Journal of Alloys and Compounds 508 (2010) 191–195

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

A comparative study of CrAlN films synthesized by *dc* and *pulsed dc* reactive magnetron facing target sputtering system with different pulse frequencies

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ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form 10 August 2010
Accepted 13 August 2010
Available online 19 August 2010

Keywords:
CrAlN
dc Magnetron sputtering
Pulsed magnetron sputtering
Pulse frequency
Balanced magnetron sputtering

ABSTRACT

CrAlN films were prepared using a *balanced* magnetron sputtering system operated in *dc* and *pulsed* condition (with different pulse frequencies), and their phase composition were then determined through XRD analysis. In order to investigate the relationship between the mechanical properties and microstructure of the films, hardness measurements were taken using a nanoindentation system. All films exhibited NaCl-type CrN structure in both *dc* and *pulsed* conditions. Plastic hardness, H_{pl}, of the films ranged between 15 to 36 GPa. *Pulsed* prepared CrAlN films showed higher hardness, higher internal stress values, and smaller grain sizes than *dc* prepared CrAlN film. Moreover, plastic hardness and internal stress of *pulsed* prepared CrAlN films increased on increasing pulse frequency.

1. Introduction

The engineering of thin films is complicated by their deposition mechanism. One current problem is that in each deposition process there are many deposition parameters operating simultaneously, which can change the structure and properties of the film. Musil suggests that this problem can be solved by controlling the energy delivered to the film during its growth [1]. When a large number of energetic particles hit the surface of the growing film, several effects occur. First of all, when energetic ions attack the surface of the growing film, their kinetic energy transfers to other atoms. This kinetic energy excites the surface atoms, causing them to move around on the surface and find energetically proper sites. Increasing ion bombardment causes formation of films with high density and smooth surface, which results from the resputtering of the surface atoms that fill the voids [2–8]. In addition, ion bombardment of the growing film can increase nucleation sites and permit the formation of nanocrystalline films. Recently, highly energetic species (up to hundreds eV) were formed in plasma by pulsing the power of the target during *pulsed* magnetron sputtering [7–16]. However, little is currently known about the role of pulse frequency on the microstructure of films prepared in *pulsed dc* balanced magnetron sputtering systems.

Ternary nitrides find widespread use as hard protective films on cutting tools and as corrosion and abrasion-resistant layers on optical and mechanical components. Among ternary nitrides, CrAlN films have some outstanding properties like high toughness, high compressive residual stress, excellent film adhesion, low surface energy and high wear resistance [17–22]. The combination of these properties makes CrAlN films suitable for many applications. In our previous report we showed that in a *pulsed dc balanced* magnetron sputtering system, increasing the energy of bombarding particles while decreasing the total sputtering pressure (p_{T}) leads to the formation of CrAlN films with higher internal stress and hardness [23]. 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 a few reports on these effects in a *balanced* system. Lin et al. showed that during sputtering of CrAlN film in a *pulsed dc unbalanced* system, a change in pulse frequency from 100 to 350 kHz leads to a cubic to hexagonal phase transformation [16]. Unfortunately, there is no report on the relationship between pulse frequency and microstructure of CrAlN films produced in a *pulsed dc balanced* system, and accordingly, the purpose of the present work is to address this topic. In this study, CrAlN films were synthesized in a *balanced* magnetron sputtering system, through both *dc* and *pulsed* reactive sputtering at various pulse frequencies. Comparative studies of the microstructure and properties between *dc* and *pulsed* CrAlN films were then performed.

2. Experimental procedure

CrAlN films were prepared in a magnetron sputtering apparatus having a pair of targets facing each other. This is referred to as the facing target-type sputtering (FTS) (Osaka Vacuum Co., Ltd., FTS-2R), as shown in Fig. 1, where a magnetic field of about

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doi:10.1016/j.jallcom.2010.08.042

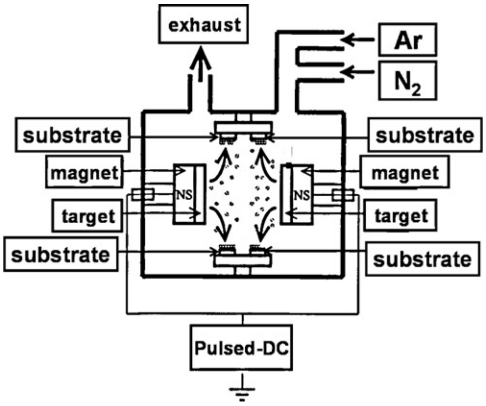

Fig. 1. Schematic drawing of a facing target-type sputtering apparatus.

0.02 T is applied perpendicular to the target planes to confine the plasma between the two targets, thereby maintaining discharge even under a gas pressure lower than the limit for planar magnetron sputtering. The sputtering system can be operated in both *dc* and *pulsed* conditions. Two rectangular plates (100 mm × 160 mm × 10 mm thickness) of alloy targets (Cr/Al = 50 at%/50 at%) (99.9%) were sputtered in a mixture of argon and nitrogen, both of 99.9999% purity. Details of the film deposition and magnetron pulsing parameters are summarized in Table 1. The system was evacuated to a vacuum down to 5×10^{-5} Pa (=3.8×10^{-7} Torr) prior to deposition. The flow rate of each gas (Ar/N_2) was independently controlled using a mass-flow controller. In order to avoid target poisoning and to precisely control the nitride formation, the argon flow rate was fixed and the nitrogen flow rate was reduced from a high nitrogen flow rate to a lower nitrogen flow rate, along the hysteresis loop of reactive sputtering [24,25]. A mirror-polished 25 mm square silicon wafer was used as the substrate. All the substrates were cleaned ultrasonically with acetone, ethanol, and 2-propanol, in that order, before sputtering deposition. The input power of *pulsed dc*, was applied to both targets synchronously and the target-to-substrate distance was fixed at 115 mm. The substrates kept at floating potential during the deposition. The substrate temperature increased to 150 °C during deposition due to particle bombardment of the substrate even without bias application and substrate heating. The N_2/Ar flow rate was fixed at 20/15 sccm for all samples. For the *pulsed* prepared CrAlN films, pulse frequency ranged between 80 and 240 kHz; the pulse power was 1.5 kW and the duty cycle was 79%. The film thickness was controlled between 1.8 and 2 μm by controlling the sputtering time.

The Ar intensity of the films was evaluated by electron probe microanalysis (EPMA) measurement (JEOL model JXA-8200D). Because of the lack of a standard sample for argon, the argon intensities of the films are compared.

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

The evaluation of the film internal stress was carried out using a surface profile and roughness measuring instrument (MITUTOYO, SV-624). Alterations in the sample curvature, caused by the deposited film, were investigated using this instrument. The film stress, σ, was calculated from the following equation derived from the Stoney equation:

$$\sigma = \left[\frac{ET^2}{3(1-\upsilon)L^2 t} \right] \times 4\delta \qquad (1)$$

where E, υ, T and L are Young's modulus, Poisson's ratio, substrate thickness, and substrate length, respectively. In this case, t is the thickness of the film ($t \ll T$) and δ is the deformation in the center of substrate after deposition.

The crystal structure of the films was determined 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 taken in the grazing angle mode (Seeman–Bohlin mode) with an incident beam angle of 1°.

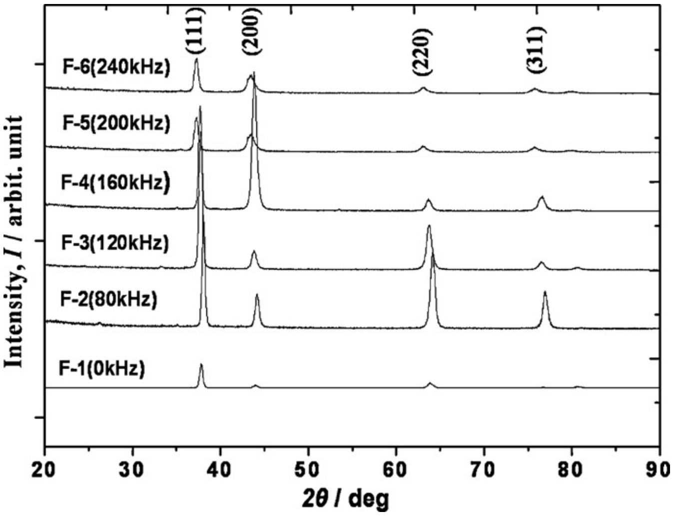

Fig. 2. X-ray diffraction patterns of CrAlN films at different pulse frequencies measured by TF mode.

TEM samples were prepared and observed perpendicular (cross-sectional view) to the film surface. The samples were milled with a focused ion beam milling system (HITACHI, FB-2100), and TEM studies were carried out with a (TOPCON, EM-002B type) TEM operated at 120 kV.

3. Results

The XRD patterns of the CrAlN films deposited at *dc* and *pulsed* conditions are presented in Fig. 2. All films exhibited NaCl-type CrN structure; however, the diffraction peaks of the *pulsed* sputtered CrAlN films showed a clear shift to lower diffraction angles compared to that in *dc* sputtered CrAlN film. The film composition for F-3 and F-6 films is shown in Table 1. There is a small difference in composition between the films at low and high pulse frequencies. Accordingly, the shifting of XRD peaks to a lower angle cannot be related to the changes in the chemical composition of the films by pulsing frequency. This peak shift indicates a possible increase in the film internal stress with increasing pulse frequency.

Using *pulsed dc* sputtering also affected the internal stress value of the films. Figure 3 shows the internal stress values of the CrAlN films synthesized in *dc* and *pulsed* conditions; all stress values in the films are compressive. *Pulsed* CrAlN films showed higher internal stress values compared to *dc* sputtered film. Moreover, internal stresses of *pulsed* CrAlN films increased with increasing pulse frequency. Since the measured residual stress can be generated by both thermal and intrinsic sources, it is good to examine their relative contributions. It has been demonstrated that the intrinsic stress dominates over thermal stress when the ratio of T_s/T_m is smaller than 0.3, where T_s is substrate temperature and T_m is the melting temperature of the films materials [26]. The melting point of AlN and CrN is 2572 and 1773 °C, respectively. According to the rule

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

Sample no.	N_2/Ar	Power (kW)	Duty cycle (%)	Pulse width, τ_p (ns)	Frequency (kHz)	Ar intensity	Composition (at%)		
							Al	Cr	N
F-1	15/20	1.5	–	–	0	–	–	–	–
F-2	15/20	1.5	79	2073	80	–	–	–	–
F-3	15/20	1.5	79	1096	120	334	24.4	26.5	49.1
F-4	15/20	1.5	79	1256	160	–	–	–	–
F-5	15/20	1.5	79	1056	200	–	–	–	–
F-6	15/20	1.5	79	896	240	1295	24.6	26.1	49.3

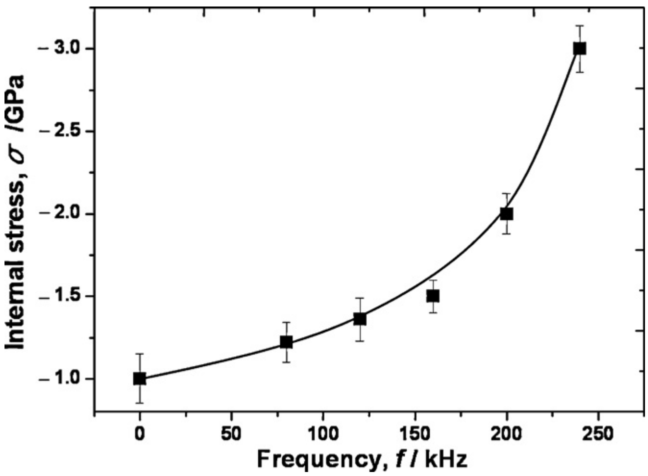

Fig. 3. Influence of pulse frequency on internal stress values of CrAlN films.

of mixture the melting point of CrAlN film will be around 2172 °C. Since the substrate temperature fixed at 150 °C during deposition the ratio of T_s/T_m will be 0.05 which is smaller than 0.3. Moreover, it is well known that the thermal stress σ_{th} is related to difference in coefficient of thermal expansion between substrate and film material. Here we used the rule of mixture between CrN and AlN, using the following values: $\alpha_{CrN} = 2.3 \times 10^{-6}\,k^{-1}$ [27], $\alpha_{AlN} = 5 \times 10^{-6}\,k^{-1}$ [28]. This gives $\alpha_{CrAlN} = 3.6 \times 10^{-6}\,k^{-1}$. Thermal expansion coefficient of Si is $3 \times 10^{-6}\,k^{-1}$, and $\Delta\alpha$ will be $0.6 \times 10^{-6}\,k^{-1}$. Since T_s/T_m ratio is smaller than 0.3 and the difference in thermal expansion coefficient between substrate and film is small, we believe that the measured residual stress is dominated by the intrinsic stress since the contribution from thermal stress is small. The argon intensities of F-2 and F-6 films are shown in Table 1. It can be seen that the Ar intensity of F-6 film is higher than that of F-2. This suggests that at higher pulse frequencies, more Ar becomes inserted in to the lattice, thus forming CrAlN films with higher internal stress [29].

The dependence of the plastic hardness of the films on the pulse frequency is shown in Fig. 4. Plastic hardness, H_{pl}, of the films varied between 16 and 36 GPa. The *pulsed* sputtered CrAlN films showed higher plastic hardness than *dc* sputtered film. Moreover, the plastic hardness of the films increased with increasing the pulse frequency.

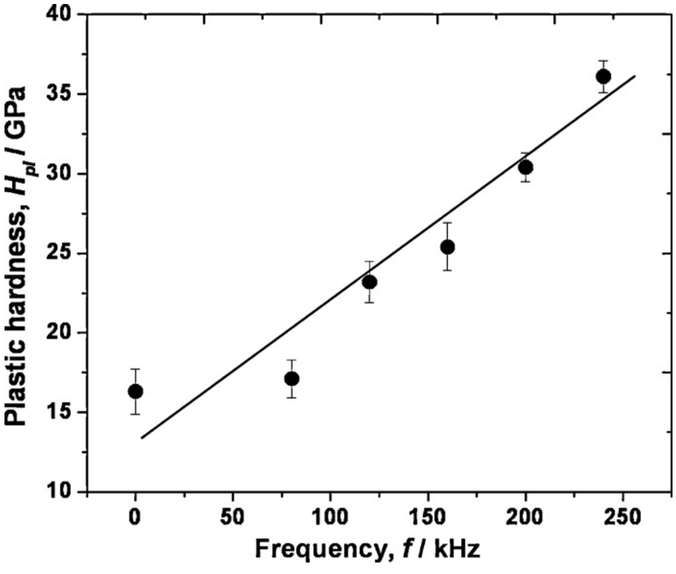

Fig. 4. Influence of pulse frequency on plastic hardness, H_{pl}, of CrAlN films.

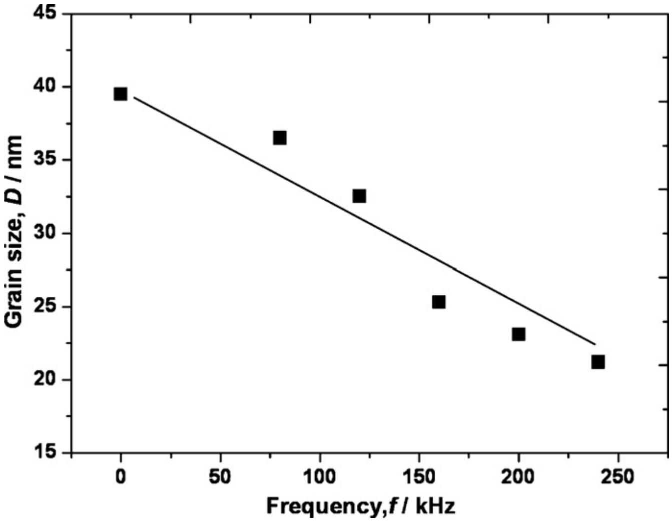

Fig. 5. Influence of pulse frequency on grain size of CrAlN films.

Figure 5 shows the change of film grain size with pulse frequency. The grain sizes calculated from the XRD peak width of the films in θ–2θ scan mode. The width of the XRD peaks reveals, using the Scherrer equation, the average length of the columnar grains as the grain size. The *pulsed* sputtered CrAlN films exhibited smaller grain sizes in comparison with *dc* sputtered film. Previous reports demonstrated that the energetic bombardment of the growing film in the *pulsed* plasma can effectively transfer the energies to the adatoms, which increase the adatoms mobility and nucleation sites, thereby decreasing the grain size of the *pulsed* sputtered films [16,29].

In order to compare the grain size of the films prepared at low (F-2) and high pulse frequencies (F-6), cross-sectional dark field TEM images of each film are shown in Fig. 6(a) and (b), respectively. The columnar width and columnar height of F-2 film at low pulse frequency of 80 kHz (F-2) were estimated from the cross-sectional dark field image of the TEM sample to be in the range of 30–100 and 120–300 nm, respectively. However, the columnar width and columnar height of F-6 film at the higher pulse frequency of 240 kHz (F-6), ranged from 10 to 30 and 50 to 150 nm, respectively. Therefore, the grain size of the *pulsed* CrAlN films decreased with increasing pulse frequency.

4. Discussion

It has been shown that film properties, such as high compressive stresses and high roughness can be explained by the energy of the incident species on the surface of the growing film [30,31]. It is shown that when the energy of the incident species on the film surface is low, their energy transfers to the surface of the growing film and affects the surface roughness [5,31,32]. On the other hand, the species are supplanted into the film when their energy increases, which, in turn, forms higher internal stresses [33–36]. Lee et al. reported that the ion density and energy flux increase with increased pulse frequency in *pulsed dc* plasma. They claimed that these increases are due to the stochastic heating generated by the fast oscillation in the target voltage wave form [37]. Moreover, Glocker [38] analyzed the plasma generated by a *pulsed dc* power supply and found that pulsing increases the time-averaged electron temperature and density as compared to *dc* sputtering discharges. This gives rise to greater ion fluxes at the substrate and significantly higher ion energy fluxes per arriving atom at the growing film. In

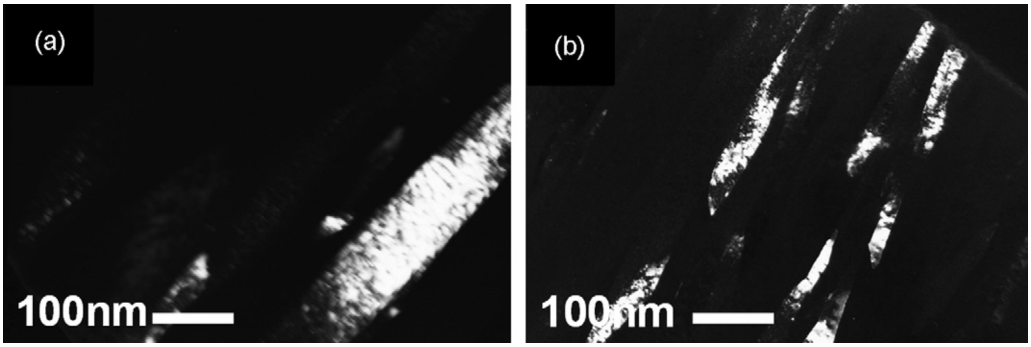

Fig. 6. Cross-sectional dark field TEM images of CrAlN film with different pulsing frequencies (a) F-2, *f* = 80 kHz and (b) F-6, *f* = 240 kHz.

the present study, we argue that energy of the incident species on the surface of the growing film is probably higher for *pulsed* CrAlN films. A possible correlation was sought between energy of the incident species on the surface of the growing film and changes in structural properties like internal stress and grain size. In the following, we examine this attempted correlation.

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 correlated with the energy delivered to the growing film by the bombarding ions and condensing particles [39]. As shown in Fig. 3, *pulsed* sputtered CrAlN films have higher internal stress values than that of *dc* sputtered film. Moreover, films those are prepared at higher pulse frequencies show higher values of internal stress, which might be related to an increased energetic bombardment of the films with increased pulse frequency [5].

As shown in Figs. 5 and 6, grain sizes obtained from XRD and TEM analysis are smaller for *pulsed* CrAlN films, which decrease continuously with increasing pulse frequency. Lee et al. [37,40] revealed that the time average ion flux and energy flux increase as the pulse frequency increases. Consequently, more surface defects on the growing film are produced by the higher energy of incident ions when pulsing frequency increases. With an increasing number of preferential nucleation sites, the grain size of thin film will be decreased. The smaller grain size of the *pulsed* CrAlN films is another piece of evidence that there is increased energetic bombardment at higher pulse frequencies [16,29].

As discussed above, the grain sizes of *pulsed* CrAlN films are smaller than that of *dc* CrAlN film and the grain size decreases with increasing pulse frequency. Moreover, the *pulsed* CrAlN films show higher internal stress values compared to *dc* CrAlN film, and the internal stress values of *pulsed* CrAlN films increases gradually with increasing pulse frequency. With a decrease in grain size down to approximately 20 nm, multiplication and mobility of dislocations are hindered and the hardness of the material increases according to the Hall–Pech relationship. Consequently, it is most likely that the existence of a higher internal stress or smaller grain size is responsible for the higher hardness of the films in *pulsed* CrAlN films at higher pulse frequencies.

Here we conclude that the microstructure and properties of CrAlN films strongly change in the *pulsed* sputtering condition in *balanced* magnetron sputtering system.

5. Conclusions

Microstructural studies of the films allow us to draw the following conclusions:

(1) All films had an fcc-CrN crystalline structure.
(2) *Pulsed* sputtered CrAlN films showed higher internal stress values, which increased with increasing pulse frequency.
(3) *Pulsed* sputtered CrAlN films showed smaller grain sizes, which decreased with increasing pulse frequency.
(4) The plastic hardness of the films increased from 16 to 36 GPa when increasing the pulse frequency. *Pulsed* synthesized CrAlN films showed higher plastic hardness values compared to *dc* synthesized CrAlN film.
(5) The microstructure and properties of CrAlN films can strongly vary in the *pulsed* sputtering condition in *balanced* magnetron sputtering system.

Acknowledgement

The authors wish to express their thanks for the financial support by a grant for scientific research from Japan Society for the Promotion of Science.

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