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STRUCTURE AND MORPHOLOGY OF INDIUM NITRIDE THIN FILMS GROWN BY PLASMA ASSISTED PLD: THE IMPACT OF NITROGEN FLOW AND SUBSTRATE TEMPERATURE

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Abstact. We provide insight on how the substrate temperature and flow of nitrogen influence the structure and morphology of InN thin films grown by plasma assisted pulsed laser deposition on *c*-cut sapphire substrates. Structures were obtained following ablation of an In metal target by a 193 nm laser beam. Our results show a significant difference between the ways in which the variations of these two parameters influence the properties of the thin films.

Key words: pulsed laser deposition, III-nitrides, thin films.

1. INTRODUCTION

Owing to properties such as 0.65 eV band gap [1] and high electron saturation velocity [2], InN has been consider for a variety of applications, including solar cells, high speed integrated circuits, light emitting diodes (LEDs) and laser diodes covering a wide spectral range. In fact, InN has found applications in heterostructure based optoelectronic devices as a ternary alloy along with GaN [3]. However, growth of high-quality InN and InN-alloy based heterostructures is met with serious challenges, especially due to the fact that InN decomposes at temperatures above 550° C [4]. As a result, the diffusion length of the growth precursors used in conventional epitaxial growth techniques such as molecular beam epitaxy (MBE) and chemical vapour deposition (CVD) is severely reduced. This shortcoming can be overcome by using pulsed laser deposition (PLD) of an In metal target, allowing ablated species to achieve high kinetic energies when they impinge onto the surface of the substrate [5]. Moreover, the addition of highly reactive nitrogen plasma generated by a radiofrequency (RF) discharge source is aimed at improving the interaction efficiency with the ablated In species, allowing for the formation of InN. In fact, recent reports demonstrate the viability of plasma assisted PLD as an alternative technique for the epitaxial growth of high quality InN thin films [6].

Our present study is motivated by the fact that while the effects of temperature and plasma/precursor flow on the structure and morphology of the films have been properly documented for the case of InN growth by MBE [7] and CVD [8], the scientific literature contains little information on this topic for the case of PLD. The investigation of these aspects was demonstrated to be particularly useful since it has been shown that the variation of In/N precursors and/or temperature have a significant impact on the functional properties of InN films, e.g. their photoluminescence. In this work we provide insight on how the substrate temperature and flow of nitrogen influence the structure and morphology of InN thin films grown by plasma assisted PLD. Structural differences between the resulting films were investigated by means of X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to analyze the morphology of the structures.

2. EXPERIMENTAL

The samples were prepared by pulsed laser ablation of an In metal target (>99.99% purity) in controlled reactive nitrogen atmosphere. The beam from an ArF excimer laser (λ = 193 nm, τ = 20 ns, 10 Hz pulse repetition rate, 2 J/cm2 fluence) was focused onto the target at a 45° angle of incidence. Samples were obtained following the ablation of the In target by 36,000 laser pulses. The ablated material was collected on *c*-cut sapphire substrates mounted on a heater, 4 cm away from the target. The entire ablation procedure was assisted by the presence of nitrogen plasma. High purity N_2 gas (>99.99% purity) was fed through a mass flow controller into the radiofrequency plasma generator operating at 300 W discharge power. During the deposition, the pressure in the reaction chamber was kept at a constant 5 Pa, for all samples discussed here. The target was pre-ablated for 15 minutes in nitrogen atmosphere prior to each deposition in order to remove possible contamination with indium oxide.

Table I summarizes growth parameters that were varied in order to study the influence of nitrogen flow and substrate temperature on the structure and morphology of the resulting films. The five samples presented in the table can be grouped into two sets: i) one grown at different nitrogen flows and constant substrate temperature of 550° C (samples A1, B1, and C1, respectively); ii) and one obtained at different substrate temperatures and constant nitrogen flow of 100 sccm (samples A1, A2, and A3, respectively).

Table 1

Growth conditions of selected samples

Sample (name)	N_2 flow (sccm)	Substrate temp. (° C)
A1	100	550
B1	20	550
C1	5	550
A2	100	300
A3	100	50

A PANalytical X'Pert PRO MRD diffractometer was used for the XRD analysis of the resulting structures. The morphology of the samples was studied with an FEI Inspect S50 scanning electron microscope.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the X-ray diffraction spectra for samples grown at different nitrogen flow rates and substrate temperature of 550° C, whereas Fig. 2 illustrates their corresponding surface morphologies (from bottom to top: A1, B1, and C1, respectively). The XRD spectrum of sample A1, obtained in a nitrogen flow of 100 sccm, demonstrates the growth of highly oriented InN, also illustrated by the SEM image for this sample showing the formation of nanostructures with sizes of the order of ~100 nanometers, grown along the *c*-axis of the sapphire substrate. This result was shown to be a fingerprint of InN growth in N-rich conditions [9].

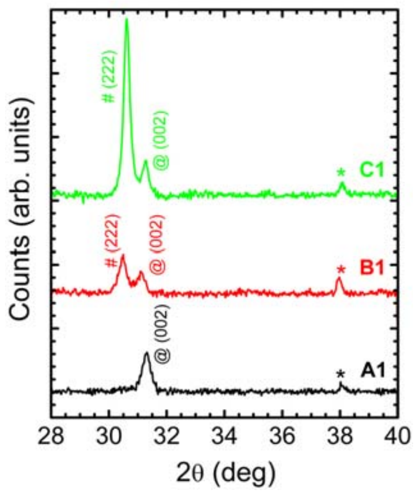

Fig. 1 – XRD curves of the symmetrical 2θ/ω scans for samples grown at different nitrogen flow rates and substrate temperature of 550° C (from bottom to top: A1, B1, and C1, respectively). The '@' symbol was assigned to peaks corresponding to InN, whereas In_2O_3 peaks are marked with '#'. The diffraction peaks marked with '*' are a contribution of the sapphire substrate. The spectra are shifted in intensity for clarity.

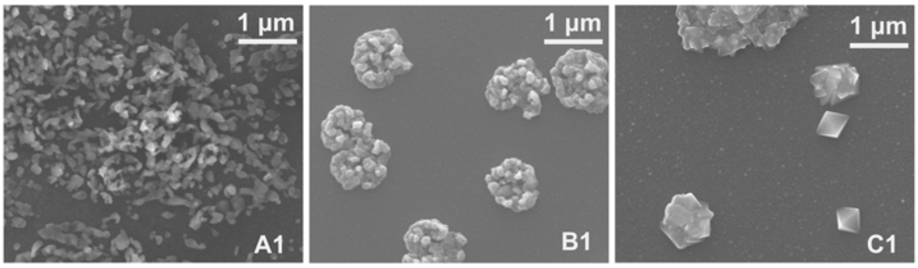

Fig. 2 – SEM images of samples A1, B1, and C1, respectively.

A decrease of the nitrogen flow by a factor of five appears to result in significant In_2O_3 contamination of sample B1 and in the formation of more bulky, micron-sized structures on the substrate surface. A possible explanation for this occurrence could be due to the fact that although we decreased the nitrogen flow, we maintained the pressure in the deposition chamber at a constant value of 5 Pa by adjusting the rotation speed of the turbo molecular pump. The decrease in the pump rate of the vacuum system is likely to have resulted in contamination with O_2 from the ambient atmosphere.

Contamination with In_2O_3 is even more pronounced when further decreasing the nitrogen flow to 5 sccm (sample C1), although it is interesting to note that formation of highly oriented InN structures is still present, as evidenced by the XRD spectrum. Moreover, the comparable intensities of the InN (002) peaks in the XRD spectra of samples A1, B1, and C1, respectively, suggest that the rate of formation of InN is largely unaffected by the decrease in the nitrogen plasma flow, the only negative effect of this reduction being the huge contamination of the films with In_2O_3.

The XRD spectra (Fig. 3) and SEM images (Fig. 4) for the second set of samples illustrate changes in the structure and morphology, respectively, of samples grown at different substrate temperatures and constant nitrogen flow rate of 100 sccm (from bottom to top: A1, A2, and A3, respectively).

Rather than contamination with In_2O_3, the main effect of substrate temperature decrease appears to be the formation of In droplets on the surface. This can be explained through the fact that the diffusion length of the ablated In species is tightly related to the temperature at the surface on which the diffusion process takes place, and therefore a reduction in temperature will result in a reduced diffusion length. Thus, In species will be more likely to condense on the surface in the form of droplets, rather than interacting with the nitrogen plasma to form InN, as the substrate temperature decreases. This effect is less significant at 300° C (sample A2) and much more pronounced at around room temperature (sample A3).

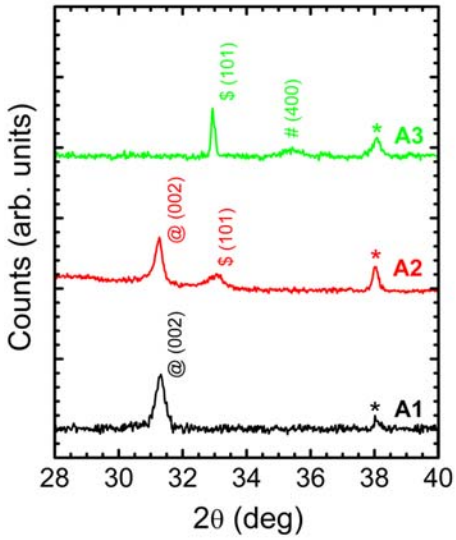

Fig. 3 – XRD curves of the symmetrical 2θ/ω scans for samples grown at different substrate temperatures and nitrogen flow rate of 100 sccm (from bottom to top: A1, A2, and A3, respectively). The '@' symbol was assigned to peaks corresponding to InN. Metallic In peaks are highlighted with '$', whereas In_2O_3 is marked with '#'.The diffraction peaks marked with '*' are a contribution of the sapphire substrate. The spectra are shifted in intensity for clarity.

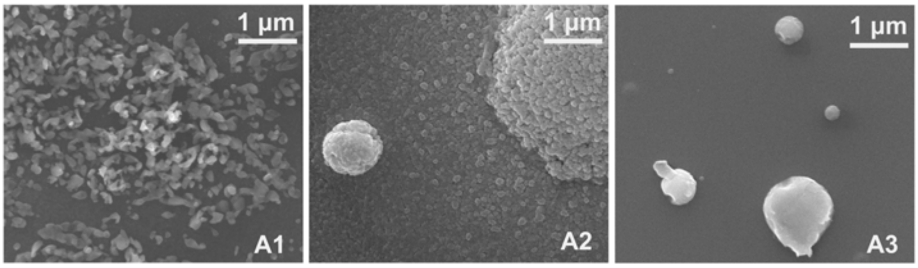

Fig. 4 – SEM images of samples A1, A2, and A3, respectively.

Although formation of metal In droplets is evidenced both by the XRD spectrum and the SEM image of sample A2, this temperature still favours the growth of highly oriented InN. A very different outcome is observed after further decreasing the substrate temperature to near room temperature. The XRD spectrum of sample A3 shows no evidence of InN formation, only the presence of In and some In_2O_3. At this temperature the surface is practically covered entirely by In droplets. The disappearance of InN is likely caused by the reduced kinetic energies of the ablated In species at lower substrate temperatures, *i.e.* by a greatly reduced diffusion length, eventually inhibiting the formation of InN and allowing for the formation of In droplets.

The results from these two sets of samples illustrate the very different ways in which substrate temperature and nitrogen flow affect the mechanisms of InN formation during the plasma assisted PLD process.

4. CONCLUSIONS

Two sets of InN thin films were prepared by plasma assisted PLD in order to study the influence of temperature and nitrogen flow on the structure and morphology of the samples. The degree of contamination of the samples with In_2O_3 was found to strongly increase with decreasing the nitrogen flow, although formation of InN was largely unaffected. On the other hand, the substrate temperature reduction caused an increase in In and a decrease in InN contents in the resulting films. The reduction in temperature is likely to result in a decreased diffusion length of the species on the substrate surface, eventually inhibiting the formation of InN at near room temperature and allowing for the formation of In droplets on the surface of the films.

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