

## Synthesis and Quality of Cr-doped AlN Thin Films Grown by RF Sputtering

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The AlCrN films were grown by RF reactive sputtering method under the selected conditions. The Cr concentration was varied by the number of Cr pieces placed on the Al target. The sample quality has been studied by XRD, Auger spectroscopy, optical absorption and electrical resistant measurements. The XRD and Auger results show that the samples consist of a major phase with the  $Al_{1-x}Cr_xN$  formula, which has a hexagonal structure, and a few percents at. of oxygen, which may form  $Al_2O_3$ . There exist the Cr clusters in the samples with high concentration of Cr. The optical absorption measurement provides the information about the band gap that relates strongly to the quality of samples. The quality of samples is also clearly reflected in electrical measurement, i.e., the temperature dependence of resistance exhibits a semiconductor characteristic only for the samples that have no Cr cluster. In these cases, the values of ionization energies  $E_a$  can be derived from  $R(T)$  plots by using the function  $R(T) = R_0 \exp(E_a/k_B T)$ .

**Keywords :** thin films, diluted magnetic semiconductor, energy band gap

### 1. Introduction

Recently, semiconductor devices based on the control and manipulations of electron spins have got considerable attention. Diluted magnetic semiconductors (DMS), which referred to transition metal-doped semiconductors, are extensively investigated due to their potential in combining ferromagnetic and semiconducting properties in a single material [1-3]. The realization of devices that can operate at room temperature will require a substantial high Curie temperature ( $T_c$ ) in DMS systems. By using the mean field Zener model of ferromagnetism, Diet *et al.* [4] predicted that  $T_c$  of wide band gap semiconductor such as GaN and ZnO doped with ~5 at.% of Mn can be exceeding room temperature. AlN is a host semiconductor that has widest band gap (6.2 eV) [5]; consequently, one can expect a very high Curie temperature in AlN-based DMS's. Among the transition metal elements, only Cr and Mn are expected to have a high stability of the ferromagnetic state in AlN-based DMSs [6]. In the previous work, the above room temperature magnetism in Cr-doped AlN films grown by DC sputtering technique was reported

[7]. However, the disadvantage of this technique is the interruption of plasma caused by the high resistance of AlN material. This problem may influence the properties of samples.

In this work, we used the RF sputtering technique and, for the first attempts, we concentrated to the effect of Cr-doped concentration on the quality of samples.

### 2. Experiments

AlCrN samples were deposited on (100) silicon and quartz substrates in a reactive RF magnetron sputtering system. The substrates were sequentially cleaned in ultrasonic baths of trichloroethylene, acetone, and ethanol for 5 minutes each and dried by  $N_2$  gas. The composite target included a high purity (99.999%) aluminum disk with a diameter of 3 inches and a number of square Cr pieces of  $5 \times 5$  mm in size, which were placed symmetrically on the surface of the Al disk. The samples were named AlCrN<sub>n</sub>p, where n is the number of Cr pieces that ranges from 1 to 6. The base vacuum in the chamber was approximately  $5 \times 10^{-7}$  Torr. The deposition conditions were optimized and fixed as following: the working pressure of Ar and  $N_2$  gas mixture (50% Ar, 50%  $N_2$ ) was 7 mTorr, the substrate temperature was 400°C, and the sputtering power was

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120 W. Before starting the sputtering process, a 15-min pre-sputtering was performed. All the films were uniform and perfectly adhesive to the substrates. The thickness of the films determined by absorption spectra's fringes was about 400 nm, corresponding to the deposition time of 60 minutes.

The XRD measurements were carried out in grazing mode using Cu- $K_{\alpha}$  radiation. Spectra of Auger electron spectroscopy (AES) was measured to determine the concentration of samples. The optical absorption was carried out for the samples deposited on quartz substrates over the wavelength from 200 to 900 nm in transmittance mode. The resistance of the films was measured as a function of temperature ( $R(T)$ ) ranging from 77 K to 300 K by four-probe technique. The maximum measurable resistance in our set-up was  $\sim 108 \Omega$ .

### 3. Results and Discussion

The XRD results indicate that only the films AlCrN1p and AlCrN2p are single phase with a hexagonal structure (wurtzite) AlN. No cubic metastable AlN phase was found. We present XRD patterns of 03 selected films (AlCrN2p, AlCrN4p and AlCrN6p) in Fig. 1. The grain size, one of manifestations of sample quality, are about 10 nm estimated by Scherrer formula. The peak, which relates to the second phase of Cr clusters, starts appearing in the XRD pattern of sample AlCrN3p and increases when the number of Cr pieces increases.

The AES results show the almost linear change of Cr doped concentration with the number of Cr pieces, e.g, 4.3; 8.4; 17; and 25 at.% for the samples with  $n = 1; 2; 4$

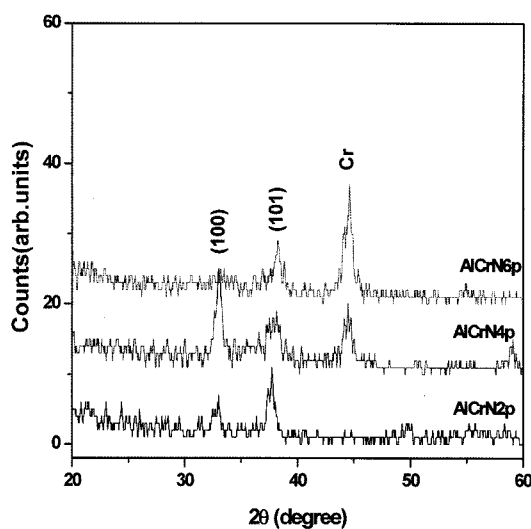


Fig. 1. XRD patterns of 03 selected samples (AlCrN2p, AlCrN4p and AlCrN6p).

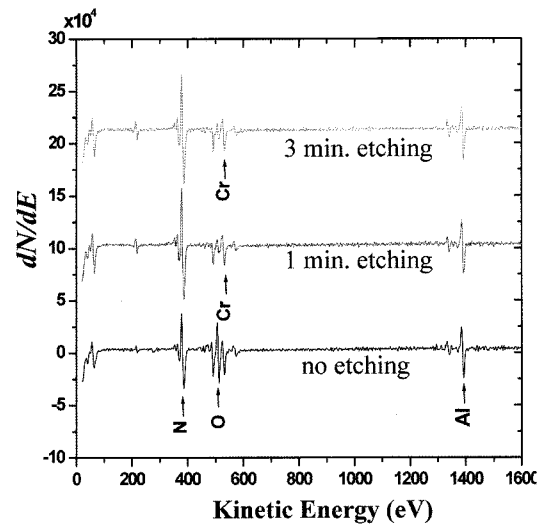


Fig. 2. AES spectra of AlCrN2p sample with different etching times.

and 6, respectively. For each sample, the AES measurements have been carried out several times with different etching time that range from 0 to 3 min. We show an example of AES spectra for AlCrN2p sample in Fig. 2. For this sample, from the spectrum of "no etching measurement, we can see the top surface of sample containing a large amount of oxygen. AES spectra of all "etching measurements are almost the same. The concentration data derived from these spectra suggest that the sample consists of a major phase with the approximate formula  $Al_{0.83}Cr_{0.17}N$  and a few atomic percents of oxygen. We are not aware of the reason of oxygenation; however, we are suspicious about the quality of gas used in reactive sputtering technique.

Similarly, the chemical formulery of the AlCrN1p sample can be estimated as  $Al_{0.91}Cr_{0.09}N$ . For the samples that contain Cr clusters, it is impossible to have an opinion

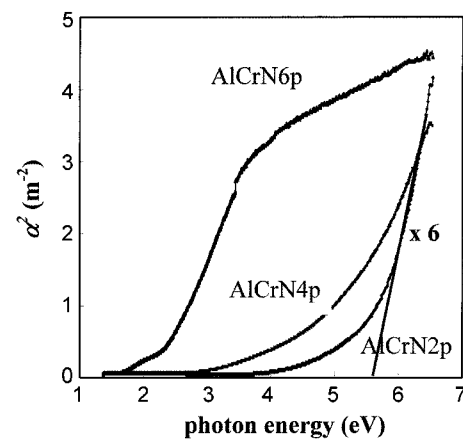
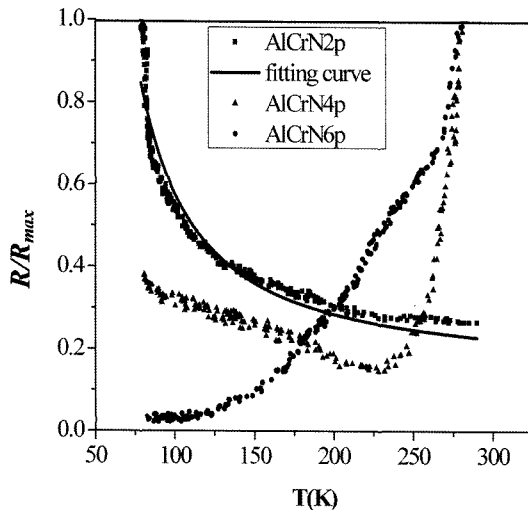


Fig. 3.  $\alpha^2$  vs.  $h\nu$  plots of 03 selected samples (AlCrN2p, AlCrN4p and AlCrN6p).



**Fig. 4.** The temperature dependence of relative resistance of selected samples (AlCrN2p, AlCrN4p and AlCrN6p).

about the chemical formulary of the main phase.

Fig. 3 shows  $\alpha^2$  vs.  $h\nu$  plots for 03 samples with  $n = 2$ ; 4 and 6 ( $\alpha$  is absorption coefficient and  $h\nu$  is photon energy).

Among these plots, we can see clearly that only the one of AlCrN2p still remains a direct band characteristic of AlN. The band gaps determined by extrapolating the linear portion of the absorption edge to zero value are 5.7 and 5.2 eV for AlCr1p and AlCrN2p, respectively. We consider that these band gaps correspond to the transition of electron from the top of the impurity band, which is located near the valence band, to the bottom of the conduction band. Impurity band broadening occurs when Cr concentration increases, leading to a narrowing of band gap. Our explanation is similar to that of Hashimoto *et al.* [8] for the observed band gap in GaCrN film. For two others samples, the tail at the edge of plots should relate to the impurity bands induced by second phases.

The temperature dependence of resistance of selected samples are shown in Fig. 4. Because the absolute values of resistance are in big different scale for different samples, we present these results in relative value. We can see in this figure that, only for the sample AlCrN2p, the resistivity decreases with the increasing of temperature, following the semiconductor characteristic  $R \sim \exp(E_a/k_B T)$ , where  $E_a$  is the activation energy of the sample (i.e the required energy to excite the carriers from the top of the valence band to the bottom of the impurity band). This means that for this sample the substituting of Cr for Al in the host lattice produces the charged carriers. This resistivity behaviour of AlCrN2p is similar to that of the sample AlCrN1p. The values of  $E_a$  determined by fitting  $R(T)$  plot are about 0.08 and 0.06 eV for the samples AlCrN1p

and AlCrN2p, respectively. These  $E_a$  values are quite high compared with thermal energy ( $k_B T = 0.026$  eV at 300 K), explaining why the resistance of these samples are very high. In Fig. 4, we also see that when the Cr concentration reach to a substantial value (the cases of AlCrN4p and AlCrN6p), the Cr clusters make the electrical conducting property become metallic. Especially, for the sample AlCrN4p, the temperature dependence of resistivity reflects the combination of both semiconductor and metal characteristics.

## 4. Conclusion

The results of the XRD, AES, optical absorption and resistivity measurements are in agreement to indicate that, under the limit of about 8 at.%, Cr atoms will substitute for Al atoms in AlN matrix, leading to a major  $Al_{1-x}Cr_xN$  phase. When Cr doped content exceeding this value, the Cr clusters start being formed. However, a few percents of oxygen are still observed in all samples. In order to improve the quality of samples, it is needed to find a solution for this problem. In the samples without Cr clusters, the substitution of Cr for Al has changed the material from insulator to semiconductor. The studies of other properties of samples are in progress.

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