# Effect of Total Pressure on the Structure of TiCrN Thin Films Prepared from Mosaic Target by Reactive DC Magnetron Sputtering

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## Abstract

Titanium chromium nitride (TiCrN) nanocrystalline thin films were prepared on Si(100) wafers by reactive DC magnetron sputtering technique using a mosaic Ti-Cr target. The effects of the total pressure in the range of $3.5 \times 10^{-3}$ - $8.0 \times 10^{-3}$ mbar on the structure of the TiCrN films were investigated. The crystal structure, microstructure, surface morphology, thickness, and chemical composition were characterized by glancing incident X-ray diffraction (GI-XRD), field emission scanning electron microscopy (FE-SEM), and energy dispersive X-ray spectroscopy (EDS) technique, respectively. The results have shown that the TiCrN thin films were formed as a solid solution of (Ti,Cr)N. The films showed a nanocrystalline structure of TiCrN with crystal sizes of less than 54 nm, which were ranging from 21.5 to 53.4 nm. While, the lattice constance were ranging from 4.139 to 4.213 Å. The film thicknesses increased from 137 nm to 462 nm with an increasing in the total pressure. The chemical composition, Ti Cr and N contents, in the as-deposited films, varied with the total pressure. Lastly, the as-deposited TiCrN films showed compact columnar and dense morphology as a result of changed in the total pressure.

*Keywords: TiCrN, Thin films, Reactive magnetron sputtering, Total pressure, Mosaic target*

## 1. Introduction

Over the last several years, surface engineering has been an important process used to revise the wear, oxidation, and corrosion resistance of industrialized materials subjected to strong wear environments, with which require surfaces with a high hardness and corrosion resistance (Krelling et al, 2017). Generally, transition metal nitrides are extensively used due to their excellent properties: hardness, high melting point, chemical stability, and wear resistance (Santheccia et al, 2015). Notably among the best-known hard coating is titanium nitride (TiN), which is one of the first synthetic coatings whose mechanical properties has been generally reported in numerous researches for its thicknesses in the order of micron (Solis-Pomar et al, 2016). TiN is a hard ceramic material, which is generally known to crystallize in the B1-NaCl structure with a nitrogen concentration in the range of 37.5–50%. As a result of its vigorous wear and corrosion resistant properties, it is frequently deposited into cutting tools in order to extend their lifespan (Santheccia et al, 2015). Nevertheless, TiN coatings still have its limitation in high temperature processes by oxidizing at above 500 °C to form a brittle layer of $TiO_2$, it can result in an easily induced shear off of the TiN coating and contributes to the degradation (Komarov et al, 2016).

In order to overcome these problems and improve the properties of 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 and Buranawong, 2017). It has been reported that the thermal stability of TiN films is significantly better by the addition of another element, especially chromium into its structure, which leads to significant heightened thermal oxidation resistance of TiN. Whereby the Cr atoms are located in crystalline lattice sites substitutes the Ti atoms to form a solid solution (Vishnyakov et al, 2006). The TiCrN films have excellent mechanical properties: wear resistance, chemical stability, and thermal stability with the oxidation temperature at above 700 °C (Krzanowski et al, 2014). Moreover, the composition of Cr in the TiCrN films can protentially affect the microstructure and various properties of coatings (Chang et al, 2007).

Physical vapor deposition (PVD) techniques namely, evaporation, magnetron sputtering, and ion plating are commonly used to deposit the ternary hard coating of TiCrN. In which, the reactive magnetron
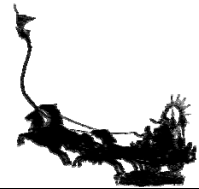
sputtering is one of the most commonly used techniques to deposit uniformly surfaced and strong adhesion films, with high deposition rate and low substrate temperature during the deposition process (Thampi et al, 2016). A tactic which evolves the method of magnetron sputtering for depositing multicomponent thin films with any content of elements using a single magnetron is the use of a mosaic target (a target that consists of a matrix of one metal with inserts of other metals). The sputtering by mosaic target is suitable for deposited films with low mutual solubility or with a great difference in the melting temperatures (Golosov et al, 2012).

Nowadays, it is commonly known that the properties of the sputtered thin films depend on the structure of the films, which relate to the deposition processes parameters such as working gas flow rate, sputtering power, depositions time, and/or total pressure. Therefore, the effects of these parameters on the structure of TiCrN thin films are still crucial and necessary to investigate. Presently, the studies of the TiCrN thin film deposition, mostly, have been focused on the effects of the deposition parameters on the crystal structure, microstructure, and properties of TiCrN thin films. However, the studies of the TiCrN film which, deposited from magnetron sputtering by using a mosaic target are still scarce. This research work is thus aimed at growing nanostructured TiCrN films on unheated Si-wafers by reactive DC unbalanced magnetron sputtering from the mosaic target, by varying the total pressure to investigate the influences of total pressure on the structure of the as-deposited films.

## 2. Objectives
1. To prepare nanostructured TiCrN thin films on Si-wafer at room temperature without substrate heating and biasing by reactive DC magnetron sputtering, using the mosaic target at different total pressure.
2. To study the effects of total pressure on the structure of the as-deposited TiCrN thin films.

## 3. Materials and Methods
The TiCrN thin films were grown on an unheated substrate, Si(100) wafers, by reactive DC magnetron sputtering technique from a "homemade" coating system (Figure 1), without external heating and voltage biasing. The mosaic target is pure metal Ti (99.97%) disk inserted with Cr (99.99%) in the center of the high sputtering rate zone of the target, as shown in Figure 2(Witit-anun & Buranawong, 2019). The distance from the substrate to the target was constant at 15.0 cm. The high purity process gases of Ar (99.999%) and $N_2$ (99.999%) were used as the sputtering and reactive gases, respectively.

The chamber was evacuated by the vacuum pumps to a base pressure at $5.0 \times 10^{-5}$ mbar, before the deposition process. Then, the target was treated as a pre-sputtered process with an Ar atmosphere for 10 minutes, while the substrates were shielded by a shutter, in order to clear the surface contamination. Thin films were deposited after Ar and $N_2$ flowed into the chamber with an optimized constant flow rate at 16 and 6 sccm, respectively (Witit-anun & Buranawong, 2019). The total working pressure varied in the range of $3.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, $6.5 \times 10^{-3}$, and $8.0 \times 10^{-3}$ mbar. The sputtering power was maintained at about 200 W through deposition time at 30 minutes. The details of deposited TiCrN thin films are presented in Table 1.
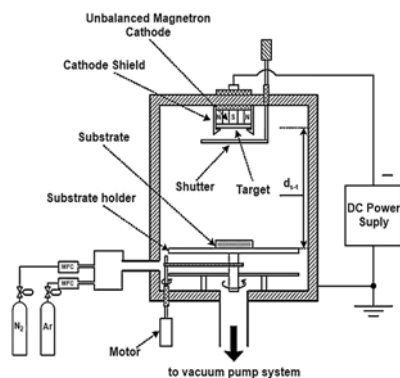


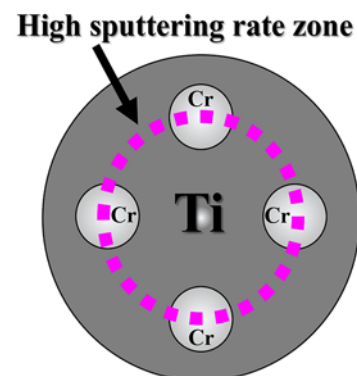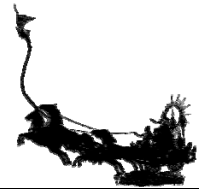**Figure 1** The diagram of the coating system



**Figure 2** The mosaic target of Ti-Cr

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The as-deposited TiCrN thin films were characterized by three main techniques. The crystal structure was analyzed by glancing incident X-ray diffraction (GI-XRD: Bruker D8) as the incident angle of 3° with 2θ-scan wide-ranging from 20° to 80°. The phases were identified using the JCPDS files and the crystal size was calculated applying Scherrer's equation. The chemical composition was measured by energy dispersive X-ray spectroscopy (EDS: EDAX). The microstructure and thickness were detected by Field Emission Scanning Electron Microscope (FE-SEM: Hitashi s4700).

**Table 1** Conditions for the deposition TiCrN films

| Parameter | Detail |
|---|---|
| Sputtering target | mosaic Ti-Cr |
| Substrate | Si (100) |
| Substrate temperature | room temperature |
| Substrate to target distance | 15.0 cm |
| Flow rate of Ar | 16 sccm |
| Flow rate of $N_2$ | 6 sccm |
| Base pressure | $5.0 \times 10^{-5}$ mbar |
| Total working pressure | $3.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, $6.5 \times 10^{-3}$ and $8.0 \times 10^{-3}$ mbar |
| Sputtering power | 200 W |
| Deposition time | 30 minute |

## 4. Results and Discussion

TiCrN thin films were deposited on Si-wafer by reactive DC unbalanced magnetron sputtering from the mosaic target by varying the total working pressure, whereas maintainingthe other deposition parameters, such as thesputtering power, flow rate of sputtering gas, flow rate of reactive gas and base pressure, as constant.The tendency of the deposition rate as exhibited in Figure 3, is calculated from the ratio of thickness per deposition time, as a function of the total working pressure. The results indicated that the deposition rates were coincidingly increased with an increasing in the total working pressure. In addition, the deposition rate of the films increased from 4.6 nm/min to 15.4 nm/min with increasing of the total pressure from $3.5 \times 10^{-3}$ mbar to $8.0 \times 10^{-3}$ mbar. Owing to the direct variation of deposition factors: number of bombarding $Ar^+$ ions, number of sputtered atoms, and the total pressure, lead to expressively increase in the sputtering rate of the TiCrN films.
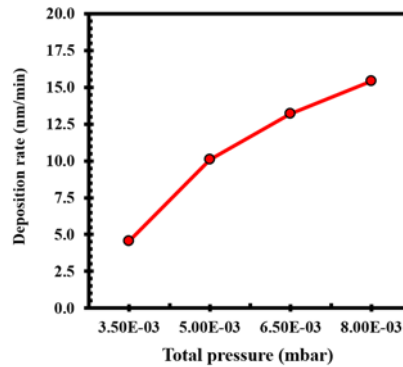
**Figure 3** Effect of total pressure on the deposition rate of the as-deposited thin films

Table 2 presented the chemical composition of the TiCrN films from EDS technique. It can be clearly examined that the nitrogen content in the films increased from 61.2 to 66.0 at.% with an increasing of the total working pressure, whereas the $N_2$ flow rate was maintained constant at 6.0 sccm. Nevertheless, the Ti content was decreased from 13.8 to 8.9 at.%, while the concentration of the Cr content in the films was rather constant at about 25.0 – 26.8 at.%. This result can be explained by the mean free path of bombarding ions, which was also decreased with an increasing of the total pressure during the sputtering process, leading to an energy decrease of these ions. Due to the fact that the enthalpy of TiN is higher than CrN, therefore, this process can increase the incorporation of N atoms and also reduces the incorporation of Ti atoms in the films. Moreover, it also shows the ratio x of Cr content in films defined as $x = Cr/(Ti+Cr)$, the ratio of N content in films defined as $y = N/(Ti+Cr)$, and the film composition $Ti_{1-x}Cr_xN_y$ as a function of the total pressure. It was discovered that the Cr content was in the range of 0.64 to 0.74, while the N content was ranging from 1.58 to 1.94. Hence, the film composition from varied total working pressure at $3.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, $6.5 \times 10^{-3}$ and $8.0 \times 10^{-3}$ mbar were $Ti_{0.36}Cr_{0.64}N_{1.58}$, $Ti_{0.28}Cr_{0.72}N_{1.69}$, $Ti_{0.26}Cr_{0.74}N_{1.89}$ and $Ti_{0.26}Cr_{0.74}N_{1.94}$, respectively. In addition, the ratio of the nitrogen to the metals (y) was more than 1, indicating that all of the as-deposited thin films were over stoichiometry.

**Table 2** Chemical composition, Ti (x value) and N (y value), and film composition as a function of total pressure

| Total pressure (mbar) | Chemical composition (at.%) | | | $x=Cr/(Ti+Cr)$ | $y=N/(Ti+Cr)$ | Film composition $(Ti_{1-x}Cr_xN_y)$ |
| --- | --- | --- | --- | --- | --- | --- |
| | Ti | Cr | N | | | |
| $3.5 \times 10^{-3}$ | 13.8 | 25.0 | 61.2 | 0.64 | 1.58 | $Ti_{0.36}Cr_{0.64}N_{1.58}$ |
| $5.0 \times 10^{-3}$ | 10.4 | 26.8 | 62.8 | 0.72 | 1.69 | $Ti_{0.28}Cr_{0.72}N_{1.69}$ |
| $6.5 \times 10^{-3}$ | 9.1 | 25.4 | 65.5 | 0.74 | 1.89 | $Ti_{0.26}Cr_{0.74}N_{1.89}$ |
| $8.0 \times 10^{-3}$ | 8.9 | 25.1 | 66.0 | 0.74 | 1.94 | $Ti_{0.26}Cr_{0.74}N_{2.94}$ |

The X-ray diffraction spectra of the as-deposited TiCrN films prepared on Si (100) wafer at various total working pressure are displayed in Figure 4. Of which, the lines at 2θ values of standard TiN and CrN with (111), (200) and (220) planes were showed for comparison purposes. The results from XRD technique revealed that the crystal structure of TiCrN films is significantly depended on the total pressure. The diffraction peaks at (111), (200), and (220) were found in the TiCrN thin films deposited at a total pressure of $3.5 \times 10^{-3}$, $5.0 \times 10^{-3}$ and $6.5 \times 10^{-3}$ mbar. Furthermore, the 2θ values of diffraction spectra were found between the 2θ values of TiN and CrN at the low total pressure ($3.5 \times 10^{-3}$ and $5.0 \times 10^{-3}$ mbar). Whereas, at a high total pressure ($6.5 \times 10^{-3}$ and $8.0 \times 10^{-3}$ mbar), the diffraction peak showed a more significant shift from the standard peak of TiN, the films may be possible to form as CrN. Thus, the diffraction angle for TiCrN spectra is significantly shifted toward a

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higher angle. This phenomenon may be explained by the fact that the mean free path of $Ar^+$ ions was also decreased with an increasing of the total pressure in the vacuum chamber, which led to the energy reduction of ion bombardment. Consequently, the energy of sputtered atoms might be less than the energy that was used to formed TiN, whereby the N affinity of Ti and Cr are $\Delta H_{TiN}$ = -337.65 kJ/mol and $\Delta H_{CrN}$ = -117.15 kJ/mol, respectively (Paksanchai et al, 2014). It can be evidently understood that the total working pressure in the sputtering gas mixture (Ar/$N_2$) during the sputtering process meaningfully impacted the orientation growth behavior for TiCrN thin films.

Additionally, the sharpen peak for the total pressure at $5.0 \times 10^{-3}$ mbar exhibited a well-crystallize (Ti,Cr)N phase was formed. Due to the total pressure during the sputtering process strongly relevant to the energy of sputtered atoms for enhanced crystalline growth of films, therefore, the total pressure at $5.0 \times 10^{-3}$ mbar is an optimized condition to deposited high crystallinity films. The (Ti,Cr)N is a solid solution of TiN and CrN that have a similar crystal structure and nearby lattice parameter (Choi et al, 2009). Reports from other literature, have founded that the fcc B1-NaCl phase of the (Ti,Cr)N film was achieved by sputtered deposition (Paksanchai et al, 2012; Thampi et al, 2016). In fact, the solid solution was formed whereby the Ti atoms were substituted by Cr atoms in the TiN structure owing to the atomic radius of Cr atom (0.1249 nm), which is smaller than that radius of Ti atom (0.1445 nm) (Paksanchai et al, 2012). From the Table 2, the crystal sizes of the as-deposited films calculated by the full width at half maximum (FWHM) of XRD spectra from the Scherrer's equation were in the range of 21.5 to 53.4 nm. Finally, the lattice constant of the TiCrN films was slightly decreased with an increasing in the total working pressure. In this work, the constant was in the range of 4.139 to 4.213 Å, between that of CrN (4.148 Å; JCPDS 77-0047), and TiN (4.238 Å; JCPDS 87-0633), which confirms that the Cr atoms have absolutely incorporated into the TiN structure.
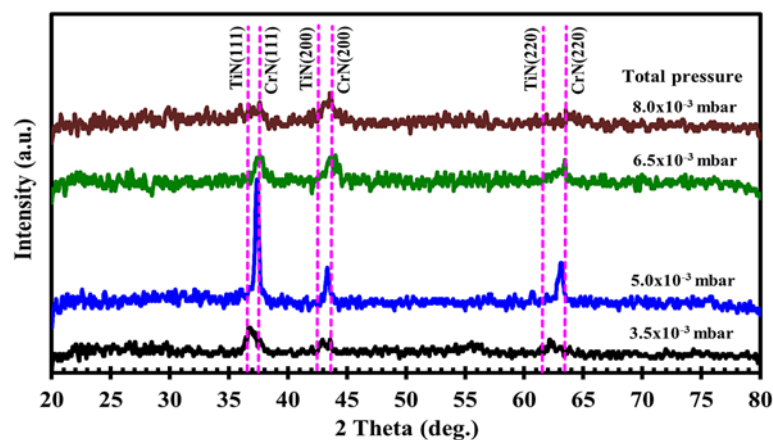


**Figure 4** XRD pattern of TiCrN thin films deposited at various the total working pressure

**Table 3** Thickness, crystal size and lattice constant of the as-deposited TiCrN thin films as a function of total pressure.

| Total pressure (mbar) | Thickness (nm) | Crystal size (nm) | | | Lattice constant (Å) | | |
|---|---|---|---|---|---|---|---|
| | | **(111)** | **(200)** | **(220)** | **(111)** | **(200)** | **(220)** |
| $3.5 \times 10^{-3}$ | 137 | 21.5 | 34.1 | 34.4 | 4.213 | 4.206 | 4.212 |
| $5.0 \times 10^{-3}$ | 303 | 52.4 | 53.4 | 53.3 | 4.162 | 4.170 | 4.161 |
| $6.5 \times 10^{-3}$ | 397 | 30.0 | 27.6 | 43.4 | 4.140 | 4.139 | 4.150 |
| $8.0 \times 10^{-3}$ | 462 | 31.1 | 35.6 | NA | 4.140 | 4.148 | NA |

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The cross sections and surface morphology of the as-deposited TiCrN thin films at different total working pressure are as shown in Figure 5. It revealed that thin films have small grains and smooth surface at the lowest total pressure ($3.5 \times 10^{-3}$ mbar) as shown in Figure 5(a). Then, the morphology of the films was generally composed of incalculable grains like islands varying in sizes randomly dispersed on the surface, and were enlarged with increasing of the total pressure (Figure 5(b), 5(c) and 5(d)).

It can be explained that as the total pressure reached the lowest at $3.5 \times 10^{-3}$ mbar, the grain size on the surface of the as-deposited film became smaller compare to the film grown at a higher total pressure, resulting in a smooth surface and dense structure film. High energy atom of sputtered atoms including Ti and Cr, moving to the substrate during the sputtering process at low total pressure can enhance nucleation growth of films.

The thickness of the as-deposited TiCrN thin films, in this work, indicated that the thickness was significantly increased from 137 to 462 nm with an increasing of the total pressure. This effect may be explained by the fact that the number of bombarding ions ($Ar^+$) was increased with an increasing of the total pressure, which leads to an increase of the sputtered atoms from the target with Ti and Cr in TiCrN films. Additionally, the as-deposited films show columnar structure, which was grown continuously from the substrate to the top of the surface, and correspond to the zone 2 of the Thornton's structure zone model (SMZ) at a high total pressure. The columns are smaller defected and are consistently facetted at the surface.



(a)　　　　　　　(b)　　　　　　　(c)　　　　　　　(d)
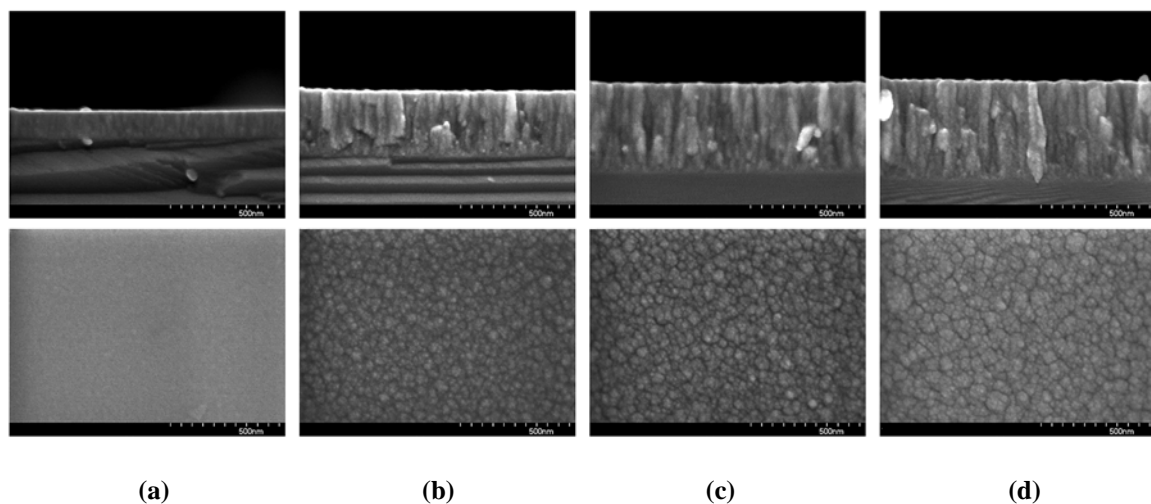
**Figure 5** FE-SEM image of TiCrN thin films deposited at various the total working pressure
(a) $3.5 \times 10^{-3}$ mbar (b) $5.0 \times 10^{-3}$ mbar (c) $6.5 \times 10^{-3}$ mbar (d) $8.0 \times 10^{-3}$ mbar

## 5. Conclusion

The nanostructure of TiCrN thin films was successfully prepared on Si (100) wafers from a mosaic Ti-Cr target by reactive DC magnetron sputtering technique with various total working pressure. The effects of the total pressure in the range of $3.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, $6.5 \times 10^{-3}$, and $8.0 \times 10^{-3}$ mbar on the structure of the as-deposited TiCrN films were investigated. The crystal structure, microstructure, surface morphology, thickness, and composition were characterized by GI-XRD, FE-SEM, AFM and EDS technique, respectively. The results have shown that the TiCrN thin films were formed as a solid solution of (Ti,Cr)N. The films showed a nanocrystalline structure of TiCrN with crystal sizes of less than 54 nm, which the sizes of films were ranging from 21.5 to 53.4 nm. The lattice constants were ranging from 4.139 to 4.213 Å. The film thicknesses increased from 137 to 462 nm with an increasing of the total pressure. The nitrogen content of TiCrN films was slightly increased, while the titanium content was decreased with an increasing of the total pressure. Lastly, the TiCrN films shown compact columnar and dense morphology because of changes in the total pressure**.**

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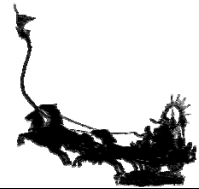
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