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Effect of Cr Content on Structure and Hardness of TiCrN Thin Films

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Abstract

The aim of this study was to investigate the effects of chromium (Cr) content on the structure and hardness of titanium chromium nitride (TiCrN) thin films deposited on Si substrates using reactive direct current magnetron sputtering from mosaic Ti-Cr targets. The crystal structure, chemical composition, surface morphology, microstructure, and hardness of the thin films were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FE-SEM), and nano-indentation. The results showed that the as-deposited films were formed as (Ti, Cr)N solid solutions with face-centered cubic structures in the (111), (200), and (220) planes, as determined from the XRD patterns. The lattice parameters were in the range of 4.206–4.282 Å with a nanocrystalline structure, and the average crystal size was 13.3–15.7 nm. According to the EDS analysis results, the Ti, Cr, and N contents were observed at different ratios. According to the microscopic FE-SEM image, the Cr content influences the surface morphology and cross-section of the deposited film. According to the nano-indentation results, the hardness of the deposited films increased and then decreased (12.17–15.64 GPa) with increasing Cr content. The highest hardness was obtained at a Cr content of 20.28 at.% with an average crystallite size of 13.4 nm.

Keywords: Chromium content, Hardness, Hard coating, Thin film, TiCrN, Reactive magnetron sputtering

1. Introduction

Thin-film deposition with high adhesion, hardness, and toughness can be employed in various industrial components, including protective layers and hard coatings of cutting and machining tools. Thus, thin-film deposition can improve mechanical properties, including wear, erosion, and hardness degradation, during operation, resulting in a longer tool life. A single-layer titanium nitride (TiN) thin film is popular for its superior wear resistance and mechanical qualities, making it ideal for surface improvement in dies, molds, and cutting tools. [1,2]. However, high-load activities when subjected to extreme oxidizing conditions degrade its mechanical and tribological characteristics at high temperatures, revealing the inadequacy of TiN thin films, leading to the development of new generation thin films. Titanium chromium nitride (TiCrN), a ternary nitride compound with solid solubility of Ti and Cr, has been a good choice for its exceptional mechanical, wear, and oxidation properties [3], and its mechanical properties have been extensively studied [4,5].

Magnetron sputtering is one of the most widely used methods for producing thin films because of its several advantages, including a rapid deposition rate and the use of low-energy particle bombardment for deposition on heat-sensitive materials [6,7]. The production of single-element thin films using single magnetron sputtering has been extensively explored and presents no substantial problems. However, the deposition of intermetallic thin films, which include two or more metal elements, proves to be a more complex process because controlling the sputtering rate of materials from each magnetron target complicates the process of obtaining a thin film with a specific composition and sputtering machines with several magnetrons are more expensive. These technologies are costly, particularly when large-scale goals are required but cannot be achieved in small laboratories or at a

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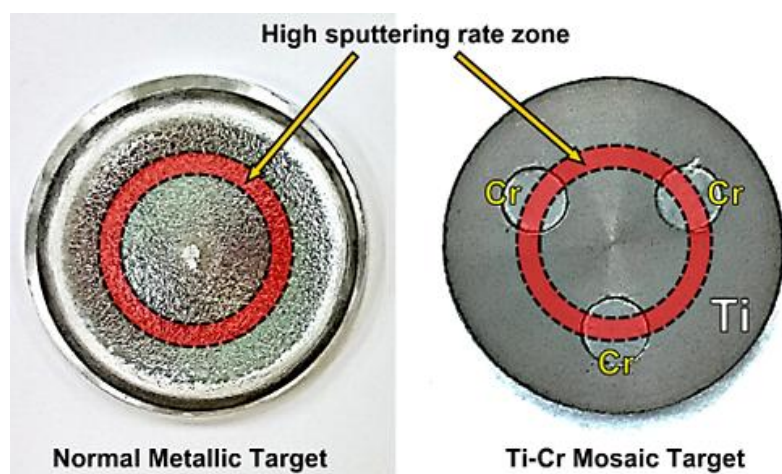
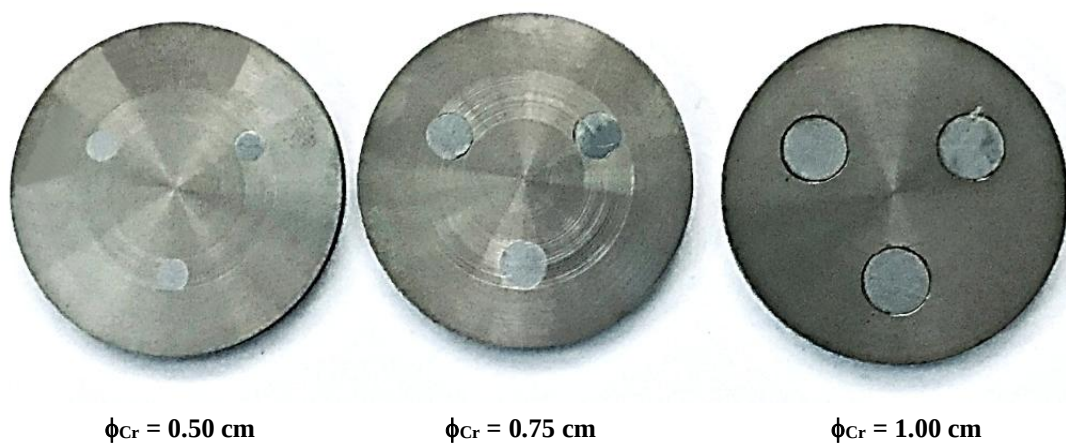


Figure 1 Concept of fabricating mosaic coating target.

(A)



(B)



Figure 2 Position and diameters of Cr inserts in Ti target: (A) three inserts and (B) four inserts.

2.2 Characterization of TiCrN thin films

The chemical composition, surface morphology, microstructure, and thickness of the films were characterized by energy-dispersive X-ray spectrometry (EDS, EDAX LEO1450VP) equipped in a field emission scanning electron microscope (FE-SEM, Hitachi S4700). The phase evolution of TiN due to chromium addition was clarified using glancing incident angle X-ray diffraction (GIXRD, Bruker D8) at an incident angle of 3° with a Cu-K α X-ray source. The θ - 2θ scan mode ranging from 20° – 80° was operated. Peak profile analysis of X-ray diffraction (XRD) patterns and calculation of the full width at half-maximum (FWHM) of the diffraction peaks were performed using the Scherrer equation to obtain the crystallite size (Equation (1)) [13].

$$D = K\lambda/\beta\cos\theta, \quad (1)$$

where D represents the grain size (nm), K represents Scherrer constant (0.89), λ denotes the X-ray wavelength, β denotes FWHM, and θ denotes the diffraction angle. Bragg's law was introduced to explain the XRD diffraction patterns. The lattice constants of the films were also considered in the XRD analysis.

The nano hardness was measured using a nano-indentation tester (BRUKER, Hysitron TI Premier). A diamond Berkovich indenter was used in the experiment and was always less than 10% of the thin film thickness to ensure that the film hardness was not influenced by the substrate. Ten loading and unloading indentation phases were performed on each sample. During the loading stage of the nano-indentation process of elastic–plastic materials, the total penetration depth is the sum of the elastic and plastic depths. The plastic depth corresponds to the contact depth, which is used to determine the contact area. During the unloading stage, elastic recovery occurs; thus, the contact depth can be determined by the unloading curve. After determining the contact area, the hardness of the indented material is obtained according to its normal definition (Equation (2)) [14].

$$H = \frac{P_{\max}}{A} \quad (2)$$

where $P_{\max}$ denotes the maximum load and A represents the area-depth function.

3. Results and Discussion

3.1 Elemental composition of TiCrN thin films deposited from Ti-Cr mosaic target

The TiCrN compositions as functions of the numbers and diameters of the inserts are shown in Table 2. The results indicate that the Cr atomic concentration in the films gradually increases as the numbers and diameters of inserts increase from 3 to 4 pieces and 0.50 to 1.00 cm, respectively. A Cr content of 8.60 at.% was observed for three Cr inserts and a diameter of 0.5 cm. When increased to four Cr inserts at the same diameter, the Cr content increased to 11.27 at.%. A 15.23-at.% Cr content was obtained as the diameter increased (0.75 cm) at three Cr inserts. As the number of inserts was increased (four pieces), the Cr content increased to 18.47 at.%. Up to 23.03-at.% Cr content was obtained in the thin film at a maximum number and size (diameter) of inserts of 4 and 1 cm, respectively. In addition, similar evolution trends were observed for the Ti and N contents. The Ti content was reduced by 50% (from 17.61 to 8.63 at.%), whereas the decrease from 73.89 to 68.33 at.% was observed for the maximum number and size of Cr inserts (four pieces and 1 cm (diameter), respectively).

The different Cr contents in the films were obtained by varying the number and diameter of Cr inserts and by successfully doping Cr into the thin film layers. The desired Cr content in the film was successfully controlled in this experiment. The higher number of Cr inserts (3–4) and larger insert sizes (0.50–1.00 cm) cause more Cr atoms to be sputtered from the Ti-Cr target, which results in more Cr atoms in the TiN structure during thin film formation, which explains the increase in Cr content observed using the EDS technique. Previous studies have found that the size of the inserts affects the elemental compositions of films, which is consistent with our experiment [3,15].

Table 2 Elemental composition of the TiCrN thin film deposited from Ti-Cr mosaic target.

Sample code	Number of Cr inserts	Diameter of Cr insert (cm)	Cr (at.%)	Ti (at.%)	N (at.%)
3Cr050	3	0.50	8.60	17.61	73.79
4Cr050	4		11.27	15.88	72.84
3Cr075	3	0.75	15.23	13.40	71.37
4Cr075	4		18.47	10.91	69.96
3Cr100	3	1.00	20.28	10.07	69.92
4Cr100	4		23.03	8.63	68.33

3.2 Crystal structure of TiCrN thin films

The XRD patterns of TiCrN thin films with various Cr contents are shown in Figure 3. The 2θ diffraction angles of 36.5° , 42.63° , and 61.18° were indexed at the lowest Cr content of 8.6 at.%. All peaks varied between the CrN standard (JCPDS No. 77-0047) and TiN (JCPDS No. 87-0633), implying that the films were TiCrN solid solutions with (111) (200) and (311) planes compared to the JCPDS standard. At a Cr content of 11.27 at.%, no other diffraction pattern appeared, but all peaks slightly shifted toward higher 2θ diffraction angles. The diffraction angles of the TiCrN solid solutions were still observed at Cr contents of 15.23–20.28 at.%. The highest Cr content of 23.03 at.% resulted in not only an increase in the X-ray intensities of the TiCrN (111), (200), and (220) planes (with a significant increase in that of (111) plane) but also peak shifting.

The TiCrN structure was formed when the Cr atoms in the films substituted the Ti atoms. This structure is called a TiCrN solid solution [16,17]. The variable X-ray intensity was due to varying Cr amounts, which were sputtered by varying the number and size of Cr inserts, thereby inducing the formation of more atoms on the substrate surface and increasing the thin film thickness. These results are consistent with those reported by other researchers [12,18,19]. Whatever the addition of sputtered atoms on the substrate, an increase in the X-ray intensity could be observed. In contrast, a shift toward higher angles was observed for all TiCrN peaks (Table 2). These results reveal the substitution of Ti with Cr because the atomic radius of Cr (0.136 nm) is smaller than that of Ti (0.145 nm), which is consistent with previous studies [20,21]. This substitution causes lattice distortion, which results in a peak shift based on Bragg's law [13].

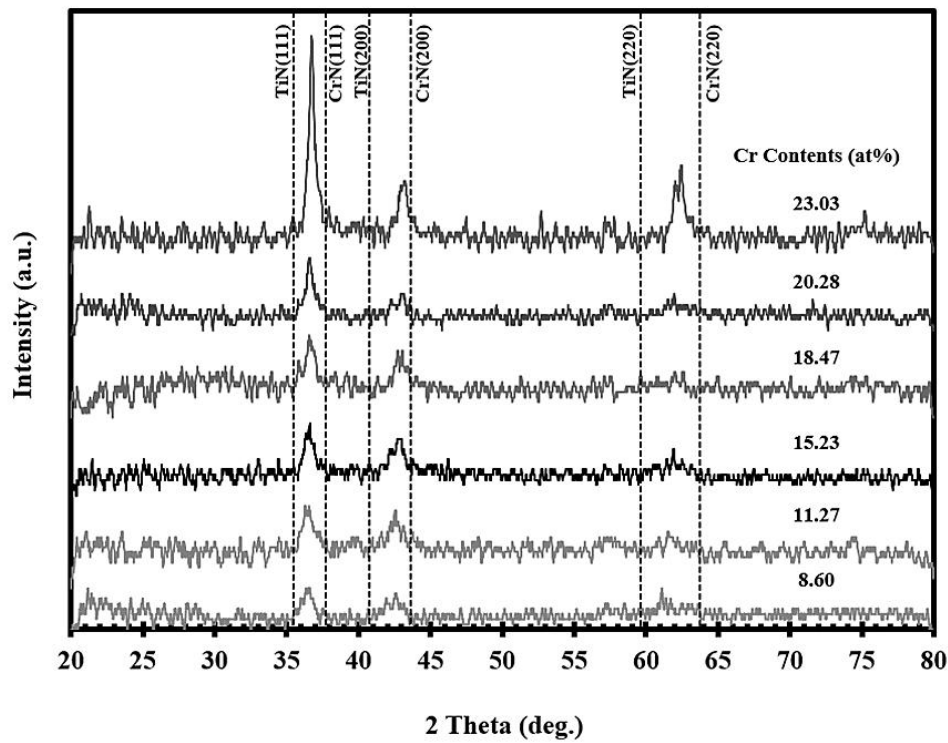
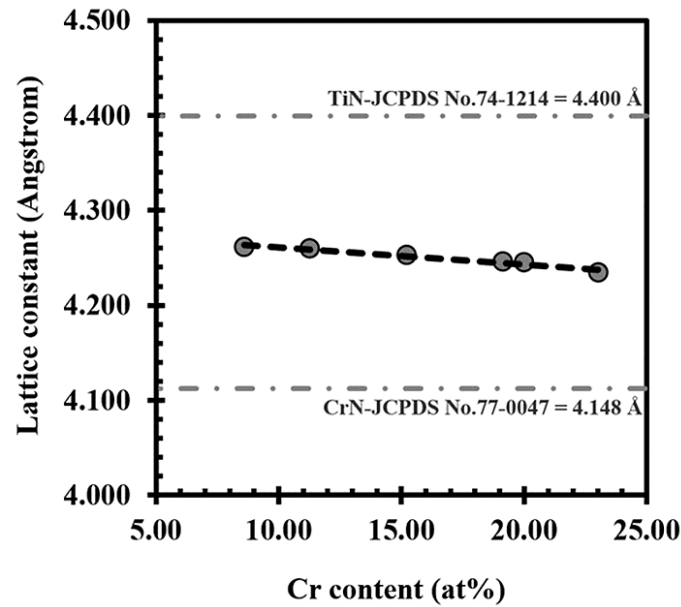


Figure 3 XRD patterns of TiCrN thin film with different Cr contents.

The average crystal size is presented in Table 3. The crystal size varied between 13.33 and 13.58 nm as the Cr content increased from 8.60 to 23.03 at.%, and the largest average crystal size was observed at the highest Cr content (23.03 at.%). The relation between the lattice constant of the TiCrN thin films and the 2θ diffraction angle from the (111) plane is shown in Table 2. The lattice constant decreased from 4.2161 nm to 4.235 Å, and the increase in the diffraction angle with increasing Cr content was investigated. The other crystal planes exhibited similar trends to the (111) plane. These trends can be explained by the substitution process, as previously mentioned. This result is also supported by the XRD results: as the Cr content increased, the lattice constant decreased because of lattice distortion, which caused all peaks to shift. In addition, the different lattice constants at different Cr contents between the TiN and CrN lattice constant standards (Figure 4) indicate that the diffraction patterns are supported by solid solution formation.

Table 3 Average crystal size and diffraction angle as functions of Cr content.

Cr content (at.%)	Average crystal size (nm)	2 θ diffraction angle (°)			Lattice constant (Å)
		TiCrN (111)	TiCrN (200)	TiCrN (220)	
8.60	13.3	36.50	42.63	61.18	4.261
11.27	13.5	36.51	42.58	61.54	4.2597
15.23	14.3	36.57	42.78	61.94	4.253
18.47	13.5	36.62	42.88	62.25	4.246
20.28	13.4	36.64	42.98	61.89	4.245
23.03	13.5	36.73	43.10	62.29	4.235

**Figure 4** Lattice constants of TiCrN thin films as functions of Cr content.

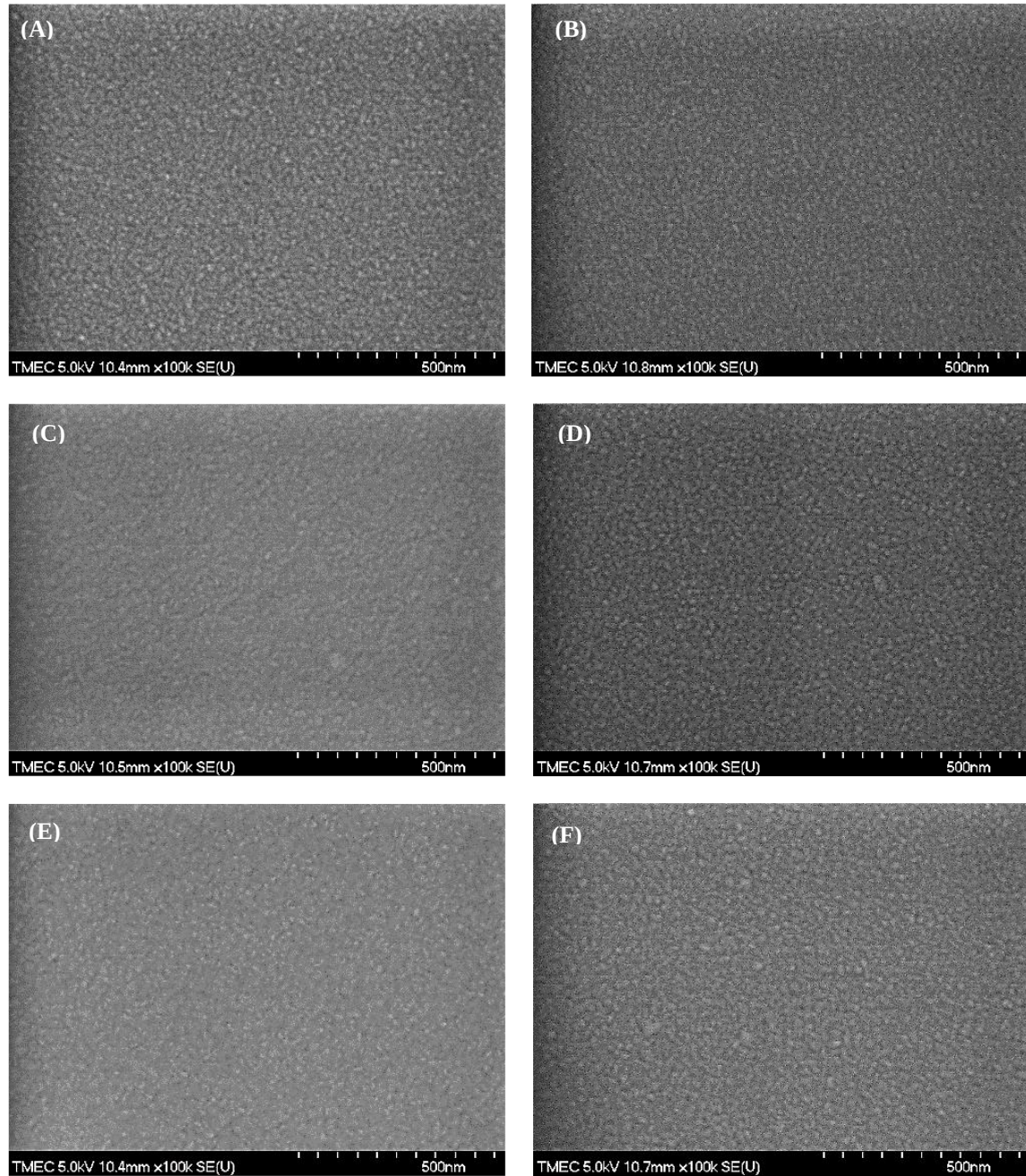
3.3 Surface morphology and microstructure of TiCrN thin films

The surface morphology of the TiCrN films was observed by FE-SEM at different Cr contents. The results are presented in Figure 5. Small individual grains that spread across the thin film surface were observed at a Cr content of 8.60 at.%. When the Cr content increased to 11.27 at.%, morphology similar to that of fine grains was observed. Note that the surface morphology did not depend on the Cr content, which changed as the number and size of Cr inserts were varied. No change in surface morphology evolution was observed as the Cr content increased from 15.23 to 23.03 at.%. Figure 5 presents typical fracture cross-sectional FE-SEM micrographs of Si substrates. The TiCrN thin films exhibit a fine, dense columnar structure at the lowest Cr content (8.60 at.%). At a Cr content of 11.27 at.%, the films exhibit a compact columnar structure. No change in cross-sectional morphology was observed when the Cr content reached 23.03 at.%. The appearance of a compact columnar structure at all Cr contents can be related to the introduction of Cr into thin films.

The thickness and deposition rate of the film as a function of Cr content are presented in Table 4 and Figure 6. The thickness of the films was measured from the boundary between the substrate and thin film layer to the top surface of the thin film. The deposition rate was calculated from the thickness over the deposition time. A thickness of 141 nm was investigated at a Cr content of 8.60 at.%. An approximately double thickness increase (256 nm) was obtained when the Cr content was increased to 23.03 at.% at a deposition rate of 4.7–8.5 nm/s. The highest thickness coating rate was obtained at the highest Cr content because many large Cr inserts were used to produce the Ti-Cr target. This resulted in a high sputtering rate on the targets, leading to a slightly higher deposition rate, thereby increasing the thickness of the high-Cr-content samples compared to the low-Cr-content samples. This result agrees well with the multicomponent coatings reported in other studies, which found the dependence of the evolution of the thickness and deposition rate on metallic atom addition in binary nitride structures [12,22,23].

Table 4 Thickness, deposition rate, average crystal size, and hardness as functions of Cr content.

Cr content (at.%)	Thickness (nm)	Deposition rate (nm/s)	Hardness (GPa)
8.60	141	4.7	13.32
11.27	154	5.1	14.18
15.23	181	6.0	14.22
18.47	192	6.4	14.13
20.28	203	6.8	15.64
23.03	256	8.5	12.17

**Figure 5** Surface morphologies of TiCrN thin films as functions of Cr content: (A) 8.60 at.%, (B) 11.27 at.% (C) 15.23 at.%, (D) 18.47 at.%, (E) 20.28 at.%, and (F) 23.03 at.%.

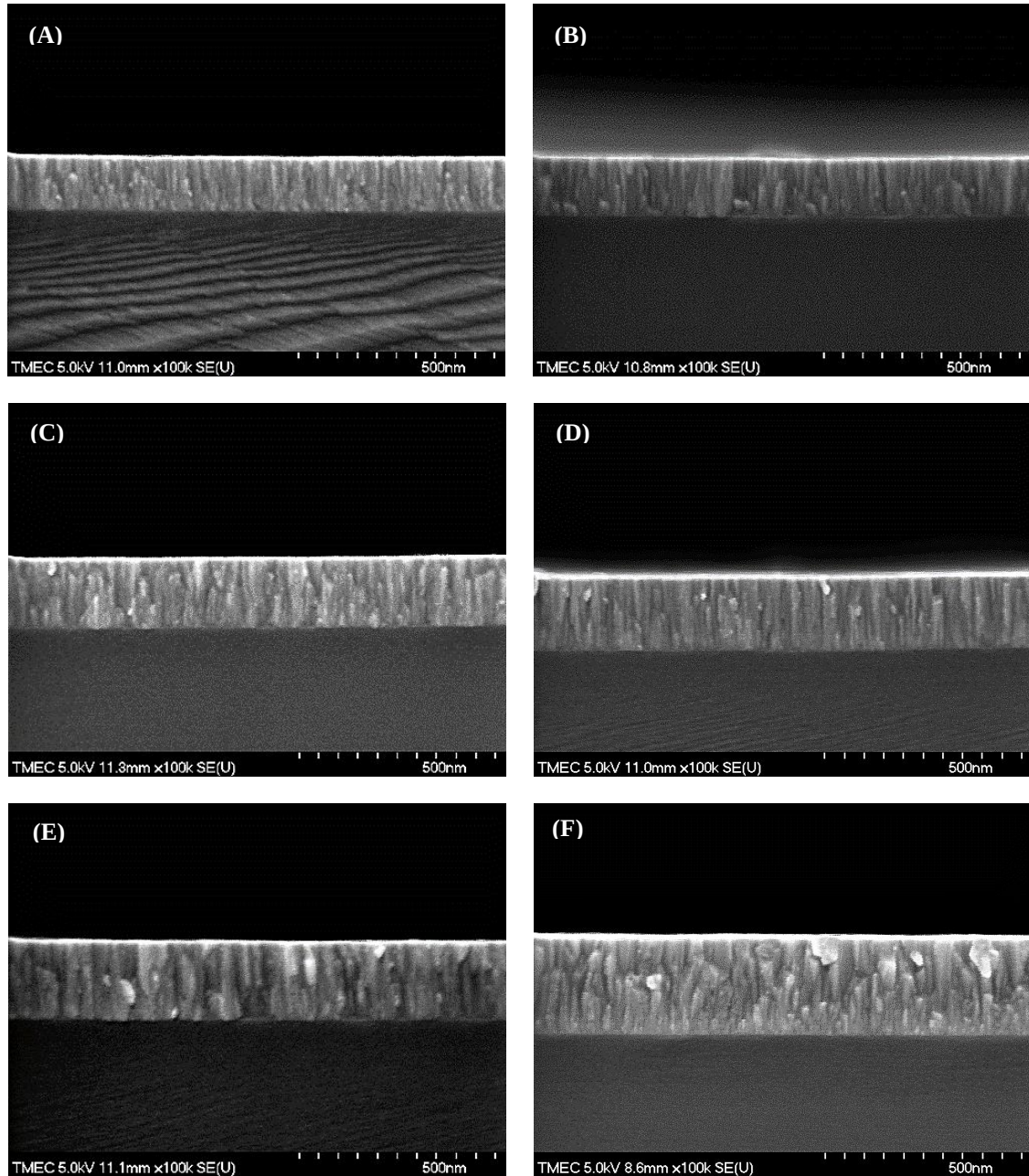


Figure 6 Cross-sectional morphologies of TiCrN thin films as functions of Cr content: (A) 8.60 at.%, (B) 11.27 at.% (C) 15.23 at.%, (D) 18.47 at.%, (E) 20.28 at.%, and (F) 23.03 at.%.

3.4 Hardness of TiCrN thin films

The hardness of the TiCrN films was measured using a nano-indenter. The results are presented in Table 4, indicating that the hardness of the films depends on the Cr content in the deposition process. A hardness value of 13.32 GPa was obtained at a Cr content of 11.27 at.%. A slight increase in hardness to 14.18 GPa was observed at a Cr content of 15.23 at.%. With a further increase in Cr content from 15.23 to 18.47 at.%, an almost constant hardness value between 14.13 and 14.22 GPa was obtained. The highest hardness value (15.64 GPa) was obtained at a Cr content of 20.28 at.%, whereas the hardness decreased to 12.17 GPa as the Cr content increased to 23.03%.

The hardness of the thin films increased and then decreased with Cr content. These results imply that by varying the Cr content, the hardness of the film can be successfully controlled. Compared with CrN coatings reported in previous studies [24,25], the hardness of the as-deposited TiCrN thin films is improved by an increase in matrix strength resulting from the addition of different soluble elements to the crystalline lattice of the base metal. This results in a substitutional or interstitial solid solution, resulting in the distortion of the atomic lattice caused by the misfit of the atomic radius, thereby inhibiting dislocation movement, which is called “solid solution

hardening” [26,27]. The increase in hardness can be explained by this reason. However, the type of metal-to-nitrogen bonding changes, becoming less covalent and decreasing in hardness at high Cr content [28]. The evolution of hardness was similar to that obtained in other studies [28-30].

In addition, the grain size influenced the film hardness. The average crystal size of the TiCrN thin film was 13.33–15.72 nm. The highest hardness was obtained at a small average crystal size of 13.35 nm. This result is attributed to the “Hall–Petch relationship,” which explains how materials can obtain strengths equal to their theoretical strengths by reducing their grain sizes. The strength continues to increase as the grain size decreases [31].

4. Conclusion

TiCrN thin films with different Cr contents, which were varied by varying the number and size of Cr inserts, were successfully deposited using Ti-Cr mosaic targets. The elemental composition, crystal structure, surface morphology, and hardness of the films were investigated in detail. The EDS analysis indicated that the Cr content increased as the number and size of Cr inserts increased, implying that the Cr content can be controlled through this approach. The XRD analysis revealed that the as-deposited thin films formed a nanocrystalline TiCrN solid solution. With increasing Cr content, the diffraction peaks were shifted to higher angles, the crystal size increased from 13.3 to 15.7 nm, and the lattice parameters decreased. Surface morphology observations based on FE-SEM revealed no change in the morphology of small individual grains. According to the cross-sectional investigation, all films exhibit columnar growth structures. The addition of Cr to TiN increased the thickness and deposition rate from 141 to 256 nm and 4.7 to 8.5 nm/s, respectively. With a higher Cr fraction, the hardness increases to its maximum at a small average crystal size of 13.4 nm. The hardening mechanism was attributed to the Hall–Petch relation, which was mainly influenced by grain size. These results may be useful for industrial applications in which cutting and machining tools are subjected to room-temperature deposition without external heating.

5. References

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