Ferromagnetic Properties in Diluted Magnetic Semiconductors (Al,Mn)N grown by PEMBE

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We present the structural, magnetic, and electrical properties in the (Al,Mn)N films with various *Mn* concentrations grown by plasma-enhanced molecular beam epitaxy. X-ray diffraction analyses reveal that the (Al,Mn)N films have the wurtzite structure without secondary phases. All (Al,Mn)N films showed the ferromagnetic ordering. Particularly, $(Al_{1-x}Mn_x)N$ film with $x = 0.028$ exhibited the highest magnetic moment per *Mn* atom at room temperature. Since all the films exhibit the insulating characteristics, the origin of ferromagnetism in (Al,Mn)N might be attributed to either indirect exchange interaction caused by virtual electron excitations from *Mn* acceptor level to the valence band within the samples or a percolation of bound magnetic polarons arisen from exchange interaction of localized carriers with magnetic impurities in a low carrier density regime.

Keywords : (Al,Mn)N, Diluted magnetic semiconductor, Wide bandgap semiconductor, Ferromagnetism, PEMBE

1. INTRODUCTION

Spintronics is expected to develop the new multi-functional devices which substitute conventional semiconductor devices, and make it possible to process the information faster and to consume the power lower than the conventional ones by controlling spin in addition to charge of carriers (electrons or holes) simultaneously[1,2]. Diluted magnetic semiconductors (DMSs) in the field of spintronics have attracted great attention and have been developed by incorporating the particular transition metals as magnetic dopants in conventional semiconductors. These materials can be applicable to the development of semiconductor spintronic devices such as spin-polarized light emitting diodes (spin LEDs)[3], spin-polarized field effect transistors (spin FETs)[4], spin-polarized resonant tunneling diodes (spin RTDs)[2] and quantum computers[1]. The theoretical studies predicted that (Ga,Mn)N should have a Curie temperature (T_C) above room temperature according to Zener model of carrier-induced ferromagnetism and the calculation based on the double exchange mechanism by Dietl et al.[5] and Sato et al.[6], respectively. Recently, several groups have successfully reported room-temperature ferromagnetism in (Ga,Mn)N[7-9]. On the other hand, Litvinov et al.[10] proposed theoretically that (Al,Mn)N might result in T_C higher than that of (Ga,Mn)N. In addition, AlN plays an important role for optoelectronic devices such as blue, violet, and ultraviolet (UV) LEDs and laser diodes (LDs) by alloying with GaN[11]. Also, it has been used as a tunnel barrier and an insulator for semiconductor-based devices. Therefore, AlN along with GaN is considered as a promising material for semiconductor spintronic devices. More recently, several groups have reported the growth and characterization in AlN-based DMSs[12,13]. For (Al,Mn)N, the indication of hysteresis were reported by Frazier et al.[13] but their magnetic moments were not saturated yet. In this paper, we report on the successful growth of ferromagnetic (Al,Mn)N films with various *Mn* concentrations by PEMBE and their magnetic properties. The (Al,Mn)N films were found to exhibit insulating characteristics and ferromagnetic ordering with T_C above room temperature. Also, we discuss the origin of ferromagnetism in (Al,Mn)N.

2. EXPERIMENT

The growth of the (Al,Mn)N films with various *Mn* concentrations was carried out in a PEMBE system under ultrahigh vacuum (UHV) conditions with a base

pressure of ~1 × 10^{-10} Torr. The source materials were high-purity *Al* (6N) and *Mn* (5N5) metals that were heated in conventional effusion cells, respectively. As the nitrogen source, high-purity nitrogen (6N) gas was supplied through a radio-frequency (rf) plasma source. For the epitaxial growth of (Al,Mn)N layers, 2 μm-thick undoped GaN templates on sapphire (0001), prepared by metalorganic chemical vapor deposition (MOCVD), were used as substrates. All the films were grown at the substrate temperature of 700 °C with *Al* cell temperature of 1200 °C. The *Mn* concentrations in the films were controlled by changing *Mn* cell temperatures from 700 °C to 800 °C, and were estimated to be 2.8 %, 3.2 %, and 4.0 %, respectively, as measured by secondary ion mass spectrometry (SIMS) which confirmed homogeneous distribution of *Mn* within the films. The thickness of the (Al,Mn)N films measured by a surface profiler was approximately 400 nm.

The crystalline quality and c-axis lattice constants of the (Al,Mn)N films was investigated by X-ray diffraction (XRD) analyses using *Ni*-filtered *Cu* K_α source. The magnetic properties were studied using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 5 – 300 K. The electrical properties were determined by van der Pauw Hall measurements at room temperature.

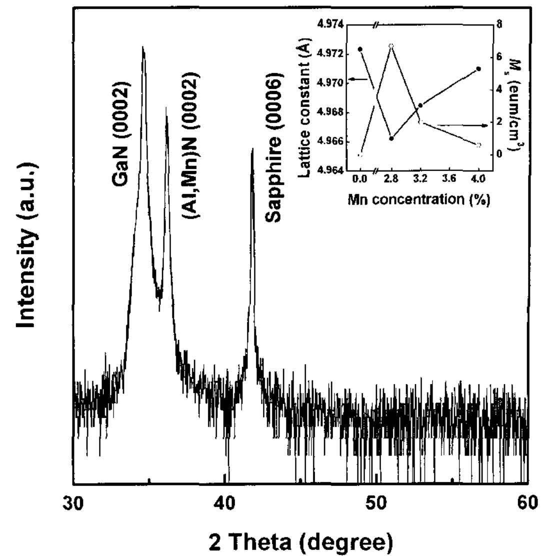

Fig. 1. Representative XRD pattern for the (Al,Mn)N films. The inset shows *c*-axis lattice constants determined by XRD analyses and saturation magnetizations at 5 K measured by SQUID magnetometer with magnetic fields applied parallel to the plane of the films as a function of *Mn* concentration.

3. RESULTS AND DISCUSSION

In order to investigate the structural properties for the (Al,Mn)N films with various *Mn* concentrations, XRD analyses were performed. Figure 1 shows the representative XRD pattern for the (Al,Mn)N films. Only the diffraction peak from wurtzite (Al,Mn)N (0002) was observed in addition to the peak from GaN (0002) and sapphire (0006). Furthermore, no additional peaks from secondary phases such as manganese nitrides and manganese clusters were found. The changes of *c*-axis lattice constants in the films are characterized using Bragg's law from the shift of XRD peak positions as a function of *Mn* concentration and the results are shown in the inset of Fig. 1. When *Mn* atoms enter into the AlN lattice, *c*-axis lattice constant decreases, indicating the introduction of *Mn* in substitutional sites[13]. As *Mn* concentrations increase over 3 %, *c*-axis lattice constants were found to expand. It is believed that *Mn* atoms do not effectively replace *Al* atoms located at the substitutional sites but partial *Mn* atoms are incorporated into the interstitial sites rather than the substitutional sites within the film. It is also confirmed from the variation of the saturation magnetizations (M_s) in magnetization versus magnetic field (*M-H*) curves at 5 K measured using SQUID magnetometer as shown in the inset of Fig. 1. As *Mn* concentrations increase, the saturation magnetizations decrease. As discussed in XRD results, *Mn* atoms which begin to locate at the interstitial sites with increasing *Mn* concentrations could cause the antiferromagnetic interaction, resulting in the deterioration of the effective magnetic moments. This tendency has been previously found in the case of (Ga,Mn)N[7]. Compared with the previous work[13], our (Al,Mn)N films seem to have higher *Mn* concentrations as deduced from *Mn* cell temperatures. Hence, the magnetic moments in our (Al,Mn)N were saturated and rather decreased with increasing *Mn* concentrations.

The magnetic properties for the (Al,Mn)N films with various *Mn* concentrations were investigated. Figure 2 shows *M-H* curves for the $(Al_{1-x}Mn_x)N$ films with (a) $x = 0.028$ and (b) $x = 0.032$ at room temperature. In addition, *M-H* curve for the sample with $x = 0.028$ at 5 K was shown in the inset of Fig. 2. The clear hysteresis loops for both films were obtained, indicating that the films exhibit the ferromagnetic ordering at room temperature. However, no hysteresis loop for the $(Al_{1-x}Mn_x)N$ film with $x = 0.040$ was observed, revealing that the film has T_C lower than room temperature owing to the enhanced antiferromagnetic interaction. In particular, for the $(Al_{1-x}Mn_x)N$ films with $x = 0.028$, the saturation magnetization and coercivity at 5 K were 6.7 emu/cm^3 and 69 Oe, respectively, and both at 300 K were smaller than those at 5 K. These saturation magnetizations are larger than those of (Al,Mn)N reported in the previous

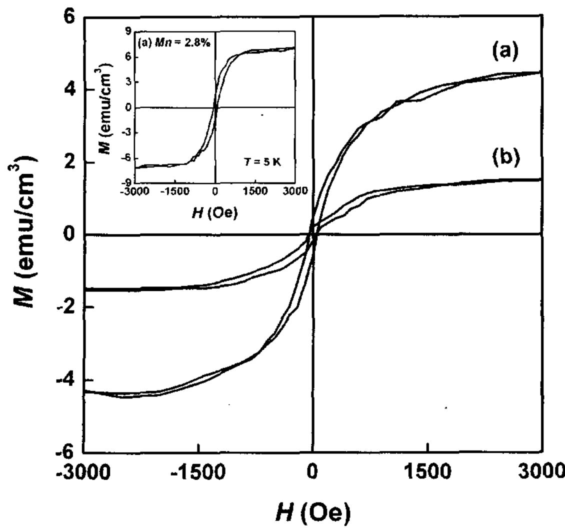

Fig. 2. Hysteresis loops for the $(Al_{1-x}Mn_x)N$ film with (a) $x = 0.028$ and (b) $x = 0.032$ at room temperature obtained by SQUID magnetometer with magnetic fields up to 3000 Oe applied parallel to the plane of the samples. The inset shows the hysteresis loop for the sample with $x = 0.028$ at 5 K. For the (Al,Mn)N films, the non-magnetic contributions of GaN templates and sapphire substrates and experimental apparatus have been subtracted from the data.

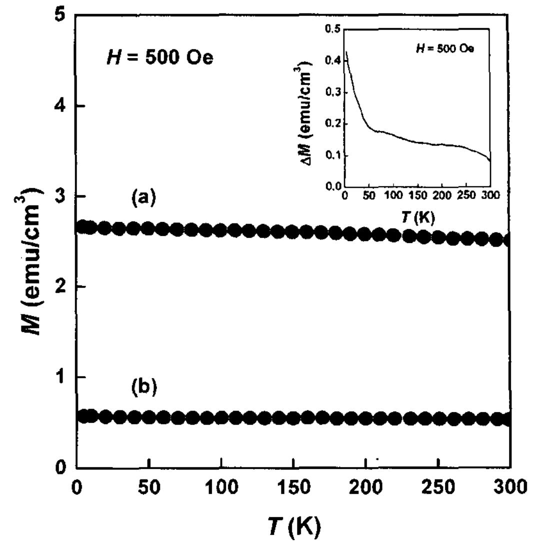

Fig. 3. Temperature dependence of FC magnetizations for the $(Al_{1-x}Mn_x)N$ films with (a) $x = 0.028$ and (b) $x = 0.032$ measured by SQUID magnetometer in a magnetic field of 500 Oe. The inset shows the difference (ΔM) between FC and ZFC magnetizations for the $(Al_{1-x}Mn_x)N$ film with $x = 0.028$ as a function of temperature in a magnetic field of 500 Oe.

work[12] and the effective magnetic moments calculated from M_s are 0.51 μ_B/Mn and 0.34 μ_B/Mn at 5 K and 300 K, respectively.

The temperature dependence of field-cooled (FC) magnetizations for the $(Al_{1-x}Mn_x)N$ films with (a) $x = 0.028$ and (b) $x = 0.032$ in a magnetic field of 500 Oe measured by SQUID magnetometer is shown in Fig. 3. The magnetizations for the (Al,Mn)N films decrease slowly and continuously without the abrupt drop as temperature increases. This behavior indicates that the (Al,Mn)N films obviously exhibit the ferromagnetic ordering in the temperature range 5 – 300 K and T_C of the films exceeds room temperature. The inset of Fig. 3 illustrates the difference ($\Delta M = M_{FC} - M_{ZFC}$) between FC and zero-field-cooled (ZFC) magnetizations for the $(Al_{1-x}Mn_x)N$ film with $x = 0.028$ as a function of temperature in a magnetic field of 500 Oe. This subtraction method points out the presence of hysteretic ferromagnetic regime if the difference is nonzero[14]. The (Al,Mn)N film obviously maintains nonzero magnetization over 300 K. It corresponds to the observation of hysteresis at room temperature in *M-H* curves.

The electrical properties in the (Al,Mn)N films were determined by van der Pauw Hall measurements at room temperature. The Ohmic contact to (Al,Mn)N films was made using indium. All the films exhibit highly resistive characteristics (~60 M-Ohm), indicating the insulating behaviors of the films. Therefore, the origin of ferromagnetism in (Al,Mn)N might not be attributed to carrier-mediated Ruderman-Kittel-Kasuya-Yosida(RKKY) interaction which is frequently reported in III-V and IV-VI DMSs such as (Ga,Mn)As[2] and PbSnMnTe[15], respectively. Another possible explanation for this ferromagnetism is due to the formation of secondary phases such as manganese nitrides and manganese clusters. However, the presence of such secondary phases in XRD measurements is not observed. These results demonstrate the feasibility that the ferromagnetic ordering in our insulating (Al,Mn)N comes from the intrinsic property. The other possible origin of the ferromagnetism is indirect exchange interaction caused by virtual electron excitations from *Mn* acceptor level to the valence band within the films[10]. Finally, it can be explained by a percolation of bound magnetic polarons arisen from exchange interaction of localized carriers with magnetic impurities in a low carrier density regime[16]. It has been used to understand the ferromagnetism in (Ga,Mn)As with low *Mn* concentration showing an insulating behavior[17]. However, it is still unclear and further studies including microstructure analyses are necessary to clarify the origin of ferromagnetism in (Al,Mn)N.

4. CONCLUSION

In summary, we have investigated the structural, magnetic, and electrical properties in (Al,Mn)N films with various *Mn* concentrations grown by PEMBE. XRD analyses did not identify the presence of any secondary phases within wurtzite (Al,Mn)N films. The lattice constants of *c*-axis determined by XRD measurements were found to decrease with increasing *Mn* concentrations, indicating the presence of the substitutional *Mn* atoms. The $(Al_{1-x}Mn_x)N$ films with $x = 0.028$ and $x = 0.032$ exhibited the ferromagnetic ordering with T_C above room temperature while the film with $x = 0.040$ showed the ferromagnetic ordering at 5 K. Considering that the (Al,Mn)N films show the insulating characteristics, the origin of ferromagnetism in our (Al,Mn)N might be due to either indirect exchange interaction caused by virtual electron excitations from *Mn* acceptor level to the valence band within the samples or a percolation of bound magnetic polarons arisen from exchange interaction of localized carriers with magnetic impurities in a low carrier density regime.

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