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Research articles

Effects of thermal annealing on structural and magnetic properties of Mn ions implanted AlInN/GaN films

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ABSTRACT

In the search of functional diluted magnetic semiconductors, a study of effects of Mn ions implantation on structural and magnetic properties of AlInN/GaN/sapphire films is reported. Mn ions at 200 keV were implanted into the layers at three doses $5 \times 10^{14}\,cm^{-2}$, $5 \times 10^{15}\,cm^{-2}$ and $5 \times 10^{16}\,cm^{-2}$. The as-implanted samples were thermally annealed and investigated by using X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS) and vibrating sample magnetometry (VSM). The structural analysis of the samples indicated that the sample implanted at dose of $5 \times 10^{14}\,cm^{-2}$ and thermally annealed at 750 °C exhibited good crystalline recovery. The ferromagnetism of the samples was investigated by recording magnetization as a function of applied magnetic field. The magnetic characterizations exhibited well shaped hysteresis at room temperature which indicates presence of high temperature ferromagnetism in the samples. The findings of this work pointed out that AlInN/GaN samples implanted with Mn ions at dose of $5 \times 10^{16}\,cm^{-2}$ and annealing at 750 °C exhibited maximum magnetization. On the basis of first principles calculations, it is predicted that p–d interaction is the mechanism of ferromagnetic ordering in the material.

1. Introduction

The synthesis strategies for diluted magnetic semiconductors (DMS) and other materials for applications in devices have been focused by material researchers [1,2]. There are several techniques based on chemical and physics principles to prepare DMS materials but majority of them face drawbacks. The major hurdles encountered in fabrication of these materials are limited solid solubility, incorporation of magnetic species on desired lattice sites of the host, phase segregation, issue of magnetically inactive atoms, structure disorders etc [3]. Besides the other methods, ion implantation offers an attractive procedure to prepare the materials having desired dopant profile including concentration, depth etc without restrictions on solid solubility limits [4]. Furthermore, this technique is quick, controlled and offers incorporation of magnetic dopants after the growth of host materials as ex-situ processing of the semiconductors [5].

The search of functional diluted magnetic semiconductors (DMS) often attract the researchers towards III-nitride family of semiconductors due to its unparalleled advantages and potential for device grade applications [6,7]. Though, major research related to this class of materials refers to GaN but when tunable properties are concerned, the ternary alloys AlGaN, AlInN and InGaN have been focused [8]. The role of band gap in controlling the properties and understanding the mechanism of exchange interactions is very crucial in spintronics. Out of the entire series of possible alloys in III-nitride family, $Al_{1-x}In_xN$ is such an alloy which offers very large range of materials starting from narrow gap material InN for $x = 1$ (having band gap of 0.7 eV) and ending at wide gap material AlN for $x = 0$ (having band gap of 6.2 eV). AlInN is the only alloy in nitrides family which gives flexibility in tuning the lattice parameters and the band gap. The AlInN is lattice matched to GaN when indium concentration is 17% in the alloy. Since DMS are simultaneously semiconductors and magnetic materials, there should be relation between band gap and Curie temperature of the material. Dietl, on the basis of Zener model, explained the role of band gap in magnetism of semiconductors and mentioned that Curie temperature of wide gap semiconductors is higher [9]. It was predicted that p-type GaN and ZnO can exhibit high temperature ferromagnetism at 5% Mn doping when these materials contain 3.5×10^{20} holes/cm^3. AlInN is very interesting material by ferromagnetic point of view since it can offer different mechanism of exchange interactions due to wide range of

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band gap values. InN in its undoped form has been reported to exhibit ferromagnetism due to indium vacancies [10]. On the other hand, in case of AlN, ferromagnetism has been witnessed by doping the matrix with transition and rare earth metals [11,12]. There is very less work done on ferromagnetism in AlInN which demands detailed investigations of AlnN based DMS for spintronic applications [13,16,17]. This work involves structural and magnetic characterization of AlInN DMS prepared by implantation of Mn ions. A detailed study of the implanted materials has been made by using XRD and RBS with the idea that the structural properties have deep impact on ferromagnetic properties of materials.

2. Experimental

The samples used in this study were layered thin films of $Al_xIn_{1-x}N$/GaN/sapphire heterojunctions grown in low pressure metal organic chemical vapor deposition reactor. The precursors used for achieving the target material were Trimethylgallium (TMGa), Trimethylaluminum (TMAl), Trimethylindium (TMIn), Silane (SiH_4) and Ammonia (NH_3) as sources of Ga, Al, In, Si and N respectively. The carrier gas to facilitate the atomic species was hydrogen. The growth conditions for the samples are described elsewhere [13]. The thickness of epitaxial AlInN layer as per in-situ reflectivity records was about 200 nm whereas the GaN template was about 4 μm thick. The indium content ‘x’ of as-grown layer $Al_xIn_{1-x}N$ in the sample found from X-ray diffraction measurements by applying Vegard’s law for end products AlN and InN was 3.4% [13]. Mn ions with 200 keV were implanted at room temperature onto the samples by setting incidence of the beam at angle of 7° by using ion implanter system LC-4. The projected ion ranges estimated by using SRIM simulations was 202 nm from the surface of the samples. The implantation conditions and sample names are given in Table 1.

The samples after implantation were thermally annealed by using rapid thermal annealing system at 750 °C and 850 °C for 30 sec in nitrogen ambient. Detailed structural characterizations of the samples were made by using X-ray diffraction (XRD) and Rutherford Backscattering spectroscopy (RBS). Triple axis XRD measurements in full range of $2\theta = 20°–100°$ and high-resolution measurements of symmetric (0 0 0 2) reflections in range $2\theta = 34°–36°$ were carried out by Rigaku SLX-1A X-ray diffractometer. On the other hand, in case of RBS measurements, a beam of 2 MeV He ions having 1 mm diameter was employed to bring the structural information of the samples. The backscattered particles were detected at 165° with a silicon detector which had resolution of 18 keV and an aperture diameter of 5 mm. The detector was adjusted 80 mm away from the samples holder to detect the backscattered ion. The RBS analysis helps in compositional analysis of the materials whereas XRD helps investigate the structural properties of the materials.

The magnetization of the implanted samples was measured by recording magnetization as a function of applied magnetic field (MH curves). These measurements were carried out at room temperature by placing samples perpendicular to the field using vibrating sample magnetometer of model DMS 4HF. The as-implanted sample AMn31 was tested for magnetic field annealing by placing in the field of 1 kOe for one hour. The magnetic annealing was carried out to explore the relation between ion-implantation induced changes in microstructure and magnetic properties of the materials. The preliminary measurements are given in the manuscript whereas detailed investigations are in progress. The diamagnetic contribution of the samples was subtracted. The first principles calculations were performed within supercell approach at the level of GGA-PBE implanted in ADF-BAND Package [14]. The supercells with compositions $Al_{87.5}In_{12.5}N$ and $Al_{81.25}Mn_{6.25}In_{12.5}N$ were used for the calculations. The structures were fully relaxed with convergence criterion was selected as 10^{-5} eV.

Table 1
Ion implantation conditions and sample’s names used in this study.

Dose	Sample name	Beam current
As-Grown	A1	–
5×10^{14} cm^{-2}	AMn11	3 μA
5×10^{15} cm^{-2}	AMn21	10 μA
5×10^{16} cm^{-2}	AMn31	20 μA

3. Results and discussion

The results obtained after characterization of as-grown and ion implanted samples were carefully examined to explore the effects of ion implantation. Following sections give a representation of the results and their interpretations.

The X-ray diffraction measurements of the materials under investigation are shown in Fig. 1. The curves recorded in 2θ range of 20°–100° to do the structural phases analysis show peaks 2θ values of 34.56°, 35.7°, 41.7°, 72.8° and 73.2°, and 90.2°. These peaks correspond to reflections from (0 0 0 2) GaN, (0 0 0 2) AlInN, (0 0 0 6) Sapphire, (0 0 0 4) GaN, (0 0 0 4) AlInN and (0 0 0 1 2) Sapphire respectively. This analysis points to presence of the expected phases and absence of any secondary phase, within the experimental accuracy of the measurements, which may have caused the phase segregation of host structure or clustering of the implanted ions in response to the implantation and subsequent thermal annealing. Further, in order to investigate the effects of the implantation on epilayer, high resolution measurements were carried out to scan the (0 0 0 2) symmetric reflections in the region of first peak related to GaN and its shoulder peak.

The results shown in Fig. 1 (right penal) shows (0 0 0 2) reflection of GaN at $2\theta = 34.56°$ for as-grown as well as ion implanted samples regardless of the ion dose. However, the peak related to (0 0 0 2) reflection of AlInN which is observed at $2\theta = 35.77°$ for as-grown sample shown noticeable modification after ion implantation. The peak is shifted towards lower angle to the value $2\theta = 35.65°$ for the samples implanted with lowest dose of 5×10^{14} cm^{-2}. The change in separation of the peak of epilayer with respect to that of the template, i.e; ($\Delta\theta = \theta_{AlInN} - \theta_{GaN}$) points to variation of lattice constant and hence tensile strain as per $\varepsilon^{\perp} = -cot\theta_B.\ \Delta\theta$ [15].

The decrease in value of $\Delta\theta$ indicates an increase in perpendicular strain in the epilayer which may be interpreted in two ways. First, it may be the related to substitutional incorporation of guest Mn (having 0.64 Å size) ions in place of host Al (having 0.67 Å size) or In (having 0.94 Å size) cations when taken in 3+ state. The placement of Mn on either Al or In is expected to produce induce compression because the foreign ion is smaller in comparison to that of host elements. The substitutional settlement of the implanted atoms can be verified by independent techniques like magnetic characterization which shall be discussed in later parts of the manuscript. The second possibility is to exclude the incorporation of Mn on Al or In sites. It is related to the shift of XRD peak related to the epitaxial layer is production of strain due to implanted-ion to host-lattice interaction effects which are known as interstitialcy interaction [13]. However, considering the results and deeper look of the literature, we are now of the opinion that these are two extreme situations whose subsistence is less likely. There is more likelihood of presence of both these situations in superposition in which substitutional incorporation of the foreign atoms and ion-lattice interactions to produce interstitial defects take place simultaneously. A detailed investigation may help to know the exact mechanism and exploring which of these two competing processes dominate.

In contradiction with the sample AMn11, the peak related to AlInN has disappeared in case of higher implantation doses of AMn12 and AMn13. It points to sever crystalline damage of the epitaxial AlnN layer and survival of the layer when implantation dose was 5×10^{14} cm^{-2}.

A closer look into the XRD curves on lower angle shoulder of (0 0 0 2) reflection of GaN points to asymmetry in case of Mn ions