World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:6, No:1, 2012

Formation of (Ga,Mn)N Dilute Magnetic Semiconductor by Manganese Ion Implantation

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Abstract**—**Un-doped GaN film of thickness 1.90 μm, grown on sapphire substrate were uniformly implanted with 325 keV Mn^+ ions for various fluences varying from 1.75 x 10^{15} - 2.0 x 10^{16} ions cm^{-2} at 350^0 C substrate temperature. The structural, morphological and magnetic properties of Mn ion implanted gallium nitride samples were studied using XRD, AFM and SQUID techniques. XRD of the sample implanted with various ion fluences showed the presence of different magnetic phases of Ga_3Mn, $Ga_{0.6}Mn_{0.4}$ and Mn_4N. However, the compositions of these phases were found to be depended on the ion fluence. AFM images of non-implanted sample showed micrograph with rms surface roughness 2.17 nm. Whereas samples implanted with the various fluences showed the presence of nano clusters on the surface of GaN. The shape, size and density of the clusters were found to vary with respect to ion fluence. Magnetic moment versus applied field curves of the samples implanted with various fluences exhibit the hysteresis loops. The Curie temperature estimated from zero field cooled and field cooled curves for the samples implanted with the fluence of 1.75 x 10^{15}, 1.5 x 10^{16} and 2.0 x 10^{16} ions cm^{-2} was found to be 309 K, 342 K and 350 K respectively.

Keywords**—**GaN, Ion implantation, XRD, AFM, SQUID

I. Introduction

GALLIUM nitride based diluted magnetic semiconductor (Ga,Mn)N has potential applications in optoelectronic devices, such as blue ultra-violet light emitting diodes and laser diodes, as well as high-temperature and high power devices [1-3]. In past, many methods i.e. molecular beam epitaxy, metal oxide chemical vapor deposition, hydride vapor epitaxy etc. have been developed to synthesize (Ga,Mn)N structure but obstacle occurs to maintain certain percentage of Mn to achieve III-V semiconductors magnetic [4-7]. Ion implantation has been obvious advantages to overcome this problem by introducing impurities without solubility limit. Magnetic and structural properties of 180 keV Mn ions implanted p-type GaN with the fluence of 5 x 10^{16} ions cm^{-2} were investigated using SQUID and XRD techniques. The result of SQUID study showed the strongest ferromagnetic behavior after rapid thermal annealing of the sample at 800^0 C for 30 s and XRD study showed Mn-N binary phases of $Mn_6N_{2.58}$ and Mn_3N_2 after annealing at 900 ^{0}C [4]. SQUID and XRD studies of 1 keV Mn ion implanted GaN/Al_2O_3 for the fluence of 2.5 x 10^{14} ions cm^{-2} showed hysteresis loop at 293 K and the (Ga,Mn)N structure respectively [5]. SQUID, AFM and PL studies of 200 keV Mn^+ ion implanted GaN for the fluence of 5 x 10^{16} ions cm^{-2} showed the ferromagnetic behavior up to the temperature 270 K. AFM images showed the magnetic clusters and PL measurement showed the transitions at 2.5 and 3.0 eV corresponds to (e,Mn) and (D,Mn) respectively after rapid thermal annealing at 850^0 C for 20 s. [6]. XRD and SQUID studies of 200 keV Mn ion implanted GaN for the fluence of 1 x 10^{16} ions cm^{-2} showed the shift in the diffraction peak towards lower angle and ferromagnetic properties after annealing the sample at 900 ^{0}C [7]. In this paper, we reported structural, morphological and magnetic properties of 325 keV Mn^+ ions implanted gallium nitride at different fluences.

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II. Experimental Details

Un-doped GaN film of thickness 1.90 μm, grown on sapphire substrate by metal organic chemical vapor deposition (MOCVD) were uniformly implanted with 325 keV Mn^{+2} ions at 350 ^{0}C substrate temperature using 1.7 MV Tandetron accelerator at IGCAR, Kalpakkam, India. The beam current density was about 50 nA cm^{-2} during implantation. The scanned beam was further collimated through a collimator of diameter 12.5 mm for uniform implantation over the entire area of the sample. During implantation, the vacuum in the target chamber was maintained at 10^{-7} mbar. Three samples of gallium nitride were implanted with manganese ions for fluence of 1.75×10^{15}, 1.50×10^{16} and 2.0×10^{16} ions cm^{-2}. The structural properties of samples were recorded using X-ray diffractometer (X'pert PRO, PANalytical model) equipped with Cu Kα (λ~ 0.1540 nm) radiation source. The primary excitation current for the experiment was 30 mA at 40 kV. The detection period and step size were kept 1.0 degree per minute and 0.02 degree respectively. Atomic Force Microscope measurements of non-implanted and implanted samples were performed using diCaliber form Veeco instrument. The quantitative analysis was carried out using Veeco SpmLab analysis software. All the AFM measurements were performed in tapping mode (for both trace and retrace information) using a silicon nitride tip at ambient temperature. The magnetic properties of Mn^+ implanted gallium nitride samples were studied using superconducting quantum interference devices (SQUID) magnetometer (MPMSXL-Quantum design Co. Ltd.). The implanted samples were mounted plane parallel to the applied field during SQUID experiment. Magnetization was measured as function of applied magnetic field and temperature to determine the coercive field and other magnetic properties. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves as function of temperature were recorded. In the ZFC mode, the samples were cooled in zero fields from 350 K to 1.8 K. After stabilization of the temperature, the constant field 500 (Oe) was applied and the data were recorded while heating the sample. In the FC mode, the samples were cooled from 350 K to 1.8 K in the presence of a constant magnetic field 500 (Oe) and then the measurements were carried out while heating the sample in the same field.

III. Results and Discussion

A. X-ray Diffraction (XRD) Studies

X-ray diffraction spectra of gallium nitride film grown on sapphire substrate and implanted with 1.75×10^{15}, 1.50×10^{16} and 2.0×10^{16} ions cm^{-2} recorded in the 2θ range between 40°-80° were presented in Figures 1(a), 1(b), 1(c) and 1(d) respectively. The non-implanted sample showed a peak at 72.86° attributed due to GaN from (004) plane [Fig. 1(a)]. After implantation with Mn ion, XRD peaks of implanted GaN samples from (004) plane shifts towards lower 2θ values with respect to that of the non implanted sample. The difference in 2θ values between implanted and non implanted GaN sample indicates the lattice expansion due to incorporation of Mn ion in gallium nitride [8]. The sample implanted with the fluence 1.75 x 10^{15} cm^{-2} showed peaks at 44.764^0, 64.721^0 and 77.832^0 corresponds to Mn_3Ga, $Ga_{0.6}Mn_{0.4}$ and Mn_4N magnetic phase respectively. Whereas, other peaks at 44.121^0 and 65.160^0 could not be identified. These phases also appeared in sample implanted for fluence of 1.5 x 10^{16} ions cm^{-2}. However, the intensity of these magnetic phases was increased. Further increase in the ion fluence of 2 x 10^{16} ions cm^{-2} did not show these magnetic phases. The lattice constant of tetragonal gallium nitride structure calculated using following equation; [9]

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

where, d is inter planar distance, h, k and l are the planes, a, c are the lattice constants. The c plane lattice constant for the samples implanted with the fluence of 1.75 x 10^{15} and 1.5 x 10^{16} cm^{-2} were found to be 0.5188 and 0.5213 nm respectively. Whereas the corresponding estimate for non-implanted GaN sample was found to be 0.5186 nm. The increase in the lattice constant showed the Mn atoms are incorporated in the wurtzite GaN structure as substitutional on the Ga sub-lattice [9]. The bond length b calculated by considering the Ga and N along the c plane of GaN structure using following equation; [10]

$$b = \frac{c_{GaN}}{2\,[1 + \sin(19^0)]} - \left[\frac{r_{Ga} + r_N}{2}\right] \qquad (2)$$

where, r_{Ga} (= 0.1218 nm) and r_N (= 0. 075 nm) are the atomic radii for Ga and N respectively. The bond length for the samples implanted with the fluence of 1.75 x 10^{15} and 1.5 x 10^{16} cm^{-2} were found to be 0.0973 and 0.0982 nm respectively. Whereas the corresponding estimate length for non-implanted GaN sample was found to be 0.0972 nm.

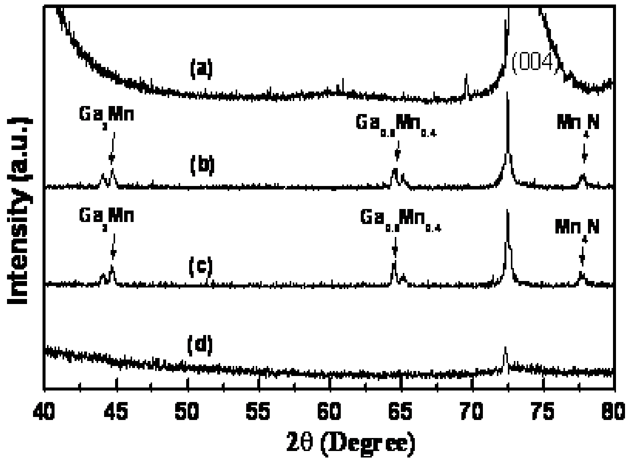

Fig. 1 XRD spectra of (a) non-implanted sample and samples implanted with 325 keV Mn^+ ions for the fluence of (b) 1.75 x 10^{15}, (c) 1.5×10^{16} and (d) 2×10^{16} ions cm^{-2}.

B. Atomic Force Microscopy (AFM) Studies

Two dimensional (3 µm x 3 µm) AFM images and corresponded line analysis across the surface of the non-implanted and samples implanted with 325 keV Mn^+ ion for the fluence of 1.5 x 10^{16}, 1.75 x 10^{15} and (c) 2 x 10^{16} ions cm^{-2} shown in Figure 2(a), 2(b), 2(c) and 2(d) respectively. The AFM image of non-implanted sample showed roughness on the surface [Fig. 2(a)]. After implantation with Mn ion, the roughnesses observe to be reduced. The estimated values of rms surface roughness and average size of cluster were given in Table I. The decrease in the rms roughness may be due to flattening of the surface due to ion impact. However, sample implanted with 2 x 10^{16} ions cm^{-2} showed increase in the rms surface roughness than that of the sample implanted with 1.5 x 10^{16} ions cm^{-2} [Fig. 2(d)]. The shape and size of clusters were found to vary with respect to ion fluence [Table-I]. Figure 3(a), 3(b), 3(c) and 3(d) showed three dimensional AFM (3 µm x 3 µm) images of non-implanted and samples implanted with 325 keV Mn^+ ion for the fluence of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} respectively. The sample implanted with the fluence 1.75 x 10^{15} ions cm^{-2} showed that the hillocks surrounded with craters. Further increase in the ion fluence (1.5 x 10^{16}), the hillocks and surrounded craters were reduced and became uniform [Fig. 3(c)]. Whereas, the density of hillocks were found to increase for the sample implanted with 2 x 10^{16} ions cm^{-2} [Fig. 3(d)]. In this measurement the average heights of hillocks were measured using SPIP software. The average height of hillock of samples implanted for the fluence of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} were found to 6 nm , 5 nm and 8 nm respectively. However, the average height for non-implanted sample was found to 7 nm.

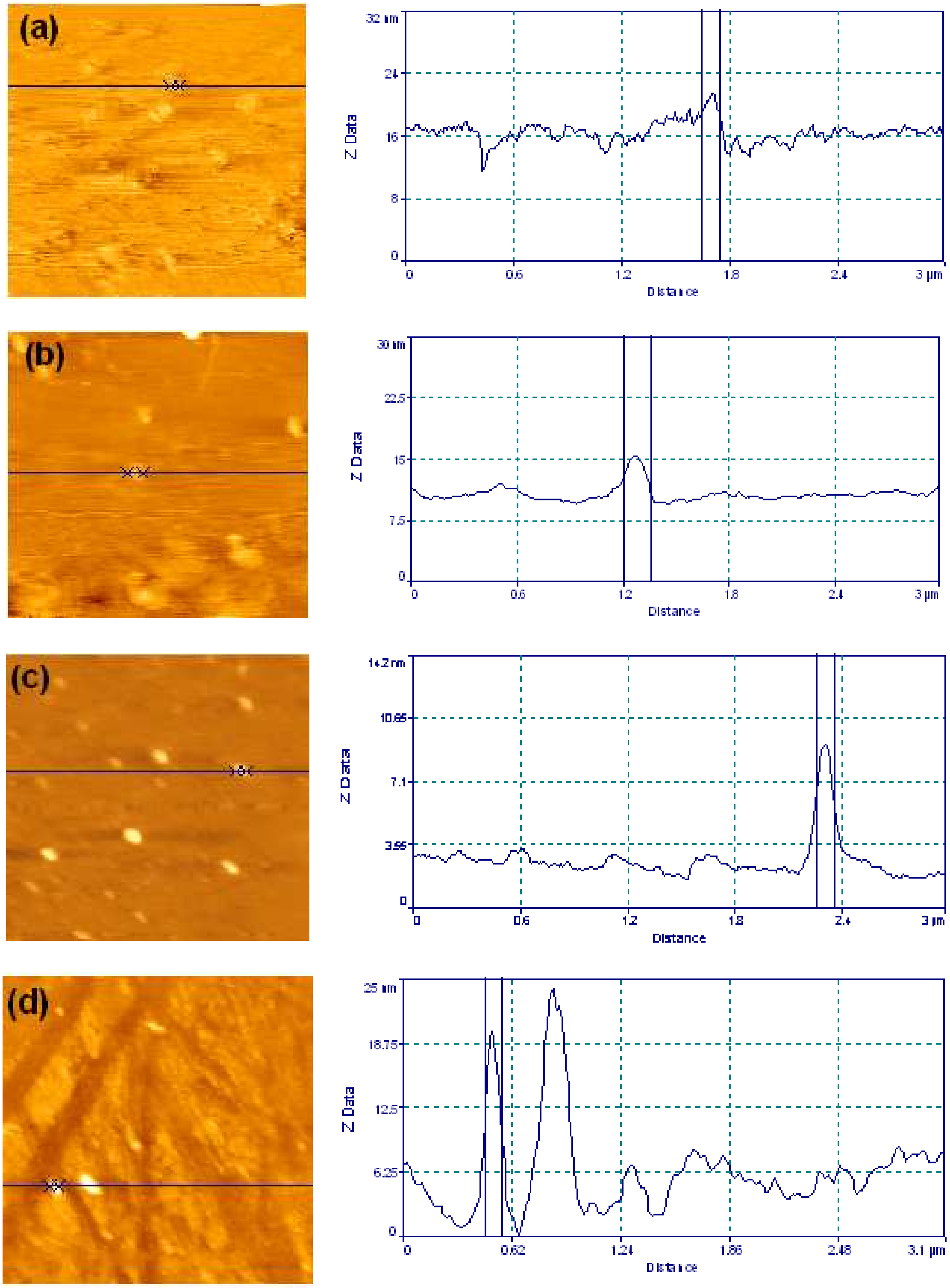

Fig. 2 Two dimensional AFM images of 3 × 3 µm scanned areas and corresponded line analysis across the surface of; (a) non-implanted GaN and samples implanted with 325 keV Mn^+ ion for the fluence of (b) 1.75 x 10^{15}, (c) 1.5 x 10^{16} and (d) 2 x 10^{16} ions cm^{-2}

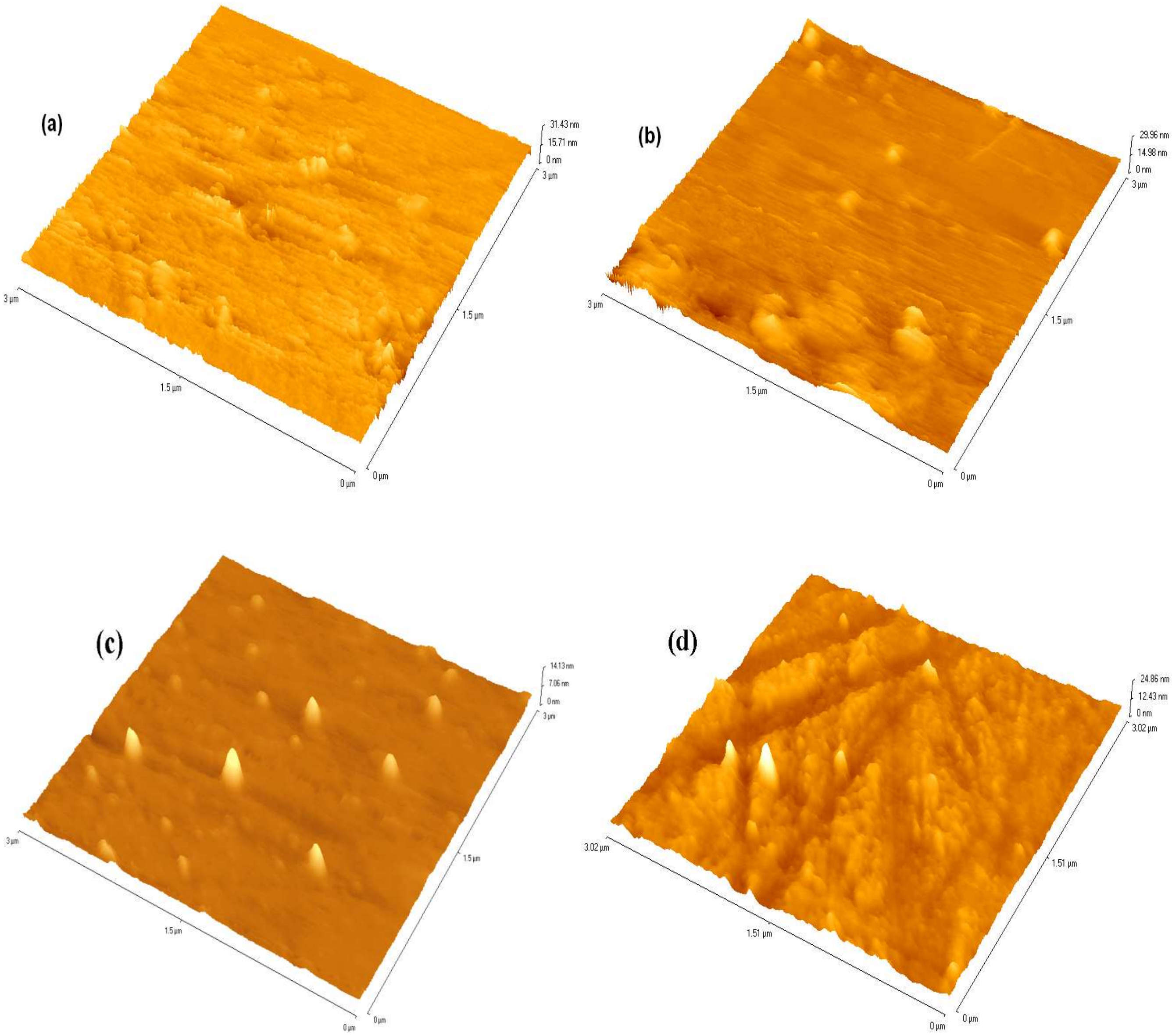

Fig. 3 Three dimensional AFM images of 3 × 3 µm scanned areas of; (a) non-implanted GaN sample and samples implanted with 325 keV Mn^+ ion for the fluence of; (b) 1.75 x 10^{15}, (c) 1.5 x 10^{16}, (d) 2 x 10^{16} ions cm^{-2}

TABLE I
VARIATION OF AVERAGE SURFACE ROUGHNESS AND RMS SURFACE ROUGHNESS OF NON-IMPLANTED AND SAMPLES IMPLANTED WITH VARIOUS FLUENCES OBTAINED FROM AFM

Fluence (ions.cm^{-2})	Rms surface roughness R_q (nm)	Average size of cluster (nm)
Non-implanted	2.1717	134
1.75×10^{15}	1.5811	160
1.50×10^{16}	0.7675	130
2.00×10^{16}	2.1419	154

Fig. 4 showed the plot of power spectral density (PSD) function versus spatial frequency of non-implanted and samples implanted for the fluences of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2}. The area 3 µm x 3 µm was used for power spectral density analysis. The PSD curves exhibited typical features consisting of a plateau with the low spatial frequency and an inverse slope with high spatial frequency. The plateau height in the lower spatial frequency regions indicated the roughening of sample surfaces. The slope (p) of power spectral density function estimated from Figure 4 for higher spatial frequency region ($q > q_0$). The values of plateau height extracted from PSD curves [Fig. 4] of the samples implanted for the fluences of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} were found to be 77, 26 and 156 nm^4 respectively. However, the value of plateau height for non-implanted sample was 106 nm^4. The values of p with respect to ion fluence estimated from power spectral density curve [Fig.4] for higher spatial frequency region of the samples implanted for the fluence of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} were found to be 18.33, 3.99 and 35.08 respectively. However, the value of p for non-implanted sample was 14.65.

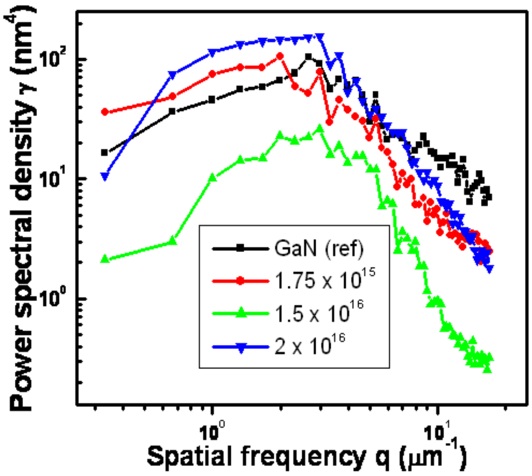

Fig. 4 Plot of power spectral density function vs. spatial frequency of 325 keV Mn$^+$ ions implanted gallium nitride at difference fluences

C. Magnetic Studies

Magnetization (M-H) curves of implanted gallium nitride samples for ion fluences 1.75 x 10^{15} to 2 x 10^{16} ions cm^{-2} shown in Figure 5. The sample implanted with 1.5 x 10^{16} ions cm^{-2} showed the increased in the magnetic properties as compared to other samples implanted with fluence of 1.75 x 10^{15} ions cm^{-2} and 2 x 10^{16} ions cm^{-2}[Fig 5 (a)]. The saturation magnetization in the samples implanted with 1.75 x 10^{15} , 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} were found 1.15 x 10^{-5}, 5.07 x 10^{-4} and 1.51 x 10^{-5} emu respectively. The coercive field of implanted gallium nitride sample increased with ion fluence. The changes in the properties are due to variations of concentration of Mn ions and the defects occurred in the samples due to ion implantation.

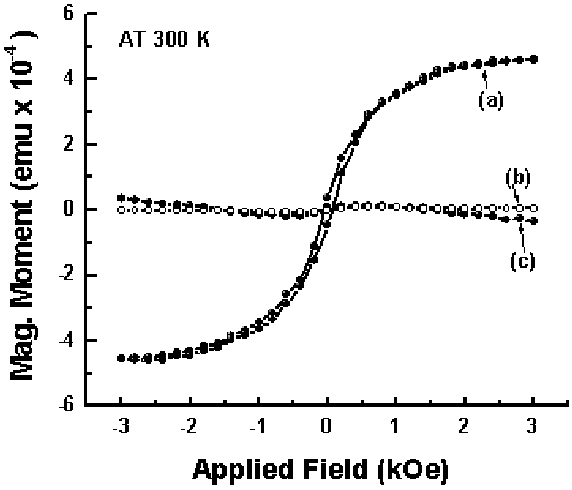

Fig. 5 M-H curves of 325 keV Mn$^+$ implanted GaN with the fluence of (a) 1.5 x 10^{16}, (b) 1.75 x 10^{15} and (c) 2 x 10^{16} ions cm^{-2}

Temperature dependent of the difference ($\Delta M = M_{FC} - M_{ZFC}$) between zero field cooling and field cooling magnetization curves (H = 500 Oe) of Mn implanted gallium nitride samples with various fluences 1.5 x 10^{16}, 1.75 x 10^{15} and 2 x 10^{16} ions cm^{-2} shown in Figs 6(a), 6(b) and 6(c) respectively. The FC- ZFC subtraction becomes more effective in case of small amount of ferromagnetic material in the presence of large diamagnetic /paramagnetic background. This subtraction simultaneously indicates the presence of hysteresis if the difference is non zero [11].

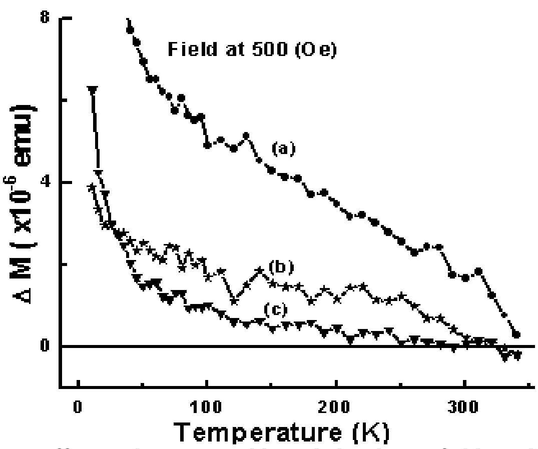

Fig. 6 Difference between Field-Cooled and Zero field- cooled magnetization of 325 keV Mn$^+$ implanted GaN with fluence of (a) 1.5 x 10^{16}, (b) 1.75 x 10^{15} and (c) 2 x 10^{16} ions cm^{-2}

All implanted samples showed the positive magnetization above room temperature. The Curie temperature has been estimated from the field cooled and zero field cooled curves of samples implanted with 325 keV Mn ions for the fluences of 1.75 x 10^{15}, 1.5 x 10^{16} and 2 x 10^{16} ions cm^{-2} were found to 309 K, 342 K and 350 K respectively. It can observe from Figure 6 that the magnetization decreased drastically up to the temperature ~ 30^0 K and later decreased slowly. It may be due to the implanted damage which is the positional disorder of interacting spin and carriers [12]. This result indicated the presence of one or more element to the magnetization and attributed the different phases, which may be responsible for observing ferromagnetic behaviors. However, the sample implanted with 1.5 x 10^{16} ions cm^{-2} exhibited the higher magnetization compare to other sample [Fig. 6(a)].

IV. Conclusions

We have characterized the properties of 325 keV Mn^+ ion implanted gallium nitride samples for various ion fluences using XRD, AFM and SQUID techniques. XRD showed the new peaks correspond to Mn_3Ga, $Ga_{0.6}Mn_{0.4}$ and Mn_4N magnetic phases. It revealed that increase in the lattice constant with ion fluence indicated the Mn atoms were incorporated in the wurtzite GaN structure as substitutional on the Ga sub-lattice. AFM images showed nano clusters on the surface of GaN. The surface morphology found to decrease with ion fluence. The magnetic properties of the samples implanted with various fluences exhibited the hysteresis loops. ZFC and FC magnetization showed the persistence of magnetism above the room temperature.

Acknowledgments

The Authors are thankful to Professor P. L. Paulose and Ganesh Jangam (TIFR, Mumbai, India) for SQUID measurements.

References

[1] H. Ohno, Science 281 (1998) 951.
[2] T. Jungwirth, Jurgen Konig, Jairo Sinova, Physical Rev. B 66 (2002) 12402.
[3] C. Ronning, P.X. Gao, Y. Ding, Appl. Phys. Lett. 85 (2004)783.
[4] Jeong Min Baik, Jong Lam Lee, Yoon Shoon, Journal of Appl.Phys. 93 (2003) 9024.
[5] Fugiang Zhang, NuoFu Chen, Xianglin Liu, Jour. of Cryst.Growth 262 (2004) 287.
[6] Yoon Shon, Young Hae Kwon, Appl. Phys. Lett. 93 (2003) 1546.
[7] Lili Sun, Fawang Yan, Junxi Wang, Phys. Status Solidi. A 206 (2009) 91.
[8] Jeong Baik, Yoon Shon, Jong-Lam Lee, App. Phy. Lett. Vol.84(2003), 1120-1122.
[9] Thaler G.T., Overberg M.E., Gila B., Frazier R., Abernathy C.R., Pearton S. J., Appl. Phys. Lett. 80 (2002) 3964.
[10] Budy Mulyanti, A. Subagio, ITB Jour. Sci. 40 A, 2,(2008),97-108.
[11] Doo Suk Han, Jeungee Park, Kung Won Rhie, Appl. Phys.Lett. 86 (2005) 032506.
[12] A.F. Hebard, R.P. Rairigh, J.G.Kelly,J.Phys. D:Appl. Phys. 37 (2004) 511.