnO) thin films have become very attractive nanostructures because of their potential applications in optoelectronic devices. These structures were deposited on Si substrates by RF reactive magnetron sputtering method. In order to characterize the obtained films, Atomic Force Microscopy (AFM) and Rutherford Backscattering Spectrometry (RBS) were used. AFM gave information regarding the surface topography while RBS was employed to determine stoichiometry and thickness of the thin films. The AFM measurements indicated a mean roughness of about 12 nm for InN films and 27 nm for ZnO films. The RBS measurements revealed the In_xN_{1-x} and Zn_xO_{1-x} stoichiometry of the films. It was also found that the stoichiometry of the InN films was affected by the substrate temperature.

Key words: Indium nitride, zinc oxide, RF-magnetron sputtering, Rutherford Backscattering Spectrometry, Atomic Force Microscopy.

1. INTRODUCTION

Indium nitride (InN) and zinc oxide (ZnO) semiconductors have become very attractive because of their wide-ranging applications potential [1]. InN thin films show interesting properties: band gap in the 0.7 - 1.9 eV region [2, 3], high electron mobility, the possibility of modifying the band gap by impurities using ternary compounds like InGaN and InAlN [4]. InN could be used for THz emission devices [5, 6, 7]. ZnO is a compound semiconductor having wide band gap energy of 3.37 eV [8], large exciton binding energy, high-efficiency UV emission at room temperature [9] and it is an important material for next-generation short-wavelength optoelectronic devices, sensors, transducers and biomedical applications [10].

One of the challenges regarding these structures is the measurement of their properties. Nowadays there are a lot of advanced techniques which are able to reveal their properties, but most of them are destructive and in order to obtain quantitative results a standard is required, so the need for nondestructive methods is a demand from the materials manufacturers.

Rutherford Backscattering Spectrometry (RBS) [11, 12] and *Atomic Force Microscopy* (AFM) [13] are two ideal techniques for the analysis of thin films [14].

AFM microscopy was employed to reveal the surface topography of the thin layers and to measure their roughness. The RBS method was used to determine stoichiometry and thickness of deposited InN and ZnO thin films.

This paper reports on the characterization of InN and ZnO using AFM and RBS methods. The information gained using these methods helps materials manufacturers to understand, optimize and improve the growth condition of the thin films.

2. EXPERIMENTAL

2.1. SAMPLE DESCRIPTION

InN and ZnO thin films were deposited onto Si substrates by magnetron sputtering at the National Institute for Optoelectronics – INOE 2000. The experimental device used was an AJA ATC ORION 5 UHV unit; a detailed procedure of the deposition method is described elsewhere [15]. Substrate temperature was kept constant at a value of 400°C for ZnO samples. For InN two substrate temperatures were used, 350°C for InN_1 sample and 550°C for InN_2 sample. The deposition time was 60 minutes. Two samples of InN and two samples of ZnO deposited on Si were analyzed.

2.2. AFM MEASUREMENTS

The surface topography of the thin films was investigated using *Tapping Mode – Atomic Force Microscopy* (TM-AFM) MultiModeNanoScope IIID Controller (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA). Images were acquired at room temperature using a RTESP (Phosphorus (n) doped Si) cantilever with a spring constant of 20–80 N/m. Data acquisition and offline analysis was performed using AFM software v531r1. Surface roughness root mean square (RMS) values were measured over 1×1 μm^2 and 5×5 μm^2 areas for InN samples and 2×2 μm^2 and 7×7 μm^2 areas for ZnO samples.

2.3. RBS MEASUREMENTS

RBS is an accelerator-based analytical technique with direct application in materials science. In RBS, a beam of monoenergetic ions (H^+ or He^+) is directed at a target, and the energies of the ions which are scattered backwards are analyzed [16]. RBS is used for the quantitative analysis of the stoichiometry, thickness, and depth profiles of thin solid films or solid samples.

The samples were irradiated, at the tandem Van-de-Graaff accelerator from the *Horia Hulubei Institute of Physics and Nuclear Engineering* (IFIN-HH), using

a He^{2+} ion beam with energy of 4.5 MeV [17, 18]. The pressure inside the reaction chamber during the experiments was around 10^{-5} Torr. Energy calibration was determined using a $^{241}Am^{244}Cm$ mixed nuclide source and the spectrum from a thin C layer deposited on an Al/Au target.

Backscattered particles were detected at an angle of 167° with respect to the beam using an ORTEC ultra ion-implanted detector, with an active area of 450 mm^2 and a resolution of 12 keV at full width half maximum. Data analysis was performed off-line using the code SIMNRA [19, 20]. Physical thicknesses were calculated using the assumed values of 6.5 $x10^{22}$ atoms·cm^{-3} (6.81 g/cm^3) for the volume density of InN and 8.29 $x10^{22}$ atoms·cm^{-3} (5.6 g/cm^3) for the volume density of ZnO.

3. RESULTS AND DISCUSSION

3.1. AFM ANALYSIS

The AFM images of the InN thin films grown on silicon substrate are presented in Figs. 1 and 2. The root mean square (RMS) roughness (Rq) parameter, which represents the standard deviation of the surface heights values within a given area, was measured over the entire image using the roughness analysis option of the AFM software [21]. The RMS (R_q) values of InN were measured for two different scanning areas of the sample image (1×1 μm^2 and 5×5 μm^2). The RMS (R_q) values for InN_1 sample are 10.2 nm for the scanning area of 1x1 μm^2 and 11.2 nm for the scanning area of 5×5 μm^2 while for InN_2 sample the corresponding values are 12.9 nm and 13.1 nm. The height scale (z axis) of the AFM images (Figs. 1 and 2) is 200 nm/div.

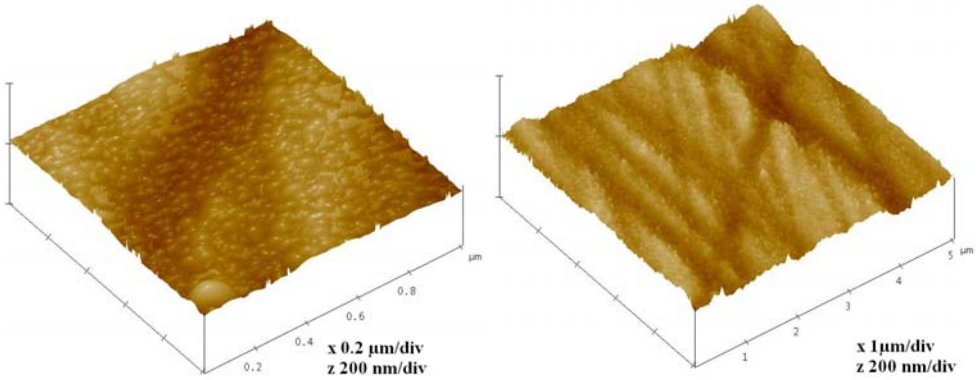

Fig. 1 – AFM images of InN film on Si substrate, InN_1 sample.
The scan size is 1x1μm^2 (left side) and 5×5 μm^2 (right side).

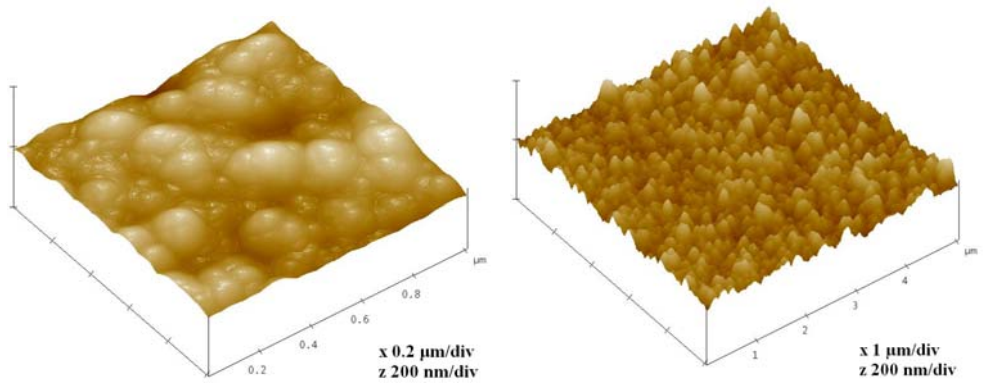

Fig. 2 – AFM images of InN film on Si substrate, InN_2 sample.
The scan size is 1x1µm^2 (left side) and 5×5 µm^2 (right side).

The Figs. 3 and 4 show the AFM images of the ZnO films deposited on Si. The roughness of the ZnO films is estimated for scans of 2×2 µm^2 and 7×7 µm^2. The RMS (R_q) values for ZnO_1 sample are 22.8 nm for the scanning area of 2×2 µm^2 and 41.1 nm for the scanning area of 7×7 µm^2 while for ZnO_2 sample the corresponding values are 16.6 nm and 27.2 nm. The height scale of AFM images of ZnO thin films deposited onto Si is 400 nm/div.

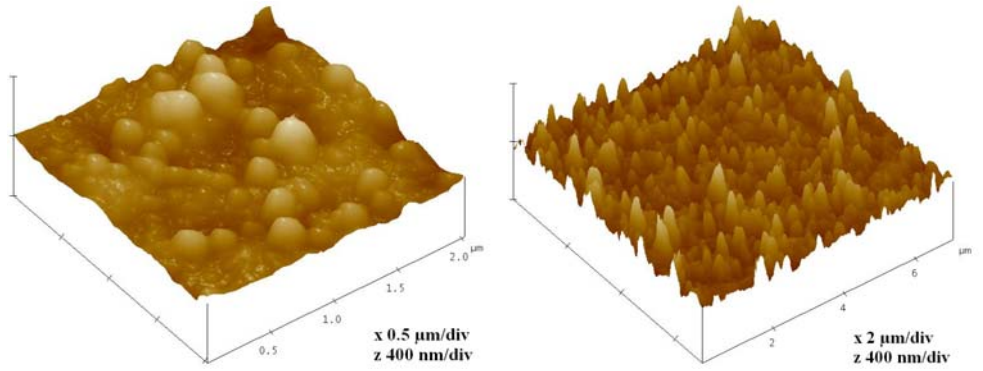

Fig. 3 – AFM images of ZnO film on Si substrate, sample ZnO_1.
The scan size is 2x2µm^2 (left side) and 7×7 µm^2 (right side).

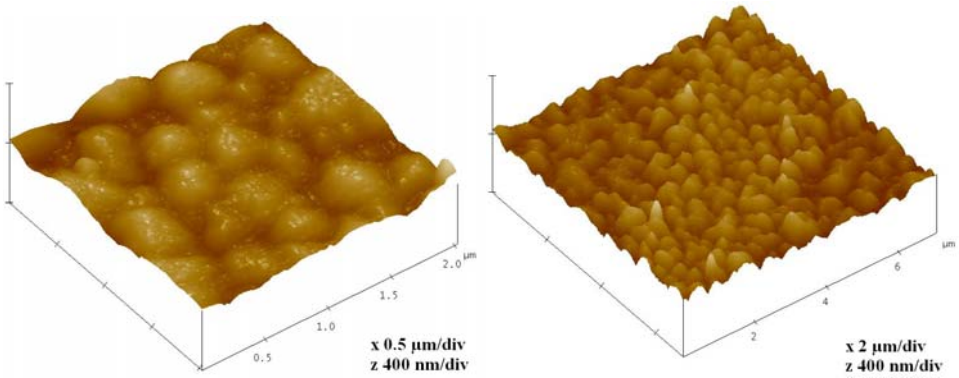

Fig. 4 - AFM images of ZnO films on Si substrate, sample ZnO_2.
The scan size is 2x2µm^2 (left side) and 7×7 µm^2 (right side).

3.2. RBS ANALYSIS

The RBS measurements are usually performed using alpha particles having energy smaller than 3 MeV [15]. If the alpha beam energy is increased over 3 MeV nuclear reaction channels are opened. Due to the poor stability of the alpha beam at low energies we have used 4.5 MeV energy. Another reason for using this energy is because light elements like N, have a higher cross-section for this particular energy and can be distinguished from the substrate signal. For the substrate signal RBS indicates the presence of nuclear resonances. The fitting code for the data analysis, SIMNRA, takes into account this fact so the spectra analysis can be done without introducing artifacts.

SIMNRA fits the simulation over experimental data and gives information regarding the stoichiometry and areal concentration (multiples of 1e15 atoms/cm^2). The physical thickness, measured in nm, can be obtained by dividing the areal concentration to the volume density. Because we did not measure the volume densities, we assumed the values of the bulk materials densities. Taking into account the volume densities, from section 2.3, and the areal concentration obtained from the SIMNRA fit of the experimental data we can obtain the physical thicknesses of the samples.

Fig. 5 shows the simulation of one-layer structure of InN and the RBS experimental data for InN_1. In the vicinity of the substrate-film interface a SiO_2 layer is detected, having a thickness of ~88 nm. The InN layer has a thickness of 192 nm and the stoichiometric composition is $In_{0.3}N_{0.7}$.

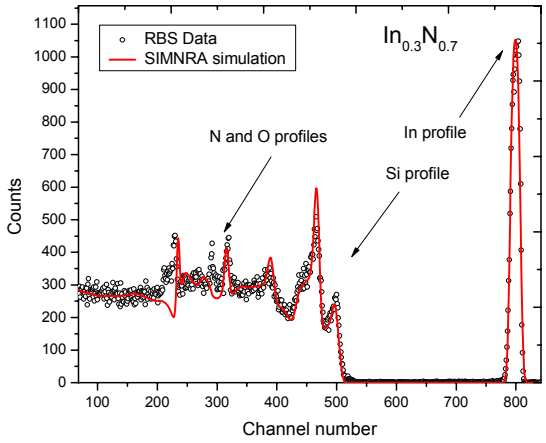

Fig. 5 – RBS spectrum of a ~ 192nm thick InN film on Si, along with SIMNRA fitting for a one-layer film structure of $In_{0.3}N_{0.7}$ at substrate temperature of 350°C.

Fig. 6 shows the simulation of one-layer structure of InN and the RBS experimental data for InN_2. In the vicinity of the substrate-film interface we have found the same SiO_2 layer but this time having a smaller thickness of ~ 28 nm. The InN layer has a thickness of 108 nm and the stoichiometric composition is $In_{0.45}N_{0.55}$.

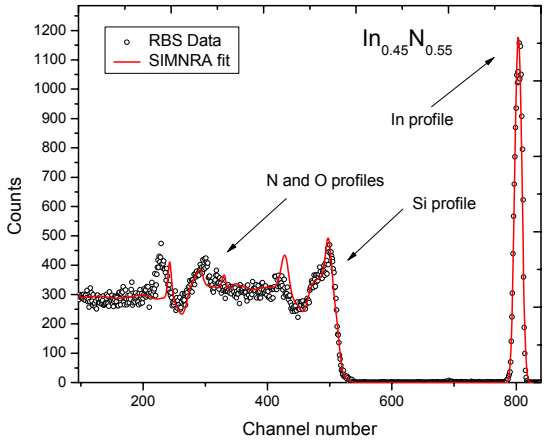

Fig. 6 – RBS spectrum of a ~ 108nm thick InN film on Si, along with SIMNRA fitting for a one-layer film structure of $In_{0.45}N_{0.55}$ at substrate temperature of 550°C.

In the Figs. 7 and 8 we present the simulation of a one-layer structure of ZnO and the RBS experimental data for sample ZnO_1 and sample ZnO_2. The ZnO layer has a thickness of 254 and 328 nm respectively and the stoichiometric composition is $Zn_{0.45}O_{0.55}$. The RBS results are presented in Table 1.

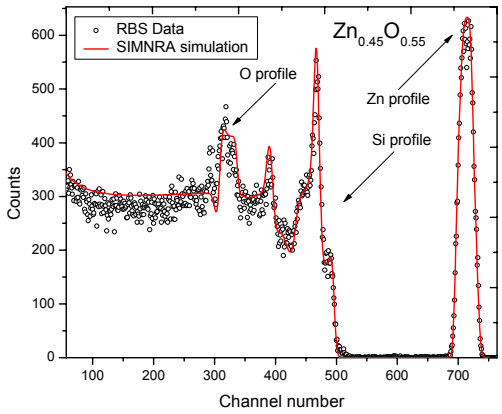

Fig. 7 – RBS spectrum of a ~ 254nm thick ZnO film on Si, along with SIMNRA fitting for a one-layer film structure of $Zn_{0.45}O_{0.55}$ at a substrate temperature of 400°C.

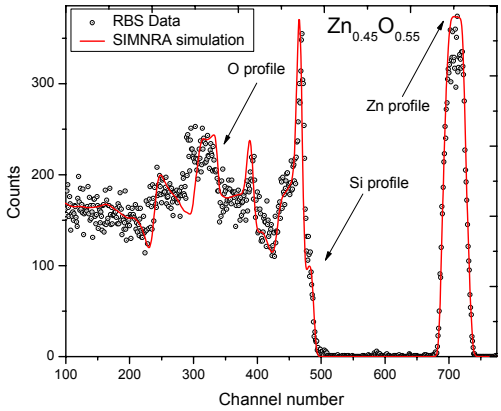

Fig. 8 – RBS spectrum of a ~ 328 nm thick ZnO film on Si, along with SIMNRA fitting for a one-layer film structure of $Zn_{0.45}O_{0.55}$ at a substrate temperature of 400°C.

Table 1

The RBS results for InN and ZnO samples

Sample	Thickness [nm]	Stoichiometry
InN_1	192	$In_{0.3}N_{0.7}$
InN_2	108	$In_{0.45}N_{0.55}$
ZnO_1	254	$Zn_{0.45}O_{0.55}$
ZnO_2	328	$Zn_{0.45}O_{0.55}$

In all the spectra a threshold is present at the silicon interface, this is due to the presence of a thick SiO_2 layer on the Si surface. The SiO_2 layer thickness is in the order of tenths of nm. One possible explanation for the presence of this SiO_2 layer is the exposure of the Si substrate to atmospheric air.

From Table 1 it can be seen that the two InN samples have different stoichiometries. For a substrate temperature of 350°C the stoichiometry is $In_{0.3}N_{0.7}$ while for 550°C it is $In_{0.45}N_{0.55}$. This means that InN stoichiometry is affected by the substrate temperature. From the N/In ratios it can be seen that the films are nitrogen rich.

All the deposited layers are In_xN_{1-x} and Zn_xO_{1-x} type (Fig. 9). Samples were analyzed on the assumption that the substrate used (Si) has an infinite thickness.

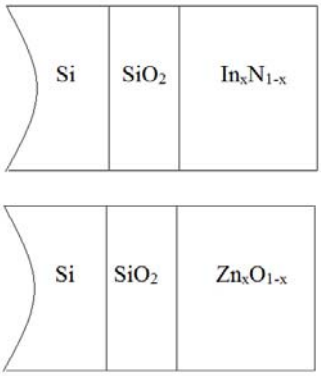

Fig. 9 – Schematic representation of the InN and ZnO samples.

The error of the RBS measurements is estimated to be less than 5%; this is due to the lack of experimental values for the cross section for scattering of ^{4}He on ^{14}N for the 4.5 MeV at the scattering angle of 167°. It is worth to mention that even though oxidation is common among III-V compounds, the oxygen at the surface of the two InN samples is not present. Oxygen is present in the RBS spectra only through the layer of SiO_2 coming from the air atmosphere exposure of the silicon substrate.

4. CONCLUSIONS

Several InN and ZnO thin films deposited by reactive magnetron sputtering onto Si substrate have been analyzed by AFM and RBS.

The AFM measurements indicated a mean roughness of about 12 nm for InN films and 27 nm for ZnO films. These values had no impact on the RBS measurements because the alpha beam diameter is about 2 mm being by far larger than the length of the crystallites in the film deposition.

The RBS measurements revealed the In_xN_{1-x} and Zn_xO_{1-x} stoichiometry of the films and the fact that oxygen is not present at the surface of the two InN samples. It was found that the substrate temperature affected the stoichiometry of the InN films.

The information obtained using these methods helps materials manufacturers to understand, optimize and improve the growth condition of the thin films.

Future experiments using Resonant Nuclear Reaction Analysis are planned for a better understanding of these structures.

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