Effect of Zr content on the structure and morphology of CrZrN thin films prepared by reactive DC magnetron co-sputtering method

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Abstract. In this research, nanostructured chromium zirconium nitride (CrZrN) thin film has been deposited on Si(100) substrates by reactive DC magnetron co-sputtering method without in situ substrate heating and post-deposition annealing. The effects of Zr content on thin film structure and morphology were investigated. The Zr content in the films were varied by applied the sputtering current of Zr target (I_{zr}) in the range of 300 to 900 mA, whereas the current of Cr target was kept at 300 mA. The crystal structure, microstructure, morphology, thickness, and chemical composition were characterized by glancing angle X-ray diffraction (GA-XRD), field emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDS) techniques, respectively. The results showed that the increase of I_{zr} not only increased the deposition rate, but also increased the Zr content of the as-deposited film ranging from 3.9 to 26.5 at%. The as-deposited thin films were formed as a (Cr,Zr)N solid solution, with fcc structure in (111) and (200) plane, where Cr atoms were replaced by Zr atoms in the CrN lattice. The 2θ diffraction peaks were shifted to the lower value as increase of Zr content which was obtained by increased I_{zr}. The nanocrystalline CrZrN structure with crystal sizes smaller than 10 nm structure were calculated for as-deposited thin films. The lattice parameters increased from 4.187 to 4.381 Å, whereas the crystal size decreased from 8.3 to 6.4 nm. The FE-SEM images of all the CrZrN films exhibited compact columnar with dense morphology as a function of Zr content. Moreover, the thickness of the CrZrN thin films was increased of 302 – 421 nm.

1. Introduction

For many years, surface engineering have been widely studied in research area because of the modern industrial requirement for novel and excellent surface properties for many applications such as machine parts, forming, and cutting tools. The transition metal nitrides for example TiN, VN, and CrN are good candidated of hard coating applications. These metal nitrides' film possesses a higher hardness than the traditional steel and cabides because of improve both mechanical and tribological properties [1].

Compared to the other nitride films, CrN has become the good choice as coating in many industrial applications due to their superior hardness, corrosion resistance, wear behavior, and easy to deposit. Therefore, CrN film was investigated in many industrial applications [2]. A drawback of using CrN thin films as high-speed machining processes was occured when operated at high-temperature (> 700 °C), the formation of porous oxides on film surface was found resulting the degradation of their mechanical properties [3]. To overcome these problems, it can be done by alloying the other elements, such as Ti, Al, and Zr, in the CrN structure to form the ternary nitride thin films, for example, CrTiN, CrAlN, and

CrZrN, which have excellent properties. Among these films, CrZrN showed unique characteristics as mechanical properties enhancement and a achieving low surface roughness through the Zr content in the film [4], so it could be one of the most promising solution for practical applications.

The CrZrN thin film can be synthesized by various techniques, especially sputtering. Many research groups have been dedicated to synthesized the CrZrN thin films, used substrate heating, and biased to improve the film structure These processes cause the substrate to heat up, increasing manufacturing costs and was unsuitable for thermally sensitive substrates. Therefore, it is important to synthesized these films without heating and biasing. In addition, most previous studies have focused on the tribological property, which is limited to hardness, friction, and wear. However, the study of the effect of film's composition on the structure and morphology of the CrZrN thin films is still limited.

In this research, as a part of the ongoing research projects that effort to develop the ternary nitride thin films of the Cr-based hard coating for hard coating applications, CrZrN films with various Zr content were synthesized by reactive DC unbalanced magnetron co-sputtering at room temperature with unheated and no substrate bias process, and characteristics such as the crystalline structure, surface morphology and microstructure of the as-deposited films were investigated at different Zr content.

2. Materials and methods

The CrZrN coatings were deposited on Si(100) substrates at room temperature without heating and biasing using separate metallic disc sputtering target of Cr (99.95%) and Zr (99.95%) with a 75° magnetron cathode arrangement by the reactive DC magnetron co-sputtering method. The high purity processing sputtering gases of Ar (99.999%) and reactive gases of N_2 (99.999%) were injected into a chamber. The deposition chamber pressure was reduced to a base pressure of 5×10^{-5} mbar before each deposition. The total pressure was 5×10^{-3} mbar with fixed of Ar and N flow rate were 10 sccm and 12 sccm, respectively. In the deposition process, the sputtering current of the Cr target (I_{Cr}) was kept at 300 mA, whereas the sputtering current of the Zr target (I_{Zr}) were 300 mA, 600 mA and 900 mA with constant deposition time of 60 minutes. The target to substrate separation was 150 mm

The thin films were characterized by various techniques. The element composition analysis was carried out by EDS (EDAX). The phase and crystal structures were examined by a glancing angle X-ray diffractometer (BRUKER D8) using Cu Kα radiation at grazing incidence angle of 3°. The crystallite size is calculated by Scherrer's equation. The microstructure, cross-sectional morphology, and thickness were studied by Field Emission Scanning Electron Microscope (FE-SEM, Hitachi s4700).

3. Results and discussions

The CrZrN films were successfully deposited by reactive DC magnetron co-sputtering technique using separate metallic Cr and Zr targets on Si substrates. The chemical composition of the as-deposited CrZrN thin films results from the various sputtering current of the Zr target was evaluated by the EDS technique is listed in table 1. It was showed that the enhancement of Zr content in films but the reduction of Cr content was found as a function of sputtering current on the Zr target. Although film No.1 used the same sputtering current of Zr and Cr target, the Cr content is obviously superior compared to Zr content. This can be attributed to the fact that the sputtering yield of Cr (~ 0.87) is higher than Zr (~ 0.41) [5]. It also shows that the atomic ratio of the Zr and N content is defined as x = Zr/(Cr+zr) and y = N/(Cr+zr). It was found that the atomic ratio of Zr content (x) increased from 0.15 to 0.78 at% as sputtering current of Zr target increased, while the N content (y) in all deposited films decreased from 2.76 to 1.93 at%. Moreover, the atomic ratio of nitrogen to metals (Cr+Zr) (y) was higher than 1 implied that the over stoichiometry of CrZrN thin films were investigated.

Table 1. Thickness, composition, crystal size, and lattice constant of the CrZrN thin films.

| No.	I_{Zr} (mA)	Thickness (nm)	Composition (at.%)			Atomic ratio		Crystal size (nm)		Lattice constants (Å)	
			Cr	Zr	N	x=Zr/(Cr+Zr)	y=N/(Cr+Zr)	(111)	(200)	(111)	(200)
1	300	302	22.7	3.9	73.4	0.15	2.76	8.2	8.3	4.210	4.187
2	600	363	9.3	20.5	70.2	0.69	2.35	7.8	7.4	4.263	4.242
3	900	421	7.6	26.5	65.9	0.78	1.93	6.4	6.9	4.381	4.357
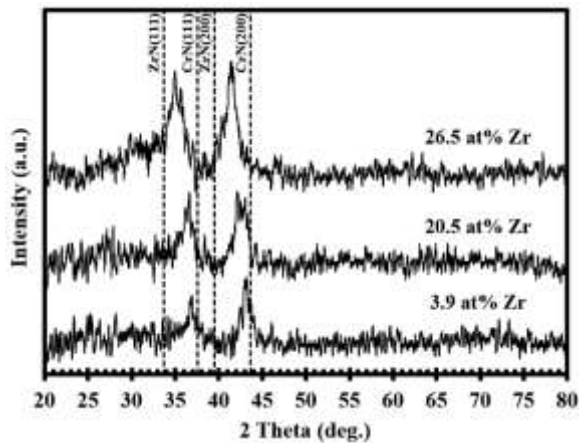
Figure 1. XRD diffraction patterns of the CrZrN thin films with different Zr content.
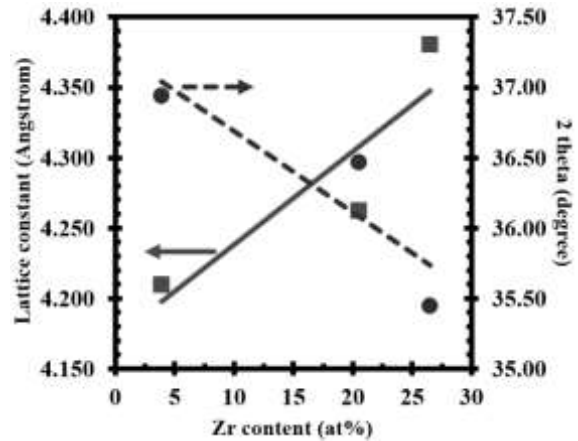
Figure 2. 2θ position and lattice constants of the CrZrN thin films with different Zr content.

XRD patterns of the as-deposited CrZrN films deposited on Si substrates through different Zr content are illustrated in figure 1. For comparison, the standard diffraction peaks for the (111) and (200) planes of ZrN (JCPDS No. 78-1420) and CrN (JCPDS No. 77-0047) were included. The results showed that the diffraction peaks are located between the standard diffraction peaks of ZrN and CrN. This result implied that the solid solution of (Cr,Zr)N with FCC structure formation. On the other hand, there are no corresponding 2θ peaks for pure ZrN and CrN phases. The CrZrN peaks are shifted to lower 2θ angles as Zr content increased due to the replacement of larger atomic radius of Zr (0.161 nm) to the position of the smaller atomic radius of Cr (0.136 nm) [1], which result in a change in the lattice constants were identified for all as-deposited films. The result was agreed with the reference [6]. According to Bragg Law, the film's lattice constants are calculated from the CrZrN (111) plane. Figure 2 show the 2θ position and lattice constants of CrZrN(111) films as a result of Zr content. It can be seen that as the Zr content increases, the 2θ position and the lattice constant were both increases. When using Scherrer's equation from the FWHM of the XRD pattern, the crystal size of CrZrN thin films was calculated as a result of the Zr content performed in Table 1, were decreased from 8.5 to 6.4 nm for (111) plane and 8.3 to 6.9 nm for (200) plane as increasing of the Zr content.
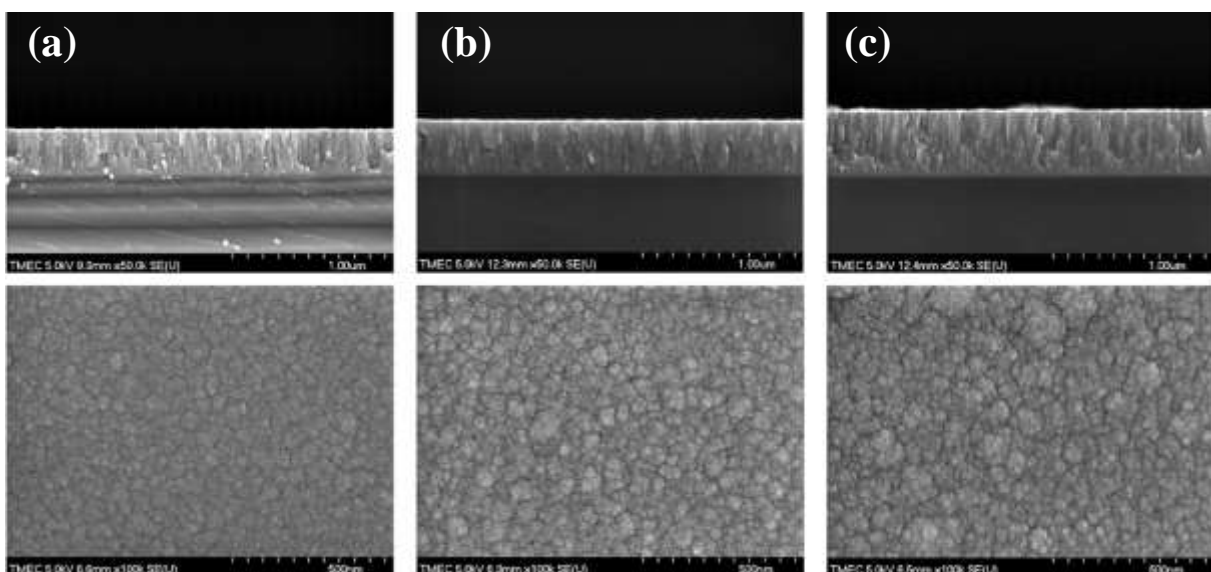
Figure 3. Surface morphologies of the CrZrN thin films with Zr content of (a) 3.9 at%Zr (b) 20.5 at%Zr and (c) 26.5 at%Zr.

The microstructure and morphologies of the CrZrN thin film with different Zr contents were analyzed by the FE-SEM technique (figure 3). At low Zr content (3.9 at%), it was found that the granule shape pattern with almost same size was indentified along the film surface but exhibited the grain boundaries between each grain. The grain aggregation across the surface resulting the enhancement of granule grain size were cleary indentifiled at higher Zr content (20.5 at%). More over, the grain boundaries were also investigated. The grains were kept the same shape but became bigger size with more void between each grain at highest Zr content (26.5 at%). The grain size increased can be explained that the larger the kinetic energy of sputtered deposited atom reaching to the surface of substrate [7].

The cross-sectional structure and thickness of FE-SEM micrograph were also listed and illustrated in figure 3 and table 1, respectively. At low Zr content (3.9 at%), the competitive grain growth with columnar structure were found. At highest Zr content of 26.5 at%, the porous microstructure which more open grain boundaries accompanied with fibrous grain along the coating were indentified. The cross-section pattern were well agreement with Zone T of Thornton's zone model [8]. According to table 1, the thickness increased from 307 to 401 nm as a function of Zr content which increase by increasing the target sputtering current (I_{zr}) from 300 to 900 mA. The higher of sputtering current helps to increase the growth rate of deposited atom resulting the increase of film thickness [7].

4. Conclusion

The nanocrystalline CrZrN thin films were grown on Si(100) by reactive DC magnetron co-sputtering without heating and biasing to the substrate at a low sputtering current in order to analyse the effect of Zr incoperation on their structure and morphology. It was found that the films crystallographic orientation in (111) and (200) were found which implied that the solid solution with FCC structure of (Cr,Zr)N was successfully deposited even though Zr content less or more than Cr content. The 2θ diffraction peaks shifted to the lower angle wheareas the lattice constants were increase. An decrease in crystal size was observed as the Zr content in the films increase. The nanocrystalline structure of CrZrN film was performed due to a crystallite size of the film less than 10 nm. Higher composition and atomic ratio of Zr were investigated. The thickness of films increased when the Zr content increase. The microstructure showed columnar with more open grain boundaries as Zr content enhancement.

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