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Influence of total gas pressure on the microstructure and properties of CrAlN films deposited by a pulsed DC balanced magnetron sputtering system

S. Khamseh [a,*], M. Nose [b], T. Kawabata [a], K. Matsuda [a], S. Ikeno [a]

[a] *Department of Materials Science and Engineering, Faculty of Engineering, University of Toyama, 3190, Gofuku, Toyama 930-8555, Japan*
[b] *Faculty of Art and Design, University of Toyama, Takaoka 933-8588, Japan*

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ABSTRACT

CrAlN films have been prepared using a pulsed DC reactive sputtering system. The effects of N_2/Ar ratio and pulse width on the film's structure and properties have been investigated.

The total sputtering pressure decreased with increased N_2/Ar ratio. All CrAlN films showed NaCl-type CrN structure, while mixed structures of wurtzite-type Cr_2N, wurtzite-type AlN and NaCl-type CrN phases formed in the films produced under lower sputtering pressure and higher pulse width. Increasing the sputtering pressure resulted in a decrease in the films internal stress. Moreover, the plastic hardness of the films prepared under different pulse widths was higher at the lower sputtering pressure.

1. Introduction

It is well known that the energy delivered to a growing film by bombarding particles (E_{pi}) has a strong effect on its microstructure and properties [1–5]. Polakova et al. [6] showed that, in a collisionless discharge, the energy delivered per deposited volume can be determined from three measured quantities, i.e. the substrate bias (U_s), the substrate ion current density (i_s) and the deposition rate (a_D) of the film, according to the following formula:

$$E_{pi} = \left(\frac{i_s U_s}{a_D}\right) \exp\left(-\frac{L}{\lambda_i}\right) \quad \text{at } T_s = \text{const} \tag{1}$$

where (L) is the sheath thickness, (λ_i) is the mean free path of the ion for collisions leading to losses of the ion energy in the sheath [6]. In DC magnetron sputtering system it has been found that changes in sputtering rate (a_D), caused by a change in the partial pressure of reactive gas (p_{RG}) (RG = N_2, O_2, CH_4, etc.) under constant deposition conditions, induce very large changes in the energy (E_{pi}) delivered to the film during its growth [6,7]. Therefore, it can be expected that changes in the properties of the reactively sputtered films will strongly depend on the partial pressure of reactive gas [7]. Previous reports demonstrated that pulsed DC magnetron sputtering enhances both the plasma density and electron temperature, and therefore increases the ion energy and ion flux to the growing film at the substrate [8–11]. However, little is currently known about the role of the partial pressure of reactant gas on the microstructure of the films prepared in pulsed DC magnetron sputtering systems.

CrAlN films are well known for their outstanding properties such as high toughness, high compressive residual stress, excellent film adhesion, low surface energy and high wear resistance [12–20]. Over recent years a general approach aimed at improving the properties of CrAlN film has been to increase its Al content to improve its structure and increase its thermal stability. In our previous report we showed that, with a Cr/Al (=30/70 (at.%)) alloy target in the pulsed DC balanced magnetron sputtering system, CrAlN films with moderate hardness and a mixed structure of NaCl-type CrN and wurtzite-type AlN form [21]. However, these CrAlN films did not show good mechanical properties. In contrast, using a Cr/Al (=50/50 (at.%)) alloy target and different pulse widths, CrAlN films with the correct microstructure and good mechanical properties were formed [22]. There are some reports on the effect of sputtering conditions and pulsing parameters on the properties and structure of CrAlN film in unbalanced magnetron sputtering systems, but there are only few reports on these effects in a balanced magnetron sputtering system. Facing target-type sputtering is one of the balanced magnetron sputtering systems, frequently used for the deposition of magnetic materials [23,24], hard coatings [25] and transparent conducting coatings [26]. We need to investigate the effect of sputtering conditions and pulsing parameters on the microstructure and mechanical properties of CrAlN films in balanced magnetron spattering system. In this paper, we report on CrAlN films prepared in a balanced magnetron sputtering

* Corresponding author.
E-mail address: srkhamseh@yahoo.com (S. Khamseh).

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Table 1
Details of deposition parameters and properties of the films that prepared under different deposition conditions.

Sample No.	Total sputtering pressure (Pa)	N_2/Ar	Pulse width, τ_p (ns)	Composition (at.%)			Internal stress (GPa)	Hpl (GPa)
				Cr	Al	N		
S-1	2.7×10^{-1}	20/15	576	26.1	24.6	49.3	-2.7 ± 0.4	28 ± 2.5
S-2	2.6×10^{-1}	20/15	1136	–	–	–	-2.6 ± 0.7	30 ± 1.5
R-1	2.3×10^{-1}	30/10	576	–	–	–	-3.5 ± 0.9	33 ± 2.5
R-2	2.2×10^{-1}	30/10	1056	24.1	24.5	51.4	-3.6 ± 1.1	42 ± 2.8

system under different N_2/Ar ratios and pulse widths with a Cr/Al (=50/50 (at.%)) alloy target. The microstructure and properties of the deposited films were studied.

2. Experimental procedure

CrAlN films were prepared in a pulsed DC sputtering apparatus with facing target-type sputtering (FTS) configuration (Osaka Vacuum Co., Ltd., FTS-2R). For more details about the deposition conditions of the films we refer to our previous reports [21,22]. A mirror-polished silicon wafer 25 mm square was used as the substrate. All the substrates were cleaned ultrasonically with acetone, ethanol, and 2-propanol, in that order, before sputtering deposition.

The hardness was measured by a nanoindentation system (Fischer scope, H100C) at room temperature. The load was selected to keep an impression depth not more than 10% of the film thickness, so that the influence of the substrate could be neglected.

The measurement of the internal stress value of the films is described in detail in our previous articles [21,22].

The crystal structure of the films was assigned using X-ray diffractometry (Cu Kα radiation) with either a thin film or θ–2θ goniometer (Philips X'pert system). When using the thin film goniometer, scans were made in the grazing angle mode (Seeman–Bohlin mode) with an incident beam angle of 1°.

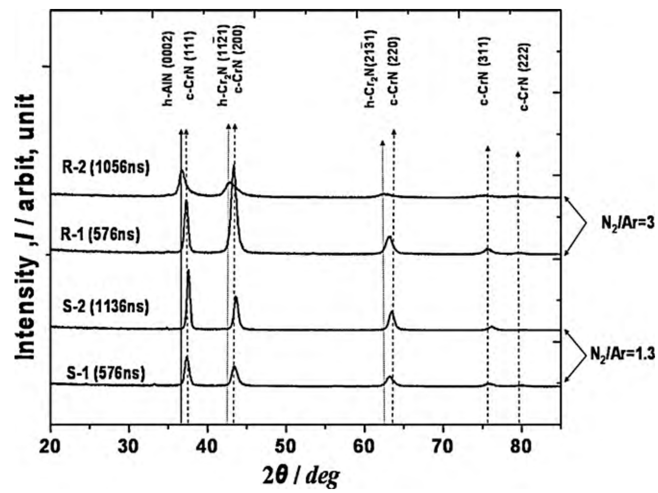

Fig. 1. X-ray diffraction patterns of CrAlN films at different deposition conditions.

3. Results and discussion

Details of the deposition of films and magnetron pulsing parameters for each N_2/Ar ratio are summarized in Table 1. Films were prepared at two different pulse widths (low and high) with two N_2/Ar ratios of 1.3 (named group-S) and 3 (named group-R). The pulsing power was 1.5 kW and the frequency 240 kHz. The total sputtering gas pressure ranged between 0.26 and 0.27 Pa for group-S, and 0.22–0.23 Pa for group-R.

As shown in Table 1 the total sputtering pressure is lower for films of the group-R which are prepared under higher N_2/Ar ratio. On increasing the nitrogen flow rate in group-R, target poisoning became apparent. Moreover, with increased nitrogen flow rate, the Ar flow rate decreased simultaneously. Consequently, the number of whole sputtered species decreased as a result of combined actions of target poisoning and lower Ar partial pressure. Finally, the total sputtering gas pressure was lower at higher N_2/Ar ratio.

The development of XRD patterns for CrAlN films, prepared at different N_2/Ar ratios and pulse widths is given in Fig. 1. Films prepared at the lower N_2/Ar ratio (S-1, 2) and one film prepared at higher N_2/Ar ratio and lower pulse width (R-1), exhibited a NaCl-type CrN structure. In contrast, a film prepared at higher N_2/Ar ratio and higher pulse width (R-2) showed a mixed structure of wurtzite-type Cr_2N and wurtzite-type AlN phases in addition to some weak peaks of NaCl-type CrN phase at high diffraction angles. For more details about the formation of mixed structure in the R-2 film, we refer to our previous paper (this sample is named as D-5 film) [22].

An increase in sputtering pressure also affected the internal stress values of the films. The residual stress values in CrAlN films deposited at different deposition conditions are summarized in Table 1. All stress values in CrAlN films are compressive. The CrAlN films deposited at lower sputtering pressure (group-R) exhibited higher compressive stress values compared to the films deposited at higher sputtering pressure (group-S). The intrinsic stress occurs as a consequence of an accumulation of crystallographic defects that are built in to the film during its deposition and is connected with the energy delivered to the growing film by bombarding ions and condensing particles [11]. According to Eq. (1) this energy (E_{pi}) is determined not only by (i_s), (a_D) and (U_s) but also by the total sputtering pressure (p_T). Thus, a decrease in total sputtering pressure at higher N_2/Ar ratios will increase the mean free path of ions (λ_i) which in turn increase the delivered energy to the growing film (E_{pi}). It has been shown that, when the incident species on the surface of the growing film have relatively low energies and subplantation ratios, their energy is transferred to the surface of the growing film and affects the surface roughness [27–31]. On the other hand, when the energy of the incident species increases, their energy is dissipated in the bulk of the film which, in turn, results in higher internal stresses [30,32,33]. The film composition for S-1 and R-2 films is shown in Table 1. It can be seen that the percentage of atomic nitrogen in the R-2 film is higher than that of S-1. We conclude that more nitrogen species with higher energy are incorporated into the films of group-R which result in the observed higher internal stress.

The hardness values of CrAlN films deposited at different sputtering pressures and pulse widths are summarized in Table 1. CrAlN films prepared at lower sputtering pressures (group-R) showed slightly higher hardness, ranging between 33 and 42 GPa, compared to the films prepared at higher sputtering pressures (group-S) which ranged between 28 and 30 GPa. Polakova et al. reported formation of super hard (Ti,Al,V)N films at lower total sputtering gas pressures [6]. However, they demonstrated that super hard film can be formed only at energies (E_{pi}) greater than a minimum (threshold) energy (E_{pi}) but a certain minimal energy (E_{pi}) is only a necessary condition to enhance film's hardness and is not the single dominating one. A second condition necessary to cause high hardness in the film is an optimum structure [6]. In this study, films at higher sputtering pressures show higher internal stress values. Moreover, the R-2 film shows mixed structure of wurtzite-type and the NaCl-type phases. In our previous article, the R-2 film was characterized as a nanocomposite film composed of a mixture of grains with different chemical composition [22]. These together can yield an optimal structure which can result in higher hardness values of group-R.

4. Conclusions

From the results of the present study, the following conclusions can be drawn:

(1) An increase in the N_2/Ar ratio leads to a decrease in total sputtering gas pressure. This decrease can increase the energetic bombardment of the growing film.
(2) All CrAlN films showed NaCl-type CrN structure, while mixed structures of wurtzite-type Cr_2N, wurtzite-type AlN and NaCl-type CrN phases were formed in the film with lower sputtering pressure (higher N_2/Ar ratio) and higher pulse width.
(3) Higher energetic bombardment of the films at lower sputtering pressure leads to the formation of CrAlN films with higher internal stress and hardness.
(4) An increase in the energy of bombarding particles with decreasing total sputtering pressure (p_T) significantly influences the structure and properties of deposited films in a pulsed DC balanced magnetron sputtering system.

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