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Structural, magnetic and nanomechanical properties in Ni-doped AlN films

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ABSTRACT

Synthesis and characterization of structural, magnetic and nanomechanical properties of Ni-doped AlN films deposited by magnetron sputtering are reported. The films exhibited ferromagnetism with a Curie temperature above 400 K. The observed room temperature saturation magnetization tended to decrease with increasing Ni concentration, which has the maximum 4.56 emu/cm^3. The nanomechanical analysis testified that the degradation of crystalline quality in the films with high Ni content results in the decreasing hardness, Young's modulus and slight decrease of friction coefficient. $Al_{1-x}Ni_xN$ films for $x = 0.021$ exhibited favorable nanomechanical properties and outstanding ferromagnetism which confirm the possible application in spin electronics.

1. Introduction

Dilute magnetic semiconductor (DMS) materials have been attracting considerable interest for their potential applications in the field of spintronic and nonvolatile storage [1,2]. Ferromagnetic semiconductors with Curie temperature (T_c) above room temperature are of special interest from the viewpoints of both fundamental research and practical applications [3,4]. Following theoretical predictions [5], high temperature ferromagnetism (FM) has recently been reported in doped oxides and nitrides, such as ZnO [6,7], TiO_2 [8], SnO_2 [9], GaN [10], and AlN [11]. Among them, AlN possesses attractive advantages such as direct-wide band gap (6.2 eV), high thermal conductivity (2.85 W/cm K), and high breakdown field ($1.2–1.8 \times 10^6$ V/cm) [12].

Recently high-temperature FM has also been observed in transition metals doped AlN host semiconductors. Cr-doped AlN films with a T_c higher than 900 K was reported by Kumar et al. [13]. Nonmagnetic element, Cu, doped AlN film with $T_c \sim 360$ K has been experimentally observed by Ran et al. [14]. In previous studies, ferromagnetic Ni-doped GaN and ZnO films with T_c above room temperature have been successfully synthesized both by reactive sputtering and by pulsed-laser deposition, which suggesting Ni dopant can induce ferromagnetic in non-ferromagnetic semiconductors. And room-temperature ferromagnetic behaviors in Ni-doped AlN nanostructure and polycrystalline powders have been reported [15,16].

Moreover, the successful fabrication of devices based on the epitaxial AlN thin films requires better understanding of the mechanical characteristics in addition to its electrical performances, since the contact loading during processing or packaging can significantly degrade the performance of these devices [17,18]. Consequently, there is a growing demand of investigating the mechanical characteristics of materials, especially in the nanoscale regime, for device applications.

In the present investigation, we report on the magnetic and nanomechanical characteristics of room temperature ferromagnetism (RTFM) in $Al_{1-x}Ni_xN$ films synthesized by reactive sputtering. RT-magnetism, favorable mechanical properties and strong adhesion with the substrate of Ni-doped AlN films are reported. The effects of Ni concentration on the ferromagnetic and nanomechanical properties were investigated. The origin of RTFM the Ni-doped AlN films was also discussed in detail.

2. Experimental

The thin film samples of composition $Al_{1-x}Ni_xN$ ($x = 0.021$, 0.047, 0.064, and 0.082) were deposited on *p*-type (100) Si substrate by reactive sputtering from Al and Ni purity 99.999% targets in a sputtering system (GJP 450). $Al_{1-x}Ni_xN$ films were prepared by alternatively depositing AlN and Ni films. A constant partial gas pressure ratio of Ar:N_2 = 2:3 with a total pressure of 0.5 Pa and a RF power of 150 W was applied for depositing AlN film. A sputtering pressure of pure Ar gas with 0.5 Pa was applied for doping Ni with the RF power of 60 W. The base pressure in the chamber was below 2.0×10^{-4} Pa and the substrate temperature was held on 300 °C. The

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thickness of Ni doping and AlN film is about 5–10 nm and 100 nm, respectively, for each layer. The whole films had a thickness of about 600 nm. The dopant concentration of Ni was controlled by varying the sputtering time, which was 15 min for AlN film and 2–8 s for Ni doping, respectively. Both the beginning and the end of the layers are AlN films to prevent Ni atoms from permeation to substrate and oxidation.

The dopant concentration of Ni was determined by X-ray fluorescence (XRF, XRF 1800). Structural properties were characterized by field emission scanning electron microscopy (SEM, JSM-7100F), X-ray diffraction (XRD, D8 Advance) and atomic force microscope (AFM, Nanoscope IIIA). Photoluminescence (PL) spectra of the samples were collected at RT excited by the 250 nm line of a Xe lamp as excitation source at RT. The magnetic property was performed on a superconducting quantum interference device magnetometer (SQUID, MPMS XL-7) which features a sensitivity of 10^{-8} emu. Nanomechanical properties including nanohardness and scratch were measured by Nanoindenter (Hysitron TI 950). The hardness (H) and Young's modulus (E) of $Al_{1-x}Ni_xN$ films were determined adopting Oliver and Pharr model from the load–displacement curves with a diamond Berkovich indenter tip. During the nanoscratch tests, the load was ramped from 0 to 8 mN in 10 s and the scratch length was set as 15 μm with spherical indenter. The coefficient of friction was calculated by dividing the lateral force encountered during the scratch by the normal force. At least 5 independent indents and scratches were conducted for each sample. An in situ imaging analysis was used to observe the surface morphologies around the scratch marks after the nanoscratch.

3. Results and discussion

Cross-sectional SEM image of the 2.1 at.% Ni-doped specimen indicates that the monolayer and homogeneity structure of AlN films, as shown in Fig. 1(a). Fig. 1(b) shows the typical XRD pattern for $Al_{1-x}Ni_xN$ thin films with different Ni concentrations deposited on p-type (100) Si substrate. There is only one sharp peak, corresponding to (100) of the AlN structure in the pattern, which indicates all the films has the hexagonal wurtzite structure without any other impurity phases such as NiN, Ni_2N_3, NiO, Ni_2O_3 or Ni clusters. The lattice constants a as a function of Ni contents are shown in Table 1. It can be seen from the table that the (100) peak position shifts to higher angles as Ni concentration from 2.1 to 8.2 at.% and the lattice parameter, a, slightly shrinks with the increase of Ni doped concentration, probably due to the Ni substitution for Al. This tendency has been found in Si-doped AlN films and provides the clear evidence that the doping ions were incorporated into the substitutional sites in the AlN structure [19]. However, the tendency is in the opposite direction of Cr-doped AlN films, in which the c-axis lattice constant decreases as a function of Cr doping concentration [20]. A possible reason for the different tendency could be the orientation of the film, since the AlN (002) oriented in the Cr-doped films but AlN (100) in our present work. It also can be observed that the intensity of (100) peaks was decreased with increasing Ni concentration. The decreasing crystalline property may be due to the Ni doping induced defects in the AlN films.

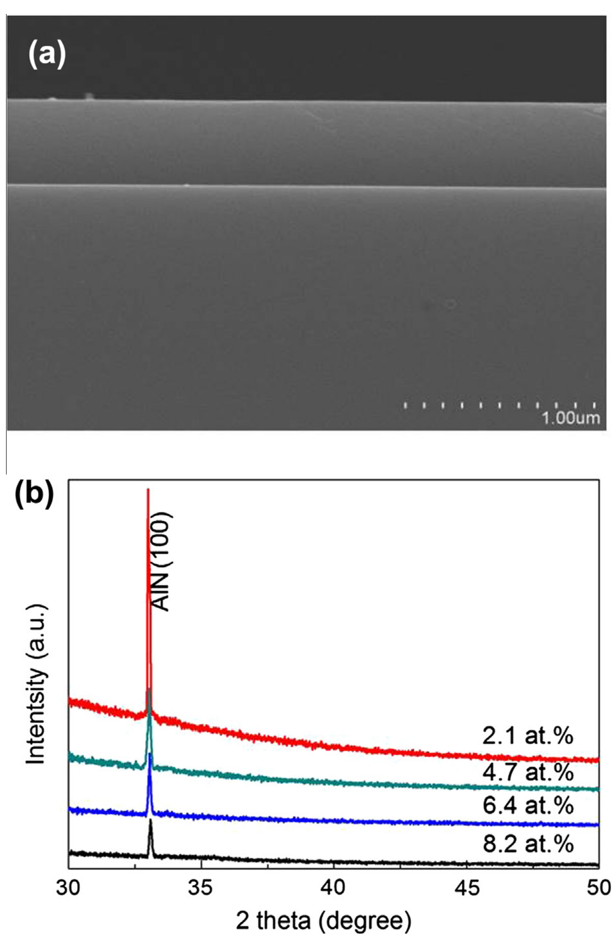

Fig. 1. (a) Cross-sectional SEM image of the 2.1 at.% Ni-doped AlN and (b) X-ray diffraction patterns of $Al_{1-x}Ni_xN$ samples with varying Ni composition deposited on p-type (100) Si substrate at 300 °C.

Moreover, the Scherrer's formula shown below was employed to estimate the average grain size of Ni-doped AlN (100) films [21]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where D, λ, B and θ are denoted as the average grain size, the wavelength of the X-ray (1.5406 Å), the full-width at half-maximum of (100) peak, and the corresponding diffraction angle, respectively. Thus, the estimated average grain sizes of 2.1, 4.7, 6.4 and 8.2 at.% Ni-doped AlN (100) films are 43.2, 35.1, 28.7, and 25.6 nm, respectively, indicating a decreasing average grain size with increasing Ni concentration.

The AFM measurement technique was employed to discuss the effect of Ni concentrations on the surface morphology of Ni-doped AlN films. Fig. 2 shows the three-dimensional surface morphologies acquired over a 1 μm × 1 μm area. It can be seen that the surface of AlN thin film with 2.1 at.% Ni doping is relatively smooth (Fig. 2(a)). As Ni concentration increasing to 8.2 at.% the grain size of AlN films reduced and the surface roughness increased obviously. The result is in agreement with the result of XRD. The root mean square (RMS) surface roughness of 2.1, 4.7, 6.4 and 8.2 at.% doped AlN films are 2.48 nm, 3.46 nm, 6.61 nm and 7.46 nm, respectively. Since the XRD result illustrates no exist of secondary phase in Ni-doped AlN film, this indicates that more Ni atoms dissolving into the AlN lattice brought down the surface activity of the grains and leaded to uneven nucleation, therefore, the grain growth was inhibited and the surface roughness was increased. A similar trend of increasing surface roughness or decreasing grain size with increasing doping content is reported for Fe-doped ZnO film [22] and Na-doped CdS film [23].

The photoluminescence (PL) spectra of undoped and Ni doped samples were carried out to confirm that the Ni incorporated into the AlN lattice indeed (Fig. 3) for some transition metal doped AlN materials were expected to have strong luminescence properties [24]. No emission peak was found in the spectrum range of 300–460 nm. However, obvious blue emission peaks located at

Table 1
Variation of peak position, and lattice parameter of the samples with Ni doped concentration.

Ni concentration (at.%)	(100) Peak position, 2θ	Lattice parameter, a (Å)
2.1	33.24	3.1095
4.7	33.28	3.1055
6.4	33.30	3.1036
8.2	33.36	3.0984