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CRYSTALLINE PHASES AND HARDNESS OF $(Ti_1-xAlx)N$ COATINGS DEPOSITED BY REACTIVE SPUTTERING

Chong Kwan Park, Joo Dong Park, and Tae Sung Oh

Department of Metallurgy and Materials Science, Hong Ik University, Seoul 121-791, Korea

ABSTRACT

(Til-xAlx)N films were deposited on high speed steel and silicon substrates by reactive sputtering in mixed $Ar-N_2$ discharges. Crystalline phases and microhardness of $(Ti_{1-x}Al_x)N$ films were investigated with variation of the film composition and substrate RF bias voltage. With Al content x of about 0.6, crystalline phase of $(Ti_{1-x}Al_x)N$ films was changed from single-phase NaCl structure to two phase mixture of NaCl and wurtzite structures. Microhardness of $(Ti_{1-x}Al_x)N$ films was largely improved by applying RF bias voltage above 50 V during deposition. Hardness of $(Ti_{1-x}Al_x)N$ films reached a maximum value for Al content x of about 0.4, and 1900 kg/㎟ was obtained for 1㎛-thick $(Ti_{0.6}Al_{0.4})N$ films.

INTRODUCTION

With high mechanical hardness and low friction coefficients, polycrystalline TiN coatings have been widely used as wear-resistance coatings to increase the lifetime of cutting tools, forming tools and dies[1-3]. A critical disadvantage of TiN hard coatings, however, is that TiN oxidizes rapidly to form rutile TiO_2 at temperatures above 500℃. Instead of forming a stable passive layer on the TiN film surface, this oxide layer spalls at a critical thickness due to the large difference in TiO_2 and TiN molar volumes. As a result, unoxidized TiN is exposed to further oxidation until the entire TiN coating is consumed. Thus, applications of TiN coatings, as hard coatings for high speed cutting tools and high temperature dies, have been limited[1-4].

Recently, (Ti,Al)N coatings have been extensively investigated to overcome the oxidation problem of TiN coatings[3-7]. When (Ti,Al)N coatings are used at high temperatures, oxidation of coatings can be protected by formation of a passive layer of amorphous Al_2O_3[8]. It has been also reported that wear resistance properties of (Ti,Al)N coatings are superior to those of TiN[9].

In this work, $(Ti_{1-x}Al_x)N$ films were deposited on high speed steel and silicon substrates by reactive sputtering in mixed $Ar-N_2$ discharges. Crystalline phases and microhardness of $(Ti_{1-x}Al_x)N$ films were investigated with variation of the film composition and substrate RF bias voltage.

EXPERIMENTAL PROCEDURE

$(Ti_{1-x}Al_x)N$ films, with x ranging from 0 to ~0.6, were reactively deposited on high speed steel (HSS) and silicon substrates by d. c. magnetron sputtering in mixed $Ar-N_2$ dis

charges. Composition of $(Ti_{1-x}Al_x)N$ films was controlled by changing the area fraction of Al chips on the erosion zone of Ti sputtering target. Ar and N_2 gases were admitted into the sputtering chamber using separate mass flow controllers. Total flow rate of Ar and N_2 gases was kept constant at 20 sccm, resulting in a sputtering pressure of 0.65 Pa. After characterizing the crystalline phases of TiN films which were sputtered at various flow ratio of N_2 gas to total $(Ar+N_2)$ gas, flow ratio of N_2 gas was fixed to be 0.1 for deposition of all $(Ti_{1-x}Al_x)N$ films. Substrate temperature during deposition was maintained at either room temperature or 300℃, and substrate RF bias voltage was applied in the range of 0~100 V.

Film thickness was controlled to be 1㎛. Compositions of $(Ti_{1-x}Al_x)N$ films were determined by energy dispersive spectroscopy(EDS). Crystalline phases of the films were characterized by X-ray diffractometry(XRD), and lattice parameter of $(Ti_{1-x}Al_x)N$ films was determined with (111) diffraction peak. Microstructure of the films was observed using scanning electron microscopy (SEM), and hardness of the films was measured using Vickers microhardness test at indentation load of 50 gf. To evaluate oxidation behavior of the films, TG/DTA was conducted at a scan rate of 5℃/min for TiN and $(Ti_{0.52}Al_{0.48})N$ films, which were deposited on glass substrates and flaked off to be charged into DTA pot.

RESULTS AND DISCUSSION

XRD patterns of $(Ti_{1-x}Al_x)N$ films, which were deposited at room temperature without RF bias voltage, were illustrated in Fig. 1. With Al content x ranging from 0 to 0.56, crystalline phases of $(Ti_{1-x}Al_x)N$ films were determined to be single-phase NaCl structure, typical for TiN, with (111) preferred orientation. However, films with x of about 0.6 had two phases of TiN and wurtzite AlN structures, which could be clearly illustrated with Table 1. As shown in Table 1, $(Ti_{1-x}Al_x)N$ films with x near 0.6 were composed of TiN and AlN phases without depending on the RF bias voltage (0~100V) and substrate temperature. In Table 1, compositions of the films, deposited with RF bias voltage of 50V at room temperature and with 75V at room temperature or 300℃, were all less than x= 0.56 with TiN single phase.

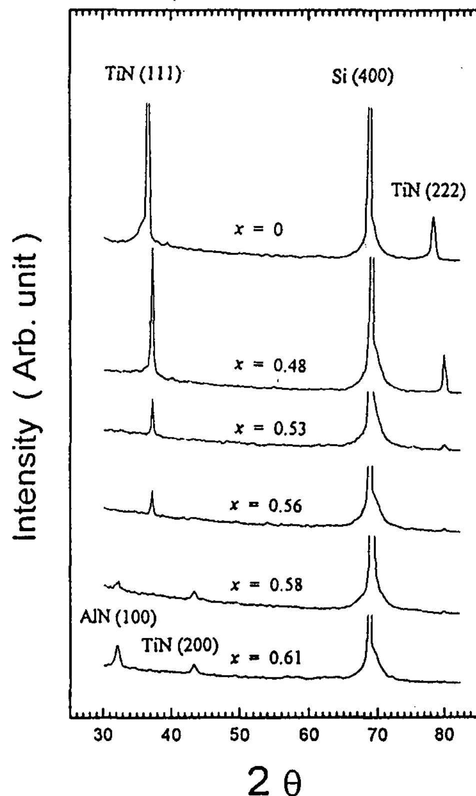

Fig. 1 XRD patterns of $(Ti_{1-x}Al_x)N$ films sputtered at room temperanture without RF bias voltage.

Table 1. Compositions of $(Ti_{1-x}Al_x)N$ films which were composed of TiN and AlN phases at various deposition condition.

RF bias voltage	0V		30V		50V		75V		100V
substrate temperature	RT	300℃	RT	300℃	RT	300℃	RT	300℃	RT
Al content x	0.58	0.61	0.60	0.59	—	0.61	—	—	0.59

Even with identical area fraction of Al chips on the erosion zone of Ti target, composition of $(Ti_{1-x}Al_x)N$ films was slightly varied with sputtering conditions. As reported for the films processed by arc deposition[10-12], it has been observed that Al content x of $(Ti_{1-x}Al_x)N$ films decreased with higher RF bias voltage due to less ionization of Al vapour[12] and also due to the difference in the sputtering rates of Ti and Al[11]. Resputtering rate of Al in $(Ti_{1-x}Al_x)N$ films is faster than Ti resputtering rate[11, 13]. Thus, Al concentration x of $(Ti_{1-x}Al_x)N$ films decreased with increasing the energy of ions by applying higher RF bias voltage.

As shown in Fig. 2, lattice parameter of $(Ti_{1-x}Al_x)N$ films decreased linearly from 0.423nm for TiN to 0.416nm for $(Ti_{0.4}Al_{0.6})N$ with increasing Al content×, due to the substitutional replacement of Ti in TiN lattice with Al having a smaller radius[3, 4]. The decrease of lattice parameter was also partly attributed to the bonding characteristics of transition-metal nitrides. Charge transfer from metal atoms to N will be reduced by substituting of Al atoms into Ti sites, resulting in the decrease of the effective radius of N and, thus, lattice parameter[4].

Scanning electron micrographs of $(Ti_{0.52}Al_{0.48})N$ films deposited at room temperature with RF bias voltage of 0V, 30V, 50V, and 75V respectively, were compared in Fig. 3. These microstructures wer typical of what

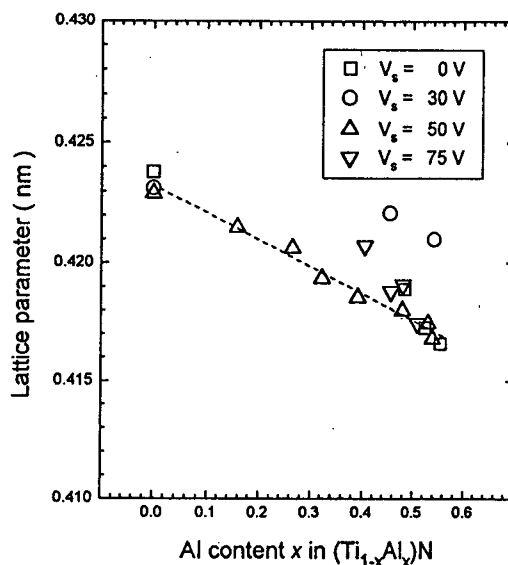

Fig. 2 Lattice parameter of$(Ti_{1-x}Al_x)N$ films vs. Al content x.

was observed for $(Ti_{1-x}Al_x)N$ films deposited with each bias voltage. Except for TiN film, mi-crostructural variation of $(Ti_{1-x}Al_x)N$ films with Al contentx$(0.16 \leq x \leq 0.6)$ could not be observed, when the applied bias voltage was identical. As shown in Fig. 3, microstructure of the films, deposited without RF bias voltage, was very porous. However, applying RF bias voltage, even of 30V, leaded to a dense microstructure possibly due to the interruption of columnar-structure growth[2]. Densification of the film structure was mainly caused by implantation and recoil processes together with forward sputtering into voided regions[2]. Thus, adatom diffusivities could be thought to be enhanced with applica

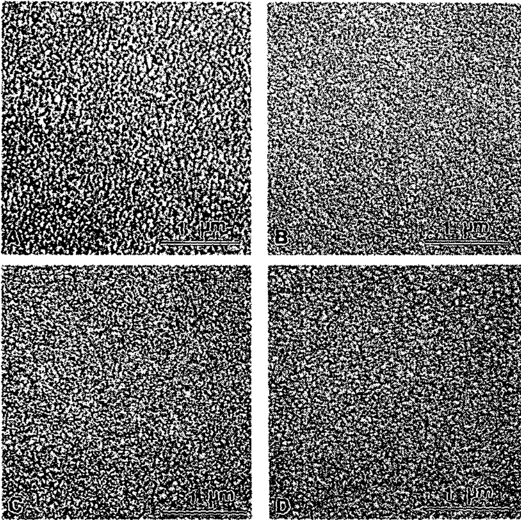

Fig. 3 Scanning electron micrographs of ($Ti_{0.52}Al_{0.48}$)N films deposited at room temperature with RF bias voltage of (a) 0 V, (b) 30 V, (c) 50 V, and (d) 75 V.

tion of RF bias voltage, resulting in more close-packed microstructure[2].

As shown in Fig. 4, the grain size of TiN films (~160nm) was larger than~75nm of (Ti1-xAlx)N films (Fig. 3) without depending on the bias voltage ranging from 0 V to 100V. Larger grain size of TiN films was possibly attributed to the lower sputtering rate of Ti compared with Al[11, 13].

Microhardness values of 1㎛-thick ($Ti_{1-x}Al_x$)N films, deposited on Si or HSS substrates at various sputtering condition, were illustrated in Fig. 5. Usually, coating thickness of at least seven times larger than indentation depth is required for hardness measurement of thin film coatings to eliminate extension of the plastic deformation field into the substrate[1,14]. In this study, however, hardness of 1 ㎛-thick ($Ti_{1-x}Al_x$)N films was measured at indentation load of 50 gf to eliminate the difficulty of measuring indentation diagonals with optical microscopy at 500ㅌ. Hardness values of ($Ti_{1-x}Al_x$)N films in Fig. 5 were lower than ones reported in the literature. Hardness of TiN coatings, which is strongly dependent on the coating thickness, has been reported to increase from 500kg/㎟ at~1㎛ thickness to 2100kg/㎟ for about 5㎛

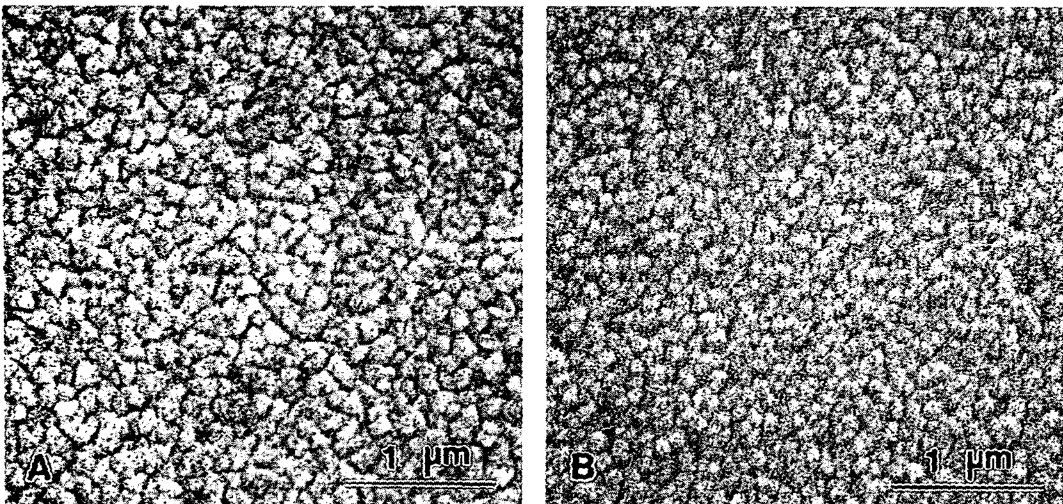

Fig. 4 Scanning electron micrographs of TiN film deposited at room temperature with RF bias voltage of (a) 0 V and (b) 50 V.

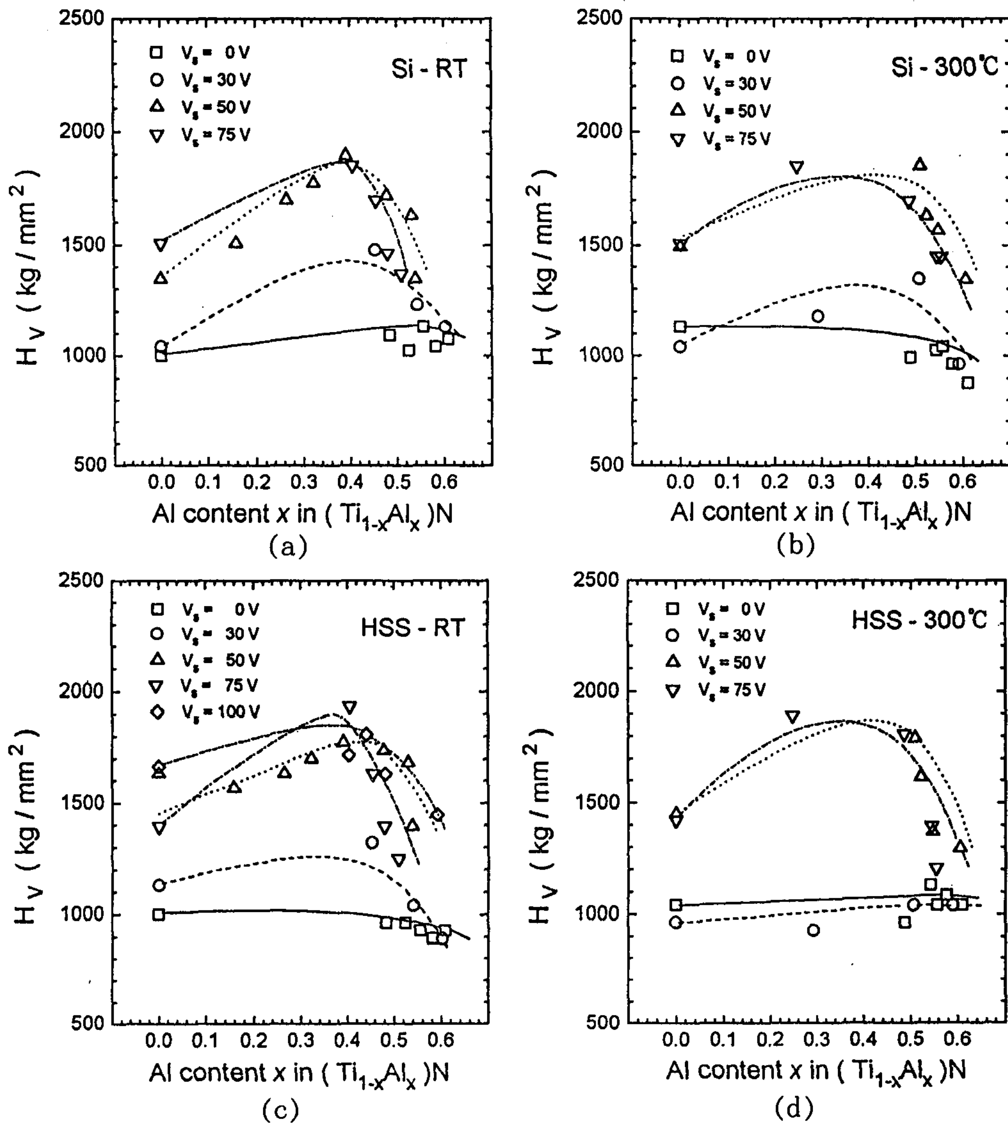

Fig. 5 Microhardness of 1 μm-trick $(Ti_{1-x}Al_x)N$ films, reactively sputtered on (a) Si substrate at room temperature and (b) at 300℃, and on (c) HSS substrate at room temperature and (d) at 300℃

-thick films[1]. Thus, hardness of $(Ti_{1-x}Al_x)N$ films (Fig. 5), fabricated by reactive sputteri *ng in this study, will increase to much higher values, when they are measured at thicker films. In fact, hardness of 1800kg/㎜^{2} and 2000kg/㎜^{2} was obtained on 3㎛-thick TiN films which were deposited at room temperature with RF bias voltage of 50V and 75V, respectively·

As shown in Fig. 5, hardness of $(Ti_{1-x}Al_x)$ N films was markedly improved by applying RF bias voltage above 50V, due to the densification of microstructure (Fig. 3 and Fig. 4) and also possibly due to the increase

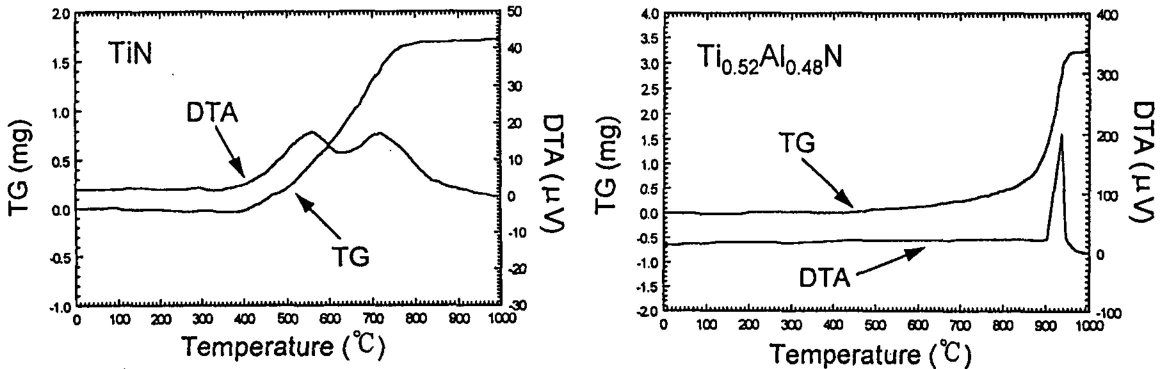

Fig. 6 TG/DTA curves of TiN curves of TiN and ($Ti_{0.52}Al_{0.48}$)N films deposited with RF bias voltage of 50 V.

of point defect density formed during film growth[2]. Hardness of ($Ti_{1-x}Al_x$)N films increased with increasing Al content x and reached a maximum value for Al content x of about 0.4. This hardness improvement with Al contentx could be attributed to the distortion of TiN lattice by substitution of Al into Ti sites. Hardness values of ~1900kg/㎟ were obtained for 1㎛-thick ($Ti_{0.6}Al_{0.4}$)N films deposited with RF bias voltage above 50V.

Oxidation behavior of TiN and ($Ti_{0.6}Al_{0.4}$)N films, deposited at room temperature with RF bias voltage of 50V, is illustrated in Fig. 6. Although the oxidation of TiN film began to occur at about 350℃, it could be retarded up to 900℃ for ($Ti_{0.52}Al_{0.48}$)N film. It has been reported that the enhanced oxidation resistance of ($Ti_{1-x}Al_x$)N film is caused by the large difference in Gibbs free energy of the oxide formation for Ti and Al in ($Ti_{1-x}Al_x$)N film[15,16]. Compared with Ti, Al is weakly bonded to the nitrogen, and more easily oxidized to form a stable and protective Al_2O_3 layer on the ($Ti_{1-x}Al_x$)N film surface[8,15,16].

CONCLUSIONS

1) Al content x of ($Ti_{1-x}Al_x$)N coatings, fabricated by reactive sputtering, was reduced by increasing the substrate RF bias voltage.

2) Without depending on RF bias voltage (0V~100V) and substrate temperature, crystalline phase of ($Ti_{1-x}Al_x$)N coatings, fabricated by reactive sputtering, was changed from TiN single phase with (111) preferred orientation to two phase mixture of TiN and AlN at Al content x of 0.6.

3) Microstructure of ($Ti_{1-x}Al_x$)N films was densified by applying RF bias voltage, even of 30V. Compared with TiN films of which grain size was about 160nm, ($Ti_{1-x}Al_x$)N films were composed of smaller grains of ~75nm.

4) Hardness of ($Ti_{1-x}Al_x$)N films increased markedly by appling RF bias voltage above 50V. Hardness of ($Ti_{1-x}Al_x$)N films reached a maximum value for Al contentx of about 0.4, and 1900kg/㎟ was obtained for 1㎛-thick ($Ti_{0.6}Al_{0.4}$)N films sputter-deposited with RF bias voltage of above 50V.

5) Although the oxidation of TiN film began to occur at about 350℃, it could be retarded up to 900℃ for $(Ti_{0.52}Al_{0.48})N$ film.

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