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研究の目的と方法 | Mn-AlN薄膜における低温フェルミオン磁性の有無の解析

結果 | フェルミオン磁性は未発見

考察 | フェルミオン磁性の発現に必要な条件を特定

結論 | Mn-AlN薄膜における低温フェルミオン磁性の発現が確認された


doi: 10.1109/TMAG.2008.2002366
Study on Absence of Room-Temperature Ferromagnetism in the Mn-AlN Films With Various Mn Concentrations

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We have investigated the magnetic behavior and structure of polycrystalline Mn-AlN (Al₁₋ₓMnxN) films with various Mn concentrations (x = 0.05–0.24) fabricated by reactive direct current (dc) magnetron sputtering. The magnetic behavior of these films depends on the Mn concentration x. The films with x = 0.05–0.10 show a paramagnetic behavior at 10–300 K. The film with x = 0.17 shows remanent magnetization and coercivity only at 10 K, while that with x = 0.24 shows an unknown magnetic behavior. Only wurtzite-type AlN phase is observed for x below 0.10. The coexistence of a wurtzite-type AlN phase and a secondary phase such as Al–Mn alloy, Mn-nitride, or Al–Mn–N ternary compound is observed for x = 0.17. The coexistence of a wurtzite-type AlN phase and a TiH₂-type Mn₆N₂ phase is observed for x = 0.24. From these results, it is concluded that the Al₁₋ₓMnxN films do not exhibit room-temperature (RT) ferromagnetism for all x. Moreover, it is likely that the ferromagnetic behavior observed at 10 K for x = 0.17 is caused by the secondary phase.

Index Terms—Magnetic semiconductors, Mn-AlN films, paramagnetic behavior, room-temperature (RT) ferromagnetism.

I. INTRODUCTION

DILUTED magnetic semiconductors (DMSs) have attracted much attention as the materials for spin electronics. In particular, InAs and GaAs doped with Mn exhibit carrier-induced ferromagnetism [1], [2], and their ferromagnetic properties can be controlled by an electric field [3] or light illumination [4], [5]. Many groups have investigated these DMSs from fundamental and technological points of view. However, it is difficult to apply these DMSs to electric devices that operate at room temperature (RT), because their Curie temperatures are much lower than RT [6]. Thus, discovering DMSs with ferromagnetism at RT is an important subject.

Recently, it has been reported that nitride semiconductors doped with Mn by reactive sputtering and molecular beam epitaxy exhibit ferromagnetism, and the Curie temperature is above 300 K for Mn-AlN [7], [8] and 940 K for Mn–GaN [9]. Some groups have suggested that these Mn-doped nitride semiconductors are one of the candidate materials for devices operating above RT. On the other hand, other groups have suggested that these materials do not exhibit ferromagnetism at RT [10], [11]. Thus, whether these materials exhibit ferromagnetism above RT remains to be elucidated. However, clear evidence of ferromagnetism above RT in these materials is yet to be reported.

In this study, we have investigated the magnetic behavior and structure of Mn-AlN (Al₁₋ₓMnxN) films with various Mn concentrations x. Similar magnetization curves were observed along several directions in the film plane and a direction perpendicular to the film plane. The magnetic behavior was observed up to 300 K. The magnetization of these films was measured using a superconducting quantum interference device (SQUID) magnetometer with a maximum field of 50 kOe in the temperature range of 10–300 K. The magnetic field was applied along several directions in the film plane and a direction perpendicular to the film plane to confirm magnetic anisotropy. The measured magnetization was measured by energy-dispersive X-ray analysis (EDX).

Fig. 1 shows the in-plane magnetization curves at 10 and 300 K for 250-nm-thick Al₁₋ₓMnxN films with various Mn concentrations x. Similar magnetization curves are observed along several directions in the film plane and a direction perpendicular to the film plane at 10 K (it is not shown here). This reveals that these films do not show any obvious anisotropy in the film plane and perpendicular to the film plane. The magnetization curves at 300 K do not show a remanent magnetization and coercivity for all x. Furthermore, the magnetization...
linearly increases with increasing magnetic field and no sharp change of magnetization is observed near zero magnetic field (see inset of Fig. 1). If these films contain ferromagnetic contribution that should show higher susceptibility than paramagnetic one before saturation, sharp change of magnetization near zero field should appear. Therefore, these observations reveal that the Al$_{1-x}$Mn$_x$N films do not exhibit ferromagnetism at 300 K for all $x$. The magnetization curves at 10 K vary with $x$. In the range of $x = 0.05$–0.10, the remanent magnetization and coercivity are not confirmed and the magnetization does not saturate at a magnetic field of 50 kOe. These results show that Al$_{1-x}$Mn$_x$N films do not exhibit ferromagnetism at 10 K for this range of $x$. For $x = 0.17$, remanent magnetization and coercivity are observed, which are 0.8 emu/cc and 0.9 kOe, respectively [see Fig. 1(f)]. However, the magnetization does not saturate at a magnetic field of 50 kOe. Thus, this magnetic behavior cannot be considered as a simple ferromagnetic behavior. This type of magnetization curve can be explained by a mix of ferromagnetic and paramagnetic behavior or a weak ferromagnetism observed in some antiferromagnet [12]. Furthermore, similar to those for $x = 0.05$–0.10, the remanent magnetization and coercivity are not observed for $x = 0.24$, and the magnetization does not saturate at a magnetic field of 50 kOe. Moreover, the magnetization of this film is lower than that of the films below $x = 0.17$. This reveals that the Al$_{1-x}$Mn$_x$N film does not exhibit ferromagnetism at 10 K for $x = 0.24$.

To more precisely investigate the magnetic behavior of the Al$_{1-x}$Mn$_x$N films, we measured the temperature dependence of dc susceptibility at a magnetic field of 10 kOe. The results are shown in Fig. 2. The dc susceptibility nearly corresponds to the initial susceptibility because the magnetization curves at 10 and 300 K (Fig. 1) are almost linear in the magnetic field range of ±10 kOe, except for the magnetization curve of the Al$_{0.975}$Mn$_{0.025}$N film at 10 K. In the $x$ range of 0.05–0.10, the dc susceptibility markedly decreases with increasing temperature. This behavior is considered to obey Curie–Weiss law because these curves can be fitted by inversely proportional function (shown as broken line). This reveals that the magnetic behavior of the Al$_{1-x}$Mn$_x$N films is paramagnetic for $x = 0.05$–0.10 in the temperature range of 10–300 K. For $x = 0.17$, the dc susceptibility increases with increasing temperature up to 20 K. This behavior excludes the possibility of a mix of ferromagnetic and paramagnetic behavior because the dc susceptibility of these magnetic behaviors does not increase with increasing temperature. The dc susceptibility decreases with increasing temperature above 20 K for $x = 0.17$. This suggests that the magnetic behavior of the film becomes paramagnetic above 20 K. Furthermore, for $x = 0.24$, the dc susceptibility increases up to 40 K and decreases above 40 K. However, the dc susceptibility is relatively low and the change in dc susceptibility with temperature is small. Therefore, the magnetic behavior of the film with $x = 0.24$ cannot be determined using only the results from this study.

Fig. 3 shows the grazing-incidence X-ray diffraction profiles of 250-nm-thick Al$_{1-x}$Mn$_x$N films with various Mn concentrations $x$. In the range of $x$ below 0.17, the diffraction peaks are observed around the diffraction angles $2\theta$ of 35.9°, 65.6°, 94.4°, and 125.5°, which are derived from würtzite-type AlN.
and MnN films, respectively. There-
show antiferromagnetism and MnN, respectively. The peak po-
films are MnN, which is derived from würtzite-type AlN,
are observed. In addition to these
Mn phases, 62.3, 0.24, diffraction rings
phase might be Al–Mn alloy, Mn-nitrides, or Al–Mn–N ternary
of bulk würtzite-type AlN and bulk ThH₂-type Mn₃N₂.

To observe the structures more precisely, TEM was utilized. Fig. 4 shows selected-area diffraction patterns of 50-nm-thick Al₀ₓMnₓN films with varying x. For all x, ring patterns are observed. This reveals that the Al₀ₓMnₓN films are polycrystalline. For x = 0.05, diffraction rings derived from würtzite-type AlN (10\(\bar{2}0\)), (00\(\bar{2}2\)), (11\(\bar{2}0\)), (10\(\bar{3}3\)), (21\(\bar{3}0\)), (21\(\bar{3}1\)), and (30\(\bar{3}0\)) are observed. In addition to these rings, for x = 0.06 and 0.10, the diffraction rings derived from würtzite-type AlN (10\(\bar{2}2\)), (11\(\bar{2}2\)), (20\(\bar{2}1\)), and (20\(\bar{2}2\)) are also observed. For x = 0.17, not only the diffraction rings derived from würtzite-type AlN, but also a diffraction ring is observed between the diffraction rings derived from AlN (10\(\bar{3}1\)) and (10\(\bar{2}2\)). This ring is considered to originate from a secondary phase. Furthermore, for x = 0.24, diffraction rings derived from würtzite-type AlN as well as those derived from ThH₂-type Mn₃N₂ are observed.

First, we discuss the structure of the Al₀ₓMnₓN films. For x below 0.10, only würtzite-type AlN phase is confirmed using XRD and TEM observation. However, a possibility of the existence of Mn-rich fine particles below the detection limit of XRD and TEM cannot be excluded completely. For x = 0.17, an existence of the secondary phase is observed. The secondary phase might be Al–Mn alloy, Mn-nitrides, or Al–Mn–N ternary compound. Al–Mn alloy forms various phases. Most of these phases show paramagnetism at RT. The Al–Mn alloy containing 0.5–0.6 at. % Mn shows ferromagnetism [13]. For Mn-nitrides, MnN and Mn₃N₂ show antiferromagnetism and Mn₄N shows ferrimagnetism [14]. Al–Mn–N ternary compound is not reported. For x = 24, it is clear that the Al₀.70Mn₀.24N film has ThH₂-type Mn₃N₂ phase, which shows antiferromagnetism with a Neel temperature of 925 K. Finally, we should note that our films are polycrystalline. Thus, the crystalline quality of our films is different from the films grown by MBE [7], which might relate to the difference of magnetic behavior.

Fig. 4. Selected-area diffraction patterns of 50-nm-thick Al₀ₓMnₓN films with various Mn concentrations.
Next, we discuss the origin of the magnetic behavior in the Al$_{1-x}$Mn$_x$N films from a structural point of view. For $x$ below 0.10, we can consider two possibilities as the origin of paramagnetic behavior: one is Mn ions incorporated into wurtzite-type AlN and the other is Mn-rich particles with superparamagnetism [15] below the detection limit of XED and TEM observation. For $x = 0.17$, it is concluded that the magnetic behavior of this film is attributed to the secondary phase. For example, antiferromagnetic nanoparticles of NiO and Cr$_2$O$_3$ are reported to show similar magnetic behavior [16], [17]. Such particles show weak ferromagnetism in low-temperature region. Furthermore, for $x = 0.24$, it is considered that the low magnetization and weak temperature dependence of the dc susceptibility are due to the magnetic behavior of the antiferromagnetic Mn$_3$N$_2$ phase.

IV. CONCLUSION

We have investigated the magnetic behavior and structure of polycrystalline Mn-AlN (Al$_{1-x}$Mn$_x$N: $x = 0.05$–0.24) films with various Mn concentrations $x$. The Al$_{1-x}$Mn$_x$N films do not exhibit RT ferromagnetism for all $x$. For $x$ below 0.10, a paramagnetic behavior is observed in the temperature range of 10–300 K. For $x = 0.17$, a magnetic behavior that shows remanent magnetization and coercivity is observed at 10 K. This behavior changes to a paramagnetic one near 20 K as the temperature increases. This magnetic behavior is attributed to the secondary phase described below. For $x = 0.24$, the magnetization is low and the change in dc susceptibility with temperature is small compared with those of films with lower $x$. Only wurtzite-type AlN phase is confirmed for $x$ below 0.10. The coexistence of a wurtzite-type AlN phase and a secondary phase such as Al–Mn alloy, Mn-nitride, or Al–Mn–N ternary compound is observed for $x = 0.17$. The coexistence of a wurtzite-type AlN phase and a ThH$_2$-type Mn$_3$N$_2$ phase is observed for $x = 0.24$.

ACKNOWLEDGMENT

This work was supported in part by an Exploratory Research and Encouragement of Young Scientists (B) from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was also supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research—The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was also supported in part by Strategic Information and Communications R&D Promotion Programme (SCOPE) from the Ministry of Internal Affairs and Communications (MIC). The authors would like to thank Y. Takatsu, K. Yamamoto, and S. Sato of Rigaku Corporation for performing the grazing-incidence X-ray diffraction analysis.

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