

STRUCTURAL AND OXIDATION BEHAVIOR OF NANOSTRUCTURED TiCrN THIN FILM DEPOSITED BY REACTIVE DC MAGNETRON CO-SPUTTERING

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Abstract

Nanostructured titanium chromium nitride (TiCrN) thin films were deposited on Si by reactive DC magnetron co-sputtering technique. The effects of N₂ gas flow rates on the structure of the TiCrN films were studied. The crystal structure, microstructure, surface morphology, thickness, composition, and hardness were characterized by GI-XRD, FE-SEM and EDS, and nanoindentation techniques, respectively. The oxidation behavior of the films was carried by annealing in the air. The oxidation activation energies were calculated using the Arrhenius equation. The results revealed that the as-deposited thin films were formed as a (Ti, Cr)N solid solution with the fcc type phase. The films showed a nanocrystalline structure with crystal sizes less than 20 nm. The lattice constants were in the range of 4.144 to 4.181 Å. The thickness of the TiCrN films decreased from 767 to 415 nm with increasing of the N₂ gas flow rates. The N content of the films was increased with increasing of the N₂ gas flow rates, while the Ti and Cr content were decreased. The TiCrN thin films showed compact columnar and dense morphology as a result of the N₂ gas flow rate. The hardness of the TiCrN thin film was in the range of 38.2 to 70.8 GPa. The oxide phases of TiO₂ structure with strong preferred orientation (101) plane has appeared from 700°C. The oxidation rate was increased from 9.29×10^{-13} to 1.32×10^{-12} cm²/s as an increase in annealing temperature. Finally, the oxidation activation energy of 10.98 kJ/mol was calculated in this work.

Keywords: TiCrN, Thin films, Hard coating, Reactive magnetron sputtering, Co-sputtering

Introduction

Surface finishing by coating the surface with the suitable materials thin films have played an important role, in both surface engineering research and the modern industrial. Thin films are generally used to modify the surfaces of the substrate materials, enhancing their mechanical, electrical, electrochemical, optical, or biological properties

and extending their useful time. Thus, the use of thin films enables the application of less expensive materials as substrates, since substrate-thin film systems are able to guarantee the desired properties. Especially, a hard coating is widely used as tribological coatings on steel substrates. These coatings enhance substrate hardness and wear

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resistance, making it possible to use coated steels as cutting tools, drills, etc. So, the major challenges in thin films technology or surface engineering are to design and synthesis new materials which have a high hardness, low coefficient of friction, and low wear rate for a wide range of working environments.

TiN has been known as the first generation of the binary metal nitrides hard coating which has been extensively studied and widely used as a protective coating for many industries due to its high hardness, high thermal stability, and good wear resistance as well as excellent corrosion resistance (Chu *et al.*, 2006). However, the mechanical properties of TiN film are degraded by thermal oxidation at a high temperature above 500°C (Chinsakolthanakorn *et al.*, 2013). In order to overcome these problems and/or to improve properties of the TiN thin films, the Ti-based ternary metal nitride films such as TiAlN, TiZrN, TiVN, and TiCrN have been developed (Witit-anun and Buranawong, 2017). Among these ternary nitrides films, the ternary TiCrN films have been attracted more attention owing to its outstanding overall properties with high hardness, high temperature oxidation resistance, and low friction coefficient (Witit-anun and Teekhaboot, 2016).

The TiCrN thin films can be synthesized by various PVD techniques such as ion plating (Lee, 2003), ion beam assisted deposition (Budzynski *et al.*, 2009), evaporation (Wolfe *et al.*, 2011), and sputtering (Paksunchai *et al.*, 2012). Among them, the sputtering technique is the most popular and suitable to grow these ternary nitride thin films due to the low-temperature process, use of non-toxic gases, and simple process (Shum *et al.*, 2004; Thampi *et al.*, 2016). 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. In addition, the characteristics and properties of the thin film prepared by the sputtering technique depend strongly on the deposition parameters such as total pressure, gas flow rate, sputtering power, external heating, and voltage biasing. So, the effect of deposition parameters on the structure of the as-deposited thin films still important to investigate.

In this research work, as a preliminary experiment of our research project effort to develop novel thin films for high temperature and hard coating applications, TiCrN thin films were synthesized by an unbalanced magnetron co-sputtering technique using metallic Ti and Cr targets at room temperature, without external heating and

biasing. The characteristics of the as-deposited films such as the crystalline structure, surface morphology, and microstructure and hardness were investigated and discussed as a function of the nitrogen gas flow rate. Moreover, the oxidation behavior of the as-deposited films was also studied.

Materials and Methods

Thin Film Deposition

TiCrN thin films were deposited on Si substrates by reactive DC magnetron co-sputtering technique from a home-made DC magnetron sputtering system. The cylindrical stainless-steel vacuum chamber was used as the coating chamber of the deposition system. The system is capable of creating a base pressure below 5×10^{-3} Pa in the coating chamber by using diffusion pump backing with a 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 side of the coating chamber. In order to setup the unbalanced magnetron cathode, the circular planar magnet of 65 mm diameter with 10 mm width was used as the outer magnet and the magnetic rod of 10 mm diameter was used as a 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 and 1500 G, respectively. A continuously variable home-made dc power supply of 1000 V and 3 A was used as a power source for sputtering.

The sputtering target used were the metallic Ti (99.97%) and Cr (99.95%), with the 54 mm diameter and a thickness of 3 mm held on a water-cooled magnetron cathode. The ultra-high purity processing gases, Ar (99.999%) and N₂ (99.999%) were used as the sputtering and reactive gases, respectively. The MKS type247D mass flow controllers were used to control the flow rate of both the Ar and N₂ gases individually.

Before deposition of each TiCrN thin film, the coating chamber was evacuated to a base pressure of 5×10^{-3} Pa. The target was pre-sputtering under the Ar gas atmosphere for 10 minutes while the Si (100) substrate was shielded by shutters in order to remove the contaminants on the target surface. The TiCrN thin films were deposited at different N₂ gas flow rate from 2 to 10 cm³/min, while deposition parameters such as sputtering power, substrate temperature and working pressure were constant. The main deposition parameters used are summarized in Table 1.

Table 1. The thin films deposition parameters.

Deposition parameters	Values
Sputtering target	Ti (99.97%), Cr (99.95%)
Substrate	Silicon (100)
The angle between targets	75°
The angle between substrate and targets	92°
Substrate temperature	Room temperature
Substrate biasing	Grounded
Substrate to target distance	130 mm
Base pressure	5.0×10 ⁻³ Pa
Working pressure	5.0×10 ⁻¹ Pa
Ti power	350 W
Cr power	125 W
Ar gas flow rate	10 cm ³ /min
N ₂ gas flow rate	2, 4, 6, 8, 10 cm ³ /min
Deposition time	60 min

Thin Film Characterization

The crystal structures of the TiCrN thin films were characterized by X-ray Diffraction (XRD: BRUKER D8) using a Cu K α radiation ($\lambda = 0.154$ nm) and generator setting of 40 kV and 40 mA. The XRD patterns were acquired in a continuous mode, scanning speed of 2°/min and the grazing incidence angle of 3°. 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, thickness, microstructure, and cross-section structure were investigated by Field Emission Scanning Electron Microscope (FE-SEM: Hitachi 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).

The hardness of the TiCrN thin films was determined by the penetration depth which recorded by the nanoindentation technique. Nanoindentation tests were conducted at ambient conditions using a nanoindenter (Micro materials-NanoTest) equipped with a pyramid Berkovich diamond tip. The indentation was performed at a fixed load of 3 mN, each cycle repeated 6 times, throughout in this work. The purpose of repeating was to minimize the errors and reduce the variation of each cycle.

The oxidation behavior of thin films evaluated by oxidizing the film in the ambient atmosphere after the deposition process, the as-deposited TiCrN thin film on Si-substrate was loaded into a chamber furnace (CARBOLITE: CWF 13/5) using a thermocouple to monitor the temperature during thermal oxidation by annealed in a furnace chamber while the samples were placed in small Al₂O₃

crucibles. The thermal oxidation temperature ranging from 700 to 100°C with increase step of 100°C for each sample was chosen. The annealed temperature was increase from room temperature of 30°C to the value as experiment setting. Then, the exposure time was held at 2 h throughout in this work. After that, the deposited samples were naturally cooled down until reach to the room temperature about 30°C in a furnace before moving out for next analyses. The criteria of oxidation behavior were investigated by the forming of TiO₂ which obtained from XRD EDS and FE- SEM results at a given annealing temperature.

The oxidation behavior of the TiCrN thin films at elevated temperature was identified through the oxidation rate constant ($k_p(T)$) and the oxidation activation energy (E_a) at a given temperature which follows a parabolic relation (Qi *et al.*, 2013).

The oxidation rate constant was obtained from Wagner's parabolic oxidation relation

$$d = 2\sqrt{k_p(T) \times t}$$

where d is the thickness of oxide layer from cross-sectional analysis and t is the thermal oxidation time of exposure at different temperature (2 h).

In addition, the oxidation activation energy of the films was calculated by plotting the curve from the Arrhenius-type equation with using the $k_p(T)$ from equation

$$k_p(T) = k_{po} \exp\left(-\frac{E_a}{RT}\right)$$

where k_{po} is the pre-exponential factor, E_a is oxidation activation energy, R is gas constant and T is the absolute temperature. Hence, E_a was obtained from the slope of the curve.

Results and Discussion

Deposition Rate

Figure 1 shows the variation of deposition rates, of TiCrN thin films, which determined from the thickness divided by the deposition time, as a function of the N₂ gas flow rate. The results showed a significant decrease of the deposition rate with increasing the N₂ gas flow rate. As the N₂ gas flow rate increased from 2 to 10 cm³/min, the deposition rate of the thin films decreased from 12.8 to 6.9 nm/min, because of the exceed N₂ gas are react with the surface of Ti and/or Cr targets, and form to be the thin nitride layer on the target surface, which called target poisoning (Saringer *et al.*, 2016), that reduce the Ti and Cr target sputter rate.

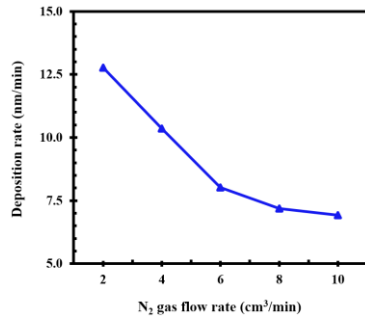


Figure 1. Effect of the N_2 gas flow rate on the deposition rate of thin films.

Elemental Composition

An increase of the N_2 gas flow rate affected the elemental composition (atomic concentrations of Ti, Cr, and N) of the as-deposited thin films, were shown in Figure 2. The elemental composition of the as-deposited TiCrN thin films was analyzed by the EDS technique. In this work, it was found that as the N_2 gas flow rate increased from 2 to 10 cm^3/min , the Ti and Cr content of the as-deposited TiCrN thin films decreased from 27.2 to 15.2 at.% and 29.4 to 23.4 at.%, respectively, while the N content increased from 43.4 to 61.4 at.% as shown 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 the N_2 gas flow rates. It was found that the Ti content almost constant about 0.36-0.48 for all N_2 gas flow rate. In addition, the N content in all films also increased with increasing of the N_2 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.

Phase Development and Crystallographic Properties

XRD patterns of the as-deposited TiCrN thin films deposited on Si substrates with different the N_2 gas flow rates from 2 to 10 cm^3/min are shown in Figure 3. The standard 2θ peak positions for the (111), (200), and (220) of the TiN and CrN structure were also included for comparison purposes. The results exhibited a low crystallinity at the N_2 gas flow rate of 2 cm^3/min , from a broad peak in an XRD

pattern, at a diffraction angle about $35.0-48.0^\circ$. As increased of the N_2 gas flow rate from 4 to 10 cm^3/min the evolution of the crystallinity was investigated. The diffraction peaks of all deposited thin films were observed. The 2θ values of diffraction peaks were about $37.23-37.39^\circ$, $42.95-43.14^\circ$ and $62.75-62.95^\circ$ which varied between the TiN and CrN from JCPDS standard structure (JCPDS films No. 87-0633, 77-0047). This result revealed that TiCrN films exhibited crystalline structure according to the TiCrN (111) (200) and (220) planes, with fcc phase.

The results for the calculated crystallite size and the lattice constants of the as-deposited TiCrN thin films in this research work are shown in Table 3. It was found that as the N_2 gas flow rate increased from 2 to 10 cm^3/min , the crystallite size of the as-deposited films calculated for the (111) peak using the Scherrer's equation, was decreased

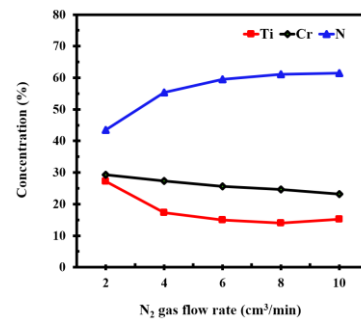


Figure 2. Effect of the N_2 gas flow rate on the elemental composition of thin films.

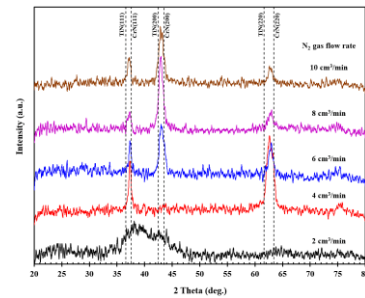


Figure 3. XRD patterns of the TiCrN thin films deposited at various of the N_2 gas flow rates.

Table 2. Composition and film composition as a function of the N_2 gas flow rates.

N_2 (cm^3/min)	Composition (at.%)			$x =$ $Ti/(Ti+Cr)$	$y =$ $N/(Ti+Cr)$	Film composition ($Ti_xCr_{1-x}N_y$)
	Ti	Cr	N			
2	27.2	29.4	43.4	0.48	0.77	$Ti_{0.48}Cr_{0.52}N_{0.77}$
4	17.3	27.3	55.4	0.39	1.24	$Ti_{0.39}Cr_{0.61}N_{1.24}$
6	14.9	25.5	59.5	0.37	1.47	$Ti_{0.37}Cr_{0.63}N_{1.47}$
8	14.0	24.9	61.1	0.36	1.58	$Ti_{0.36}Cr_{0.64}N_{1.58}$
10	15.2	23.4	61.4	0.40	1.60	$Ti_{0.40}Cr_{0.60}N_{1.60}$

Table 3. Thickness, crystal size and lattice constant of the TiCrN thin films.

N ₂ (cm ³ /min)	Thickness [nm]	Crystal size [nm]			Lattice constants [Å]		
		(111)	(200)	(220)	(111)	(200)	(220)
2	767	-	-	-	-	-	-
4	621	19.06	-	10.34	4.167	-	4.185
6	482	18.64	10.68	11.36	4.163	4.190	4.176
8	431	14.97	14.23	13.50	4.180	4.208	4.173
10	415	13.10	14.72	17.24	4.179	4.201	4.179

from 19.1 to 13.1 nm. The lattice constants of these films, which were deduced from the (111) peaks, were in the range of 4.163 to 4.180 Å, as shown in Table 3. This result suggested that the as-deposited thin films in this research work formed a solid solution of (Ti,Cr)N with the fcc phase. The result was found in other researchers, Lee *et al.* (2001) also found the fcc NaCl phase in (Ti,Cr)N film prepared by the ion-plating method. A solid solution of the TiCrN thin films from whereby the Ti atoms were substituted by Cr atoms in the TiN structure. Since the atomic radius of the Cr atom (0.1249 nm) is smaller than that of the Ti atom (0.1445 nm) (Callister, 2007), it was found that the lattice constant of the TiCrN film, increased gradually with increasing N₂ gas flow rate as shown in figure 5. Moreover, the lattice constant of the TiCrN film which in the range of 4.163 to 4.180 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.

Microstructure and Surface Morphology

The microstructure, surface morphology and the cross-sectional changes of the TiCrN thin films deposited at different N₂ gas flow rate are shown in Figure 4. The nanocrystalline TiCrN grains were formed mainly of individual grain and compact pattern with smooth surface were clearly identified from low N₂ gas flow rate (2 cm³/min). The grain like facet triangle shape accompanied with more void between grain boundaries were obtained at N₂ gas flow rate of 4 cm³/min. The same grain arrangement pattern whereas decreased their sizes were found at N₂ gas flow rate ranging from 6 to 8 cm³/min. When the N₂ gas flow rate increased to 10 cm³/min, it was found that the surface composed of small nano grains size with less void and denser structure, due to high nitrogen atom can more react with titanium and chromium atoms. This result can be concluded that the evolution of microstructure and surface morphologies were depended on the N₂ gas flow rate.

The cross-section micrograph is shown in Figure 4. It revealed that the equiaxial dense structure with also exhibit good columnar pattern

was observed at N₂ gas flow rate of 2 cm³/min. As increased N₂ gas flow rate to 10 cm³/min, the more void between columnar was exhibited. The as-deposited films were good agreements with the

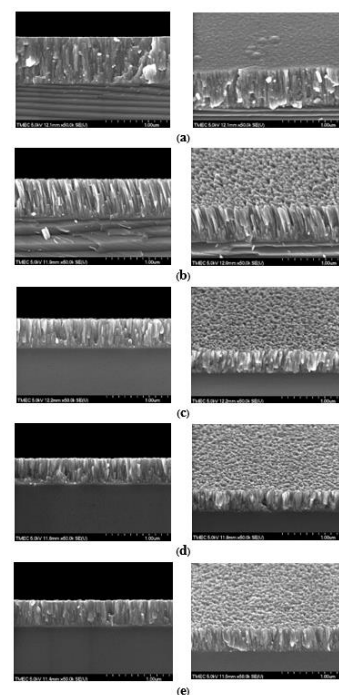


Figure 4. FE-SEM micrograph of TiCrN thin films deposited at different N₂ gas flow rates of (a) 2 cm³/min, (b) 4 cm³/min and (c) 6 cm³/min, (d) 8 cm³/min, (e) 10 cm³/min.

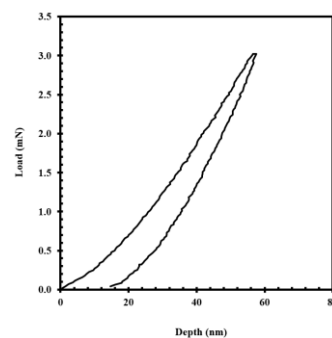


Figure 5. Load-displacement curve of TiCrN thin films.

Zone 2 structure of Thornton's zone model (Smith, 1995). From cross-section analysis were clearly identified that the thickness was decreased from 767 to 415 nm resulting formed the target poisoning when the N₂ gas flow rates increased. The cross-section observation apparently reveals the equiaxial structure with also exhibit good columnar pattern. 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.

Hardness

The hardness of the as-deposited TiCrN thin films as a function of the N₂ gas flow rate is obtained from the load-unload displacement curve (Figure 5) is present in Table 4, which was in the range of 38.2 to 70.8 GPa. In this work the TiCrN thin films deposited at less N₂ gas flow rate (2 cm³/min), with high Ti content ($x = 0.48$) and amorphous structure, exhibited maximum hardness (70.8 GPa). The hardness of the as-deposition TiCrN thin films decreased with increasing of the N₂ gas flow rate (4-10 cm³/min), with low Ti content ($x = 0.36-0.48$) and large crystallite size (10.34-19.06 nm) the lowest hardness of 38.2-40.9 GPa was obtained. This is can be explained by two hardening effects, one is the formation of a solid solution from the substitution of Ti atoms by Cr ones into TiN structure and the second is the grain boundary effects which is the number of created amorphous phases in the grain boundary that directly reduce grain size. Moreover, the hardness enhancement of thin film strongly depends on the crystallite size (Musil, 2012), which believed that the small crystallite size of the film hinders the generation of dislocation and prevents crack propagation due to the grain boundary enhancement and suppression of the grain boundary sliding (Barshilia *et al.*, 2006).

Oxidation Behavior

The elemental composition of TiCrN thin film before and after thermal oxidation was further analyzed by the EDS technique. A gradually increase of O content from 58.6 to 60.7 at.% whereas the almost constant in the Ti (22.7-24.2 at.%), Cr (2.5-2.7 at.%) but decreased of N (15.9 to 14.4 at.%), respectively, were detected as increased oxidation temperature. The increase of O contents is

due to the inward diffusion process of O from the air atmosphere diffused directly to the film by the oxidation mechanism (Chim *et al.*, 2009). The oxidation rate which calculated using the oxide layer from cross-sectional FE-SEM was depended on as a function of oxidation temperature. The enhancement of oxidation rate from 9.29×10^{-13} to 1.32×10^{-12} cm²/s was investigated when increased oxidation temperature from 700-1000°C.

The oxidation activation energy (E_a) which obtained from the slope of the Arrhenius-type equation are calculated to be 10.98 kJ/mol from the present work (Figure 6). It can be concluded that the oxidation process by increasing the annealing temperature induced the formation oxide layer and growth enhancement on underlying as-deposited thin film according to a parabolic growth law, implying that the oxidation behavior was clearly investigated from this mechanism. The oxidation activation energy of this work was different compared previous studies were 1.24-1.45 kJ/mol (Otani and Hoffmann, 1996) and 0.04 kJ/mol (Panjan *et al.*, 1996). These deviations may be related to as-deposited microstructure, defect density, and stoichiometry of the coating obtained from various deposition and oxidation conditions, which strongly influence the rate and activation energy of oxidation as a mention from other works (Chen and Lu, 2005; Qi *et al.*, 2013).

Table 4. Hardness of the TiCrN thin films as a function of the N₂ gas flow rates.

N ₂ (cm ³ /min)	Hardness (GPa)
2	70.8
4	38.2
6	40.9
8	39.8
10	40.5

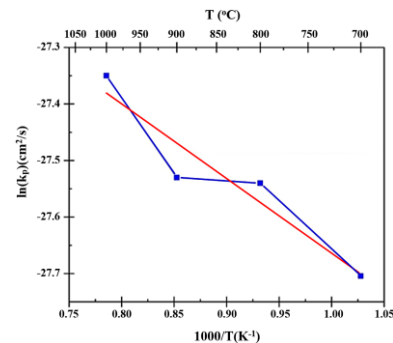


Figure 6. Arrhenius plot type of the TiCrN thin films.

Conclusions

The ternary nitride nanostructured TiCrN thin films were successfully deposited on Si substrate by reactive DC magnetron co-sputtering technique without external heating and biasing to the substrate. The as-deposited thin films formed solid solutions of (Ti,Cr)N with the fcc phase. The lattice constants of the as-deposited films gradually change with increasing the N₂ gas flow rate. Crystal size and the thickness decreased with increasing the N₂ gas flow rate. The elemental composition, Ti Cr and N contents, in the as-deposited films, were varied with the N₂ 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. The hardness of the TiCrN thin film was in the range of 38.2 to 70.8 GPa. The oxide phases of the TiO₂ structure with has appeared from 700°C. The oxidation rate, in this work, was increased from 9.29×10^{-13} to 1.32×10^{-12} cm²/s as an increase in annealing temperature. The oxidation activation energy was 10.98 kJ/mol.

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