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Effect of carbon doping on microstructure, electronic and magnetic properties of Cr:AlN films

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ABSTRACT

Carbon was doped into Cr:AlN films. Microstructure analysis demonstrated that the Cr atom kept at AlN lattice when carbon content was lower. The doped carbon atoms formed graphite phases and C–N clusters dispersing in the films, which influenced the electric and magnetic properties significantly. When the resistivity was around 10^5–10^7 Ω cm under an alternating current (AC) frequency of 210 Hz, it increased with increasing carbon content, and when the resistivity was around 10^3 Ω cm under a higher AC frequency of 800 kHz, it decreased with increasing carbon content. The magnetisms for the carbon-doped samples are stronger than those of samples without carbon doping. The atomic magnetic moment (AMM) of the sample with a carbon content of 2.3 at.% was the highest ($0.4\mu_B$/Cr). It was proposed that atomic migration of carbon might have occurred under high AC frequency. The formation of C–N compounds could consume part of the available nitrogen and then increased the density of N vacancy in the Cr:AlN lattice, which is favorable for coupling among bound magnetic polarons (BMP).

1. Introduction

Dilute doping into wide band-gap semiconductors has been intensively investigated in the past 15 years because it produces numerous novel properties and possible applications, such as materials used in spintronics and nonvolatile storage [1–3]. These novel properties are significantly and extensively sensitive to various defects. Doping can induce defects like atom substitution, interstitial atom, vacancy, cluster and deformation. It should be careful when distinguishing the defects states, their formation mechanisms and effect on the properties. It is necessary to combine many characteristic methods for detailed analysis and determination. Furthermore, scientists are attempting new doping new materials to introduce various defects, produce new phenomena and enhance properties. Normally, in oxides and nitride compounds used in spintronics, the local magnetic ordering relates to the 3d and 4f transition metals, which bring local moments into the solid. These local moments couple with each other to realize macroscopic magnetism. However, nonmagnetic materials including carbon are currently used to generate spin polarization [4].

Carbon is a typical polymorphic material. Graphene and carbon nanotubes have been intensively and extensively studied and carbon doping into a semiconductor has attracted much attention recently. Yuan et al. obtained a two-dimensional hole gas in carbon-doped (1 0 0) GaAs/$Al_{0.4}Ga_{0.6}As$ square quantum well and they were able to enhance effective *g*-factor as well [5]. Lim et al. fabricated nano-carbon doped MgB_2 bulks materials and improved the critical current density (J_c) under a high magnetic field [6]. Kwak et al. predicted that the carbon dopants can become magnetic under confinement in ZnO nanocrystals and nanowires [7]. Herng et al. obtained p-type magnetic ZnO using ion implantation [8]. Due to the polymorphism of carbon in these semiconductors, the modulation mechanisms of these properties, including carriers, local moment, and transport behaviors under magnetic field, vary significantly. Based on this, it is deserved to study extensively the effects of carbon on more semiconductors.

Wurtzite AlN is a wide-gap semiconductor with a high melting point and high thermal conductivity, which are advantages for high power devices. Cr-doped AlN has been found having high magnetic Curie temperature which is favorable for spintronics [9] and high piezoelectric response which is favorable for surface acoustic waves devices [10]. In this paper, we attempted to introduce carbon dopant into Cr:AlN and study its effect on electric and magnetic properties. After carbon doping, it was found that the conductivity varied greatly under different alternating current (AC) frequencies and that the magnetism was enhanced obviously.

2. Experimental details

The carbon and chromium co-doped AlN films were prepared using DC reactive sputtering method. The target was aluminum plate on which small graphite and

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chromium strips were placed. The compositions of C and Cr were modulated by modifying the amount of the strips. The base pressure was 4×10^{-5} Pa. The substrate was Si(1 1 1) and the substrate temperature was 250 °C. During the deposition process, the partial pressure of nitrogen and argon were kept at 0.3 and 0.5 Pa, respectively. The deposition rate was about 5 nm/min. The total thickness was kept at about 200 nm.

The contents of Cr and C were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using Shimadzu ICPS-7510. The content of Cr was monitored to be about 7.4 at.%, and that of C was 0, 2.3, 3.2 and 4.7 at.%. The structures were characterized by X-ray diffraction (XRD), Raman spectroscopy, and Cr, N and C *K*-edge X-ray absorption near edge structure (XANES). The large-angle and low-angle XRD measurements were performed on Rigaku D/max-rB equipment. Raman scattering experiments were performed at room temperature in backscattering and close-to-90° configuration using Micro-Raman spectroscopy (RM 2000, Reinishaw). An Ar^+ laser of 514.5 nm was used as an excitation source. The resolution of the Raman shift is 1 cm^{-1}. The XANES spectra were measured in the fluorescence mode using synchrotron radiation at the beam-line U7C of National Synchrotron Radiation Facility (NSRF). The magnetic property was characterized at room temperature using a vibrating sample magnetometer (VSM) with a resolution of 10^{-7} emu, which is integrated in the physical property–measurement system (PPMS) of Quantum Design cooperation. The monolayer samples, as well as Al–AlN–Al capacitor structures, with a top electrode consisting of a 0.3 mm Al disk, were also prepared to measure the resistivity at an AC frequency range of 200 Hz to 1 MHz.

3. Results and discussions

3.1. Microstructures

The Cr:AlN films without carbon had a wurtzite structure with an apparent (0 0 2) texture (Fig. 1). Such structure was maintained after a small amount (up to 3.2 at.%) of carbon was doped. The value of lattice constant *c*, which was calculated from the XRD spectra, is 4.99 Å for the sample without carbon, and it was 5.01 Å and 5.06 Å for the samples with 2.3 and 3.2 at.% of carbon, respectively. The intensity of the (0 0 2) peak dropped dramatically for the two later samples. For the sample with 4.7 at.% of carbon, the diffraction pattern of AlN was unclear. These features indicated that the specimen doped with carbon content lower than 3.2 at.% induced tensile stress perpendicular to the film plane and then elongated the lattice constant *c*. The direction perpendicular to the film plan is practically unconstrained, which might be one reason for the strain observed along the *c* direction. There was no arching or cracking occurred, which might be due to the limited thickness of 200 nm and good adhesion on the substrate with high temperature.

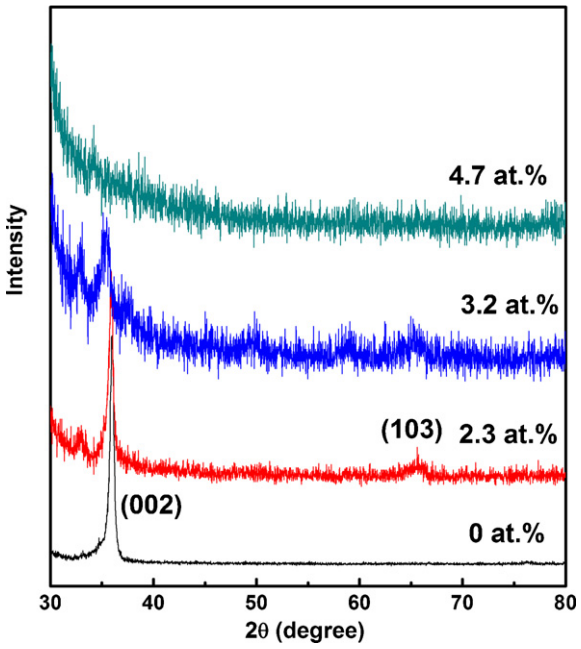

Fig. 1. XRD spectra of Cr-doped AlN films with the carbon content labeled beside every curve.

The neighboring atomic environments were important and were studied using XANES spectra (Figs. 2–4). Since the samples were still wurtzite structures when the carbon content was lower than 3.2 at.%, the atomic environments around the Cr atom was first considered in order to examine if the positions of the Cr atoms were modulated by carbon doping. The Cr *K*-edge XANES spectra and some instances which are simulated using FEFF8 code [11,12] are presented in Fig. 2. Characteristic peaks were labeled as A, B, C and D.

The features of Fig. 2(a1) for the sample without carbon are consistent with our previous study [13,14]. As discussed in Refs. [13,14], peak A in Fig. 2(a1) was due to the transition from Cr 1s electron to Al 3d–O 4p hybridized states occurring in low

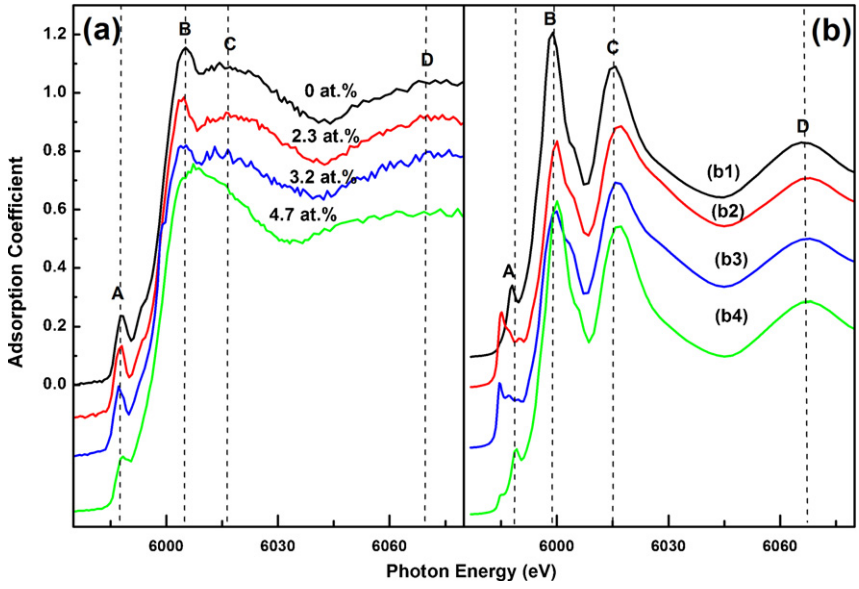

Fig. 2. Variation of the Cr *K*-edge XANES. (a) Experimental results for various carbon content; (b) simulated spectra using FEFF8 code (b1) no carbon doped; (b2) substitution of an Al atom in the second nearest neighbor by a Cr atom; (b3) substitution of an N atom in the first nearest neighbor by a carbon atom; (b4) substitution of an Al atom in the second nearest neighbor by a C atom.