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Co Ion-implanted GaN and its Magnetic Properties

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2-μm thick GaN epilayer was prepared, and 80 KeV Co^- ions with a dose of 3×10^{16} cm^{-2} were implanted into GaN at 350 °C. The implanted samples were post annealed at 700 °C. We have investigated the magnetic and structural properties of Co ion-implanted GaN by various measurements. HRXRD results did not show any peaks associated with second phase formation and only the diffraction from the GaN layer and substrate structure were observed. SIMS profiles of Co implanted into GaN before and after annealing at 700 °C have shown a projected range of ~390 Å with 7.4% concentration and that there is little movement in Co. AFM measurement shows the form of surface craters for 700 °C-annealed samples. The magnetization curve and temperature dependence of magnetization taken in zero-field-cooling (ZFC) and field-cooling (FC) conditions showed the features of superparamagnetic system in film. XPS measurement showed the metallic Co 2*p* core levels spectra for 700 °C-annealed samples. From this, it could be explained that magnetic property of our films originated from Co magnetic clusters.

Key words : magnetic semiconductor, ion implantation

1. Introduction

Dilute magnetic semiconductors (DMSs) have attracted much attention as materials for spintronic devices [1, 2]. Most of the work in the past has focused on (Ga,Mn)As and (In,Mn)As. However it is reported that these materials have too low Curie temperature (~110 K for GaMnAs and ~35 K for InMnAs) for practical application [3, 4]. The wide bandgap semiconductors GaN have recently received great interest since its Curie temperature (T_c) higher than room temperature is predicted by theoretically studies [5]. Several groups have reported Curie temperature (T_c) near or above room temperature for Mn-doped GaN [6, 7]. Although, recently Mn-doped GaN is the most intensively investigated in the group of III-V semiconductors, the systems with other transition metals as magnetic ions may also offer suitable properties [8, 9]. Co may be interesting since the T_c of Co doped TiO_2 [10] and ZnO [11] have been reported to be above room temperature. Ion implantation of magnetic ions into various semiconductors has been quite effective in surveying possible DMS system [12]. In this study, we report on the magnetic and structural properties of Co ion-implanted GaN with post annealing.

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2. Experimental Procedure

We prepared 2-μm thick undoped GaN epilayer grown on Al_2O_3 substrate by metal-organic chemical vapor deposition (MOCVD), and 80 KeV Co^- ions with a dose of 3×10^{16} cm^{-2} were implanted into GaN at 350 °C. The implanted samples were post-annealed at 700 °C by rapid thermal annealing (RTA) in N_2 atmosphere for 5 min to recrystallize the samples and to remove implantation damage. High-resolution x-ray diffraction (HRXRD), atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS) using Mg K_α radiation source ($h\nu$ = 1253.6 eV) were employed for structural characterization. Secondary ion mass spectrometry (SIMS) analysis was performed to get the depth distribution of Co, Ga, and N atoms. Magnetization measurements were carried out using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer system. In all the magnetization measurements, the magnetic field was applied parallel to the sample plane.

3. Result and Discussion

Figure 1 shows the XRD profiles of Co ion-implanted GaN samples with annealing temperature. In the as-grown sample, three main peaks correspond to the expected diffraction from the GaN epilayer and sapphire substrate structure. We examined the possibility of cobalt cluster and the reaction between Co and GaN formed during the implantation and post annealing process. Compared to the as-grown sample, Cobalt and any second phase was not observed in the as-implanted and 700 °C-annealed samples. Though XRD measurements showed the absence of impurity phases as Co clusters or Co-Ga alloys, we do not exclude the possibility of the presence of Co or Co-Ga nanoscale precipitates which cannot be measured by XRD for its insensitivity on nanoscale [13-15]. SIMS depth profiles of Co, Ga, and N atoms for before and after annealing at 700 °C are shown in Fig. 2. Co ions have shown a projected range of ~390 Å with about 7.4% concentration before and after annealing at 700 °C and that there is little movement in Co. Figure 3 shows the surface morphologies of AFM on the unimplanted and Co ion-implanted GaN with annealing temperature. The unimplanted GaN film show very smooth surface morphology. But the 700 °C-annealed sample show the formation of surface craters and very rough surface. Any magnetic islands on the implanted GaN sample were not observed.

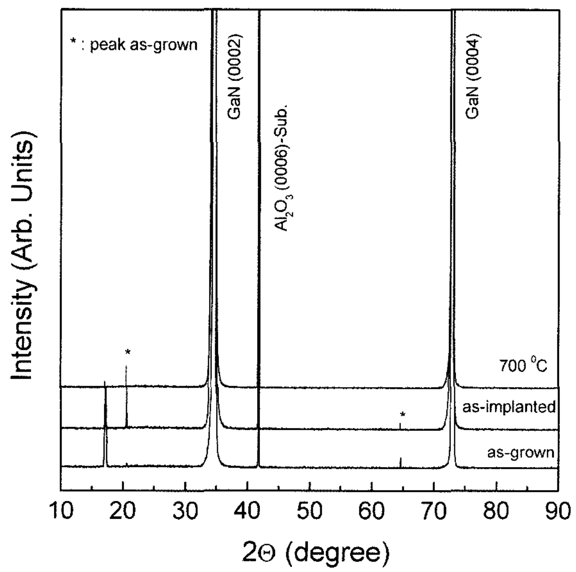

Fig. 1. XRD profile for Co ion-implanted GaN with annealing temperature.

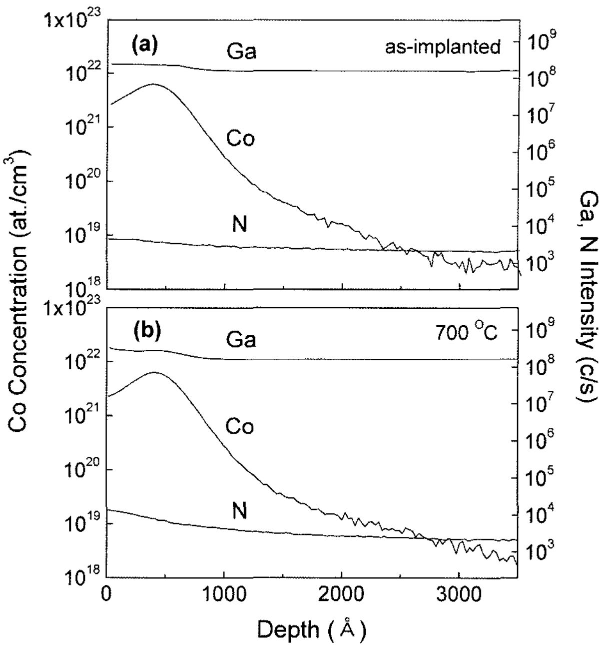

Fig. 2. Depth profile of Ga, Co, and N atoms for Co-implanted samples: (a) as-grown, and (b) after annealing at 700 °C.

The magnetization behavior of the Co ion-implanted GaN sample was investigated with SQUID magneto-

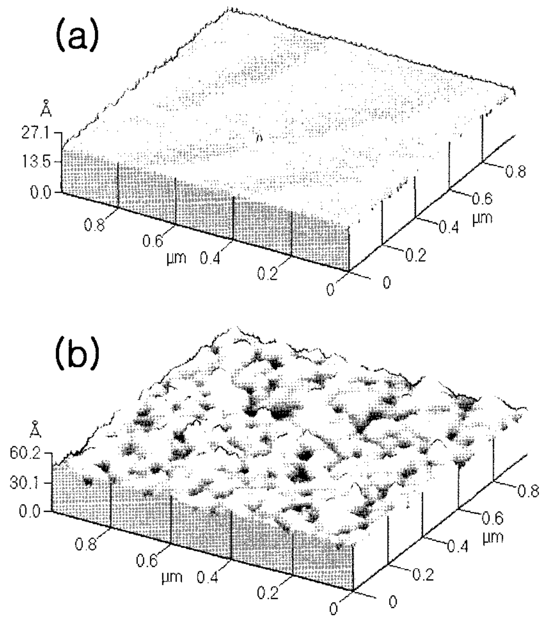

Fig. 3. AFM images for Co ion-implanted GaN with annealing temperature: (a) as-grown, and (b) 700 °C.

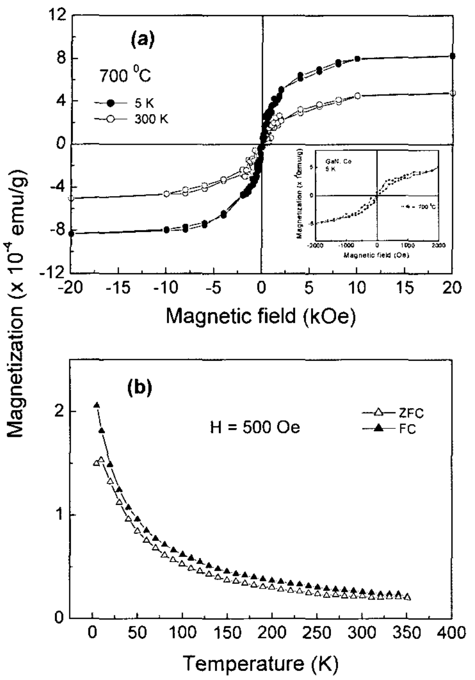

Fig. 4. (a) Magnetization curves at 5 and 300 K for samples annealed at 700 °C. (b) The temperature dependence of zero field-cooled (ZFC) and field-cooled (FC) magnetization measurements for samples annealed at 700 °C.

meter. Figure 4(a) and (b) show the magnetization curves obtained at 5 and 300 K and the temperature dependence of ZFC and FC magnetization for sample annealed at 700 °C. Inset of Fig. 4(a) shows expanded magnetization curve of sample in a low field region at 5 K. In these curves, the diamagnetic background of GaN substrate was subtracted. The magnetization curve at 5 K show clear ferromagnetic behavior with residual magnetization (M_R) and coercivity (H_c) of M_R = 5.98 × 10^{-3} emu/g and ~40 Oe for 700 °C annealed-samples. However, at room temperature, the ferromagnetic hysteresis of sample seems to have disappeared within the resolution of the measurements. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements at a applied field of 500 Oe were performed over the temperature range of 5-350 K. We have observed a cusp in the ZFC magnetization curve and a clear irreversibility of the two different conditions for the samples annealed at 700 °C. This ZFC and FC curve as well as magnetization curve of sample are characteristic of a superparamagnetic system [16]. From Fig. 4(b), the blocking temperature (T_B) was estimated to be about 10 K for the samples annealed at 700 °C.

When assigning the origin of ferromagnetism one must carefully consider magnetic impurity phase formation in DMS. In order to extract the information regarding chemical states of the elements, x-ray photoelectron

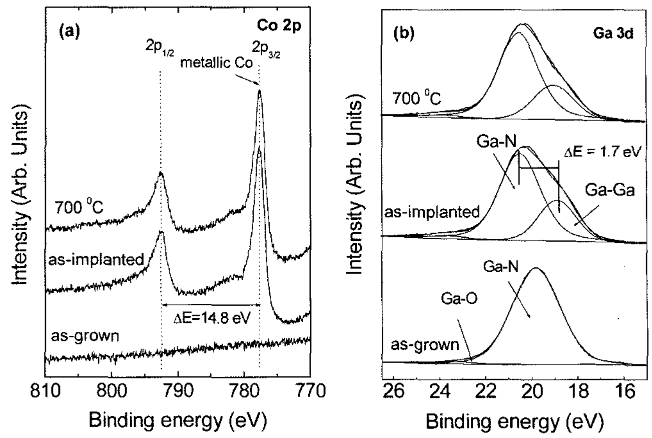

Fig. 5. Change in the XPS spectra for (a) Co 2*p* and (b) Ga 3*d* in Co ion-implanted and annealed GaN.

spectroscopy (XPS) were employed. The charge-shifted spectra were corrected using the adventitious C 1s photoelectron signal at 285 eV. Figure 5(a) and (b) show the change in XPS spectra of Co 2*p* and Ga 3*d* with annealing temperatures. XPS measurements of Co $2p_{3/2}$ core levels show only one peak at 777.6 eV for as-implanted and 700 °C-annealed samples, as shown in Fig. 5(a). The energy difference between Co $2p_{3/2}$ and Co $2p_{1/2}$ core level is 14.8 eV. This corresponds to the peak for metallic Co bonding [17]. The Ga 3*d* spectrum of the as-grown sample consists of Ga-N and Ga-O bonds are shown in Fig. 5(b). After Co implantation and post annealing, the spectrum showed asymmetry at the lower binding energy of the Ga-N bond. This means that an

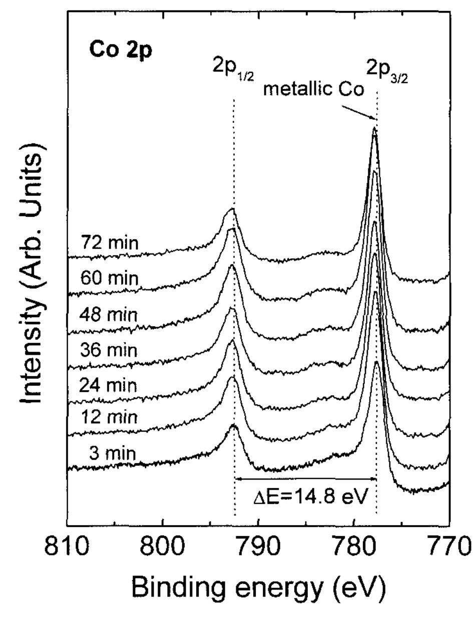

Fig. 6. Co 2*p* spectra measured by XPS with Ar sputtering time for sample annealed at 700 °C.

additional bonding is superimposed in the Ga 3*d* spectra. For the Co-implanted sample, the superimposed peak is attributed to metallic Ga atoms in GaN due to the implantation-induced loss of nitrogen atoms [18]. The difference of binding energy between Ga-N and Ga-Ga bonds is in good agreement with the reported value of 1.7 eV [17]. In order to observe the chemical states of implanted Co existing on the GaN inside, XPS depth measurement was carried out. Figure 6 shows the evolution of the Co 2*p* spectra with sputtering time. The binding energy of XPS spectrum corresponding to charge states of Co atom is observed at 778 eV for Co^0 and 781 eV for Co^{2+}, respectively. It was shown that only Co^0 is formed at the depth where Co was implanted. In terms of the microstructural point of view deduced from Fig. 5 and 6, the magnetic properties of our sample could be explained. It may be possible to consider the contribution from Co magnetic cluster for 700 °C annealed-samples.

4. Conclusion

Magnetic and structural properties of Co ion implanted GaN was investigated. No second phases were observed under our implantation and annealing condition. Films annealed at 700 °C showed superparamagnetic features. In terms of the microstructral point of view deduced from XPS measurements, it could be explained that magnetic property in our films originated from Co magnetic clusters.

Acknowledgments

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