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Epitaxial growth and magnetic properties of Cr-doped AlN thin films

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Abstract

Cr-doped AlN thin films were epitaxially grown on Al_2O_3*(*001*)* substrates at low-temperature by reactivemagnetron sputtering,and their magnetic properties were investigated. Extensive x-ray diffraction studies indicated that the films have a wurtzite-type hexagonal structure and are (001) oriented, with an epitaxial relationship of the [100] direction of the films along the [110] direction of Al_2O_3. The *c* axis lattice parameter of the films showed a linear dependence on the Cr concentration for Cr concentrations below 0.15. Room temperature ferromagnetism was observed, and the magnetic properties showed strong dependence on the Cr concentration over a wide range.

Ferromagnetic semiconductors are attracting increasing interest due to their potential applications in spintronic devices. Ferromagnetic semiconductors with Curie temperatures well above room temperature are of special interest from the viewpoints of both fundamental research and practical applications. Following theoretical predictions [1], high temperature ferromagnetism has recently been reported in doped oxides and nitrides, such as ZnO [2], TiO_2 [3], SnO_2 [4], GaN [5], and AlN [6].

AlN is one of the most promising materials for optoelectronic devices, and the realization of high temperature ferromagnetism in AlN-based materials makes it attractive for multifunctional devices. It has been reported that Cr-, Co-, and Mn-doped AlN are ferromagnetic at temperatures above 300K [6–12]. So far, Cr-doped AlN films have been grown on Si, sapphire, and SiC substrates by magnetron sputtering [6, 7], MBE [8, 9, 12], or ion implantation [10]. Notably, the solubility of Cr in AlN is much higher than that of Mn, especially in films grown at low temperatures [8]. The Cr concentration in Cr-doped AlN has been reported as high as 30% [6], which is much higher than that of Mn in the well-studied GaMnAs [13], and low substrate temperatures could favour the incorporation of Cr into AlN[8]. The high solubility of transition metals in semiconductor matrices could facilitate modulating the magnetic properties of these materials. However, there has been no systematic study of the structure and magnetic properties of Cr-doped AlN thin films with varying Cr concentrations over a wide range. In this paper, we report epitaxial growth of Cr-doped AlN thin films on sapphire substrate at low temperature by reactive magnetron sputtering, and the evolution of structure and magnetic properties with Cr concentration changing over a wide range from 0 to 20%.

Cr-doped AlN thin films, $Al_{1-x}Cr_xN$ (denoted as Cr-AlN), with x varying from 0 to 0.20, were grown on Al_2O_3*(*001*)* substrates by reactive magnetron sputtering. The base pressure of the sputtering chamber is 2×10^{-7} Torr. During sputtering the pressure of the nitrogen and argon mixture atmosphere was maintained at 0.01 Torr, and the substrate temperature was kept at 400ºC. The films are about 100 nm thick. Energy dispersive x-ray spectroscopy (EDS) was used to measure the Cr concentrations. Because the sampling depth of EDS (0.1–2 μm) is greater than the film thickness, the Al signal from the Al_2O_3 substrate would be included in direct measurements of the Cr/Al ratios of the films grown on Al_2O_3 substrate. Therefore, Si substrates were also loaded in the sputtering chamber to simultaneously prepare reference samples. The Cr concentrations of the Cr-AlN films on Si substrates were measured, and we assumed that the Cr-AlN films simultaneously grown on Al_2O_3 substrates had the same or similar Cr concentrations.

Various x-ray diffraction (XRD) techniques were used to study the structural properties of the films. θ–2θ diffraction patterns showed that all Cr-AlN films are of single phase with wurtzite structure and c axis oriented. A typical θ–2θ diffraction pattern of a Cr-AlN thin film with $x = 0.10$ is shown in **figure 1(a)** (top). Besides the diffraction peaks from the Al_2O_3 substrate (see the bottom figure of figure 1(a)), only (002) and (004) peaks from a wurtzite-type AlN hexagonal structure appeared. Figure 1(b) plots the c axis lattice parameter, c, as a function of the Cr concentration x. As x changes from 0 to 0.15, c increases almost linearly, obeying Vegard's law. This is consistent with the fact that the ion radius of Cr is larger than that of Al, and suggests that Cr does indeed enter into the lattice of AlN and occupy the Al site. The linear dependence of c on the Cr concentration does not persist as x increases beyond 0.15, probably indicating a solubility limit of Cr in AlN around 15%, although no detectable second phase has been observed in the sample with $x = 0.20$ according to XRD. The high solubility of Cr in AlN obtained here is almost twice that of Mn in GaAs. Compared with Mn, Cr also has higher solubility in AlN [8]. It has been found that the incorporation of transition metal dopants in AlN decreases as the substrate temperature increases [8]. The low film growth temperature used in this work is believed to be favourable for the incorporation of Cr into AlN.

The structural features of Cr-AlN films were further studied by means of XRD using the phi scan and pole figure modes. A typical (100) phi scan of Cr-AlN thin films (**figure 2**(a)) shows six diffraction peaks with 60º spacing in between, confirming the sixfold symmetry of the hexagonal structure. The sixfold hexagonal symmetry was also confirmed by the (102) pole figure shown in figure 2(b). These XRD results clearly demonstrated that high quality Cr-AlN films were epitaxially grown on the Al_2O_3(001*)* substrates. The phi scans of the Cr-AlN film (100) and the Al_2O_3 substrate (110) (not shown here) indicate that the [100] direction of Cr-AlN is aligned with the [110] direction of the Al_2O_3 substrate, consistent with a previous report [14]. The unit cell of Cr-AlN rotates by 30º along the c axis compared with that of Al_2O_3, with [100] of Cr-AlN parallel to [110] of Al_2O_3. The lattice mismatch between the [100] direction of AlN and the [110] direction of Al_2O_3 is 13.29%. To explain the epitaxial growth, Sun *et al* [14] proposed a crystallographic model of the epitaxial relationship between AlN films and Al_2O_3 substrate, in which an extended atomic distance mismatch is just 0.70% between eight times the Al–Al atomic distance of AlN and nine times the Al–Al distance of Al_2O_3.

Magnetic properties of Cr-AlN films were measured with a superconducting quantum interference device (SQUID) magnetometer. The diamagnetic contributions from the Al_2O_3 substrate to the total magnetization were subtracted. Room temperature ferromagnetism has been observed in all Cr-AlN films. Figure 3 shows the magnetization versus magnetic field curves for the Cr-AlN *(*$x = 0.05$*)* films at 5 and 300 K. Well-defined open hysteresis loops were observed at both temperatures, with considerable coercive field and remanence. At 5

K, the coercive field is about 355 Oe, and the saturation moment is about 0.08 μ_B/Cr. Both the saturation magnetization and the coercive field decreased as temperature increased to 300 K. The weak temperature dependence of the magnetization below 300 K is quite consistent with the previous report [7], and suggests that the Curie temperature is well above 300 K. T_C above 900 K has been reported [7, 9].

The Cr concentration dependence of the magnetic properties was investigated. As shown in figure 4, as the Cr concentration increases, both the effective magnetic moment per Cr atom (μ_{Cr}) and the coercive field (H_C) measured at 300 K gradually decrease. Similar dependences of magnetic properties on the magnetic dopant concentration have been observed

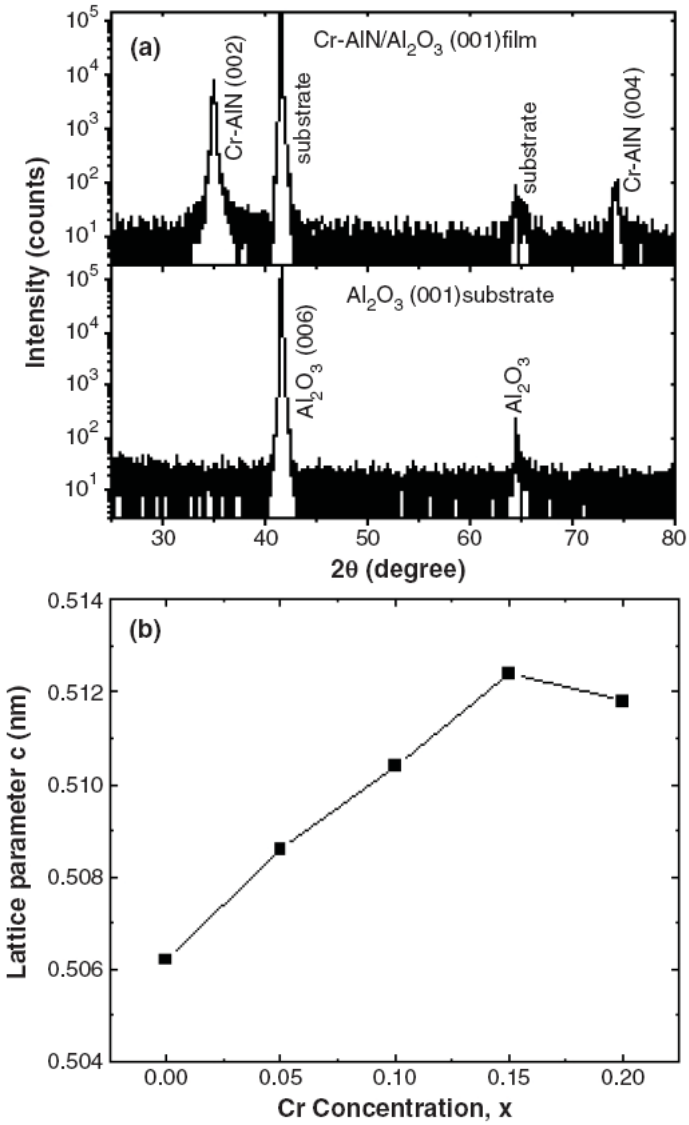

Figure 1. (a) X-ray diffraction patterns (θ–2θ scan) of a Cr-AlN *(x* = 0.10*)* film on Al_2O_3(001*)* substrate (top) and an Al_2O_3(001*)* substrate (bottom). In the Cr-AlN film, the peak around 65° is from the Al_2O_3 substrate, because it also appears in the XRD pattern of the Al_2O_3(001*)* substrate. (b) *c* axis lattice parameter *c* of Cr-AlN film as a function of Cr concentration.

in other magnetic semiconductor systems, such as Mn-doped GaAs [13], Mn-doped GaN [15], and Co-doped SnO_2 [4]. In [15], Mn-doped GaN showed lower magnetic moment at higher Mn content, which was attributed to the presence of increasing interstitial Mn due to a low Mn solubility limit of only 3%. In the Cr-AlN films reported here, the solubility of Cr is much higher (~15%). Although the possibility of the existence of interstitial Cr for $x < 0.15$ cannot be excluded, the Cr concentration dependence of the lattice parameter suggests that for $x < 0.15$, Cr mainly goes into substitutional sites, and for $x > 0.15$, Cr may mainly go into other sites. Therefore, we speculate that for $x < 0.15$, the amount of interstitial Cr (if any exists) is not expected to increase significantly as x increases, and the reduced magnetic moment at higher Cr concentrations may be mainly attributed to enhanced antiferromagnetic coupling between neighbouring substitutional Cr ions [7]; however, as $x > 0.15$, the amount of interstitial Cr may increase significantly, which further reduces the average moment. The low magnetic moment suggests that only a very small fraction of Cr contributes to the ferromagnetic ordering. The magnetic moments in our samples are in good agreement with the results observed by Kumar *et al* [7] for their Cr-AlN thin films grown by reactive sputtering at conditions similar to ours, but lower than those obtained for the films grown by the molecular beam epitaxy method [8, 9]. Film growth conditions (e.g., base pressure and growth pressure) may affect the defect states in the films and hence, as discussed below, their magnetic properties.

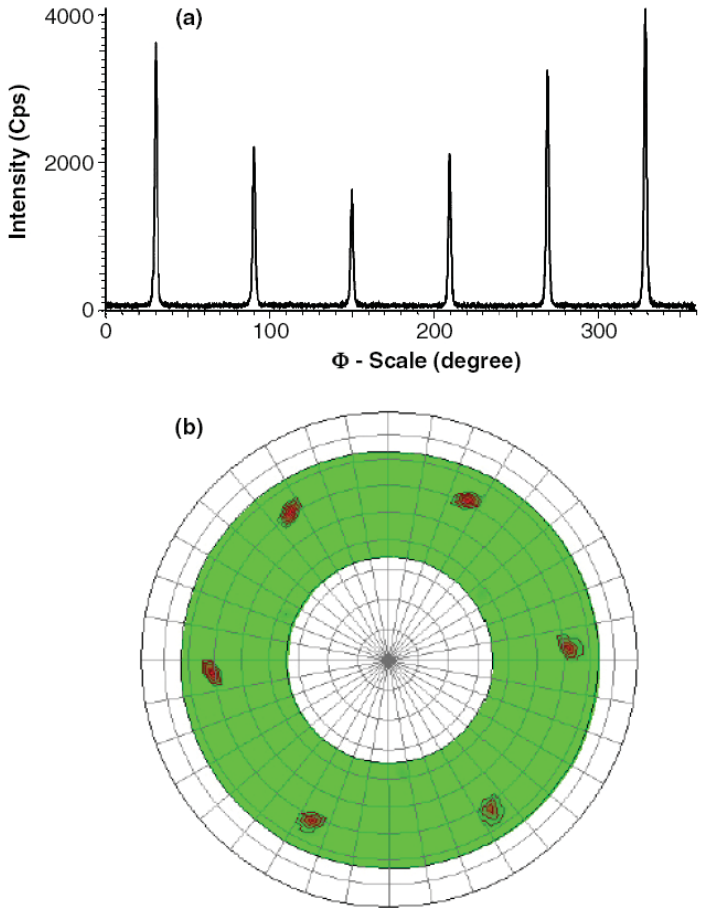

Figure 2. X-ray diffraction (100) phi scan (a) and (102) pole figure (b) of a Cr-AlN *(x* = 0.10*)* film.

The carrier-mediated ferromagnetism [1] that is well accepted for Mn-doped GaAs does not seem to be applicable in nitride [9, 10, 16] and oxide [17] systems. A double-exchange mechanism was suggested for the ferromagnetism in nitrides such as Cr-AlN [9]. Recently, Kaminski and Das Sarma [18] and Coey and co-workers [17, 19, 20] have proposed bound magnetic polaron models for ferromagnetism in poorly conducting semiconductors. Ferromagnetic exchange in dilute ferromagnetic oxides and nitrides is suggested to be mediated by localized electrons that form bound magnetic polarons, which overlap to create a spin-split impurity band. Ferromagnetism is predicted to happen at the polaron percolation threshold. The bound magnetic polarons consist of electrons surrounding defects, such as oxygen

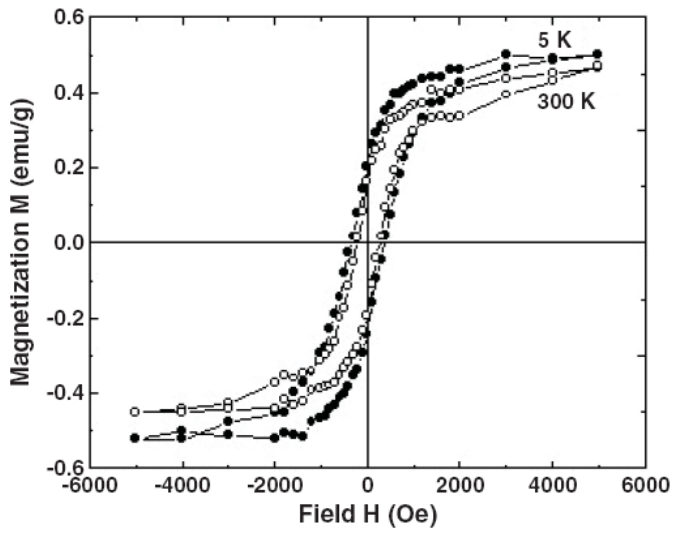

Figure 3. Hysteresis loops of one Cr-AlN film ($x = 0.05$) measured at 5 and 300 K.

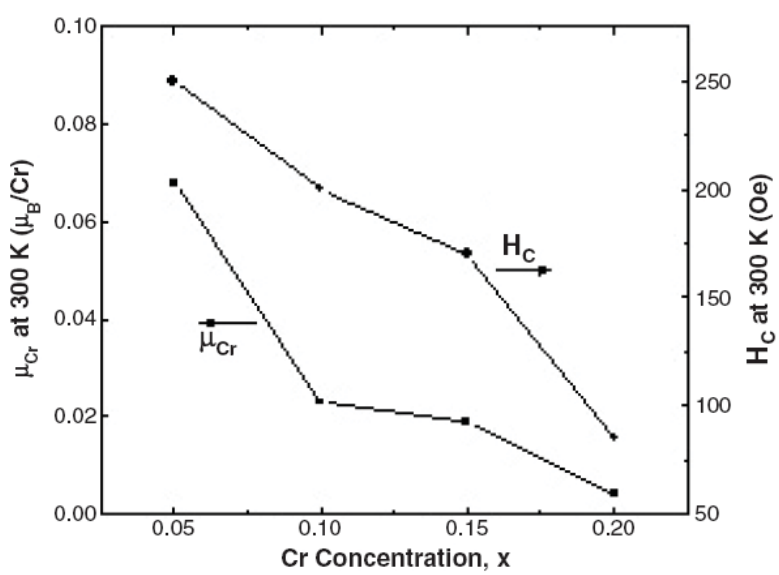

Figure 4. Cr concentration dependence of the effective magnetic moment (μ_{Cr}) and coercive field (H_C) at 300 K for the Cr-AlN films.

or nitrogen vacancies, and the Bohr orbital radius of the 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) [19, 20]. In the case of Cr-AlN, the Bohr orbital radius of polarons would be about 8.5 Å. Obviously, defects such as anion vacancies have important roles in the formation of the magnetic polarons, and hence the ferromagnetism. Taking this model into account may help us to understand the different magnetic moments obtained in the Cr-AlN films grown at different conditions as mentioned above.

In summary,we have grown ferromagnetic Cr-doped AlN films epitaxially on Al_2O_3(001*)* substrates at low temperature. The films were of wurtzite-type hexagonal structure and *c* axis oriented with the [100] direction along the [110] direction of Al_2O_3. The solubility limit of Cr in AlN is around 15%. Room temperature ferromagnetism was observed in the films, and the magnetic properties showed strong dependence on the Cr concentration in a wide range.

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