บทความวิจัย

EFFECT OF NITROGEN FLOW RATE ON STRUCTURE OF TiCrN THIN FILMS PREPARED FROM MOSAIC TARGET BY REACTIVE DC UNBALANCED MAGNETRON SPUTTERING

Nirun Witit-anun*, Adisorn Buranawong, and Surasing Chaikhun

Vacuum Technology and Thin Film Research Laboratory (VTTF), Department of Physics,

Faculty of Science, Burapha University, Chonburi, 20131

*E-mail: nirun@buu.ac.th

ABSTRACT

Titanium chromium nitride (TiCrN) thin films were deposited by reactive DC magnetron sputtering method from mosaic target. The effect of nitrogen gas flow rate on the structure of the TiCrN thin films in the range of 4 – 10 sccm were investigated. The crystal structure, microstructure, thickness, roughness and chemical composition were characterized by glancing angle X-ray diffraction (GAXRD), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and energy dispersive X-ray spectroscopy (EDS) technique, respectively. The results showed that, all the as-deposited films were formed as a (Ti,Cr) N solid solution. The as-deposited films exhibited a nanostructure with a crystal size less than 70 nm. The crystal size of all plane were in the range of 41.4 – 69.6 nm. The lattice constants were in the range of 4.169 Å to 4.179 Å. The thickness decrease from 336 nm to 382 nm with increasing the nitrogen gas flow rate. The chemical composition, Ti Cr and N contents, in the as-deposited films were varied with the nitrogen gas flow rate. The as-deposited films showed compact columnar and dense morphology as a result of increasing the nitrogen gas flow rate.

Keywords: Reactive sputtering, Mosaic target, Nitrogen flow rate, TiCrN, Thin films

Introduction

In modern industrial, surface finishing by hard coating is an important process to protect machinery parts, cutting tools and forming tools against wear, corrosion, erosion and other unexpected damage, this results in an increase in lifetime compared to uncoated. So, the major challenges in thin films technology or surface engineering are to design and synthesis new materials which having a low coefficient of friction and low wear rate for a wide range of working environments.

The binary metal nitrides such as TiN, CrN and ZrN has been known as the first generation of PVD hard coating and widely used as protective coating for many industrial (Wang et al., 2000). Among these films, TiN has been extensively studied due to its high hardness, high thermal stability and good wear resistance as well as excellent corrosion resistance. However, mechanical properties of TiN film are degraded by oxidation at high temperature above 600 ^{O}C (Paksunchai et al., 2012). In order to overcome these problems and/or to improve properties of the Ti-based binary metal nitrides thin films, the Ti-based ternary metal nitride films such as TiAlN, TiZrN, TiVN and TiCrN have been developed (Witit-anun & Buranawong, 2017). Among these ternary nitrides films, the ternary TiCrN films have been attracted more attentions owing to its outstanding overall properties with high hardness, high temperature oxidation resistance and low friction coefficient (Witit-anun & Teekhaboot, 2016).

The TiCrN thin films can be prepared by various techniques. Among them, PVD techniques are the most popular methods to grow these ternary nitride thin films especially; sputtering method is the most suitable one due to low-temperature process, use of non-toxic gases and simple process (Shum et al., 2004). In this method, various targets can be used such as, multitarget, alloy target, segment target and mosaic target. The multitarget sputtering makes it possible to accurately control the composition of the deposited films by varying the sputtering current of each cathode, but this method almost cannot be used owing to its complexity at industrial facilities. So, the tendency in ternary nitride thin films deposition is to develop the method of magnetron sputtering from single target, such as alloy target or mosaic target (Golosov et al., 2012). The alloy target is made by casting or powder metallurgical technique. The mosaic target is made from holes filled by additional elements which enabling to vary coating composition through the number and position of holes.

However, it is common knowledge that thin films synthesis by a similar process in different laboratories, or indeed, in different systems of the same laboratory, have different properties. This is because different geometry and conditions give raise to different film structures, so the effect of deposition parameters on the structure and properties still important and necessary to investigated. Nowadays, the studies of the TiCrN film deposition technique have been focused on the influences of the deposition parameters on the properties and structure of TiCrN thin films. However, investigations of TiCrN film deposition from mosaic target are still limited.

In this research work, as a part of the ongoing effort to develop novel thin films for high temperature and hard coating applications, TiCrN thin films were synthesized by an unbalanced magnetron sputtering technique using mosaic target at room temperature, without external heating and biasing. The characteristics of the as-deposited films such as the crystalline structure, surface morphology, and microstructure were investigated as a function of the nitrogen gas flow rate.

Method

Thin films of TiCrN were deposited on Si-wafer substrates by reactive magnetron sputtering technique form a homemade DC unbalanced magnetron sputtering system. The cylindrical stainless steel vacuum chamber was 310 mm in diameter and 370 mm in height was used as coating chamber of the system. The feature and diagram of the coating system has shown in figure 1. The system is capable of creating a base pressure below 5×10^{-5} mbar in coating chamber by using diffusion pump backing with rotary pump. The pressure in the system was measured by PFEIFFER Pirani–Penning gauge combination (PKR 251 compact full range gauges) with TPG 262 control and measurement unit. The unbalanced magnetron cathode was mounted on the top plate of the coating chamber so the system could be done by sputtering down configuration. In order to setup the unbalanced magnetron cathode, the circular planar magnet of 65 mm diameter with 10 mm width was used as outer magnet and the magnetic rod of 10 mm diameter was used as center magnet, placed on the backing plate of the target. The maximum magnetic field strength at the outer and the center of the target surface are about 1000 G and 1400 G. A continuously variable dc power supply of 1000 V and 3 A was used as a power source for sputtering.

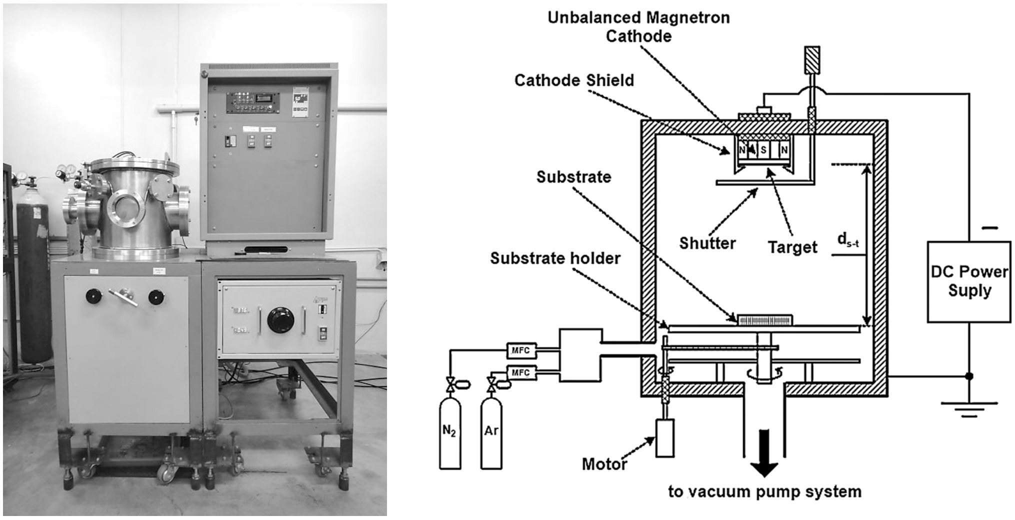

Figure 1 The feature and diagram of the coating system use in this work.

The sputtering target used was a mosaic target show in figure 2. The target matrix material is Ti (99.97%) and 4 holes positioned in the center of the erosion zone are filled with Cr (99.95%) inserts. This mosaic target is 54 mm diameter and a thickness of 3 mm held on a water-cooled magnetron cathode. The high purity processing gases, Ar (99.999%) and N_2 (99.999%) were used as the sputtering and reactive gases, respectively. MKS type247D mass flow controllers were used to control the flow rate of both the argon and nitrogen gases individually.

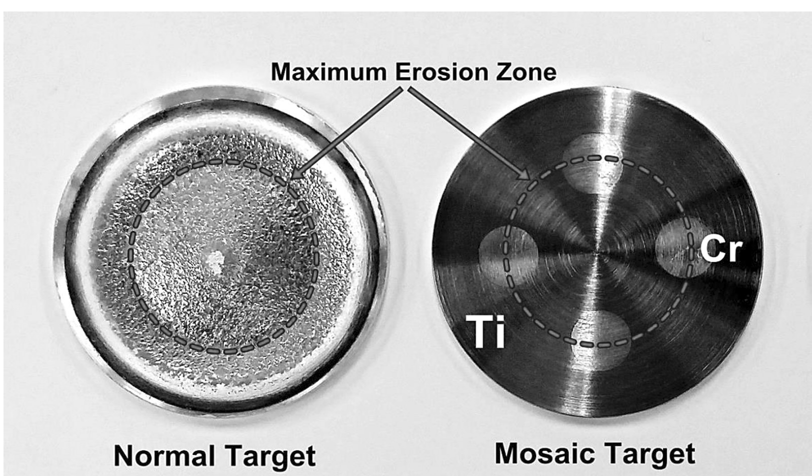

Figure 2 The feature and diagram of the coating system use in this work.

Before deposition of each TiCrN thin film, the coating chamber was evacuated to a base pressure of 5×10^{-5} mbar. The target was pre-sputtering under the Ar gas atmosphere for 10 minutes while the Si substrate was shielded by shutters in order to remove the contaminants on the target surface. The TiCrN films were deposited at different nitrogen gas flow rate from 4 sccm to 10 sccm, while deposition parameters such as sputtering power, substrate temperature and working pressure were constant. The deposition parameters used are summarized in Table 1.

The crystal structures and crystal size of the TiCrN thin films were characterized by X-ray Diffraction (XRD: BRUKER D8) using a Cu K_α radiation (λ=0.154 nm) and generator setting of 40 kV and 40 mA. The XRD patterns were acquired in a continuous mode, scanning speed of 2^{O}/min and the grazing incidence angle of 3^{O}. The phases of films were determined using Bragg's law and compared with the Joint Committee on Powder Diffraction Standard (JCPDS) files. The crystallite size calculated by Scherrer's equation. The surface morphology, and roughness of films were evaluated by Atomic Force Microscope (AFM: SEIKO SPA400) in a tapping mode with a silicon probe for observation of surface morphology and roughness with a scan size of 1.0 μm^2. The thickness, microstructure, and cross-section structure were investigated by Field Emission Scanning Electron Microscope (FE-SEM: Hitashi s4700). The chemical composition of the as-deposited TiCrN thin films was determined by Energy Dispersive X-ray spectroscopy (EDS: EDAX) equipped on Scanning Electron Microscopy (SEM: LEO 1450VP).

Table 1 Thin films deposition conditions

Parameters	Details
Sputtering target	Mosaic target of Ti (99.97%), Cr (99.95%)
Substrate temperature	room temperature
Substrate-target distances	15 cm
Base pressure	5.0×10^{-5} mbar
Working pressure	5.0×10^{-3} mbar
Sputtering power	190 W
Flow rate of Ar	16 sccm
Flow rate of N_2	4, 6, 8, 10 sccm
Deposition time	60 min

Result and Discussion

TiCrN thin films were deposited on Si-wafer by reactive DC unbalanced magnetron sputtering at from mosaic target by various nitrogen gas flow rate and keeping the other deposition parameters such as sputtering powers, substrate temperature, and sputtering pressure as constant. Figure 3 show the variation of deposition rates, which determined from the thickness divided by the deposition time, as a function of the nitrogen gas flow rate. The results show a significant decreasing of the deposition rate with increasing the nitrogen gas flow rate. The deposition rate of the films decreased form 11.2 nm/min to 9.4 nm/min with increasing the nitrogen gas flow rate from 4 sccm to 10 sccm, because of exceed nitrogen gas are react with the surface of the target, and form the thin nitride layer on the target surface, which called target poisoning, that reduce the target sputter rate.

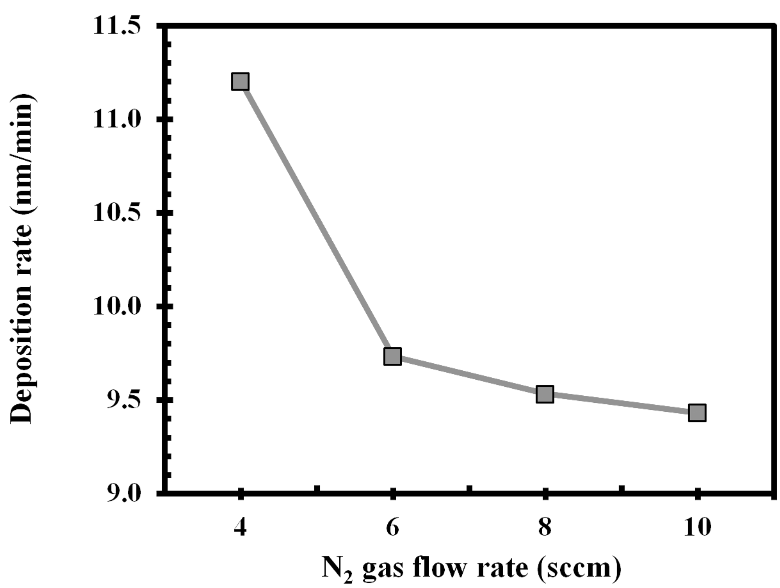

Figure 3 Effect of nitrogen gas flow rate on deposition rate of the as-deposited thin films.

The chemical composition of the as-deposited TiCrN thin films was analyzed by EDS technique as listed in table 2. In this work, it was found that as the nitrogen gas flow rate increased from 4 sccm to 10 sccm, the Ti and Cr content of the as-deposited TiCrN films decreased from 12.36 at.% to 9.80 at.% and 27.97 at.% to 23.11 at.%, respectively, while the N content increased from 59.67 at.% to 67.09 at.% as show in table 2. It also shows the Ti content and N content defined as x=Ti/(Ti+Cr) and y=N/(Ti+Cr) and film composition $Ti_xCr_{1-x}N_y$ as a function of nitrogen gas flow rate. It was found that the Ti content almost constant about 0.29-0.31 for all nitrogen gas flow rate. In addition, the N content in all films also increased with increasing of nitrogen gas flow rate. The ratio of nitrogen to metals (y) was more than 1 revealing that all of the as-deposited films were over stoichiometry.

Table 2 Chemical composition, Ti (x value) and N (y value), and film composition as a function of nitrogen gas flow rate.

N_2 flow rate	Chemical composition (at.%)			x = Ti/(Ti+Cr)	y = N/(Ti+Cr)	Film composition
(sccm)	Ti	Cr	N			($Ti_xCr_{1-x}N_y$)
4	12.36	27.97	59.67	0.31	1.48	$Ti_{0.31}Cr_{0.69}N_{1.48}$
6	10.71	25.60	63.69	0.29	1.75	$Ti_{0.29}Cr_{0.71}N_{1.75}$
8	9.99	24.13	65.88	0.29	1.93	$Ti_{0.29}Cr_{0.71}N_{1.93}$
10	9.80	23.11	67.09	0.30	2.04	$Ti_{0.30}Cr_{0.70}N_{2.04}$

Figure 4 shows the XRD patterns of the as-deposited TiCrN thin films deposited on Si-wafer substrates with different the nitrogen gas flow rate from 4 sccm to 10 sccm. The standard 2θ positions for the (111), (200) and (220) of the TiN and CrN structure were included for comparison purposes. The XRD peak position of the films showed a continuous shift from the CrN standard 2θ values with increasing of the nitrogen gas flow rate. As the nitrogen gas flow rate from 4 sccm to 10 sccm, the 2θ values for (111), (200) and (220) peak reflection of the TiCrN structure shifted toward the lower 2θ values.

This result suggested that the as-deposited thin films in this research work formed a solid solution of (Ti,Cr)N with the fcc NaCl phase. The result was found in other researcher, Lee et al. (2001) also found the fcc NaCl phase in (Ti,Cr)N film prepared by ion-plating method. A solid solution of the TiCrN films form whereby the Ti atoms were substituted by Cr atoms in the TiN structure. Since the atomic radius of Cr atom (0.1249 nm) is smaller than that of Ti atom (0.1445 nm) (Callister, 2007), it was found that the lattice constant of the TiCrN film, increased gradually with increasing nitrogen gas flow rate as show in figure 5. Moreover, the lattice constant of the TiCrN film which in range of 4.169 Å to 4.179 Å was between that of TiN (4.238 Å; JCPDS No. 87-0633) and CrN (4.148 Å; JCPDS 77-0047), which confirms that the Cr atoms have already incorporated into the TiN lattice in this case.

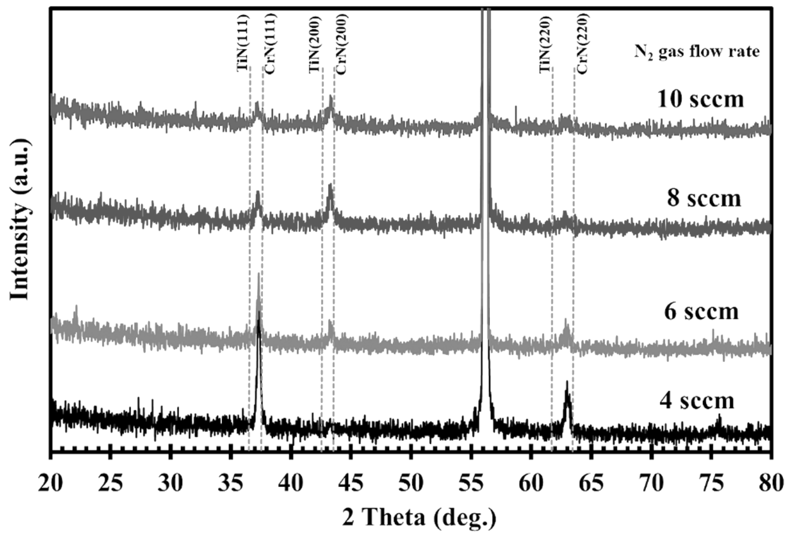

Figure 4 XRD patterns of TiCrN thin films deposited at difference nitrogen gas flow rate.

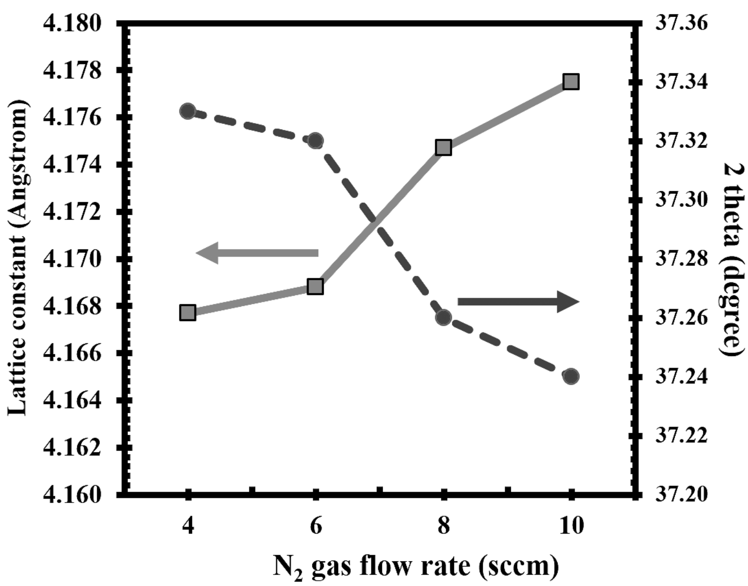

Figure 5 Lattice constant and 2θ of (111) peak as a function of nitrogen gas flow rate.

Table 3 Crystal size, roughness and thickness of the TiCrN thin films as a function of nitrogen gas flow rate.

N_2 flow rate (sccm)	Crystal size (nm)	Roughness (nm)	Thickness (nm)
4	67.1	4.8	336
6	62.1	1.8	292
8	59.9	1.4	286
10	50.8	3.2	283

The crystal sizes of the as-deposited films as a function of nitrogen gas flow rate shown in table 3 were calculated from FWHM of XRD patterns with (111) peak using the Scherrer's equation, were decreased from 67.1 nm to 50.8 nm as increasing of nitrogen gas flow rate.

The AFM technique was used to study the surface morphology, roughness, of the as-deposited films. Figure 6 shows the AFM images of the TiCrN thin films as a function of nitrogen gas flow rate. The small grains with triangle shape spread across the surface were investigated at low nitrogen gas flow rate of 4 sccm (figures 6(a)). When the nitrogen gas flow rate was increased, the coalescence of grains tend to form the bigger as the nitrogen gas flow rate increased. The RMS roughness values which obtained from AFM images were significantly decreased from 4.8 to 1.4 nm as a function of nitrogen gas flow rate. It can be noticed that the evolution of surface morphology and surface roughness were dependence on the nitrogen gas flow rate.

Figure 7 shown the FE-SEM cross-sectional images of the TiCrN thin films with different nitrogen gas flow rate. The as-deposited TiCrN thin films show columnar structure which was grown continuously from the substrate to the top surface and correspond to the zone 2 of to the Thornton's structure zone model (SMZ). The columns are less defected and are often facetted at the surface. Furthermore, the microstructure of the films also shows dense and compact columnar.

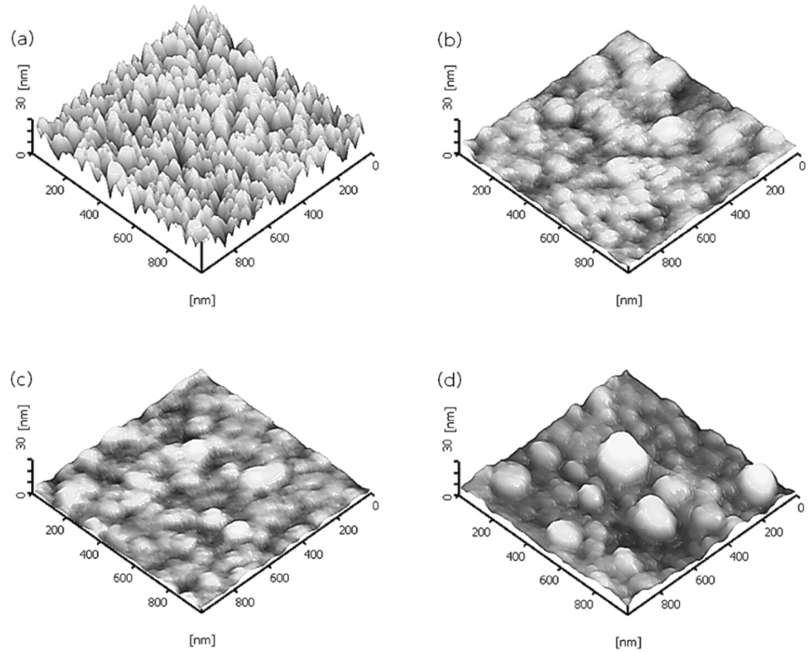

Figure 6 AFM images of the TiCrN films deposited at

(a) N_2 = 4 sccm, (b) N_2 = 6 sccm, (c) N_2 = 8 sccm, (d) N_2 = 10 sccm,

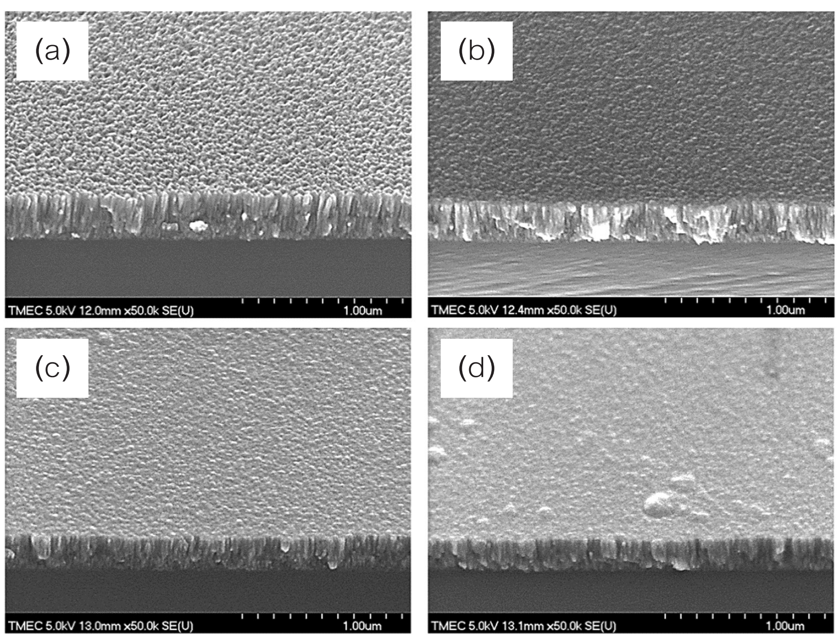

Figure 7 FE-SEM images of the TiCrN films deposited at

(a) N_2 = 4 sccm, (b) N_2 = 6 sccm, (c) N_2 = 8 sccm, (d) N_2 = 10 sccm,

Conclusion

The ternary nitride nanostructured TiCrN thin films were successfully deposited on Si-wafer by reactive DC magnetron sputtering method from mosaic target without external heating and biasing to the substrate. The as-deposited thin films formed solid solutions with the fcc NaCl phase at all nitrogen gas flow rate. The lattice constants of the as-deposited films gradually change with increasing the nitrogen gas flow rate. Crystal size and the thickness decreased with increasing the nitrogen gas flow rate. The chemical composition, Ti Cr and N contents, in the as-deposited films were varied with the nitrogen gas flow rate. The FE-SEM results revealed that the nitrogen gas flow rate affected the evolution of the microstructure. The cross section analysis showed compact columnar structure and dense morphology.

Acknowledgement

This work was financially supported by the Research Grant of Burapha University through National Research Council of Thailand (Grant no. 34/2559 - extended).

References

Callister, W.D. (2007). **Materials science and engineering: an introduction.** 7th ed. New York: John Wiley & Sons.

Golosoc, D.A., Melnikov, S.N. & Dostanko, A.P. (2012). Calculation of the elemental composition of thin films deposited by magnetron sputtering of mosaic targets. **Surface Engineering and Applied Electrochemistry.** 48(1), 52-59.

Lee, K.H., Park, C.H., Yoon, Y.S. & Lee, J.J. (2001). Structure and properties of $(Ti_{1-x}Cr_x)N$ coatings produced by the ion-plating method. **Thin Solid Films**. 385, 167-173.

Paksunchai, C., Denchitcharoen, S., Chaiyakun, S. & Limsuwan, P. (2012). Effect of sputtering current on structure and morphology of $(Ti_{1-x}Cr_x)N$ thin films deposited by reactive unbalanced magnetron co-sputtering. **Procedia Engineering**. 32, 875-881.

Shum, P.W., Li, K.Y. & Shen, Y.G. (2004). Improvement of high-speed turning performance of Ti–Al–N coatings by using a pretreatment of high-energy ion implantation. **Surface and Coatings Technology**. 198, 414-419.

Wang, W.L., Zhang, R.Q., Liao, K.J., Sun, Y.W. & Wang, B.B. (2000). Nucleation and growth of diamond films on aluminum nitride by hot filament chemical vapor deposition. **Diamond and Related Materials**. 9, 1660-1663.

Witit-anun, N. & Teekhaboot, A. (2016). Effect of Ti sputtering current on structure of TiCrN thin films prepared by reactive DC magnetron co-sputtering. **Key Engineering Materials**. 675-676, 181-184.

Witit-anun, N. & Buranawong, A. (2017). Effect of deposition time on structure of TiAlN thin films deposited by reactive DC magnetron co-sputtering. **Applied Mechanics and Materials**. 866, 318-321.