Research Article

Influence of Aluminium Contents on the Structure and Hardness of Chromium Aluminium Nitride Thin Films

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ABSTRACT

This research aims to study the influence of aluminum content in film on the structure and hardness of chromium aluminum nitride thin films, which are deposited on silicon by reactive DC unbalanced magnetron sputtering method from the Cr-Al alloy target (50:50 at%). The structure, chemical composition, morphology, and hardness were characterized by XRD, EDS, FE-SEM, and nano-indentation techniques, respectively. The results showed that the as-deposited films were formed as a (Cr, Al)N solid solution with fcc structure in the (111), (200), and (220) planes. The as-deposited film had lattice parameters in the range of 4.088-4.138 Å. The as-deposited film had nano-structure whereas the average crystallite size was in the range of 3.1-16.8 nm. The chemical composition from the EDS technique showed that the as-deposited film had chromium (Cr), aluminum (Al), and nitrogen (N) as the main component in different ratios. The FE-SEM micrograph presented that the Al content affected the surface morphology and cross-sectional of the as-deposited film. The hardness, of the as-deposited films measured by the nano-indentation technique, increased from 12.47 GPa to 67.29 GPa with the Al content while decreasing with the crystallite size. The highest hardness found in the CrAlN film with the Al content was 30.93 at% and the crystallite size was 3.1 nm.

Keywords: Hard thin films, CrAlN, Aluminium content, Reactive magnetron sputtering

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Introduction

In the past two decades, modern industrial development has generated several demands in materials technology focused on modifying and improving the surface of industrial parts such as turning, milling, drilling tools, and machinery components. Transition metal hard coatings, such as carbide or nitride compounds, are widely used to enhance the material's surface properties to increase wear and corrosion resistance, which improve their lifetime and performance, enhance productivity, and enable some new engineering applications as well [1]. These metal nitrides' thin film possesses a higher hardness than high-speed steel and cemented carbide due to their superior mechanical and tribological properties. The binary metal nitrides such as TiN, CrN, and ZrN are well known as the first generation of the physical vapor deposition (PVD) hard coating for industrial tooling and machinery parts [2, 3].

Compared to the TiN and ZrN films, Cr-based nitride film, such as CrN film has been extensively studied and used in various industries due to its high thermal stability and good wear resistance as well as high corrosion resistance. Therefore, the CrN film received extensive interest in many industrial applications [4, 5]. There are numerous studies indicating that the CrN film rapidly oxidized and deteriorated at high temperatures above 600 °C. However, several methods can resolve this problem and enhance the mechanical and chemical properties of CrN films, one of which is by alloying the other elements in the CrN films to form a ternary metal nitride coating [6]. Among these ternary nitride hard coatings, the CrAlN film has some outstanding properties such as high hardness (>30 GPa), high anti-corrosion resistance, and oxidation resistance at high temperatures [7]. Due to these advantages, the CrAlN film is a good candidate as an alternative compared to conventional CrN coating.

The CrAlN ternary nitride film can be deposited by various PVD techniques such as cathodic arc evaporation [8], RF sputtering [9], and DC sputtering [10]. Among them, the sputtering method is the most suitable and widely used because it uses non-toxic gases, a low-temperature process, and a straightforward procedure that is easy to scale up [11]. In the sputtering method, various targets can be used for the deposition processes, such as multi-target, alloy target, segment target, and mosaic target. The multi-target allows for precise control of the deposited film composition by varying the current of each cathode, but due to its complexity, this method almost cannot be used in industrial. Therefore, the development of the sputtering technique from a single target, such as an alloy target, segment target, or mosaic target, is the tendency in ternary nitride film deposition [12]. Nowadays, the studies of CrAlN film have been focused on the influences of the deposition parameters on the structure and properties. However, most of the investigations on CrAlN film have used a multi-target or co-sputtering, deposition from an alloy target is still limited.

In this work, which is a part of the ongoing projects that efforts to develop the super-hard ternary nitride coating of the Cr-based hard coating, the CrAlN thin film was prepared using a DC reactive unbalanced magnetron sputtering from a Cr-Al alloy target, without extra heating and substrate bias. The characteristics such as crystalline structure, microstructure, morphology, thickness, chemical composition, and hardness of the as-deposited thin films as a function of the Al content were investigated and discussed.

Materials and Methods

Preparation of thin films

The thin films of CrAlN were deposited on Si substrates with various aluminium (Al) atomic percent. A homemade sputtering system carried out the film deposition from an alloy target of Cr-Al (50:50 at%) (99.97%) with 50 mm diameter and 3 mm thick. The deposition chamber was made from stainless steel AISI304 of 310 mm in diameter and 370 mm high. Pure Ar (99.99%) and N_2 (99.99%), were used as the working gases, which were injected into the chamber at a continuous gas flow rate by the MKS type247D mass flow controller.

All substrates were cleaned with acetone in ultrasonic for 10 min. Subsequently, they were rinsed in deionized water, dried with N_2 gas, and placed into the sample holder in the deposition chamber. The working distance was fixed at 100 mm. Before thin film deposition, the deposition chamber was evacuated to a base pressure of 5.0×10^{-5} mbar using a diffusion pump backed with a rotary pump, before injecting the working gases (Ar and N_2). The working gas flow rates and sputtering power were controlled to achieve the various Al content in the films. The CrAlN films were deposited at a constant total working pressure of 5.0×10^{-3} mbar and a deposition time of 30 min. The deposition conditions are summarized in Table 1.

Characterization of thin films

The composition of the as-deposited films was measured by Energy Dispersive X-ray spectroscopy (EDS), which is attached to a Scanning Electron Microscopy (SEM: LEO 1450VP). The crystalline structures of the films were analyzed by a glancing angle X-ray diffraction (GA-XRD: BRUKER D8) with Cu Kα radiation (λ = 0.154 nm). The XRD patterns acquire in a 2θ continuous scan mode, with a scanning speed of 2°/min, and a grazing incidence angle of 3°. The phases of films were determined using Bragg's law and compared with the JCPDS card. The crystal size of the as-deposited films was estimated from the width of XRD peaks using Scherer's equation. The cross-sectional microstructure and thickness were investigated by Field Emission Scanning Electron Microscope (FE-SEM: Hitachi s4700). The film's hardness was measured by a nanoindentation technique (BRUKER: Hysitron TI Premier) at room temperature. The indentation was performed using a triangular Berkovitch diamond pyramid. The load was selected to keep a penetrating depth of not more than 10% of the film thickness so that the influence from the substrate can be neglected.

Table 1 Thin film deposition conditions.

Parameters	Details		
	CrAlN-20	CrAlN-25	CrAlN-30
Sputtering target	Alloy of Cr-Al (50:50 at%) (99.97%)		
Substrate-target distances	100 mm		
Base pressure	5.0×10^{-5} mbar		
Working pressure	5.0×10^{-3} mbar		
Flow rate of Ar gas	20 sccm		
Flow rate of N_2 gas	6 sccm	6 sccm	2 sccm
Sputtering power	195 W	250 W	230 W
Deposition time	30 min		

Results and Discussion

EDS composition of the CrAlN thin films

The CrAlN thin films with different Al content were successfully deposited on Si substrates by reactive DC unbalanced magnetron sputtering technique from the Cr-Al alloy target (50:50 at%) with different deposition conditions. The thickness of CrAlN films was presented in the range of 683.5 – 1549.5 nm. The chemical composition of the as-deposited CrAlN films was evaluated by the EDS technique and is summarized in Table 2. It was found that the CrAlN films were composed of chromium (Cr), aluminium (Al), nitrogen (N), with various atomic percent, and slight oxygen (O) content at about 11.43 - 18.28 at%. The CrAlN thin films in this work were classified by the Al content in the films as (1) a low Al content (CrAlN-20), which has Al = 20.11 at%, Cr = 10.26 at%, and N = 53.89 at%, (2) a moderate Al content (CrAlN-25), which has Al = 24.67 at%, Cr = 11.27 at%, and N = 45.78 at%, and (3) a high Al content (CrAlN-30) which has Al = 30.93 at%, Cr = 28.47 at%, and N = 29.17 at%.

Table 2 Thickness and chemical composition of the CrAlN films with different Al content.

Code	**Thickness (nm)**	**Chemical composition (at%)**			
		Cr	**Al**	**N**	**O**
CrAlN-20	1114.0	10.26	20.11	53.89	15.74
CrAlN-25	683.5	11.27	24.67	45.78	18.28
CrAlN-30	1549.5	28.47	30.93	29.17	11.43

XRD analyses of the CrAlN thin films

XRD patterns of the as-deposited CrAlN thin films deposited on Si substrates with different Al content were shown in Figure 1. The standard diffraction peaks (2θ positions) for the (111), (200), and (220) planes of the CrN (JCPDS No.65-2899) and AlN (JCPDS No.88-2250) were included for comparison purposes. The XRD pattern revealed that the CrAlN films with low and moderate Al content showed diffraction peaks at 2θ of about 37.60^{O} – 37.79^{O}, 43.82^{O} – 43.91^{O}, and 63.69^{O} – 63.80^{O} which according to the (111), (200), and (220) planes of CrN crystals with the fcc structures, while the CrAlN films with high Al content showed only single diffraction broad peaks at 2θ of about 44.26^{O} according to the (200) planes. The broad peak of the (200) plane indicated that the deposited film with high Al content was not well crystallized at all and is mostly amorphous [7]. In addition, in this work, no diffraction peaks were detected from the XRD results corresponding to pure CrN and AlN phases.

Furthermore, with the increase of Al content, the diffraction peaks showed a small shift to the high diffraction angle between the standard peak of CrN (JCPDS No. 65-2899) and AlN (JCPDS No.88-2250) as shown in Figure 2. Such a shift towards a higher diffraction angle of the films was attributed to a decrease of a lattice parameter in CrAlN film, the obvious gradual decrease in lattice constant of (200) plane from 4.127 Å (CrAlN-20) to 4.088 Å (CrAlN-30) as shown in Figure 2. This result suggested that the as-deposited film formed a solid solution of CrAlN with the fcc structure. In this work, a solid solution of CrAlN films forms whereby the Cr atoms were substituted by Al atoms in the CrN structures. Since the radius of the Al atom (0.121 nm) is smaller than the Cr atom (0.139 nm) [7], which confirms that the Al atoms have already incorporated into the CrN lattice, similar to the results previously reported [7,10].

The average crystal sizes of the CrAlN thin films as a function of the Al content shown in Table 3 were calculated from FWHM of the XRD patterns using Scherrer's equation. The sizes were decreased from 16.8 nm to 3.1 nm with the increase of the Al content (Figure 3).

Table 3 Crystalline size and lattice constant of the CrAlN films with different Al content**.**

Code	**Crystalline size (nm)**				**Lattice constant (Å)**		
	(111)	**(200)**	**(220)**	**Average**	**(111)**	**(200)**	**(220)**
CrAlN-20	20.9	13.4	16.1	16.8	4.138	4.127	4.128
CrAlN-25	19.9	12.9	16.7	16.6	4.118	4.119	4.121
CrAlN-30	-	3.1	-	3.1	-	4.088	-

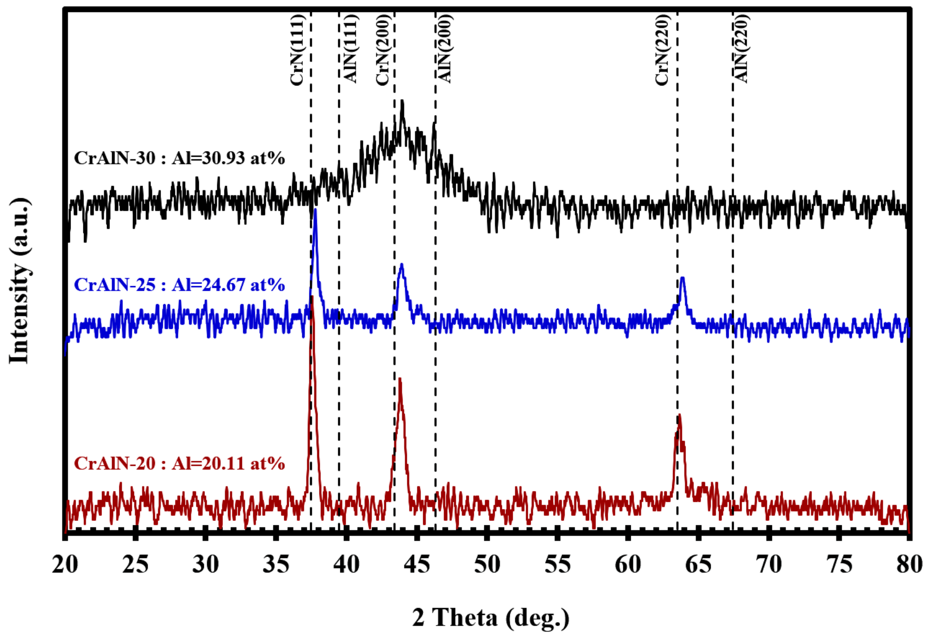

Figure 1 XRD patterns of CrAlN thin film with different Al content.

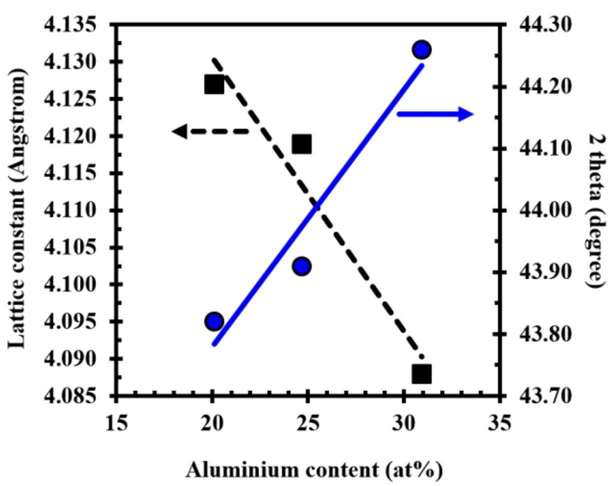

Figure 2 Lattice constant and diffraction angle of CrAlN thin film as a function of Al content.

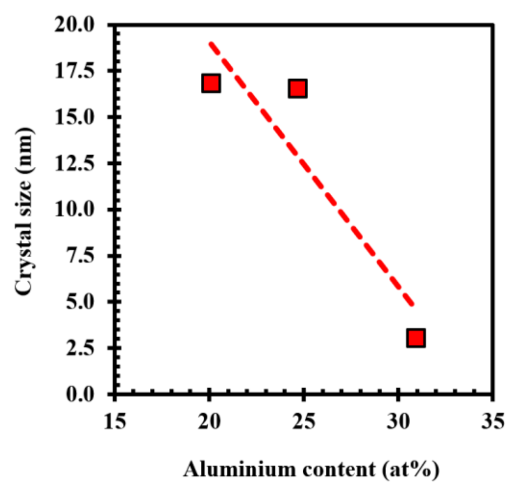

Figure 3 Average crystal of CrAlN thin film as a function of Al content.

Microstructure, morphology of the CrAlN thin films

The microstructure, surface morphology, and cross-sectional images of the CrAlN films with different Al content from the FE-SEM technique were shown in Figure 4. The surface morphology of the films with low Al content (CrAlN-20) was not smooth and slightly rough, caused by small film grains gathered in groups spread over the film surface (Figure 4(a)). With the increase of Al content, the film's surface was smoother. In the case of moderate Al content (CrAlN-25), the surface of the film was found to be smoother. The grains on the surface of the film were small and evenly distributed (Figure 4(c)). Finally, for the film with high Al content (CrAlN-30), the surface smoothness of the films was observed. The grains on the surface of the film were small and distributed evenly across the film surface (Figure 4(e)). The result in this work can be concluded that the amount of Al content in films affected the surface morphology and grain size of the as-deposited film.

The cross- sectional images of the CrAlN thin films with different Al content from the FE-SEM technique are shown in Figure 4. It was found that the films with low Al content (CrAlN-20) have no definite structure corresponding to the zone T according to the Thornton structure zone model [13] (Figure 4(b)). In the case of moderate Al content (CrAlN-25), it was found that the film was consistently densely aligned in sticks with little gaps (Void) in the film between the grains. This structure corresponded to Zone 2 according to the Thornton structure zone model [13] (Figure 4(d)). Finally, for the film with high Al content (CrAlN-30), it was found that the film had a dense structure and no gaps within the film (Figure 4(f)). In this work, it can be concluded that the Al content in the films affected the microstructure of the film. It was found that the microstructure and cross-section of the film were consistent with the Thornton structure zone model [13].

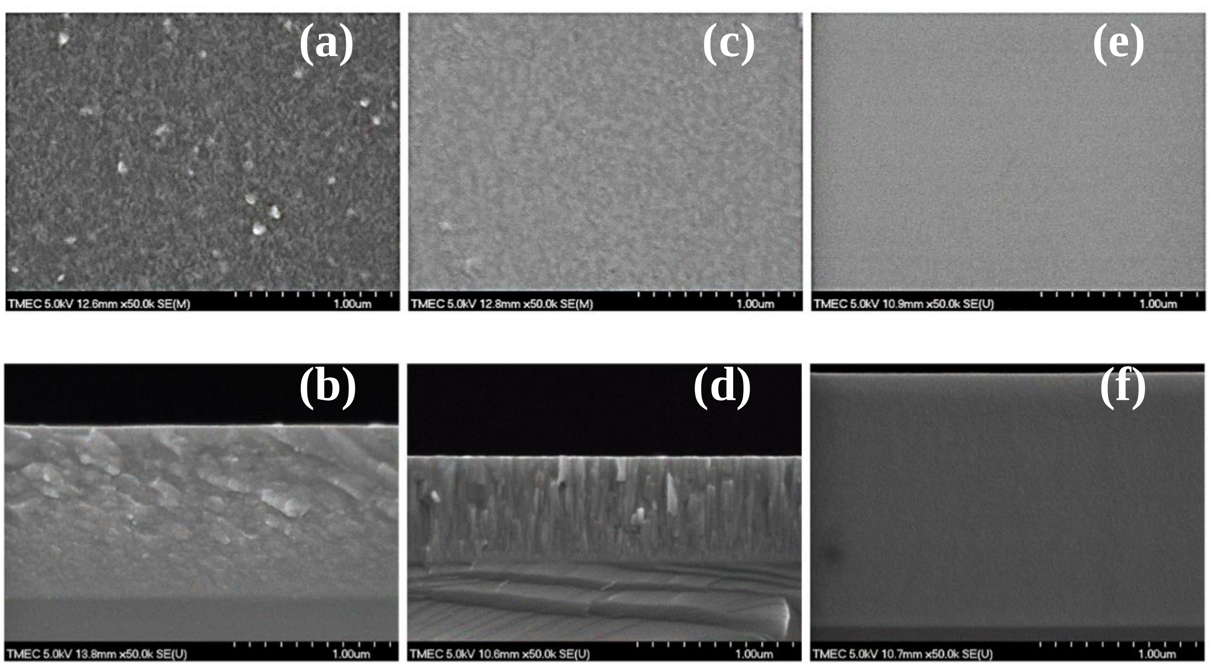

Figure 4 Surface morphology and cross-sectional of CrAlN film with different Al content**.** (a) and (b): CrAlN-20 with Al = 20.11 at%, (c) and (d): CrAlN-25 with Al = 24.67 at%, (e) and (f): CrAlN-30 with Al = 30.93 at%.

Hardness of the CrAlN thin films

According to numerous reports, the hardness of the sputtered thin film is affected by the chemical composition and crystalline size of the films. In this research work, the hardness of the as-deposited CrAlN thin films with different Al content is shown in Figure 5. The results showed that the hardness of the films with low Al content (CrAlN-20; Al=20.11 at%) and moderate Al content (CrAlN-25; Al=24.67 at%) were about 12.47 – 13.06 GPa, while the film with high Al content (CrAlN-30; Al=30.93 at%) was 67.29 GPa. As shown in Figure 5, the alloying of Al to the CrN binary nitride structure improved its hardness, and the hardness of the CrAlN film increased with the Al content increased. The maximum hardness value (67.29 GPa) was achieved when the Al content was 30.93 at%.

The hardness of thin film was also mainly affected by many factors such as grain size, internal stress, and crystal structure [14]. In the XRD results, it was shown that Cr atoms in the CrN crystal structure were replaced by partial Al atoms to form a CrAlN substitutional solid solution, and the hardness was improved due to additional atom will inhibited dislocation movement in the crystal structure which called the solid solution hardening effect. In addition, the atomic radius of the Al atom was smaller than the Cr atom which caused lattice shrinkage, while the increase in Al content could aggravate the degree of lattice distortion that hindered the dislocation movement. Therefore, the CrAlN thin film hardness can be improved compared to CrN. There are some reports that the effects of solid solution hardening as well as nanocomposite interface strain strengthening mechanisms are considered together for the hardness enhancement in the sputtered thin film [7]. This work also found that an increase in Al content resulted in the decrease of the crystallite size from 16.8 nm to 3.1 nm (from XRD results) as shown in Figure 6, consequently increasing the hardness which also suggested that high Al concentration in the film supported crystalline formation with less volume fraction of AlN amorphous regions. In the case of crystallite size, the maximum hardness value (67.29 GPa) was achieved when the smallest crystallite size of 3.1 nm was obtained.

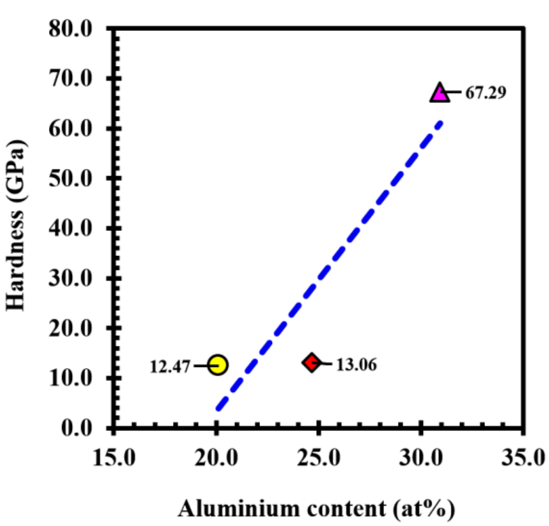

Figure 5 Hardness of CrAlN thin film as a function of Al content**.**

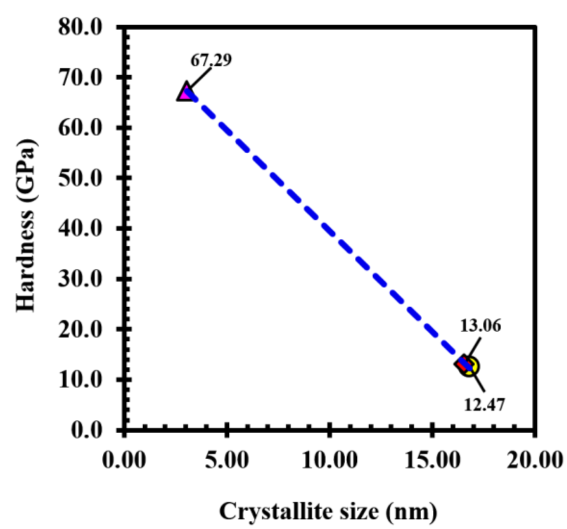

Figure 6 Hardness of CrAlN thin film as a function of crystallite size**.**

Conclusions

The nanocrystalline ternary nitride CrAlN thin films were successfully deposited without external heating and biasing to the substrate. The effect of the Al content on the crystal structure, microstructure, morphology, and hardness of the CrAlN films deposited by the DC reactive magnetron sputtering from the Cr-Al alloy target was investigated. The main conclusions are as follows: (1) The chemical composition from the EDS technique showed that the as-deposited film has Cr, Al, and N in different ratios. The as-deposited CrAlN films with low and moderate Al content composed of (111) and (200) planes with a small shift toward the higher 2θ values, while high Al content showed only single diffraction broad peaks of (200) plane. With the increase of Al content, the crystallite size decreased. When the Al content was 30.93 at%, the crystallite size was the smallest, while the surface morphology was the smoothest and densest. The cross-section showed a compact columnar structure and dense morphology with high Al content. (2) The hardness, of the as-deposited films increased with the Al content while decreasing with the crystallite size. The highest hardness of 67.29 GPa found in the CrAlN film with the Al content was 30.93 at% and the crystallite size was 3.1 nm.

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