Differences in structure and magnetic behavior of Mn-AlN films due to substrate material

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Abstract. The structure and magnetic behavior of Mn-AlN (Al1-xMnxN, x = 0.03, 0.04) films deposited on thermally oxidized Si (001) substrates and sapphire (0001) substrates were studied. Mn-AlN films deposited on each substrate had a wurtzite-type AlN phase with a preferentially oriented c-axis. Mn-AlN films that were deposited on Si (001) substrate exhibited paramagnetic behavior. In addition to paramagnetic behavior, weak ferromagnetic behavior with Curie temperatures higher than room temperature were observed for Mn-AlN films deposited on sapphire (0001) substrates.

1. Introduction
Diluted magnetic semiconductors (DMSs) have attracted much attention as materials for spin-dependent electronic devices. In particular, Mn-AlN films are promising DMSs because of their ferromagnetic behavior at room temperature [1]. Recently, we reported a Mn-AlN film deposited on a thermally oxidized Si (001) substrate that did not show ferromagnetic behavior but did show paramagnetic behavior [2]. This difference might be related to a difference in the substrate material because a ferromagnetic Mn-AlN has previously been deposited on a sapphire (0001) substrate [1]. However, the effect of substrate material on the structure and magnetic behavior of the Mn-AlN film was not investigated in detail.

In this study, we investigate the structure and magnetic behavior of Mn-AlN (Al1-xMnxN, x = 0.03, 0.04) films deposited on thermally oxidized Si (001) substrates and sapphire (0001) substrates. In particular, we discuss the difference in magnetic behavior which is due to the difference in the substrate materials.

2. Experimental procedure
Mn-AlN (Al1-xMnxN, x = 0.03, 0.04) films were fabricated by reactive dc magnetron sputtering onto thermally oxidized Si (001) substrates and sapphire (0001) substrates at substrate temperatures (Ts) of
573 K and 773 K. The base pressure was better than $5 \times 10^{-7}$ Pa. The pressure of the Ar and N$_2$ mixture was kept at 0.5 Pa and the mixture ratio was 1 : 1. The thickness of the films was 250 nm.

The structure of these films was characterized by X-ray diffraction (XRD). The magnetic behavior of these films was investigated by a superconducting quantum interference devices (SQUID) magnetometer. The valence state of Mn was estimated using X-ray photoelectron spectroscopy (XPS). The Mn concentration was measured by energy-dispersive X-ray analysis (EDX).

### 3. Results and Discussion

High-angle XRD profiles of Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates are shown in Figure 1. In addition to diffraction peaks of the substrate, diffraction peaks from a wurtzite-type AlN (0002) and (0004) were observed in each case. Although, the diffraction peak derived from the wurtzite-type AlN (0006) was not observed for Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates at a substrate temperature ($T_s$) of 773 K. This result shows that Al$_{1-x}$Mn$_x$N ($x = 0.03, 0.04$) films deposited on these substrates have a wurtzite-type AlN phase with a preferentially oriented c-axis.

To investigate the crystallographic orientation in the film plane, we obtained pole figures of AlN(1011) for the Al$_{0.96}$Mn$_{0.04}$N films that were deposited on thermally oxidized Si (001) substrates and of Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates. For Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates, the intensity increased slightly at $\chi = 28^\circ$ regardless of $\phi$. This result suggests that Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates have a random orientation in the film plane. On the other hand, the intensity increased at $\chi = 28^\circ$ and $\phi = 110, 170^\circ$ for Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates. To determine the epitaxial relationship between Al$_{0.97}$Mn$_{0.03}$N films and their sapphire (0001) substrates, we used the pole figure of Al$_2$O$_3$(1123) as shown in Figure 2(e). In this pole figure, a high intensity is observed at the same $\phi$ as AlN(1011). This indicates that Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates have an epitaxial relationship of AlN[1010] // Al$_2$O$_3$[1120].

The temperature dependence of magnetization at a magnetic field of 5 kOe for Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates are shown in Figure 3. In every case, the magnetization decreased markedly with increasing temperature. This result indicates that Al$_{1-x}$Mn$_x$N ($x = 0.03, 0.04$) films deposited on all substrates exhibit paramagnetic behavior. However, relatively high magnetization is still apparent for Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates at 300 K.
To more precisely investigate the magnetic behavior of Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates, the magnetization curves at 300 K were measured as shown in Figure 4. For Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates, no sharp change in magnetization ((a) and (b)) was observed near the zero magnetic field. This suggests that Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates do not exhibit ferromagnetic behavior at 300 K. On the other hand, for Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates, a sharp change in magnetization ((c) and (d)) was observed in the magnetic field range of ±1 kOe. This suggests that Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates exhibit ferromagnetic behavior in addition to paramagnetic behavior.

Figure 2. Pole figures of AlN(1011) for (a), (b) Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and (c), (d) Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates. (e) Pole figure of Al$_2$O$_3$(1123) for Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates.

Figure 3. Temperature dependence of magnetization for (a), (b) Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and (c), (d) Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates.

Figure 4. Magnetization curves at 300 K for (a), (b) Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates and (c), (d) Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates.
To discuss the origin of the difference in magnetic behavior, the valence state of Mn was confirmed by XPS as shown in Figure 5. The binding energy of Mn 2p$_{3/2}$ in Al$_{0.97}$Mn$_{0.03}$N films that were deposited on sapphire (0001) substrates is slightly lower than that in Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates. This reveals that the valence of Mn decreases when the substrate is changed from a thermally oxidized Si (001) substrate to a sapphire (0001) substrate. The change in ferromagnetic behavior that was caused by the change in valence state of Mn has been reported for Mn-GaN [3]. Our results are similar to their results. For this study, however, the existence of a secondary phase of fine particles below the detection limit of XRD cannot be completely ignored. Therefore, we considered this possibility. Possible secondary phases are antiferromagnetic Mn$_6$N$_5$, Mn$_3$N$_2$, Mn$_2$N and ferrimagnetic Mn$_4$N. Among these materials, ferrimagnetic Mn$_4$N which has a low valence of Mn is the possible origin of ferromagnetic behavior.

4. Conclusion
We investigated the structure and magnetic behavior of Mn-AlN (Al$_{1-x}$Mn$_x$N, $x = 0.03, 0.04$) films deposited on thermally oxidized Si (001) substrates and sapphire (0001) substrates. Al$_{0.96}$Mn$_{0.04}$N films deposited on thermally oxidized Si (001) substrates are paramagnetic while Al$_{0.97}$Mn$_{0.03}$N films deposited on sapphire (0001) substrates are a mix of ferromagnetic and paramagnetic. This difference might be related to the difference of the valence state of Mn due to the substrate material.

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