Structure and nanomechanical properties of Al$_{1-x}$Sc$_x$N thin films

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Abstract. In this study, c-axis oriented AlN and Al$_{1-x}$Sc$_x$N films have been successfully grown on Si (100) and quartz glass by DC magnetron reactive sputtering method. The crystalline structure, optical properties and nanomechanical properties of AlN thin films are investigated by X-ray diffraction (XRD), Raman spectroscopy and nanoindentation techniques, respectively. The XRD patterns show that the crystal structure of the Al$_{1-x}$Sc$_x$N films was (002) orientation. The frequency of the E$_2$ (high) mode observed in the Al$_{1-x}$Sc$_x$N films shows higher red shift compared to that observed in AlN film. The nanoindentation hardness and elastic results of Al$_{1-x}$Sc$_x$N films were 16 GPa and 190 GPa compared to that of 11.2 GPa and 110.4 GPa for AlN film.

Keywords: Thin film; Scandium; Aluminum nitride; Nanomechanical properties

1. Introduction
Wide-bandgap III–V nitride semiconductors have received much attention due to their importance in both scientific researches and technological applications [1-6]. Among the group III nitrides, AlN exhibits the largest direct band gap (6.2 eV) [3, 4], a high thermal conductivity (285 W/mK), and a high melting point (3237 K) [7, 8]. In recent years, attention has also been paid to rare-earth (RE)-doped IIIA-nitride semiconductor thin films [11], for example, scandium doping in AlN. Scandium is a RE element no.21 in the periodic system. The first principle calculation indicated that it is possible to fabricate Sc-III A-N nitrides [9, 10]. Akiyama [6] has reported that Al$_{1-x}$Sc$_x$N films with a Sc concentration of 43% exhibited a four times larger piezoelectric response than pure AlN films, which is the largest piezoelectric response among the known tetrahedrally bounded semiconductors. In a recent paper, we show the structure and optical properties of the Al$_{1-x}$Sc$_x$N films. In this work, we investigate the mechanical properties of the Al$_{1-x}$Sc$_x$N films.
The film have been prepared by various methods including radio frequency (RF) magnetron sputtering, CVD, and reactive molecular beam epitaxy [12-14]. Among them, sputtering has been the most frequently used technique to obtain the thin films. It has advantages over conventionally high temperature techniques used for thin film deposition since its simplicity, low cost, and the ability to obtain films with the properties required for many applications [15-19]. So in this work c-axis oriented AlN thin films had been successfully grown on Si(100) substrates by DC magnetron reactive sputtering method. By Sc-doping in AlN thin films, \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) alloy phase is formed. Then we investigate the effect of Sc contents on the mechanical properties related to the microstructure of \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) thin films. The structure and optical properties were characterized carefully by X-ray diffraction (XRD) and Raman spectroscopy, respectively. The mechanical properties were examined by nanoindentation measurements.

2. **Experiment**

\( \text{Al}_{1-x}\text{Sc}_x\text{N} \) thin films were prepared on Si(100) substrates by DC magnetron reactive sputtering method. The growth conditions of the films are listed in Table 1. The aluminum sputtering targets were 60mm in diameter and 99.999% of purity. In this work, we grew \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) thin films with different Sc concentrations by changing the number of Sc tips which were set on the Al target. The sputtering chamber was evacuated to a pressure below \( 3.5 \times 10^{-4} \) Pa and then high-purity argon (99.999%) and nitrogen (99.999%) gases were introduced. The growth pressure was 0.7 Pa.

| Material   | \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) |
|------------|----------------------------------------|
| Target     | Al                                     |
| Substrate  | Si (100)                               |
| Substrate temperature (°C) | Room temperature          |
| Power (W)  | 280                                    |
| Gas contents | Ar:N\(_2\)=1:1                  |
| Sputtering time | 1 hour                                |
| Sputtering pressure (Pa) | 0.7                                   |

3. **Results and discussion**

The crystal structure and orientation of the films are determined by XRD. The film thickness of \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) films is approximately about 700nm. The Sc concentration was measured by energy dispersive X-ray spectroscopy (EDS). The XRD patterns of \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) films are shown in Fig. 1(a). From Fig. 1(a) it can be found that when the films are doped with Sc, the diffraction intensity of (002) peak remarkably decreases and the peak shifts to the low angle side. Generally, the AlN has the wurtzite structure while the ScN has the rock-salt (nonpolar) [21-24]. When Sc was doped into AlN films, the Sc atoms were substituted on the Al sub-lattice. It is probably that the crystal structure of \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) films is a hexagonal intermediate phase between wurtzite AlN and rocksalt ScN.

The Raman spectra were recorded for \( \text{Al}_{1-x}\text{Sc}_x\text{N} \) films with different Sc contents. The intense band at 520 cm\(^{-1}\) is the O (\( \delta \)) phonon from the silicon substrate. The Raman peaks of
Al$_{1-x}$Sc$_x$N films at 750-800 cm$^{-1}$ can be observed from Fig. 1(b) but they are very weak. Compared to AlN E$_2$ (high) Raman peak, the Raman peak of Al$_{1-x}$Sc$_x$N films is higher red

**Figure 1.** (a) XRD patterns of Al$_{1-x}$Sc$_x$N films with different Sc mole fractions; (b) Raman spectra of Al$_{1-x}$Sc$_x$N film.

shift. With the reference to the results of our XRD, the observed peak shifting can be attributed to the change of the crystal structure.

It was reported that a red shift was observed in Raman spectra with the decrease of grain size [25]. In our cases, when AlN films are doped with Sc, the grain size decrease. These are consistent with the results of XRD. The E$_2$ (high) mode is usually being used to analyze the stress state information in the sample due to its high sensitivity to stress which affects the E$_2$ phonon frequency [26]. An increase in the E$_2$ phonon frequency indicates compressive stress, whereas a decrease points to tensile stress. In Fig. 3, the Raman peak of Al$_{1-x}$Sc$_x$N films shift to low wave number was also found with the increasing of Sc concentration, which indicates the compressive stress in Al$_{1-x}$Sc$_x$N films.

The mechanical properties of thin films were analyzed by Nanoindentation which is a very powerful technique [7,27-31]. The load-displacement response obtained by nanoindentation may be regarded as a film ‘fingerprint’ and contains a lot of information about the elastic behavior and deformation mechanism which the system is undergoing. In order to minimize the substrate effect, the maximum indentation force was limited to 2000μN so that the indentation depth was less than 10% of the film thickness. Fig. 2 gives a typical loading unloading curve of Al$_{1-x}$Sc$_x$N films. The initial loading segment contained an elastic-plastic displacement while the unloading process released the elastic energy [28-30].
Figure 2. Typical load vs. displacement curve for an Al$_{1-x}$Sc$_x$N film at 2000μN load.

Figure 3. The grain size of Al$_{1-x}$Sc$_x$N calculated using Scherrer’s equation.

Figure 4. Hardness (H) and elastic modulus (E) of Al$_{1-x}$Sc$_x$N films with different Sc mole fractions.

Fig. 4 shows the hardness and elastic modulus of Al$_{1-x}$Sc$_x$N films with different Sc contents. For the AlN film, the mean values of hardness and elastic modulus obtained from three independent measurements were 13.4 and 153.3 GPa, respectively. The hardness and elastic modulus of the films increase with increasing Sc contents, and reach a maximum value for the film with 30 at.% Sc (hardness = 17.3 GPa and elastic modulus = 190.7 GPa). With further increase in the Sc contents, both hardness and elastic modulus values decrease.
drastically. Based on the results obtained and the above discussion, the crystal structure of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ film is a hexagonal intermediate phase between wurtzite AlN and rocksalt ScN. Thus, wurtzite AlN surrounded by a matrix of rocksalt ScN will assist the relaxation of stress and restrict the generation of dislocations and defects in the film. From the results of XRD the grain size of non-doped AlN film was calculated by using the Scherrer formula [32] to be about 24.6 nm. The grain size of the $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films (shown in Fig. 3) was in the range of 14-23 nm. Then with the Sc concentration increases, the grain size of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films decreases. It is reasonable to consider that Sc may cause the Sc–N phases forming and enwrapping the AlN grains, which restrict the growth of AlN grains. These as-formed new phases play a role as a barrier to dislocation propagation, which reduces grain boundary sliding under stress, and thus hardness is improved.

4. Summary

In this study, $\text{Al}_{1-x}\text{Sc}_x\text{N}$ thin films were prepared on both Si (100) and quartz glass substrates by DC magnetron reactive sputtering method. All films show (002) preferred orientation. The nanoindentation hardness and elastic results of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films were 16 GPa and 190 GPa compared to that of 11.2 GPa and 110.4 GPa for AlN film, and reach a maximum value for the film with 30 at.% Sc. With further increase in the Sc contents, both hardness and elastic modulus values decrease drastically. From the results, we consider that the hardness enhancement appears in $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films with a proper Sc contents.

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