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We report the magnetic properties of Cr-doped AlN thin films grown by reactive magnetron sputtering under various nitrogen pressures. Ferromagnetism is observed up to the highest temperature measured, 400 K, and shows strong dependence on the Cr concentration and, especially, the nitrogen growth pressure. By varying the nitrogen pressure during film growth, the magnetic properties of the films can be changed while keeping a constant Cr concentration. The ferromagnetism is enhanced in the films that were grown at low nitrogen pressures and thus nitrogen deficient, suggesting an important role of defects in the ferromagnetism of this material. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1940131]

There is currently intense interest in ferromagnetic semiconductors (FS), since they hold unique potential for spintronics applications.[1,2] The most studied system is GaMnAs, but its Curie temperature, T_C, is far below room temperature. Following theoretical predictions,[3] many efforts have been made toward FS with high T_C, and room-temperature ferromagnetism has been observed in doped oxides and nitrides, such as ZnO,[4] TiO$_2$,[5] SnO$_2$,[6] and GaN.[7]

Recently high-temperature ferromagnetism has also been observed in AlN-based materials,[8–13] and T_C of Cr-doped AlN has been reported to be over 900 K.[12,13] Different values of saturation moment were reported in the Cr-doped AlN films fabricated by sputtering,[8,12] molecular beam epitaxy,[9,13] and ion implantation,[10] suggesting that the magnetic properties may be sensitive to the film-growth conditions. Compared to the experimental progress, the theoretical understanding of the high-temperature ferromagnetism is still rather limited. Carrier-mediated ferromagnetism[3] applied in GaMnAs does not apply to the high-temperature FS systems such as doped AlN[11] and GaN.[14] More detailed investigations of the effect of film-growth conditions will be helpful for better understanding of the ferromagnetism in these high T_C FS.

In this letter we report the effect of nitrogen growth pressure on the ferromagnetism in Cr-doped AlN (Al$_{1-x}$Cr$_x$N$_y$, referred as AlCrN hereafter) thin films grown by reactive magnetron sputtering. Ferromagnetism is observed with T_C over 400 K, and it strongly depends on the Cr concentration and the nitrogen growth pressure. The films grown at lower nitrogen pressures are more deficient in nitrogen, and show larger magnetic moments.

AlCrN thin films were grown on Si substrates at ambient temperature by reactive magnetron sputtering of pure Al and Cr targets under a mixed Ar and N$_2$ atmosphere. During sputtering, the N$_2$ partial pressure was adjusted, while the Ar partial pressure was fixed at 5 mTorr, with the N$_2$/Ar pressure ratio P_N/P_{Ar} varying from 0.5 (low N$_2$ pressure) to 2.0 (high N$_2$ pressure). The film thickness was about 50 nm. The sample compositions were measured by energy dispersive x-ray spectroscopy and x-ray photoemission spectroscopy (XPS). Structure characterization by electron diffraction clearly indicated that the AlCrN films are polycrystalline with hexagonal wurtzite structure. Transport measurement revealed a semiconducting behavior with resistivity increasing dramatically with decreasing temperature.

Magnetic properties of the AlCrN thin films were measured with a superconducting quantum interference device magnetometer (Quantum Design, MPMS XL). The diamagnetic background from the Si substrate was subtracted from the total magnetization data. Ferromagnetic behavior was observed up to the highest temperature measured, 400 K, in all films with Cr concentration x ranging from 0.05 to 0.25. Figure 1 shows a typical magnetization curve at 300 K of an AlCrN film with $x=0.15$ grown at a P_N/P_{Ar} of 0.5. It shows
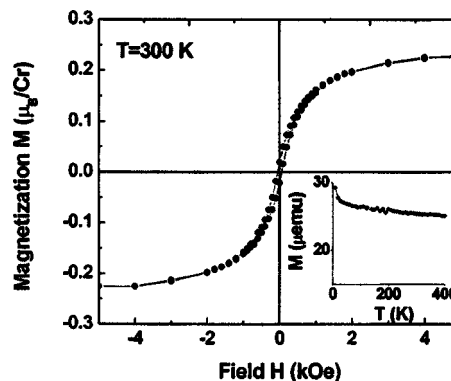

FIG. 1. Hysteresis loop at 300 K of AlCrN thin film with $x=0.15$ grown at a P_N/P_{Ar} of 0.5. The inset shows the temperature dependence of magnetization for the same sample measured at 5000 Oe.

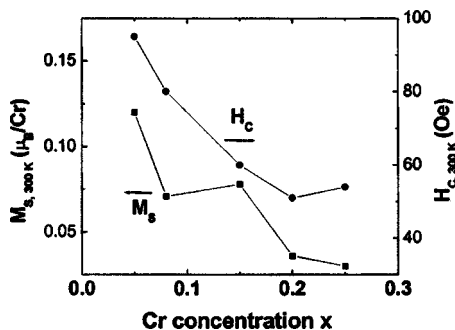[a)]Author to whom correspondence should be addressed; electronic mail: dsellmyer@unl.edu

FIG. 2. Cr concentration dependence of the saturation magnetic moment and coercivity at 300 K for AlCrN films grown at a P_N/P_{Ar} of 1.0.

FIG. 3. Hysteresis loops at 300 K for the AlCrN thin films ($x=0.15$) grown at varied P_N/P_{Ar}.

a well-defined hysteresis loop with a coercivity of 50 Oe and a saturation moment M_S of 0.23 μ_B/Cr.

The inset of Fig. 1 shows the temperature dependence of the magnetization measured at 5000 Oe for the same sample. With temperature increasing, the magnetization gradually decreases, without any ferromagnetic transition up to the highest temperature measured, 400 K. The tendency of magnetization decreasing suggests that T_C is much higher than 400 K. It has been shown that T_C of Cr-doped AlN is probably near 1000 K.[12,13] No observation of a magnetic transition as the temperature approaches 400 K indicates absence of the CrO_2 phase, which has a T_C at 390 K. This is important regarding the origin of the high-temperature ferromagnetism, which has been a concern in AlCrN.[9,10,12] The absence of the CrO_2 phase is further confirmed by XPS measurement. The XPS spectrum of Cr in the AlCrN films (not shown here) showed a peak for Cr $2p_{3/2}$ at 575.6 eV, close to the reference value of 575.7 eV for CrN, but definitely different from those of CrO_2 (576.3 eV) and Cr (574.3 eV). These results indicate that no detectable amount of CrO_2 or Cr phase formed in the sample.

The magnetic properties of the AlCrN thin films strongly depend on the Cr concentration. Figure 2 shows the saturation magnetic moment at 300 K, $M_{S, 300 K}$, and the coercivity at 300 K, $H_{C, 300 K}$, of AlCrN films grown at a P_N/P_{Ar} of 1.0 as functions of Cr concentration. In general, as Cr concentration increases from 0.05 to 0.25, both $M_{S, 300 K}$ and $H_{C, 300 K}$ gradually decrease. In this Cr concentration range, the dependence of saturation magnetic moment on the Cr concentration is consistent with previous reports,[12,13] and may indicate enhanced antiferromagnetic coupling at higher Cr concentrations.[12] The decreasing of coercivity at higher dopant concentration has also been observed in the GaMnAs system.[15]

Notably, the ferromagnetism of AlCrN films shows strong dependence on the nitrogen growth pressure. The magnetic moment is significantly enhanced in the films grown at relatively low nitrogen pressures. Plotted in Fig. 3 are the hysteresis loops measured at 300 K for AlCrN thin films with a fixed Cr concentration ($x=0.15$) but grown at different P_N/P_{Ar}. As P_N/P_{Ar} decreases from 2.0 to 0.5, i.e., nitrogen growth pressure decreases, the saturation magnetization increases significantly, while the coercivity almost does not change. Moreover, the conductivity of the films also increases with reducing the nitrogen growth pressure. The saturation moment and conductivity measured at room temperature (300 K) are plotted in Fig. 4 as functions of P_N/P_{Ar}. As P_N/P_{Ar} decreases, both saturation moment and conduc-
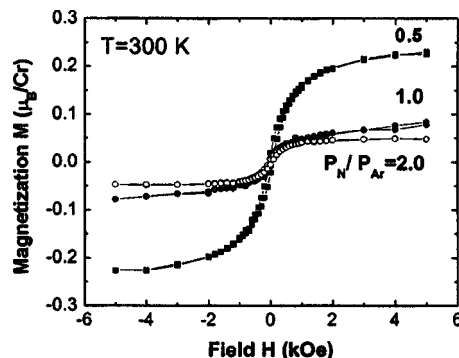
tivity increase, with a large increase occurring as P_N/P_{Ar} decreases from 1.0 to 0.5.

The change of transport properties with nitrogen growth pressure has been clarified by measuring nitrogen concentrations in the AlCrN films through XPS analysis. In the film grown at $P_N/P_{Ar}=2.0$, the ratio of N/(Al,Cr), y, is 1.0; while in the film grown at $P_N/P_{Ar}=0.5$, y is 0.7, indicating considerable nitrogen deficiencies. Although more accurate techniques would be helpful to detect the absolute value of nitrogen concentrations, considering the 5% experimental error of XPS, it is reasonable to believe that the AlCrN films grown under lower N_2 pressure are more deficient in nitrogen. Nitrogen deficiency could result in defects such as N vacancies and/or Al interstitials and produce additional electrons. So the films grown under lower N_2 pressure may have more electrons and higher conductivity than those grown under higher N_2 pressure. However, in n-type wurtzite AlN, the nitrogen vacancy has a high formation energy and is a deep donor, and therefore, this defect cannot make a significant contribution to the n-type conduction.[16,17] Other defects such as Al interstitials are also deep donors.[16] So, even in nitrogen-deficient AlCrN films, most defect-generated electrons may localize at or be trapped by the defects, and hence the concentration of itinerant electrons would be very low. This is confirmed by the carrier density data determined from Hall measurements using the van der Pauw configuration. All AlCrN films studied here are n type. The electron concentration and mobility are shown in the inset of Fig. 4 as functions of P_N/P_{Ar}. The electron mobility is in the range of 5–15 cm^2 V^{-1} s^{-1}. Although the electron concentration of the films increases as the P_N/P_{Ar} decreases, the highest concen-
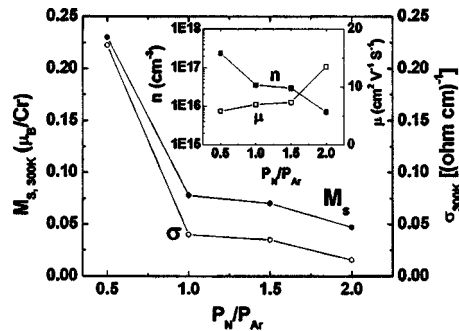

FIG. 4. P_N/P_{Ar} dependence of saturation magnetic moment (M_S) and conductivity (σ) at 300 K for AlCrN films ($x=0.15$). Inset: P_N/P_{Ar} dependence of carrier concentration (n) and mobility (μ) at 300 K for AlCrN films ($x=0.15$).

tration is still as low as 10^{17} cm^{-3}. The features of deep defect levels and low carrier densities in the AlCrN system make the carrier-mediated model of ferromagnetism unlikely for this material,[8,11–13] since this theory requires high concentration of free carriers.[3,18,19]

Although the nitrogen deficiency does not create significant numbers of free carriers, the induced defects and localized carriers may play a role in the ferromagnetism in AlCrN films. Recently, Kaminski and Das Sarma,[20] and Coey and co-workers[21–23] have proposed bound magnetic polaron models for ferromagnetism in poorly conducting semiconductors or oxides. The models associate bound magnetic polarons with localized carriers in extended Bohr orbits, and ferromagnetism is predicted to occur at the polaron percolation threshold. In the model of Coey and co-workers,[21–23] the bound magnetic polarons consist of electrons surrounding defects, such as oxygen vacancies, which trap electrons and form F centers, and the Bohr orbital radius of polaron is $\gamma\alpha_0$ (α_0 is the Bohr radius and γ is defined as $\varepsilon m_e/m^*$, where ε is the high-frequency dielectric constant, m_e is the electron mass, and m^* is the electron effective mass[22,23]). This bound magnetic polaron model may be applicable to AlCrN, in which the role of nitrogen vacancies in AlCrN is similar to that of oxygen vacancies in oxides. According to this model,[23] in the case of wurtzite AlN, the Bohr orbital radius of the associated polaron is about 8.5 Å, and the polaron percolation threshold is 0.1%, suggesting that ferromagnetism could occur in AlCrN with about 0.1% of the nitrogen sites being vacant. Although they are not expected to occur in very high concentrations, nitrogen vacancies should exist in the nitrogen-deficient AlCrN films to some extent which could satisfy the percolation threshold. As the nitrogen growth pressure decreases, the nitrogen vacancy concentration should increase, enhancing the polaron percolation and hence the ferromagnetism.

In Co-doped TiO_2 system, it was found that reducing oxygen growth pressure created Co clusters, and therefore, increased the magnetic moment and conductivity.[24,25] But a similar phenomenon involving Cr clusters in the AlCrN films appears to be unlikely. Bulk Cr is antiferromagnetic. A chemical mapping image (not shown here) for Cr in AlCrN films obtained by electron energy loss spectroscopy showed a uniform Cr distribution, ruling out the presence of Cr clusters with nanometer or larger size. Although large magnetic moment in atomic size Cr clusters has been predicted, it has not been confirmed experimentally.[26] Even if this kind of small cluster existed, one would expect to observe superparamagnetism, instead of the ferromagnetism as we show here. In addition, CrN or Cr_2N clusters, if present, would not contribute to the observed ferromagnetism, because CrN is antiferromagnetic and Cr_2N is not ferromagnetic between 85 and 500 K.[27] Thus, the presence of Cr clusters cannot be the source of the enhanced ferromagnetism in AlCrN films grown at low nitrogen pressures.

In summary, ferromagnetism was observed above room temperature in AlCrN thin films. The magnetic properties of AlCrN films strongly depended on the Cr concentration, and especially, the nitrogen growth pressure. The ferromagnetism was significantly enhanced in the nitrogen-deficient thin films that were grown under lower nitrogen pressure. The results suggest that defects like nitrogen vacancies with their associated bound magnetic polarons may play an important role in the ferromagnetism of AlCrN films.

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