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Influence of sputtering atmosphere on crystallinity and crystal orientation of AlN thin films deposited on polycrystalline $MoSi_2$ substrates

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Highly oriented AlN thin films have been deposited on polycrystalline $MoSi_2$ substrates by r.f. magnetron sputtering. The total sputtering pressure and the nitrogen concentration in the sputtering gas had a significant influence on the crystallinity and crystal orientation of the films. The film deposited at a sputtering pressure of 0.6 Pa and a nitrogen concentration of 20% indicated high crystallinity, high *c*-axis orientation ($\sigma = 3.1°$) and very low surface roughness ($R_a = 0.7$ nm). The crystallinity, crystal orientation, composition and morphology of the films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. The nitrogen concentration hardly had an effect on the composition of the films; however, it had a great influence on the shape of the fine grains constituting the films. The shape of the grains drastically changed from triangular pyramids of various sizes to uniform fine grains with increasing nitrogen concentration. *© 1998 Chapman & Hall*

1. Introduction

Human skin produces cutaneous sensations, such as of touch, pressure, pain, hot and cool, against various outer stimuli to protect the body from danger. These sensations are detected by diverse organs in the skin. Furthermore, the skin works as both a protective film and a cooler. We believe that the low reliability of a structural ceramic would be improved by preparing a film like human skin on the ceramic, because such an artificial skin could sense a change inside the ceramic to avoid sudden destruction. Aluminium nitride (AlN) is known to be a piezoelectric and a pyroelectric material, so that it is expected to respond to various physical stimuli such as mechanical impact, vibration [1], pressure and thermal change [2]. In addition, AlN possesses very high chemical stability and thermal conductivity [3, 4]. The film shows promise for use as both a protective film and a cooler. These excellent characteristics suggest that an AlN thin film would work like human skin to improve fundamentally the reliability of a structural ceramic.

AlN is not ferroelectric, poling is not available for the electric characteristics of AlN. Hence, these excellent characteristics of an AlN thin film strongly depend on only crystallinity and crystal orientation. There is no very strong statement on the crystallinity and crystal orientation of an AlN thin film deposited on a polycrystalline substrate. Generally, the crystal orientation of a substrate strongly effects the orientation of the film deposited on the substrate [5]. It was considered difficult to prepare an oriented film on a polycrystalline substrate. However, we have succeeded in preparing *c*-axis oriented AlN thin films on various polycrystalline ceramic substrates such as $MoSi_2$, Al_2O_3, SiC and Si_3N_4 [6, 7]. We have investigated the influence of substrate temperature on the physical structure of AlN thin films deposited on polycrystalline $MoSi_2$ substrates [6]. The present study focuses on the influence of total sputtering pressure and the nitrogen concentration in the sputtering gas on the physical structure of AlN thin films deposited on polycrystalline molybdenum disilicide ($MoSi_2$) substrates. The films were deposited on the polycrystalline substrates by r.f. planar magnetron sputtering using a sintered AlN target. The influence of total sputtering pressure and the nitrogen concentration on the crystallinity, crystal orientation, composition and morphology of the films have been investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2. Experimental procedure

The sputtering equipment used in this experiment was a r.f. planar magnetron sputtering system (CFS-4ES, Tokuda, Tokyo, Japan), with a (~7.6 cm) 3 in. diameter [8, 9] AlN target disc (purity 99.9%). Sintered $MoSi_2$ disc substrates were made of raw $MoSi_2$ powder (impurities: iron 0.45 at%, oxygen 1.06 at%; Nipponshinkinzoku Co. Ltd, Japan) by hot pressing at 20 MPa, 1370 °C for 10 min under vacuum [10]. The substrates were 17.0 mm diameter and 2.0 mm thick. The sputtering chamber was evacuated to

TABLE I Sputtering conditions

Equipment	R.f. planar magnetron sputtering system
Target	Aluminium nitride (99.9% purity)
Target size	Diameter 76.2 mm, thickness 5.0 mm
Substrate temperature	300 °C
Sputtering time	4 h
R.f. power	400 W
R.f. frequency	13.56 MHz
Target substrate spacing	>83.0 mm

$<4\times10^{-4}$ Pa before argon gas (purity 99.999%) was introduced. Substrate surfaces were cleaned by sputtering at 200 W r.f. power for 5 min. Argon and nitrogen (purity 99.99%) gases were then introduced. The AlN target was precleaned for 10 min with the shutter closed before the deposition process. Table I lists the other sputtering conditions.

The crystal structure and crystallinity of the AlN thin films was examined by X-ray diffraction (XRD: RAD-2, Rigaku, Japan) using CuK_α radiation. The X-ray rocking curves of the films were measured to evaluate the distribution of the crystal orientation. The composition of the films was analysed with an X-ray photoelectron spectroscope (XPS, XPS 7000, Rigaku, Japan). The morphology of the film surfaces was observed by atomic force microscopy (AFM, Nano Scope III, Digital Instruments, USA). The film thickness was measured with a surface texture measuring instrument (Surfcom, Tokyoseimitsu, Japan) and a scanning electron microscope (SEM, JSM-6400, Jeol, Japan).

3. Results and discussion

3.1. Influence of total sputtering pressure

We have investigated the influence of total sputtering pressure on the crystallinity and crystal orientation of the AlN thin films deposited on polycrystalline $MoSi_2$ substrates. In these experiments, the nitrogen concentration in the sputtering gas was 50% [11]. Fig. 1 shows the X-ray diffraction patterns of the films deposited at the total sputtering pressures of 0.2 and 1.4 Pa, respectively. The X-ray diffraction patterns of the films deposited at all pressures (0.2–1.4 Pa) consisted of diffraction peaks due to the polycrystalline $MoSi_2$ substrate and hexagonal AlN(0 0 2) and (0 0 4) planes like those shown in Fig. 1. Huffman *et al.* [12] and Takeda and Hata [13] reported AlN(1 0 0), (1 0 1), (1 0 2) and (1 0 3) diffraction peaks at high total sputtering pressures (above 0.9 Pa). However, no such AlN diffraction peaks were present in our samples, indicating that the films deposited at all pressures were *c*-axis oriented films. The *c*-axis lattice constants of the films were 0.497 nm, which was close to the reported value for the bulk AlN [14]; hence, no homogeneous strain was observed in the films.

Although the film thickness increased with decreasing total sputtering pressure, the thicknesses were almost the same (1.1–1.3 μm). The integrated intensity of the (0 0 2) peak was used to evaluate the crystallinity of the films. The crystal orientation of the films was evaluated by the X-ray rocking curves of the (0 0 2) peak [5, 15]. Presuming these curves have Gaussian distribution, the standard deviation angle, σ, was measured to evaluate the degree of crystal orientation. Fig. 2 shows the dependence of the crystallinity and crystal orientation of the films on the total sputtering pressure. The integrated intensity initially increased with increasing pressure and then began to decrease at the pressure of 0.6 Pa; consequently, the integrated intensity exhibited a maximum value at 0.6 Pa. On the other hand, σ initially decreased with the increasing pressure and increased above 0.6 Pa; σ shows a minimum of 4.2° at 0.6 Pa. These results indicate that both the crystallinity and the crystal orientation of the film deposited at a total sputtering pressure of 0.6 Pa were the highest in the range. These results were consistent with the those reported by Okano *et al.* [16], although the sputtering conditions were different.

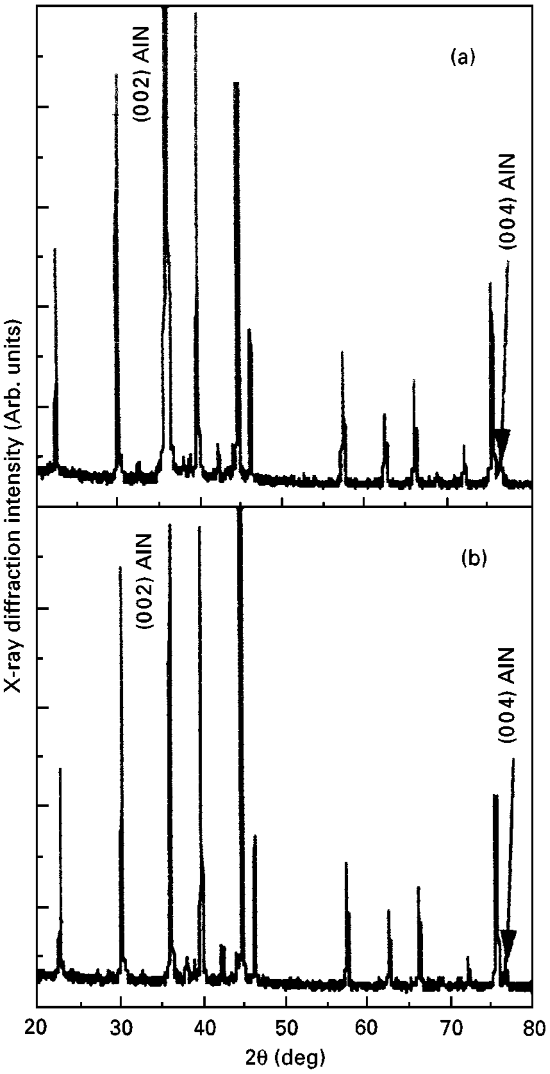

Figure 1 X-ray diffraction patterns of AlN thin films. Sputtering pressure (a) 0.2 Pa, (b) 1.4 Pa.

3.2. Influence of nitrogen concentration

We have investigated the influence of the nitrogen concentration in the sputtering gas on the crystallinity and crystal orientation of AlN thin films. In this study, the total sputtering pressure was kept to 0.6 Pa, based on the experimental results shown in Fig. 2. Fig. 3

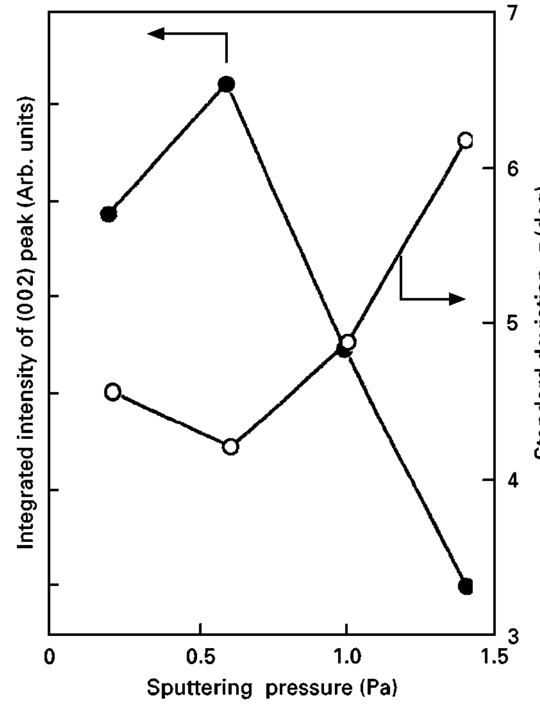

Figure 2 Dependence of crystallinity and crystal orientation of AlN thin films on sputtering pressure.

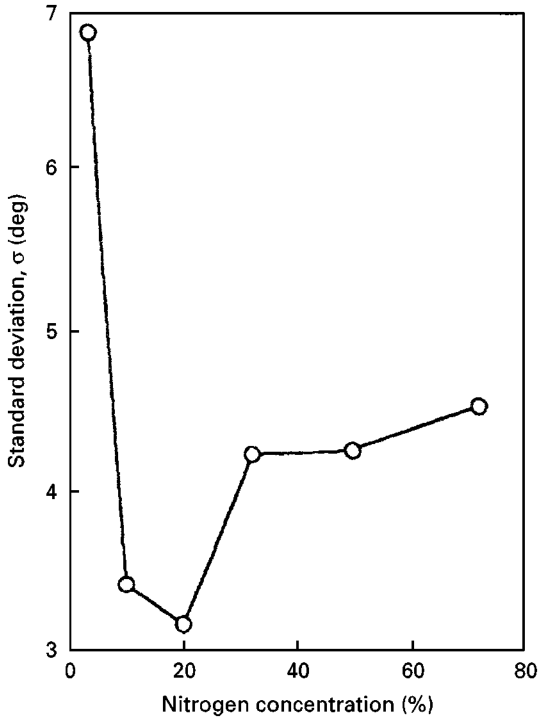

Figure 4 Dependence of crystal orientation of AlN thin films on nitrogen concentration.

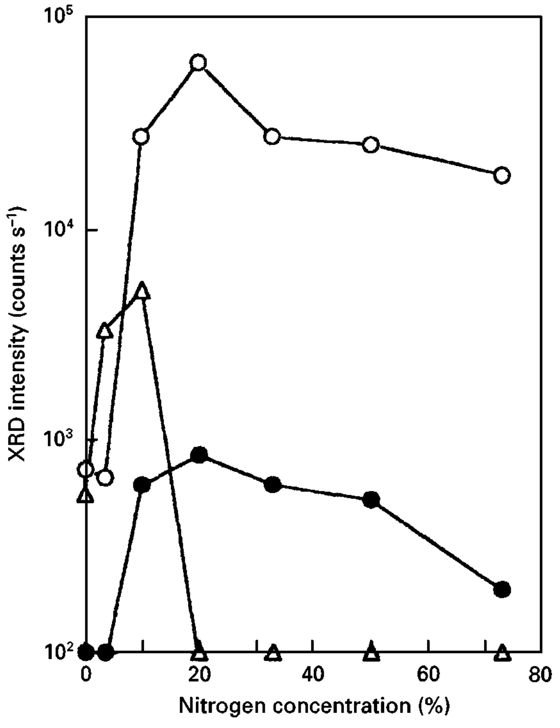

Figure 3 Dependence of X-ray diffraction intensity on nitrogen concentration. (○) 0 0 2, (△) 1 0 1, (●) 0 0 4.

shows the dependence of the X-ray diffraction intensity of each peak on the nitrogen concentration. The diffraction peaks of hexagonal AlN(0 0 2), (0 0 4) and (1 0 1) planes were observed. At a nitrogen concentration of 0%, the only weak peaks of the (0 0 2) and the (1 0 1) were observed. At 3.3%, the intensity of the (1 0 1) peak increased. At 10%, the intensity of the films increased remarkably. When the nitrogen concentration exceeded 20%, the (1 0 1) peak disappeared, and only the (0 0 2) and (0 0 4) peaks were observed. The intensity of the (0 0 2) peak exhibited a maximum value at 20%. The film thicknesses were almost the same (2.5 μm) at a nitrogen concentration of 0%–20%. Above 20%, the film thickness decreased from 2.5 μm to 1.0 μm with increasing nitrogen concentration, and the deposition rate changed from 10.5 nm min^{-1} to 4.2 nm min^{-1}. These results reveal that the films deposited at a nitrogen concentration higher than 20% had high crystallinity and *c*-axis orientation, which were in agreement with those reported by other researchers [12, 17].

Fig. 4 shows the dependence of the crystal orientation on the nitrogen concentration. The standard deviation, σ, of the X-ray rocking curve on the (0 0 2) peak decreased quickly with increasing nitrogen concentration and then began to increase at 20%; consequently, σ exhibited a minimum value of 3.1° at 20%. This result suggests that the best quality film was obtained at a nitrogen concentration of 20%. The σ value of 3.1° was as narrow as that of the piezoelectric films deposited on glass substrates [5, 17]. Okano *et al.* [16] reported that the *c*-axis orientation was improved by decreasing nitrogen concentration, because a low nitrogen concentration disturbs the formation of AlN on the aluminium target. In our study, however, the standard deviation, σ, changed independently with the formation of AlN on the target, because we used a sintered AlN target.

Because a significant effect of nitrogen concentration on the film quality was observed in the range 0%–20%, we analysed the composition of the films by XPS to investigate the influence in detail. Fig. 5 shows the dependence of the composition of the films on the nitrogen concentration. The films consisted of aluminium, nitrogen and oxygen. The composition was not changed by the nitrogen concentration and was independent of it. The existence of oxygen was reported by other researchers [16–20]. The oxygen was attributed to the possible oxidation of the sides of the grains of which the films were composed [19, 20]. The influence of nitrogen concentration on the surface morphology of the films has been investigated by atomic force microscopy (AFM). The AFM images of the films deposited at the various nitrogen concentrations of 0%, 3.3%, 20% and 73% are shown in Fig. 6. At the nitrogen concentration of 0%, the film consisted of triangular pyramids of various sizes, and the surface was very rough; the surface roughness, R_a, was 120 nm. This is an interesting phenomenon because the structure was not shown in the model proposed by Thornton [21]. At 3.3%, the film was composed of tapered grains with an improved surface roughness of 10 nm. At 20%, the film was composed of uniform fine grains and the surface was very smooth; the roughness drastically decreased to 0.7 nm. The diameter of the grains constituting the film was about 100 nm. At 73%, the film consisted of uniform fine grains, which were similar to those of the film deposited at the nitrogen concentration of 20%, and the surface was very smooth; the roughness was 1.0 nm. The deposition rate was 10.9 nm min^{-1} at the nitrogen concentration of 20% and was 4.2 nm min^{-1} at 73%, suggesting that the deposition rate strongly depended on the nitrogen concentration. However, no remarkable influence of the deposition rate was observed on the shape of the grains constituting the films in the range 20%–73%. These AFM images indicate that the nitrogen concentration remarkably changed

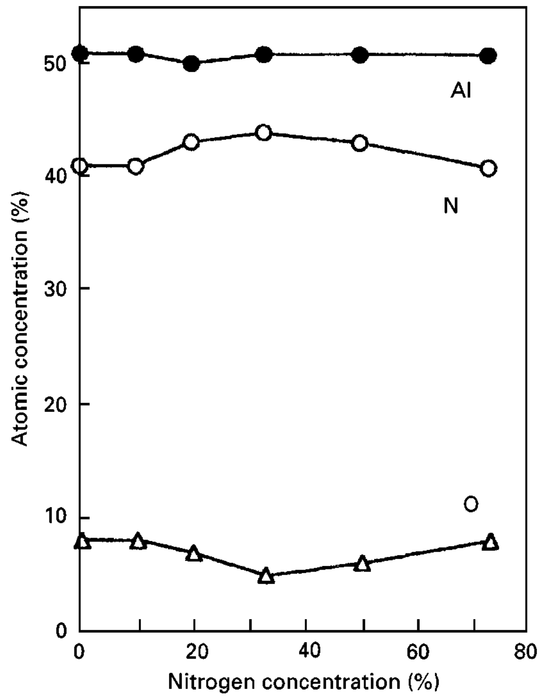

Figure 5 Dependence of the composition of AlN thin films on the nitrogen concentration.

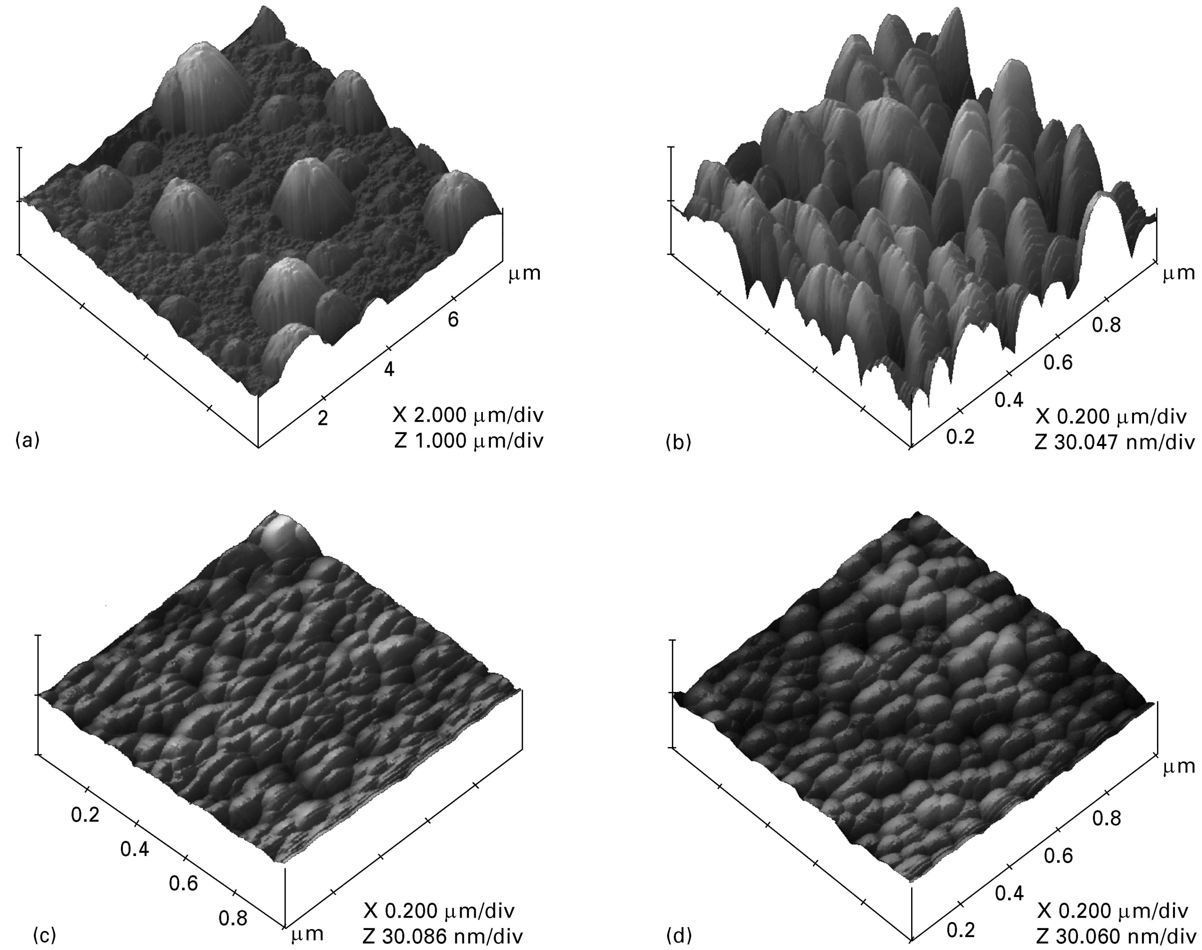

Figure 6 AFM images of surfaces of AlN thin films, at nitrogen concentrations of (a) 0%, (b) 3.3%, (c) 20%, and (d) 73%.

the shape of the grains constituting the AlN thin films deposited in the range 0%–20%; therefore, the influence of the nitrogen concentration on the crystallinity and crystal orientation of the films is probably caused by the change in shape of the grains constituting the films.

4. Conclusion

AlN thin films have been deposited on the polycrystalline $MoSi_2$ substrate by the r.f. magnetron sputtering technique. The total sputtering pressure and the nitrogen concentration in the sputtering gas was found to have a significant influence on the crystallinity and crystal orientation of the films. The X-ray diffraction patterns of the films deposited at the pressures of 0.2–1.4 Pa showed only hexagonal AlN(0 0 2) and (0 0 4) diffraction peaks. The crystal structure of the films was random at nitrogen concentrations below 10% and was perfectly *c*-axis oriented at nitrogen concentrations above 20%. The best quality film was obtained at a total sputtering pressure of 0.6 Pa and a nitrogen concentration of 20%. The standard deviation, σ, of the best film was 3.1°, and the surface roughness was 0.7 nm. The greatest effect of nitrogen concentration was observed in the range 0%–20%. The XPS and AFM results clearly indicate that the composition of the films was independent of the nitrogen concentration; however the shape of the grains constituting the films was strongly nitrogen concentration dependent. The shape of the grains changed drastically from triangular pyramids of various sizes to uniform fine grains with increasing nitrogen concentration. Therefore, the influence of the nitrogen concentration on the crystallinity and crystal orientation of the films is probably caused by the change in shape of the grains constituting the films. In order to obtain high quality AlN thin films, it is considered that careful attention must be paid to the shape of the fine grains constituting the films.

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