Study on magnetic behavior and structure of V-doped AlN films

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Abstract. Magnetic behavior and structure of V-doped AlN (Al₁₋ₓVₓN) films with various V concentrations (x = 0.03 – 0.36) were studied. These films exhibit paramagnetic behavior in the temperature range of 10 – 300 K for all x. These films have only wurtzite-type AlN phase for the range of x below 0.20. For x of 0.36, coexistence of wurtzite-type AlN phase and secondary phase is observed.

1. Introduction
Nitrides doped with various transition metals have attracted much attention as a candidate of spintronics device materials, since TM-doped AlN and GaN (TM = V, Cr, Mn) have been reported to exhibit ferromagnetism at room temperature [1-4]. Some groups have suggested that the ferromagnetism of these materials is intrinsic ferromagnetism originated from carrier-induced ferromagnetism or double exchange mechanism based on theoretical investigation [5, 6]. On the other hand, recently, other groups have demonstrated that the ferromagnetism is due to the formation of secondary phase in host semiconductor [7, 8] or that these materials do not show ferromagnetism at room temperature [9]. Thus, the magnetic behavior at room temperature of these materials is controversial. In particular, for V-doped AlN, there are few reports. K.Y.Ko et al. have reported that V-doped AlN exhibits ferromagnetism at room temperature and the coercivity is 21 Oe [1]. However, their investigation of magnetic behavior was restricted to low magnetic field range below 0.5 kOe and high temperature range above 240 K. The magnetic behavior of V-doped AlN in high magnetic field range and low temperature range remains unclear.

In this study, we prepared V-doped AlN (Al₁₋ₓVₓN) films (x = 0.03 – 0.36) using DC magnetron sputtering and investigated the magnetic behavior and structure of these films. In particular, the magnetic behavior was measured in the magnetic field range of ±50 kOe and the temperature range of 10 – 300 K.

2. Experimental procedure
The V-doped AlN (Al₁₋ₓVₓN) films were fabricated by reactive dc magnetron sputtering onto a thermal oxidized Si (001) substrate at room temperature. The base pressure was better than 9 × 10⁻⁷ Pa. The
Ar and N$_2$ mixture pressure was kept at 0.5 Pa and the mixture ratio was 1:1. The thickness of the films was 250 nm and 50 nm. The V concentration $x$ was varied from 0.03 to 0.36. The V concentration was measured by X-ray photoelectron spectroscopy (XPS).

The magnetic behavior of these films was investigated by superconducting quantum interference devices (SQUID) magnetometer with a maximum magnetic field of 50 kOe in the temperature range from 10 K to 300 K. The magnetic field was applied along the film plane. The structure of these films was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

Magnetization curves at 10 K and 300 K of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$ are shown in Fig. 1. For all $x$, remanent magnetization and coercivity are not observed at each temperature. The magnetization increases almost linearly with increasing magnetic field up to 50 kOe and does not saturate. These results reveal that the Al$_{1-x}$V$_x$N films do not exhibit ferromagnetism at 300 K and even at 10 K. Furthermore, the gradient of magnetization curves increases monotonically with increasing $x$. This shows that the magnetic behavior observed in this study is clearly originated from V doped to the Al$_{1-x}$V$_x$N films.

![Magnetization curves at 10 K and 300 K of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$.](image1.png)

**Figure 1.** Magnetization curves at 10 K and 300 K of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$.

![Temperature dependence of magnetization at the magnetic field of 10 kOe of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$.](image2.png)

**Figure 2.** Temperature dependence of magnetization at the magnetic field of 10 kOe of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$. 

In order to more precisely investigate the magnetic behavior of Al$_{1-x}$V$_x$N films, the magnetization at the magnetic field of 10 kOe was measured as a function of temperature in the range of 10 – 300 K. As shown in Fig. 2, for all $x$, the magnetization decreases markedly as temperature increases up to 100 K and becomes almost zero above 100 K. This behavior is considered to obey Curie-Weiss law. From these results, it is found that the Al$_{1-x}$V$_x$N films exhibit a paramagnetic behavior in the temperature range of 10 – 300 K for all $x$.

High-angle XRD profiles of 250-nm-thick Al$_{1-x}$V$_x$N films with various $x$ are shown in Fig. 3. In every case, several diffraction peaks derived from the thermal oxidized Si (001) substrate are observed. In addition to these peaks, for all $x$, the diffraction peaks derived from wurtzite-type AlN (10T0) and (0002) are observed at the diffraction angles $2\theta$ between 30$^\circ$ and 40$^\circ$. These peak positions are changed with $x$. For $x$ of 0.03, the diffraction peaks derived from wurtzite-type AlN (0004) and (0006) are also observed at around the diffraction angles $2\theta$ of 75$^\circ$ and 133$^\circ$. These peak positions shift to lower angle than that of bulk-AlN. From these results, it is clear that the Al$_{1-x}$V$_x$N films have wurtzite-type AlN phase for all $x$. The diffraction peak derived from wurtzite-type AlN (0002) becomes broad and the diffraction peak derived from wurtzite-type AlN (10T0) becomes sharp as $x$ increases up to 0.10. For $x$ above 0.10, the diffraction peak derived from wurtzite-type AlN (0002) becomes sharp and the diffraction peak derived from wurtzite-type AlN (10T0) becomes broad as $x$ increases. This suggests that the crystallographic orientation of these films changes from preferred c-axis orientation to coexistence of a-axis and c-axis orientation, and further to preferred c-axis orientation as $x$ increases.

![Figure 3](image-url)

**Figure 3.** High-angle XRD profiles of 250-nm-thick Al$_{1-x}$V$_x$N films with various V concentrations $x$. The broken lines denote the peak positions of bulk AlN and bulk Si.

In order to clarify the structure of the Al$_{1-x}$V$_x$N films in more detail, selected area diffraction patterns were taken as shown in Fig. 4. For all $x$, diffraction rings derived from wurtzite-type AlN (10T0), (0002), (10T1), (10T2), (1120), (1122), (2022), (2131) and (3030) are observed. In addition, for $x$ of 0.36, it slightly becomes bright between the diffraction rings derived from wurtzite-type AlN (10T1) and (10T2). This suggests that the Al$_{0.64}$V$_{0.36}$N film have a secondary phase. However, we cannot determine a species of secondary phase using only the results from this study.

Because the Al$_{1-x}$V$_x$N films have only wurtzite-type AlN phase for $x$ below 0.20, the paramagnetic behavior shown in Fig. 1 and Fig. 2 is considered to be caused by a paramagnetism of V ions.
incorporated into wurtzite-type AlN phase for $x$ below 0.20. This suggests that the magnetic interaction between V ions incorporated into wurtzite-type AlN phase is weak. For $x$ of 0.36, the secondary phase is considered to be formed in wurtzite-type AlN phase. However, the influence of the secondary phase on the magnetic behavior is not clear. This is considered that the secondary phase shows only weak magnetization. For example, the NaCl-type VN shows weak Curie-Weiss-type and Pauli-type paramagnetic behavior and the magnetization is small [10].

4. Conclusion
We investigated the magnetic behavior and structure of V-doped AlN ($\text{Al}_{1-x}\text{VN} : x = 0.03 – 0.36$) films fabricated by reactive dc magnetron sputtering. The paramagnetic behavior is observed at 10 – 300 K for all $x$. These films have only wurtzite-type AlN phase for the range of $x$ below 0.20. For $x$ of 0.36, coexistence of wurtzite-type AlN phase and secondary phase is observed.

Acknowledgements
This work was partly supported by an Exploratory Research and Encouragement of Young Scientists (B) from the Japanese Ministry of Education, Culture, Sports, Science and Technology. This work was also partially supported by “Priority Assistance of the Formation of Worldwide Renowned Centers of Research – The 21st Century COE program (Project: Center of Excellence for Advanced Structural and Functional Materials Design)” from the Japanese Ministry of Education, Culture, Sports, Science and Technology. The authors would like to thank Professor Shinji Fujimoto of Osaka University for performing the XPS measurement.

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