Preparation and characterization of nanostructured TiCrN thin films deposited from Ti-Cr mosaic target by reactive DC magnetron sputtering

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Abstract. In this research work, nanostructured thin films of TiCrN have been deposited on Si by reactive DC magnetron sputtering from a mosaic Ti-Cr target. The effects of nitrogen gas flow rates on the structure of the as-deposited TiCrN thin films were examined. The crystal structure, microstructure, surface morphology, thickness, and composition were characterized by GI-XRD, FE-SEM and EDS technique, respectively. The results revealed that the thin films were formed as a (Ti,Cr)N solid solution. The as-deposited thin films showed a nanocrystalline structure of TiCrN with the crystal sizes less than 45 nm. The lattice constants were in the range of 4.144 to 4.181 Å. The thickness of the TiCrN films decreased from 379 to 276 nm with increasing of the nitrogen gas flow rates. The nitrogen content of the as-deposited films was increased with increasing of the nitrogen gas flow rates, while the titanium and chromium content in the films were decreased. Finally, the TiCrN thin films showed compact columnar and dense morphology as a result of various the nitrogen gas flow rate.

1. Introduction

In the last decade, surface engineering is the most important technology for new industrial development, especially on improving the surface tribology properties of machinery parts. Transition metal nitride hard coating such as TiN has grown by the PVD technique is one of the most promising materials used to enhance the surface tribology properties which were used to protect the industrial parts against wear [1,2]. Both of the high hardness and toughness of the TiN coating make it outstanding for industrial applications [3]. However, a drawback of the TiN coating is rapid thermal oxidation at high temperatures above 500°C that easily induces shear off of the TiN coating and contributes to the degradation [4].

It has been reported that the thermal oxidation resistance of the TiN films is considerably increased by the addition of other element such as Al, Cr or Zr into the TiN structure, which leads to the ternary coating, such as, TiAlN, TiCrN and TiZrN [5]. Among these coatings, the TiCrN coatings have excellent properties: high hardness (25-38 GPa), good wear resistance, chemical stability and thermal stability at above 700°C [6-7]. Due to the incorporation of Cr atoms in the cubic fcc TiN structure which leads to improving the hardness and thermal oxidation resistance of the TiCrN thin films [8].

Typically, the TiCrN films can grow by many techniques, such as arc evaporation [9], ion plating [10], ion beam assisted deposition [11], and sputtering [12]. Among them, the sputtering is one of the most common used due to low-temperature process, use of non-toxic gases [13] and easy to deposited thin films with large area uniformity [14]. In the case of the sputtering, for deposited ternary nitride hard
coating, it can be done by different types of the sputtering targets, such as, multi-target, segment target, alloy and mosaic target, which has pro and con for each type. However, the use of multi-target, almost cannot be used at the industrial scale due to its complexity system. Nowadays, the tendency in the ternary nitride hard coating is to develop the sputtering method from a single target. The advantage of sputtering from a mosaic target is most obvious in the case when the films to be gotten comprise elements with low mutual solubility or a great difference in melting temperatures [15].

However, it is commonly known that the properties of the sputtered thin films depend on the structure of the films which, relate to the deposition parameters such as working gas flow rate, sputtering power, depositions time and/or total pressure. 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 limited.

The aim of this work was to prepare the nanostructured TiCrN thin films on Si at room temperature by reactive DC magnetron sputtering from the Ti-Cr mosaic target, with various of the nitrogen gas flow rates, to study the effects of the nitrogen gas flow rates on the structure of the as-deposited thin films. The characteristics such as the crystal structure, microstructure, surface morphology, thickness, and chemical composition were investigated as a function of the nitrogen gas flow rate. These relations were reported as an advanced method for recognizing the film structure. Hence, the results from this study achieved also could be actual valuable for hard coating applications.

2. Materials and methods

2.1. Thin films preparation

The TiCrN thin films were deposited on Si substrate by reactive DC magnetron sputtering technique. In the deposition chamber, all substrates are mounted at the midpoint faced to centre of the target. The distance between the Ti-Cr mosaic target and the substrate holder is about 150 mm. The system can be creating a base pressure lower than 5x10⁻⁸ mbar by using oil diffusion pump backing with a rotary pump. The pressure of the system measure by Pirani-Penning gauge combination (PFEIFFER: PKR 251) with TPG 262 measurement unit. DC power supply of 1000 V and 3 A use as a power source for sputtering. The processing gases used are high-purity argon (Ar) (99.999%) as the sputtering gas and nitrogen (N₂) (99.999%) as the reactive gas. MKS type247D mass flow controllers use to control the flow rate of both gases individually. The sputtered Ti-Cr mosaic target styled, used in this work, is made by embedding Cr rods (99.99%) into the high sputtering rate area of a Ti target (99.97%), as show in figure 1.

The coating chamber was pumped down to a base pressure of 5.0x10⁻⁸, before feeding the processing gas, Ar and N₂ gases, for each thin films deposition. The TiCrN films were deposited at different N₂ gas flow rate from 2, 6, and 10 sccm, while another deposition parameter such as Ar gas flow rate, substrate-target distances, base pressure, total pressure, sputtering current and substrate temperature were constant. The deposition parameters are summarized in table 1.

| Parameters                  | Details          |
|-----------------------------|------------------|
| Sputtering target           | Ti-Cr mosaic target |
| Substrate temperature       | room temperature |
| Substrate-target distances  | 15 cm            |
| Base pressure               | 5.0x10⁻⁵ mbar    |
| Working pressure            | 5.0x10⁻³ mbar    |
| Sputtering power            | 185-190 W        |
| Flow rate of Ar             | 16 sccm          |
| Flow rate of N₂             | 2, 6, 10 sccm    |
| Deposition time             | 30 min           |

Figure 1. The Ti-Cr mosaic target.
2.2. Thin films characterization
The crystal structures of the as-deposited TiCrN thin films were analysed by glancing incidence X-ray diffraction (GI-XRD; BRUKER D8) using a Cu Kα radiation (λ=0.154 nm). The XRD patterns were acquired in a continuous mode, scanning speed of 2°/min, and the grazing incidence angle of 3°. The phases of the thin films were identified using Bragg’s law and interplanar spacing equation and then compared with the Joint Committee on Powder Diffraction Standard (JCPD files). The crystal size can be calculated from the FWHM data acquired from the XRD pattern using Scherrer’s equation. The microstructure, surface morphology, and thickness of the thin films were observed by field emission scanning electron microscope (FE-SEM: Hitachi s4700). The chemical composition of the films was measured by energy dispersive X-ray spectroscopy (EDS; EDAX) equipped on scanning electron microscopy (SEM; LEO 1450VP).

3. Results and discussions
3.1. Crystallographic properties and phase development
The X-ray diffraction spectra of the as-deposited TiCrN films growth on silicon wafers at different of the nitrogen gas flow rates are exhibited in figure 2. The lines at a diffraction angle (2θ values) of standard TiN (JCPDS No. 87-0633) and CrN (JCPDS No. 77-0047) with (111), (200) and (220) plane are shown for comparison purposes. The diffraction peaks of all deposited thin films were observed. The 2θ values of diffraction peaks were about 37.22°-37.55°, 43.13°-43.59°, and 62.90°-63.36°, which varied between the TiN and CrN JCPDS standard structure. These results were according to the TiCrN (100), (200) and (220) planes. The XRD patterns of the as-deposited thin films showed a continuous shift of the peak positions from the standard 20 values with increasing the nitrogen gas flow rates.

![XRD spectra of the TiCrN thin films deposited at various of the nitrogen gas flow rates.](image)

Figure 2. XRD spectra of the TiCrN thin films deposited at various of the nitrogen gas flow rates.

As the nitrogen gas flow rates increased, the 2θ values of the diffraction angle for the (111), (200) and (220) peak reflection of the TiCrN structure shifted toward the lower 2θ values. It can be implied that the position of the diffraction peak was strongly influenced by the flow rate of nitrogen gas. These results indicating that the nitrogen gas flow rate in the sputtering gas mixture significantly affected
were less than 45 nm, which in the range of TiCrN thin chromium have completely incorporated into the TiN structure (lattice constant of the as deposited thin films, in this work, increased gradually with increasing nitrogen gas flow rates as shown in table 2). The crystal sizes of the as-deposited thin films, in this work, increased gradually with increasing the nitrogen gas flow rate as shown in figure 3, while the diffraction angle was decreased.

It was revealed that the lattice constant of the as-deposited TiCrN films, in this research work, was progressively increased with increasing the nitrogen gas flow rates as shown in figure 3. Moreover, the lattice constant of the as-deposited thin films were in the range of 4.144 to 4.181 Å, between that of CrN (4.148 Å; JCPDS 77-0047) and TiN (4.238 Å; JCPDS No. 87-0633), which confirms that the atoms of chromium have completely incorporated into the TiN structure. The crystal sizes of the as-deposited TiCrN thin films, in this work, calculated from FWHM of XRD spectra using the Scherrer’s equation were less than 45 nm, which in the range of 33.3 to 42.7 nm, as shown in table 2.

![Figure 3](image)

**Figure 3.** Lattice constant of the TiCrN thin films as a function of the nitrogen gas flow rates.

| N₂ gas flow rate (sccm) | Thickness [nm] | Crystal size [nm] (111) | Crystal size [nm] (200) | Crystal size [nm] (220) | Lattice constants [Å] (111) | Lattice constants [Å] (200) | Lattice constants [Å] (220) |
|------------------------|----------------|--------------------------|-------------------------|-------------------------|----------------------------|----------------------------|----------------------------|
| 2                      | 379            | 36.5                     | 36.4                    | 33.3                    | 4.144                      | 4.148                      | 4.147                      |
| 6                      | 295            | 38.1                     | 39.8                    | 39.6                    | 4.168                      | 4.168                      | 4.173                      |
| 10                     | 276            | 41.9                     | 42.7                    | 38.0                    | 4.181                      | 4.171                      | 4.175                      |
3.2. Chemical composition

The chemical composition of the TiCrN thin films were analyzed from Energy Dispersive Spectroscopy (EDS) technique as showed in figure 4 and summarized in table 3. It was indicated that as the nitrogen content of the films increased from 54.9 to 66.3 at.% with increasing of the nitrogen gas flow rates from 2 to 10 sccm while the titanium and chromium content decreased from 15.3 to 10.0 at.% and 29.8 to 23.7 at.% respectively. Moreover, it also shows the ratio x of chromium content in the as-deposited TiCrN thin films defined as x = Cr/(Ti+Cr) and thin film composition Ti\textsubscript{1-x}Cr\textsubscript{x}N as a function of the nitrogen gas flow rates. It was found that the chromium content was in the range of 0.66 to 0.70, which nearly constant. Therefore, the film composition from varied nitrogen flow rate at 2, 6 and 10 sccm were Ti\textsubscript{0.34}Cr\textsubscript{0.66}N\textsubscript{1.22}, Ti\textsubscript{0.30}Cr\textsubscript{0.70}N\textsubscript{1.74}, and Ti\textsubscript{0.30}Cr\textsubscript{0.70}N\textsubscript{1.97}, respectively. In addition, the ratio of nitrogen content to metals content (y) was more than 1 revealing that all the as-deposited TiCrN thin films in this research work were over stoichiometry.

![EDS spectra of TiCrN thin films deposited at various nitrogen gas flow rates](image)

**Figure 4.** EDS spectrum of TiCrN thin films deposited at varied the nitrogen gas flow rates; (a) 2 sccm, (b) 6 sccm, (c) 10 sccm.

**Table 3.** Composition and film composition as a function of the nitrogen gas flow rates.

| N\textsubscript{2} gas flow rate (sccm) | Composition (at.%) | x=Cr/(Ti+Cr) | y=N/(Ti+Cr) | Film composition (Ti\textsubscript{1-x}Cr\textsubscript{x}N) |
|-------------------------------------|--------------------|--------------|------------|-----------------|
| 2                                   | 15.3  | 29.8 | 54.9 | 0.66 | 1.22 | Ti\textsubscript{0.34}Cr\textsubscript{0.66}N\textsubscript{1.22} |
| 6                                   | 10.8  | 25.6 | 63.6 | 0.70 | 1.74 | Ti\textsubscript{0.30}Cr\textsubscript{0.70}N\textsubscript{1.74} |
| 10                                  | 10.0  | 23.7 | 66.3 | 0.70 | 1.97 | Ti\textsubscript{0.30}Cr\textsubscript{0.70}N\textsubscript{1.97} |

3.3. Microstructure and surface morphology

Figure 5 illustrated the microstructure (cross section and surface morphology) of the as-deposited TiCrN thin films. It can be seen thin films that the small grain and smooth surface at highest nitrogen flow rate (figure 5(c)). While the morphology was mostly composed of countless large grains like an island with different sizes distributed randomly on the surface of film at lowest nitrogen flow rate (figure 5(a)). As the nitrogen gas flow rate reached to the lowest (2 sccm), the grains size on the surface of the as-deposited film become larger compared to the film grown at high the nitrogen gas flow rate (10 sccm). It was evident that with the low nitrogen gas flow rate, the more kinetic energy of the sputtered atoms arriving at the surface of substrate and can transfer to more lattice site, which enhanced for nucleation and growth thus the grain size was enlarged [16].

From the cross-section analysis, it was visibly indicated that the thickness was decreased from 379 to 276 nm with increasing of the nitrogen gas flow rate (table 2). It can be seen that the increasing of the nitrogen gas flow rate results in the decreased of deposition rate. This effect is well known for reactive sputtering process, the increasing of nitrogen flow rate reduced the sputtering yield of a target due to target poisoning. Oppositely, since the total flow rate of the gas mixture is constant, increase in the
nitrogen gas flow rate is followed by decrease in the argon concentration. Therefore, the sputtering yield of the target reduced owing to lower momentum transfer of nitrogen comparing to argon [19]. In this work, the as-deposited TiCrN thin films show columnar structure which was grown continuously from the substrate to the top of film’s surface, which correspond to the zone 2 of the Thornton’s structure zone model (SMZ). The columns are less defected and are regularly faceted at the surface. Additionally, the microstructure of the TiCrN films also shows compact columnar.

![Figure 5. FE-SEM micrograph of TiCrN thin films deposited at varied the nitrogen gas flow rates; (a) 2 sccm, (b) 6 sccm, (c) 10 sccm.](image)

### 4. Conclusion
The nanostructure of TiCrN thin films were successfully prepared on Si substrate from a mosaic Ti-Cr target by reactive DC magnetron sputtering technique with various the nitrogen gas flow rate. The crystal structure, microstructure, surface morphology, thickness, and chemical composition of the films were characterized by GI-XRD, FE-SEM, and EDS technique, respectively. The results shown that the as-deposited films were formed as a (Ti,Cr)N solid solution. The films show a nanocrystalline structure of TiCrN film with a crystallite size less than 45 nm. The crystal sizes of films were in the range of 33.3 to 42.7 nm. The lattice constants were in the range of of 4.144 to 4.181 Å. The thickness of films decreases with increasing of the nitrogen flow rates. The nitrogen content of films was increased with increasing of the nitrogen gas flow rates. The cross-section analysis by FE-SEM showed compact columnar and dense morphology as a result of varied the flow rate of nitrogen gas.

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