Room-temperature diluted magnetic semiconductors \( p-(\text{Ga,Ni})\text{N} \)

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High concentration (5 at. %) Ni was incorporated into a chemical vapor deposition-grown GaN film by using a thin protecting Ni layer on top of the GaN film during ion implantation. After etching off the protecting layer, subsequent annealing up to 800 °C under flowing \( N_2 \) resulted in a \( p \)-type GaN with apparent ferromagnetic behavior up to \( \sim 320 \) K. In addition, the ferromagnetic behavior became more manifest with increasing annealing temperature that increases hole concentration. No presence of any other second phases nor clusters in the Ni-implanted region was identifiable, at least to the 0.2 nm point-to-point resolution of high resolution transmission electron microscopy. This novel indirect implantation process that being easy to implement appears promising for attaining room-temperature diluted magnetic semiconductors which are applicable to magnetotransport, magneto-optical and spintronics devices, among others. © 2005 American Institute of Physics.

Diluted magnetic semiconductors (DMSs) based on III-V semiconductors, fabricated by incorporating a proper concentration of magnetic ions, have attracted considerable attention in recent years because of the possibility involving charge and spin degrees of freedom in a single substance. It is expected to provide new functionality for microelectronic devices by exploiting the spin of charge carriers in the ferromagnetic semiconductors. Therefore, it is desirable to exhibit robust ferromagnetism with Curie temperature \( T_c \) above room temperature. Dietl et al.2 predicted, based on a Zener model, the possibility of ferromagnetism that GaN among the wide band-gap III-V semiconductors might have \( T_c \) values above room temperature. GaN itself also has many attractive advantages such as a large band gap, sustainable high-temperature and high-power operation, and the possibility of inclusion in visible and UV photonics.3

At present, there is no convincing results yet reported of room-temperature DMS out of GaN doped with ferromagnetic impurities, although a few studies on GaN-based DMS materials with low-temperature ferromagnetic behavior have been disclosed by using molecular-beam epitaxy4 or ion implantation5−7 to improve the typically low solubility of magnetic ions. Alternatively, ion implantation is a useful technique widely adopted nowadays in integrated circuit (IC) industries for incorporation of transition metal ions into a variety of semiconductors offering precise control of the species in both concentration and lateral distribution. Theodoropoulou et al.8 reported that transition metal ions such as Mn and Fe could be implanted into \( p \)-type GaN at doses up to the designed concentrations of 3−5 at. % resulted in ferromagnetic behavior after subsequent annealing. Meanwhile, the amorphization of the implanted area was avoided by holding the sample at \( \sim 350 \) °C during the implantation. Sato and Katayama-Yoshida9 predicted that the incorporation of the family of elements V, Cr, Mn, Fe, Co and Ni could induce ferromagnetism under the right conditions. Accordingly, Ni is also a potential acceptor in GaN and Ni ions could be easier to be extracted from target during ion implantation than other transition metals, such as Fe, Co and Mn.

In this letter, we report on the use of a thin protecting layer during implantation with Ni at a dose of \( 5 \times 10^{16} \) cm\(^{-2} \) and the study of corresponding magnetic and structural properties after subsequent annealing.

The GaN samples were grown by metal-organic chemical vapor deposition (MOCVD) on sapphire (\( \text{Al}_2\text{O}_3 \)) substrates. To avoid damaging effects during ion implantation, a 10 nm Ni thin film was pre-deposited on GaN by sputtering to serve as a protecting layer during ion implantation. Computer simulations using the transport-of-ions-in-matter (TRIM) software at the energy of 72 KeV showed that a top layer Ni with 10 nm thickness could shield most damages and still save sufficient concentration of ions with almost flat distribution for the first 40 nm. \( \text{Ni}^+ \) ions were implanted by using a Tandem (9SDH-2) accelerator for a long time (\( \sim 12.6 \) h) under an energy of 72 KeV to a dose \( 5 \times 10^{16} \) cm\(^{-2} \) that corresponds to average volume concentrations of 5 at. % in the top \( \sim 40 \) nm. The protecting Ni layer was subsequently etched away by using wet-etching process for the sake of avoiding the formation of secondary phases such as \( \text{Ni}_3\text{Ga} \) at the Ni/GaN interface during high-temperature annealing. Subsequent annealing was carried out at 500, 700, and 800 °C for 1 h, 15 min and 5 min, respectively, under flowing \( N_2 \) with the samples faced down. The structural properties of the implanted region were characterized using a high-resolution transmission electron microscope (HRTEM, JEOL 2010F) coupled with a Gatan energy filter (GIF), while magnetic properties and carrier concentration of these samples were studied by a superconducting quantum interference device magnetometer (SQUID, MPMS 5; under a field −0.2 to 0.2 T), and the van der Pauw measurement (EGK, HEM 2000; under a fixed field 0.5 T), respectively.

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TEM studies showed that a 5 at. % Ni-implanted GaN sample contained island-like Ni$_3$Ga grains enveloped with an amorphous region that arises from ion-implantation damages (figures not shown). The detailed analyses will be given elsewhere. It seemed that the high energy and long time ion bombardments decomposed some of the Ga–N bonding at the damaged zone and the decomposed N tended to escape from the surface due to the gaseous nature. As a consequence, the free Ga will react with Ni forming on the interface the nano-grain Ni$_3$Ga, which is a stable phase in the Ga–Ni binary phase diagram. In addition, the implanted region under island-like Ni$_3$Ga still held the initial wurtzite structure without any indication of other secondary phases despite of the relatively large density of lattice defects therein.

We then proposed the feasibility to lessen or to avoid the enormous defects generated by the ion implantation: a thin protecting layer the same material as the ion-implanting species (in this case Ni) atop the GaN surface. Reported hereafter are results from such a modified ion implantation. Figure 1(a) shows the cross-sectional TEM image and SAD analysis of a 5 at. % Ni-implanted GaN sample with the Ni protecting layer during ion implantation. Although implantation damages are still abundant, there are no obvious extra spots contributed from secondary phases, and only the streaking diffraction spots from the GaN hexagonal crystal structure are observed. The streaking diffraction spots are resultant from lattice defects caused by the damages of ion implantation, including dislocation loops or stacking faults, consistent with those reported by Pearaton et al.

The magnetic properties of the 5 at. % Ni-implanted GaN sample with subsequent annealing were investigated by the SQUID magnetometer. Figure 2 shows the magnetization versus magnetic field (M–H) curves at 5 K for the 5 at. % Ni-implanted GaN samples at the as-implanted, 500, 700 and 800 °C annealed states, respectively. Clearly, it depicts the enhanced magnetic property with increasing annealing temperature and the ferromagnetic behavior becomes most manifest after 800 °C annealing for 5 min. Typical magnetization (M) versus temperature (T) curves, field cooled (FC) and zero-field cooled (ZFC), were measured under an applied field 500 Oe for the 800 °C annealed sample as shown in Fig. 3. The ferromagnetic behavior is similar for both curves, and ferromagnetic hysteresis loops were obtained between 5 and 300 K as shown in the inset of Fig. 3. These results show, somewhat surprisingly, that the ferromagnetic contribution is present up to 300 K with an extrapolated Curie temperature of about 320 K.

Since the presence of ferromagnetism in a given III-V DMS material is sensitive to factors such as crystallinity, location of transition-metal dopant (substitutional or interstitial), the concentration, sign and magnitude of the charge carrier, the 5 at. % Ni-implanted GaN sample after 800 °C for 5 min annealing was further investigated in order to clarify crystallinity and carrier concentration. The cross-sectional HRTEM image and corresponding selective area diffraction (SAD) pattern for the 800 °C annealed sample, shown in Fig. 1(b), depict visibly much less stacking faults as indicated with an arrow, comparing with that of the as-implanted sample [Fig. 1(a)]. Furthermore, stacking fault density is roughly estimated from HRTEM image to give a more insight. The detailed description of such derivation, being the same method as that of a recent report, is given elsewhere. The estimated stacking fault density is about 3.2±0.5 extended defects per 100 nm$^2$, which is much lower than those of the as-implanted cases (13±3 extended defects per 100 nm$^2$). This reveals that the lattice structure is 77% recovered. Meanwhile, the single-crystalline wurtzite structure is identical to that of as-implanted sample. It also shows that not any clusters nor second phases are observable in the 5 at. % Ni-implanted GaN after 800 °C annealing for 5 min, at least to the resolution of HRTEM (0.2 nm point to point), and SAD analysis. Hence, the apparent ferromagnetic behavior is not attributed to superparamagnetism arisen from clusters within the sensitivity of HRTEM.

The possibility of ferromagnetic ordering in GaN-based semiconductor was predicted by Dietl et al. They considered the ferromagnetism to be mediated by delocalized or

**FIG. 1.** The cross-sectional HRTEM image and SAD analysis of a 5 at. % Ni-implanted GaN with the Ni protecting layer during ion implantation, (a) as-implanted and (b) postannealing (800 °C for 5 min).

**FIG. 2.** The magnetization vs magnetic field (M–H) curves at 5 K for the 5 at. % Ni-implanted GaN samples at as implanted and that annealed for 1 h at 500 °C (inset), annealed for 5 min at 700 °C (closed circle) and 800 °C (open circle), respectively.

**FIG. 3.** Typical magnetization (M) vs temperature (T) curves (FC: field cooled, ZFC: zero-field cooled) measured in an applied field of 500 G for the 800 °C annealed sample.
weakly localized holes in p-type materials. Hence, the type of carrier and carrier concentration are very important. Figure 4 shows the dependence of hole concentration for the 5 at. % Ni-implanted GaN samples. The Hall measurements under a fixed field 0.5 T revealed p-type GaN with a hole concentration which sharply increases with increasing annealing temperature. The hole concentration is $p = 10^{18}$ cm$^{-3}$ after annealing at 800 °C for 5 min. This indicates that the thin protecting layer during implantation stops not only the implantation defects, but also reduces greatly the decomposition of GaN, hence the incorporated Ni ions have the chance, during annealing (800 °C for 5 min for example), to contribute to the hole concentration. In analogy with the report of Wahl et al. for Fe implanted GaN, we expect that some fraction of Ga is substituted by Ni after implantation. Moreover, the postimplantation annealing assured the migration to the correct (cation) lattice site of most of the implanted dopant ions. If Ni occupies the Ga sites substitutionally and the valance of Ni is +2, a kind of Ni center will be formed in GaN, namely, the type of the neutral Ni center is $\text{Ni}^{2+}$ Ga$(3d^5) + e^{-}$, and thus mediates the characteristic of a ferromagnetic semiconductor through the delocalized hole. With increasing annealing temperature, more implanted Ni ions migrate to the cation lattice sites, resulting in higher hole concentration, and consequently the more mediated ferromagnetic property. The characterization done by using electron energy loss spectroscopy (EELS) also supports our suggestion. Calculation on the ratio of the integrated intensity counts for the $L_3$ and $L_2$ absorption edge of Ni, obtained from several different places in the Ni-implanted GaN film, leads to a valence state of +2. Detailed description of such derivation will be given elsewhere.

The theoretical treatment suggests that higher hole densities ($> 10^{20}$ cm$^{-3}$) are necessary for carrier-mediated ferromagnetism. Despite the hole density obtained experimentally ($< 10^{18}$ cm$^{-3}$) being lower than that theoretically predicted, we could not be blind to the observed enhancement of magnetic property related to the increasing hole concentration accompanying with subsequent annealing. Since the Curie temperature is expected to be a strong function of both the Ni ion concentration and the hole density, it would be necessary to have both values as high as possible. In our study, we consider the Ruderman–Kittel–(Kasuya)–Yosida (RKKY) model, which elucidates that the exchange interaction between nearest neighbor transition-metal ions is mediated by the carriers and gives rise to ferromagnetism.

Unexpectedly, our research led to an astonishing result that through our modified ion implantation, p-type GaN semiconductors, that have been feasible only by Mg doping during MOCVD growth of GaN films in technologies nowadays, become readily possible. This is extremely meaningful both in diluted magnetic semiconductors as well as in III-V IC industries.

In summary, by the use of a thin protecting layer during ion implantation, the 5 at. % Ni-implanted GaN exhibits obvious ferromagnetism above room temperature after annealing at 800 °C for 5 min. In addition, the ferromagnetic behavior becomes gradually manifest with increasing annealing temperature that in turn sharply increases hole concentration. There is not any evidence of secondary phases nor Ni clusters, at least to the sensitivity of a JEOL 2010F microscope (0.2 nm point to point) and SAD analyses. The discrepancy between the resultant hole concentration and the theoretical predicted optimum value sufficient to induce carrier-mediated ferromagnetism in Ni-implanted GaN requires further work to clarify. Future work should involve the trials to improve Curie temperature by increasing the hole concentration in the GaN and to explore the difference in the electronic properties around Ni atoms before and after annealing by using EELS, at the ferromagnetic state.

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