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Structural and compositional analysis of transition-metal-doped ZnO and GaN PLD thin films

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Abstract

We have studied the structural and magnetic properties of thin films of ZnO and GaN semiconductors doped with magnetic and non-magnetic transition-metals. The films were prepared on sapphire substrates by pulsed laser deposition from doped ceramic targets. Room temperature ferromagnetism was observed in ZnO (doped with Sc, Ti, V, Fe, Co or Ni) and in Mn-doped GaN films. In both cases, single crystal epitaxial growth was observed. The higher dopant:Zn ratio observed in the films is attributed to the preferential sputtering of Zn by energetic ions in the laser ablation plasma plume.

Keywords: Pulsed laser deposition; Ferromagnetic semiconductor; Sputtering

1. Introduction

Ferromagnetic semiconducting materials, particularly doped materials such as GaN or ZnO [1,2], are currently of great interest for high density data storage applications [3], since predictions of room temperature ferromagnetism appear to have been confirmed experimentally [4,5]. The effect of introducing transition-metals such as Mn or Co on the structural quality in such semiconductors is of considerable importance. At present, the solubility limits for various growth techniques are well established [6,7]; whereas, characteristics such as texture, strain and epitaxy of doped films require a better understanding.

Pulsed laser deposition (PLD) has proved to be an attractive option for diluted magnetic semiconductor (DMS) growth [8,9], primarily due to its suitability for the preparation of multi-component films. Furthermore, it appears that the solubility limit is extended when using PLD as compared to other film growth techniques. This is particularly important for many DMS materials where the transition-metal equilibrium solubility is no more than a few percent. However, recent studies indicate that the film stoichiometry can differ significantly from that of the target [10].

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Therefore, it is of interest to identify how the deposition parameters affect the film composition.

In this paper, we discuss some of the structural characteristics of two wide bandgap semiconductors, ZnO and GaN, doped with transition-metal elements. The variation of film stoichiometry in ZnO doped with different transition-metals is correlated with the particle energy distribution of the laser ablation plasma.

2. Experimental details

Ceramic targets of $Zn_{0.95}TM_{0.05}O$ (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni or Cu) and $Ga_{1-x}Mn_xN$ (x = 0.005–0.1) were synthesized from stoichiometric amounts of high purity powders using the approach outlined in Ref. [9]. The films were deposited by PLD using a KrF excimer (23 ns, 248 nm) with pulse repetition rate of 10 Hz on R-cut (0 1 2) and C-cut (0 0 1) Al_2O_3 substrates positioned 35 mm from the target and maintained at a fixed temperature within the range 600–900 °C. The laser fluence on the target was ~2.5 J cm^{-2} and the background gas pressure was maintained in the range 10^{-4} to 10^{-1} mbar during the deposition. A 1 mm^2 flat Langmuir ion probe biased at −20 V was placed at the substrate position before deposition to measure the ablation plasma ion energy distribution. Details of the ion probe configuration and time-of-flight (TOF) data acquisition technique are discussed in detail elsewhere [11]. Film growth was monitored using an in situ optical reflectometry technique (635 nm), which allowed extraction of parameters such as the growth rate, surface roughness and refractive index [12]. The film thickness was independently calibrated by small angle X-ray diffraction (XRD). Structural analysis was carried out using XRD with Cu Kα radiation, 0.154 nm, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Compositional analysis and mapping were done using energy dispersive X-ray analysis (EDAX) and magnetisation measurements were made in a superconducting quantum interference device (SQUID) magnetometer at 300 K.

3. Results and discussion

In Fig. 1, we show a small angle XRD spectrum measured on a 65 nm thick Co-doped ZnO film. The simulated spectrum was obtained using a RMS roughness of 0.4 nm, which is the same as the value obtained by AFM. The s-polarized optical reflectivity (R_s) as a function of the number of laser shots, measured during the deposition of a thicker film of about 200 nm, is shown in the inset.

A θ–2θ XRD pattern of a Co-doped ZnO film grown on R-cut sapphire is shown in Fig. 2(a). The only peaks observed are at 2θ = 25.6° and 52.6°, corresponding to

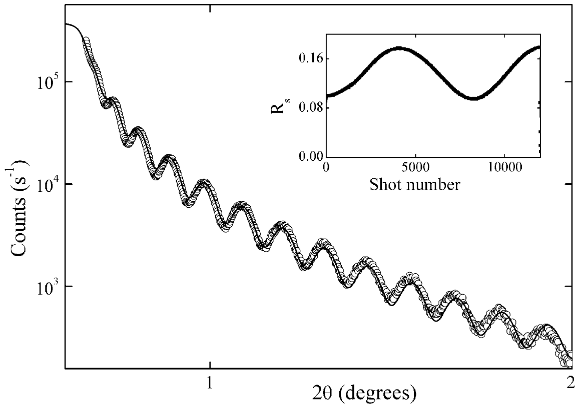

Fig. 1. Small angle XRD measurement (circles) and simulation (continuous line) for a 65 nm thick $Zn_{0.935}Co_{0.065}O$ film with RMS roughness of 0.4 nm and optical reflectivity (inset) of a thicker film (~200 nm).

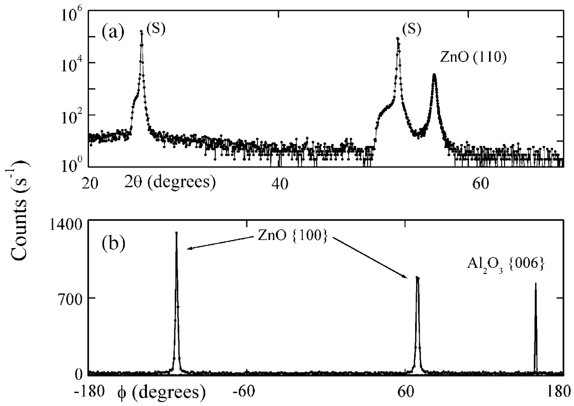

Fig. 2. (a) θ–2θ XRD pattern for a $Zn_{0.935}Co_{0.065}O$ film on R-cut (0 1 2) sapphire. Only the ZnO (1 1 0) peak and the substrate (0 1 2) and (0 2 4) peaks (marked as S) are observed. (b) ϕ-Scans for the same film, where the ZnO {1 0 0} reflections at $\phi = -113°$ and 69° and the Al_2O_3 {0 0 6} reflection at $\phi = 159°$ are shown. The epitaxial relations ZnO (1 1 0)//Al_2O_3 (0 1 2) and ZnO [0 0 1]//Al_2O_3 [1 2 $\bar{1}$] are deduced.