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Room-temperature ferromagnetism of Cu-implanted GaN

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1 MeV Cu^{2+} ion was implanted into GaN with a dose of 1×10^{17} cm^{-2} at room temperature. After implantation, the samples were subsequently performed by rapid thermal annealing at 700, 800, and 900 °C for 5 min. Both nonmagnetic Cu ion implanted samples annealed at 700 and 800 °C exhibit the ferromagnetism at room temperature, and the saturation magnetization of these samples is estimated to be $0.057\mu_B$ and $0.27\mu_B$ per Cu atom from *M-H* curve, respectively. However, the sample annealed at 900 °C does not show ferromagnetism due to clustering of Cu during the annealing process. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2431765]

Recently, diluted magnetic semiconductors (DMSs), semiconductors that exhibit ferromagnetism by the substitutional doping of transition metal (TM) ions in semiconductor host, based on III-V semiconductors have attracted a great deal of attention due to their application in spintronics device as spin-field-effect transistors and spin-light-emitting diodes.[1] Among the various semiconductors, GaN and ZnO doped by TM (V, Cr, Mn, Fe, Co, and Ni) have been widely studied because their Curie temperature was reported to be near or above room temperature both theoretically and experimentally.[2–9] Recently, it was reported that Fe and Ni doped GaNs are intrinsic insulators.[10] Therefore, Fe and Ni doped GaNs could not be used for DMS materials unless additional dopants are introduced. The most probable candidates for DMS applications were predicted to be Co or Cu-doped GaNs.[10]

Until now, it remains to be unclear whether the observed ferromagnetism is from the magnetic substitutional ion in the lattice or from the secondary magnetic phases and metal precipitates. The origin of ferromagnetism is still under debate because commonly TM dopants themselves are intrinsically magnetic, and thus their clusters or precipitates may also contribute to the observed ferromagnetism.[11] To avoid these controversies, we have chosen Cu, a nonmagnetic element itself, as a magnetic doping element in GaN. Since metallic copper and all possible phases in Cu-doped GaN are not ferromagnetic, Cu-doped GaN has no possibility of having ferromagnetic precipitations. Cu-doped ZnO has been predicted to be ferromagnetic,[12] and its ferromagnetic behavior was reported by Buchholz *et al.*[13] However, room-temperature ferromagnetism in Cu-doped GaN has not yet been experimentally reported although theoretically Cu-doped GaN was recently predicted by Wu *et al.*[11]

It is presented here that Cu-doped GaN shows ferromagnetic behavior at room temperature using implantation and subsequent annealing processes.

A 2-μm-thick GaN was deposited on the sapphire (0001) substrate using a metal organic chemical vapor deposition at 1040 °C and 500 Torr. Prior to the 2-μm-thick GaN growth, 35-nm-thick GaN was grown at 540 °C as a buffer layer. Moreover, Rutherford backscattering spectroscopy/channeling spectrum of the as-grown sample was measured in order to confirm the crystallites (not shown in here). The channeling yield $\chi_{\min}$ was 3.04% at the low energy edge of the surface peak. It implies the high crystalline quality of GaN. 1 MeV Cu^{2+} ion was implanted into GaN with a dose of 1×10^{17} cm^{-2} at room temperature. The direction of the incident ion beam was tilted by 7° to surface normal to prevent possible channeling during ion implantation. By calculating the SRIM 2003 simulation code,[14] the projected range (R_p) of the implanted Cu ion is ~480 nm and the Cu peak concentration is ~6.2 at. % around R_p, almost the same Cu concentration predicted theoretically in the paper of Wu *et al.* (6 at. %). After implantation, the samples were subsequently subjected to a rapid thermal annealing at 700, 800, and 900 °C for 5 min in nitrogen ambient at a pressure of 1 Torr. The magnetic properties were measured by a superconducting quantum interference device (SQUID) magnetometer. An atomic structure were investigated by x-ray diffraction (XRD) measurement using the bending magnet 10C1 beam

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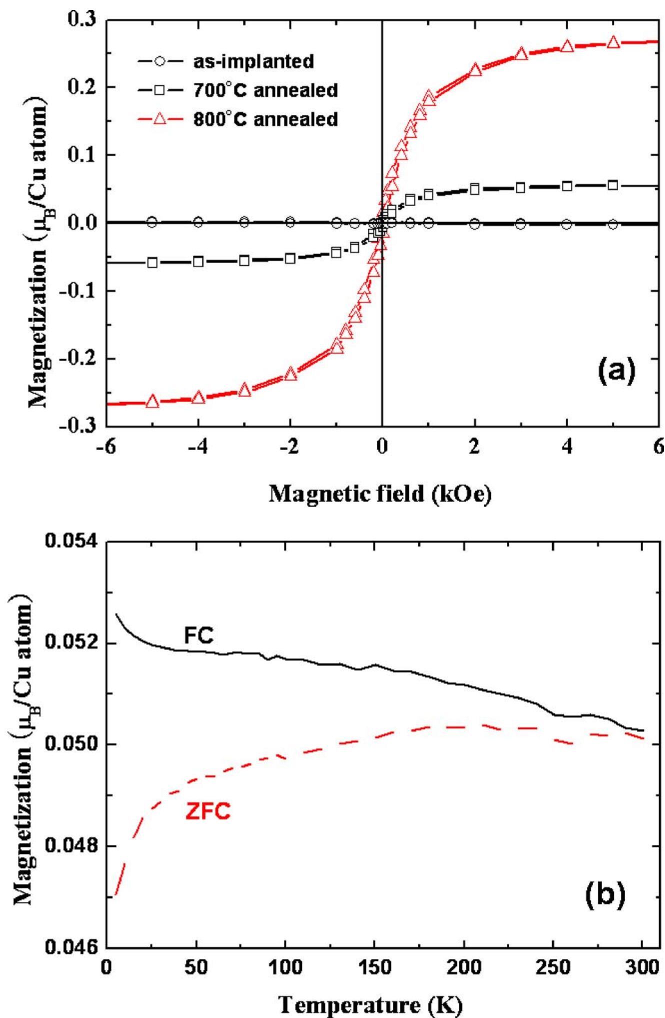

FIG. 1. (Color online) (a) Magnetization-field (*M-H*) curves at room temperature (300 K) for the as-implanted sample, and 700 and 800 °C annealed samples after the Cu implantation into high quality GaN. (b) Temperature dependence of magnetization at field-cooled (FC) and zero-field-cooled (ZFC) conditions at a magnetic field of 500 Oe for the 800 °C annealed sample.

line at Pohang Accelerator Laboratory. Also, Hall-effect measurements were performed for measuring carrier density using the standard van der Pauw technique.

A room-temperature ferromagnetism of Cu implanted GaN samples was investigated by the SQUID, as shown in Fig. 1. Figure 1(a) shows the magnetization-field (*M-H*) curves at room temperature (300 K) of as-implanted and annealed samples after implantation into GaN. *M-H* curves were corrected for the diamagnetic background of substrate. The as-implanted, unannealed, sample does not have ferromagnetic hysteresis within the resolution of the measurements. On the contrary, the annealed samples at 700 and 800 °C exhibited the ferromagnetic behavior, and the calculated magnetic moments from the saturation magnetization (M_s) are ~0.057 and 0.27 Bohr magnetons (μ_B) per Cu atom at 6 kOe, respectively. The magnetic moment tremendously increased about five times as an annealing temperature increases. The coercive field is approximately 77.5 Oe, while the sample annealed above 900 °C does not show ferromagnetic properties. Figure 1(b) shows the temperature dependence of the magnetization under a magnetic field of 500 Oe for the 800 °C annealed sample. The two curves remain separated throughout the entire temperature range (5–300 K). The two curves coincide at the Curie temperature T_C, when the hysteresis disappears.[15] It means that T_C is at least higher than room temperature (300 K).

In order to exclude possible effects of contamination and ion beam induced damage, samples were fixed to the copper substrate holder using the silicon wafers during implantation and were cleaned with an acetone prior to measurement by SQUID. In addition, an implantation technique is well known as a clean process. Venkatesan *et al.*[16] and Hong *et al.*[17] reported about d^0 magnetism assumed to cause defects or oxygen vacancies that might lead to a source of magnetism. Therefore, to confirm the damage effects, defects or vacancies, created by ion beam on the magnetism, arsenic ion implantation with an energy of 1 MeV was performed. Arsenic ion, non-TM, was chosen due to its atomic mass similar to Cu and the amount of damage caused by the implanted Cu ion. Arsenic ion implanted GaN does not exhibit magnetism. Consequently, the ferromagnetism of Cu implanted GaN is not caused by the effect of damage. The ferromagnetism in Cu implanted GaN was confirmed through several repetitive experiments. Cu implantation in GaN was performed three times for testing reproducibility, and it was confirmed that all samples annealed at 800 °C show a ferromagnetic behavior.

The magnetic property depends on annealing temperature. In other words, the damage recovery and an atomic structure after the annealing process affect the magnetic property. Wu *et al.* reported that Cu-doped GaN favors ferromagnetic ground state by *p-d* hybridization mechanism when Cu atoms substitute Ga sites.[11] XRD was measured to find the damage recovery and atomic structure. As can be seen in the XRD result [Fig. 2(a)] Ga peaks appear due to the decomposition of GaN and GaN (0002) peak shifts to a low angle after Cu implantation, indicating that the crystal lattice has been slightly expanded due to implanted Cu ions in interstitial sites. After subsequent annealing at 700 and 800 °C, Ga peaks gradually disappear and GaN (0002) peak shifts to a high angle. Therefore, it can be assumed that a certain portion of decomposed Ga and implanted Cu replaces the host Ga site in GaN during the annealing process. As previously mentioned in SQUID, these subsequently annealed samples show the ferromagnetism. These SQUID and XRD results agree with the theoretical result of Wu *et al.* although the value of the magnetic moment in the Cu-implanted sample ($0.27\mu_B$/Cu atom) did not reach the value of the magnetic moment in the prediction of Wu *et al.* ($2\mu_B$/Cu atom) due to different concentrations in a depth and the existence of unsubstituted Cu atoms to the Ga site. However, an unidentified phase peak (2θ=43.9°) in the sample annealed at 900 °C was shown in Fig. 2(b). It is conceivable that this peak is associated with a clustering of implanted Cu ions due to a relative high annealing temperature compared with annealed samples at 700 and 800 °C. Therefore, a sample annealed at 900 °C did not show ferromagnetism due to Cu metal clustering during the annealing process. And three peaks, $GaCu_2$ peaks,[18] appear after Cu implantation. This secondary phase, $CuGa_2$, is not ferromagnetic. If the $CuGa_2$ phase is ferromagnetic, the as-implanted sample must show the ferromagnetic behavior regarding to XRD spectra. However, the ferromagnetism was not observed from the as-implanted sample. It is noted that the ferromagnetism of annealed samples does not result from a secondary phase.

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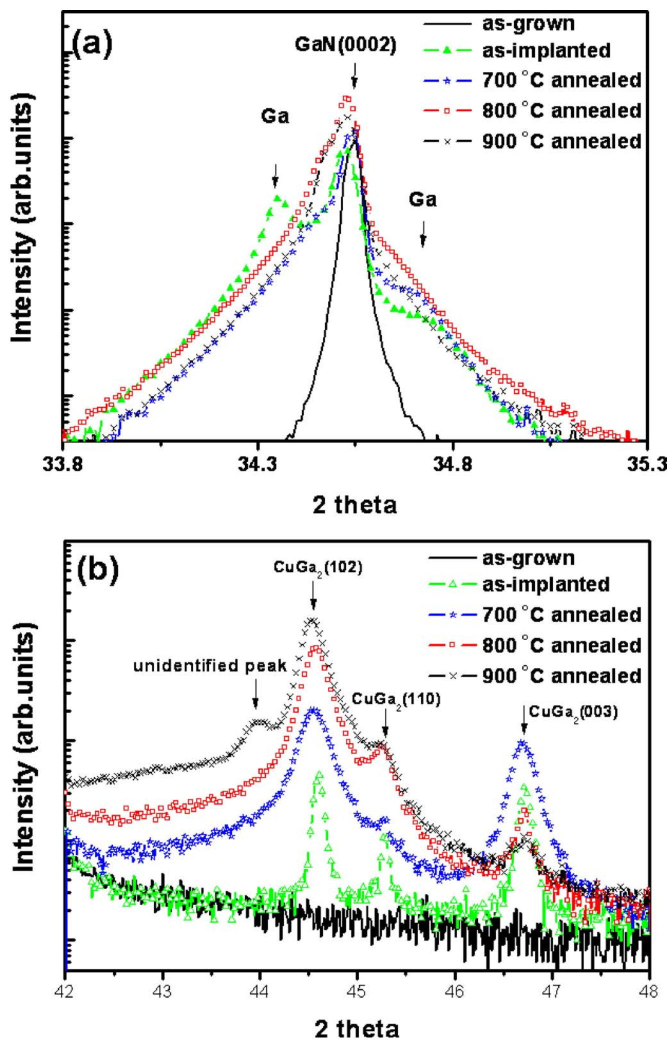

FIG. 2. (Color online) XRD spectra of as-grown and Cu implanted GaN samples.

All samples were *n* type from the Hall-effect measurements. The carrier density of the as-implanted sample (7.6×10^{19} cm^{-3}) increases more than two orders compared with that of the as-grown sample (1.1×10^{17} cm^{-3}) due to defects created by implantation. However, the carrier density of samples annealed at 700, 800, and 900 °C decreases to 1.1×10^{19}, 3.1×10^{18}, and 5.5×10^{18} cm^{-3} owing to the damage recovery after annealing, respectively.

The origin of the ferromagnetism of Cu implanted GaN is not clearly explained. However, it is proven in this letter that ferromagnetic property is not caused by the effect of damage and secondary phase. According to Bozdog *et al.*, Cu^{2+} (d^9) has been observed in Cu-doped GaN as a substitute on the Ga sublattice.[19] Cu^{2+} (d^9) can play a role of magnetic ion in GaN with a total spin of 1/2 by Hund's rule. To confirm an electronic state of implanted Cu, x-ray magnetic circular dichroism, near edge x-ray absorption fine structure spectroscopy, etc. must be measured. However, unfortunately, an electronic state of Cu was not observed for our samples from those analyses due to a large penetration depth of implanted Cu ion and a damage created by 1 MeV Cu implantation. Experimental work is in progress to clarify an origin of ferromagnetism in this system using a growth of Cu-doped GaN.

In summary, this is the experimental report of room-temperature ferromagnetism of Cu implanted GaN. Nonmagnetic Cu ion with an energy of 1 MeV was implanted into GaN. After subsequent annealing process at 700 and 800 °C, the ferromagnetism was observed at room temperature. This ferromagnetism was not caused by the secondary phase and the defects induced by ion irradiation. On the other hand, sample annealed at 900 °C did not show ferromagnetism due to Cu metal clustering. Further investigation is needed to find the origin of ferromagnetism.

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