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Effect of electron beam rapid thermal annealing on crystallographic, structural and magnetic properties of $Zn_{1-x}Sm_xO$ thin films

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ABSTRACT

Trivalent rare earth ions (Sm^{3+}) doped ZnO dilute magnetic semiconductor thin films ($Zn_{1-x}Sm_xO$, where $x=0.02$, 0.04 and 0.06) of different thickness are grown on silicon (100) substrates using radio frequency magnetron sputtering and post annealed in high vacuum by electron beam rapid thermal annealing (ERTA) technique. X-ray diffraction analysis indicates that the thin films have a ZnO's hexagonal wurtzite structure. The unit cell constants a, c and the cell volume increases in the as-deposited sample as '*x*' increases, whereas ERTA has a reverse effect on them. Topographic analysis by atomic force microscopy on as-deposited thin films shows nonlinear change in grain size as a function of Sm concentration, whereas annealed thin films show linear change. Magnetization studies by vibrating sample magnetometer on as-deposited and annealed $Zn_{1-x}Sm_xO$ thin films show ferromagnetic response, due to the oxygen vacancies introduced by Sm doping. The as-deposited 100 nm $Zn_{0.94}Sm_{0.06}O$ thin film is weakly ferromagnetic (24 μemu), which after annealing becomes comparatively stronger (60 μemu). This indicates that apart from higher doping concentration of Sm, ERTA plays an important role in inducing oxygen vacancies.

1. Introduction

Dilute magnetic semiconductor (DMS) thin films have been widely studied for decades because of its potential use in magneto-electric, magneto-optic and spintronic applications. Reports on DMSs indicate a possible room temperature (RT) ferromagnetism in semiconductors when doped with transition/rare-earth metals using Zener's/bound-magnetic-polaron model for ferromagnetism [1–4]. These reports also suggest that it is important to ensure that the DMS thin films are homogeneous, and that their magnetic property does not arise from a separate phase, especially in the case of applications like spintronic devices. Zinc oxide thin films are known for its wide band gap of 3.37 eV and large exciton binding energy of 60 meV, which can be tuned by doping group V elements [5]. This makes ZnO an interesting material for applications in the field of electronics, like transparent electrode and light emitting diodes [6–8]. Samarium (Sm^{3+}) doped ZnO thin films are well known for their opto-electronic properties. Therefore the optical and electronic properties of Sm^{3+} doped ZnO thin films are widely studied and reported, but their magnetic property are rarely reported [9,10]. Reports on Sm^{3+} doped ZnO thin films suggest that five 4f electrons of Sm dopant defines the electric and magnetic properties of the system [9]. ERTA is primarily used in semiconductor manufacturing for dopant activation, thermal oxidation and modification of thin film interfaces. Unlike conventional annealing techniques, ERTA can anneal samples in the temperature range of 200–2000 °C on a timescale of <60 s, with the ramp rates typically 20–200 °C/s. There is no report on the effect of post annealing by ERTA on the magnetic properties of Sm^{3+} doped ZnO thin films. In this article, we have reported the crystallographic, chemical, topographic and magnetic properties of $Zn_{1-x}Sm_xO$ thin films (where *x* is 0.02, 0.04 and 0.06) and the effect of electron beam rapid thermal annealing on the same.

2. Materials and methods

Commercially purchased ZnO and Sm_2O_3 powders of 5n purity from Sigma Aldrich are mixed in three stoichiometric ratios to obtain $Zn_{1-x}Sm_xO$ (where *x* is 0.02, 0.04 and 0.06) in bulk quantities. The mixed powders are calcined at 1000 °C for 10 h and

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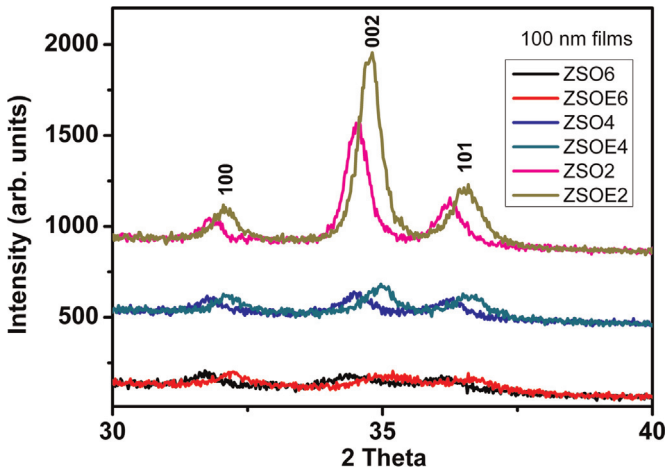

Fig. 1. GIXRD patterns acquired from 100 nm ZSO before and after annealing.

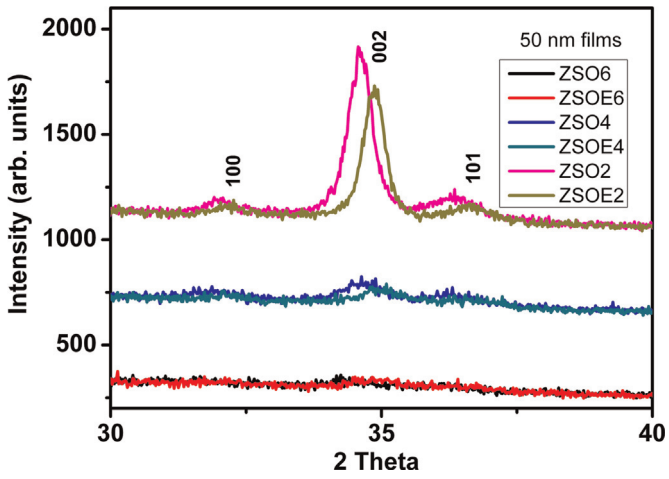

Fig. 2. GIXRD patterns acquired from 50 nm ZSO before and after annealing.

pressed into 2 in. pellets using hydraulic press. The pellets are then sintered at 1200 °C for 12 h and their surface is cleaned before using them as sputter targets in the radio frequency (RF) magnetron sputtering system.

The base pressure of the RF magnetron sputtering system's deposition chamber is brought to 5.1×10^{-3} mbar and by using Ar (working gas), the working pressure is brought to 1.2×10^{-1} mbar. $Zn_{1-x}Sm_xO$ thin films of 50 nm and 100 nm thicknesses are deposited at room temperature on silicon (100) substrates (The as-deposited thin films with x values of 0.02, 0.04 and 0.06 will be mentioned hereafter as ZSO2, ZSO4 and ZSO6 respectively). The as-deposited thin films are vacuum annealed at 5.6×10^{-6} mbar using ERTA. During the ERTA process, the rear of the deposited substrates are raster scanned with electron beam current of 3 mA for 20 s, which in turn increases the temperature to ~2000 °C in few seconds and then force cooled by circulated water. ERTA process maintains the atomic stoichiometry of the thin films by providing high temperature to the thin films in a short duration, just enough for the recrystallization to happen but not long enough for the atoms to escape the thin film through evaporation (The thin films after ERTA with x values of 0.02, 0.04 and 0.06 will be mentioned hereafter as ZSOE2, ZSOE4 and ZSOE6 respectively.). The crystallographic properties of the thin films are studied using PANalytical X'Pert Pro x-ray diffractometer (XRD) equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) in grazing incidence mode, topographic analyses are done using Agilent Technologies Molecular Imaging atomic force microscopy (AFM) and magnetic properties of the thin films are studied using PPMS-(Quantum Design) vibrating sample magnetometer (VSM).

3. Results and discussion

The GIXRD patterns of 100 nm (Fig. 1) and 50 nm (Fig. 2) $Zn_{1-x}Sm_xO$ thin films acquired before and after ERTA matched well with the calculated pattern of zinc oxide's hexagonal wurtzite structure. It is observed in both as-deposited thin films and thin films post ERTA that, the diffraction peak intensity reduces as the Sm concentration of the thin films increases. The reduction in the diffraction peak intensity with increase in Sm concentration of $Zn_{1-x}Sm_xO$ thin films has been reported earlier [10]. The observed

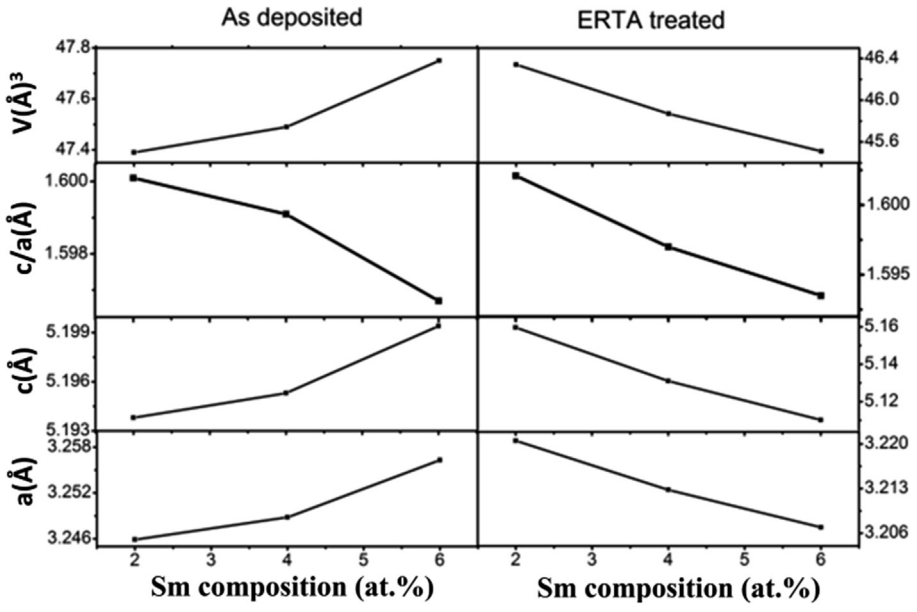

Fig. 3. Lattice parameters of 100 nm $Zn_{1-x}Sm_xO$ (where $x = 0.02$, 0.04 and 0.06) thin films before/after ERTA. GIXRD patterns of 100 nm films were used for the above calculations (The peak intensity of 50 nm films is not sufficient enough for cell parameter calculations).