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Investigation of deposition parameters on the structural properties and hardness of TiAlN films deposited via reactive pulsed DC magnetron sputtering

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Abstract

In this work, titanium aluminum nitride (TiAlN) films were deposited on a silicon substrate via reactive pulsed DC magnetron sputtering. The effect of deposition parameters such as nitrogen gas flow rate, substrate temperature, and bias voltage on the structural and mechanical properties of TiAlN films was investigated. The crystal structure, morphology, and hardness of TiAlN films were characterized via X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM, and nanoindentation. An improved crystallinity of TiAlN films was obtained by varying the substrate temperature and bias voltage. The morphology of the TiAlN film exhibited a columnar structure, and the morphology gradually changed with the increase in bias voltage. The films thickness decreased upon increasing the nitrogen gas flow rate, substrate temperature, and bias voltage. In addition, the hardness of the TiAlN film was enhanced by adjusting the nitrogen gas flow rate, substrate temperature, and bias voltage, and a suitable elemental component ratio was obtained. A maximum hardness of approximately 28.9 GPa was obtained for the TiAlN film with a nitrogen gas flow rate of 4 sccm, substrate temperature of 500ºC, bias voltage of 100 V, and an elemental composition Al/(Al + Ti) of approximately 34.35%.

1. Introduction

Hard ceramic film coatings such as titanium nitride (TiN) films are widely used industrial applications, particularly as surface protection coating on cutting tools for improved machining performance. However, TiN films have some limitations, including the inability to resist oxidation at temperatures over 900°C, resulting in the decrease of the hardness properties of the TiN films. This problem can be solved by adding aluminum (Al) in the TiN structure to form a ternary compound of titanium aluminum nitride (TiAlN) films. Moreover, the ternary compound hard coating also shows greater hardness than the binary compound hard coating. TiAlN films exhibit low friction coefficient and corrosion resistance [1], high thermal stability, and high hardness (approximately 34 GPa [2], and they resist oxidation at temperatures up to 900°C. Thin films of TiAlN can be deposited using various techniques. However, thin films are usually prepared via reactive magnetron sputtering technique because it allows a high deposition rate, high film hardness, good adhesion, and precise control [2,3]. The Ti–Al metal alloy is used as the sputtering target, and the nitrogen gas is fed and mixed with the sputtering gas to react with the sputtered atoms and form the desired compound films at the substrate. Deposition parameters are investigated on the microstructure and mechanical properties of TiAlN films. Hakansson *et al.* [3] found that a higher bias voltage produced fine grains with reduced porosity and interrupted the columnar structure of the TiAlN film. Gredic and Zlatanovic [4] revealed that the deposition rate, aluminum to titanium ratio, and metal to nitrogen ratio of TiAlN films increased with higher sputtering power. Jalali *et al.* [5] reported that the crystallinity of TiAlN films can be improved from amorphous to crystalline structure when increasing the substrate temperature at 400°C. Ali *et al.* [6] investigated the effects of nitrogen gas flow rate in the range of 2-10 sccm on the properties of TiAlN films prepared via the magnetron co-sputtering method. They found that the hardness and corrosion resistance increased with the increase in nitrogen gas flow rate. However, these studies rarely discussed the relationship of elemental composition, which impacts the microstructure and directly affect the mechanical properties of TiAlN films [7].

In this work, we investigated the effects of the deposition parameters such as the bias voltage, nitrogen gas flow rate, and substrate temperature on the microstructure and mechanical properties of TiAlN films. TiAlN films were deposited on a silicon (Si) substrate via reactive pulsed DC magnetron sputtering. The relationship of TiAlN films' hardness and their properties such as morphology, crystal structure, and elemental composition are discussed in this paper.

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2. Experimental procedure

TiAlN films were deposited on Si (100) substrates via reactive pulsed DC magnetron sputtering. An alloy TiAl (70 at% of Ti and 30 at% of Al) target with 99.8% purity, a diameter of 50.8 mm, and a thickness of 6 mm was used as the sputtering target. The Si substrates were cleaned with acetone using an ultrasonic cleaner and dried in ambient air. A turbo-molecular pump backed by a scroll pump was used to achieve a base pressure of 1×10^{-5} Torr. The distance between the target and substrate was fixed at 10 cm. The target was pre-sputtered under pure argon gas (Ar, 99.999% purity) for 10 min to remove the oxide on the target surface while the substrate was shielded by the shutter. After pre-sputtering, the reactive gas (N_2, 99.999% purity) was injected into the chamber. Both mixing gases were controlled using a mass flow controller (MKS Inc., Type 647C). The working pressure was kept at 3 mTorr, which was monitored using a vacuum gauge (DCU 400, display control unit with integrated power supply, Pfeiffer Vacuum). To find the relation of the sputtering condition and the properties of TiAlN films, three deposition parameters were studied: (i) N_2 gas flow rate was varied from 2 to 4 sccm, and the Ar gas flow rate was fixed at 20 sccm. (ii) The negative substrate bias was carried at 0, 100, and 200 V. (iii) The Si substrate was preheated at temperatures of 400ºC and 500ºC. The sputtering power was kept at 150 W with a frequency of 50 kHz and a period of 4.0 μs. Table 1 lists the details of the deposition conditions. The surface morphology and cross-sectional morphology of the TiAlN films were investigated using field emission scanning electron microscope (FE-SEM, Tescan/Mira3, Czech Republic), and the elemental composition was determined using energy-dispersive X-ray spectrometer (EDX). The crystal structure of the TiAlN films was investigated via X-ray diffraction (XRD, TTRAX III-RIGAKU). Finally, the films' hardness was determined using nanomechanical tester instruments (HYSITRON, SPM Probe Model: ACST Part# ACST-50, USA).

Table 1. Deposition conditions.

Samples	**Ar/N_2**	**Bias voltage (V)**	**Substrate temperature (°C)**	**Thickness (nm)**
TAN1	20/2	0	400	822
TAN2	20/2	100	400	676
TAN3	20/4	0	400	573
TAN4	20/4	100	400	530
TAN5	20/4	200	400	368
TAN6	20/4	100	500	405
TAN7	20/4	200	500	314

3. Results and discussion

3.1 Crystal structure

The XRD patterns of all deposited TiAlN films shown in Figure 1 reveal that the TiAlN films exhibit a NaCl type face-centered cubic (fcc)structure (PDF#04-005-5251(RDB)) with crystal plane orientations of (111) (200), and (220) for all TiAlN films. Increasing the substrate temperature in the range of 400°C - 500°C is beneficial for generating the crystallization of sputtered atoms on the surface of the substrate [8]. Table 2 shows the crystallite size calculated using Scherrer equation as shown in equation (1).

$$L = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where L is the mean size of the crystalline domains, k is a dimensionless shape factor related to crystallite shape with a typical value of about 0.9, λ is the X-ray wavelength (nm), β is the line broadening in the 2θ axis at half the maximum intensity (FWHM) in radians, and θ is the Bragg's angle.

The films exhibited a small crystallite size in the range of 8.33-17.09 nm. The smallest crystallite size was obtained from TAN6, which enhanced the hardness of TiAlN films [9]. XRD peaks considerably shifted toward lower angles under the application of bias voltages of 100 and 200 V. The application of a bias voltage enhanced the energy of the adatom via ion bombardment and affected the arrangement of the crystal structure. These suggest that all TiAlN films showed larger d-spacing and lattice parameters (Table 2) at higher bias voltages according to equations (2) and (3). The results were consistent with those obtained by Wuhrer and Yeung [10].

Bragg's equation and the relation of the d-spacing and lattice parameter of fcc (a = b = c) are given by the following equations:

$$2d \sin\theta = n\lambda \tag{2}$$

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \tag{3}$$

where d indicates the distance between the atomic layers or d-spacing, n is an integer, and hkl are the Miller indices.

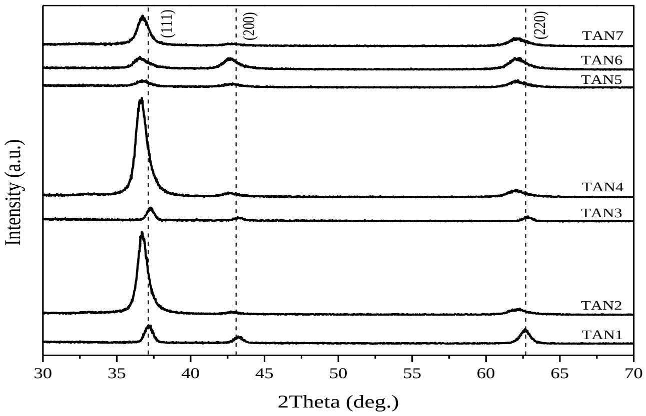

Figure 1. XRD patterns of TiAlN films deposited at various bias voltages, nitrogen gas flow rates, and substrate temperatures.

3.2 Morphology and elemental composition

Figure 2 shows the cross-sectional FE-SEM images of TiAlN films. The samples of TAN1 and TAN3 without bias voltage were found to exhibit a columnar structure, whereas the samples of TAN4 and TAN6 with bias voltage showed a reduced columnar structure compared to that of TAN1 and TAN3. In general, the columnar structure does not have a positive effect on the hardness of TiAlN films [11]. A dense and compact cross-sectional morphology is clearly revealed at the samples of TAN2, TAN4, TAN5, TAN6, and TAN7 under an applied bias voltage. Moreover, the films' thickness is measured from the cross-sectional FE-SEM images (Table 1). The film thickness clearly decreased with increased bias voltage and N_2 gas flow rate because the bias voltage allows the bombardment by ions on the film surface. Ions bombard the film surface, allowing the film to pack tightly and better align the atoms; however, this caused some atoms to fall apart or re-sputter. Moreover, a high N_2 gas flow rate can generate more TiAlN on the TiAl target surface (called target poisoning), which affected the lower deposition rate.

The elemental composition in TiAlN films was investigated as shown in Figure 3. The obtained N composition reached over 50 at%, which is higher than Ti and Al. Results showed a sufficient N_2 content to form nitride during sputtering in the compound mode. The N_2 gas flow rates were increased from 2 to 4 sccm, resulting in increased nitride formation on the TiAlN film and also on the target surface [12]. Thus, the number of Ti atoms decreased, but the number of Al atoms increased. Upon increasing the bias voltage from 100 to 200 V, the number of Ti atoms increased but the number of Al atoms decreased. The ratio of Al/(Al+Ti) is computed as shown in Table 2. TAN3, TAN4, and TAN6 samples showed a high ratio of Al/(Al+Ti) in the range of 34-35%.

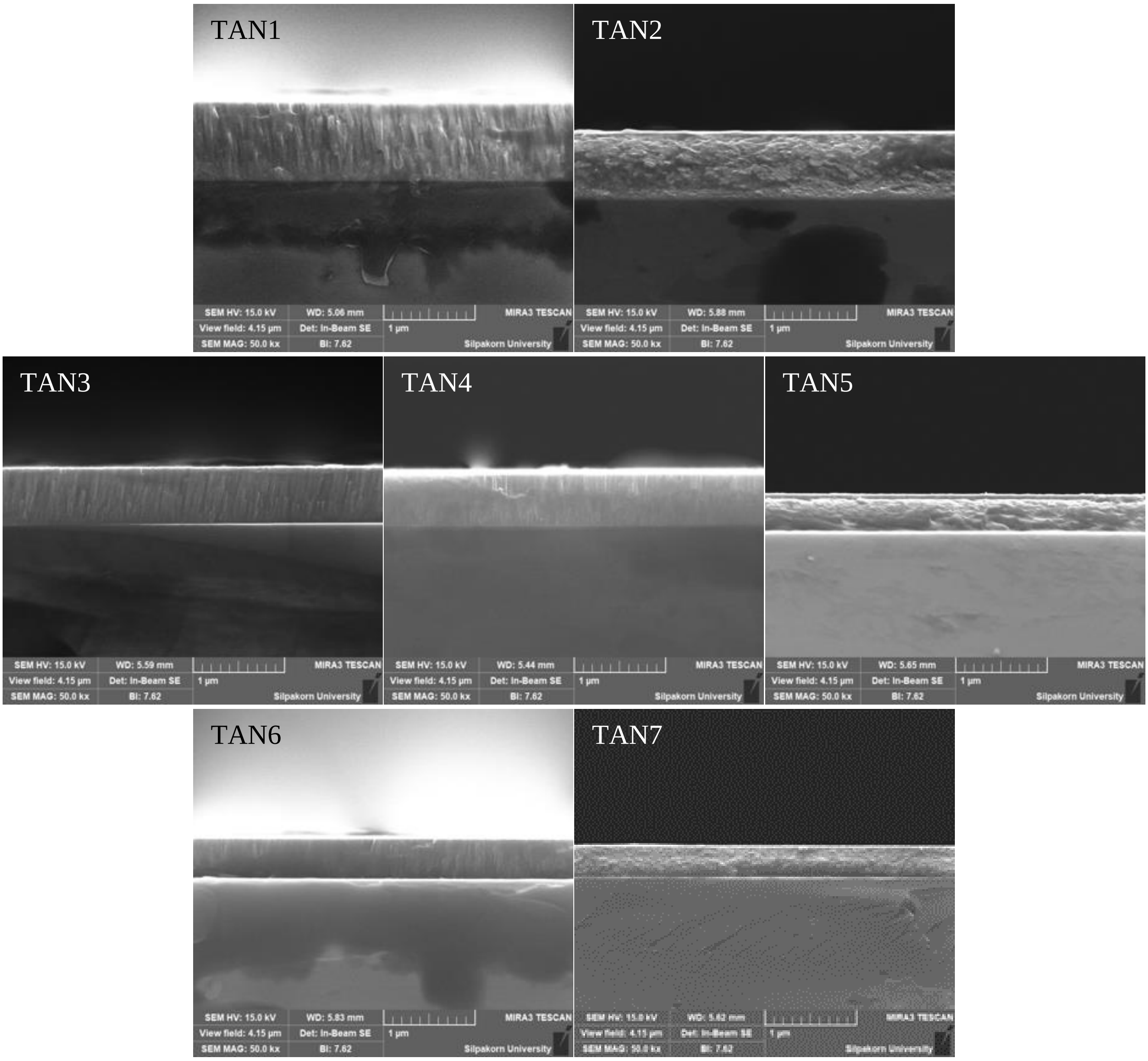

Figure 2. Cross-section morphologies of TiAlN films deposited at various bias voltages, nitrogen gas flow rates, and substrate temperatures.

Table 2. Elemental composition, d-spacing, lattice parameter, and crystallite size of TiAlN thin films.

Samples	**Elemental composition (at%)**			**Al/(Al+Ti) (%)**	**d-spacing (Å)**			**Lattice parameter (Å)**	**Crystallite size (nm)**
	Ti	**Al**	**N**		**(111)**	**(200)**	**(220)**		
TAN1	32.69	14.52	52.79	30.76	2.417	2.091	1.482	4.1864	13.06
TAN2	32.07	13.27	54.66	29.27	2.443	2.111	1.493	4.2249	9.24
TAN3	29.98	15.94	54.08	34.71	2.410	2.090	1.478	4.1784	17.09
TAN4	29.72	15.40	54.88	34.13	2.448	2.117	1.494	4.2333	8.96
TAN5	29.46	14.10	56.44	32.37	2.531	2.107	1.492	4.2729	8.78
TAN6	28.98	15.16	55.87	34.35	2.449	2.115	1.492	4.2308	8.33
TAN7	31.12	11.42	57.46	26.85	2.442	2.111	1.492	4.2246	9.22

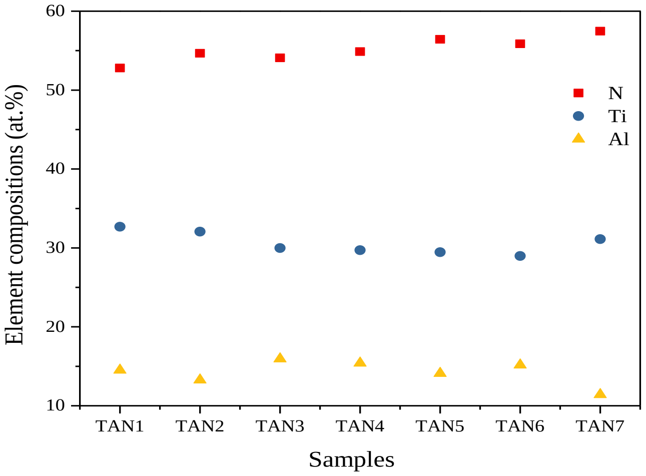

Figure 3. Elemental composition (%) of TiAlN films deposited at various bias voltages, nitrogen gas flow rates, and substrate temperatures.

3.3 Hardness

Hardness is a crucial evaluation parameter for the effect of deposition parameters. This property is related to the crystal plane, crystallite size, morphology, and elemental composition. Figure 4 shows the change of load and displacement of TAN6, which can be used to calculate the hardness of TiAlN film using equation (4).

$$H = \frac{P_{max}}{A_s} = \frac{P_{max}}{24.56\,h_c^2} \qquad (4)$$

where P_{max} is the maximum load, A_S is the ideal projected area function for a Berkovich indenter ($A_S = 24.56h_c^2$), h_c is the contact depth during indentation full load ($h_c = h_{max} - 0.75\frac{P_{max}}{S}$) at the maximum displacement data point, and h_{max} is the total displacement.

The hardness values of all TiAlN films were obtained, and a maximum value of 28.905 GPa was achieved by TAN6 (Figure 5). The hardness of TiAlN films decreased in the order TAN6 > TAN7 > TAN4 > TAN2 > TAN5 > TAN1 > TAN3. TAN3 exhibited the lowest hardness value of about 19.94 GPa under a high N_2 gas flow rate, low substrate temperature, and without bias voltage. This could be explained using the relationship of hardness with morphology. The columnar structure of TAN1 and TAN3 clearly exhibited low hardness because of the void between the columnar in films [13]. Although TAN4 and TAN6 showed columnar structures, the structures were not as clear as that of TAN1 and TAN3, resulting in greater hardness values. Moreover, the higher crystallite size mainly resulted in the lower films' hardness such as in the cases of TAN1 and TAN3. In addition, the proportion of Al/(Al + Ti) approaches 35%, indicating high hardness as reported by Wang *et al.* [7]. TAN3, TAN4, and TAN6 exhibited an Al/(Al + Ti) ratio of approximately 35% with the TAN3. Therefore, the morphology and crystallite size must also be considered.

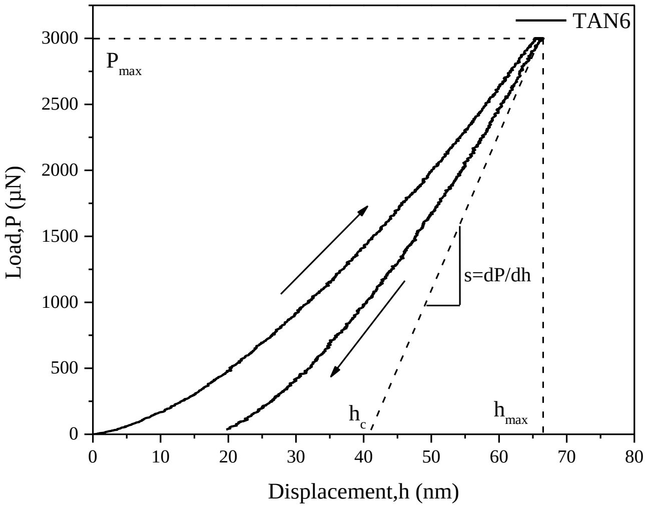

Figure 4. Relationship between load and displacement for the hardness test of TiAlN film for TAN6.

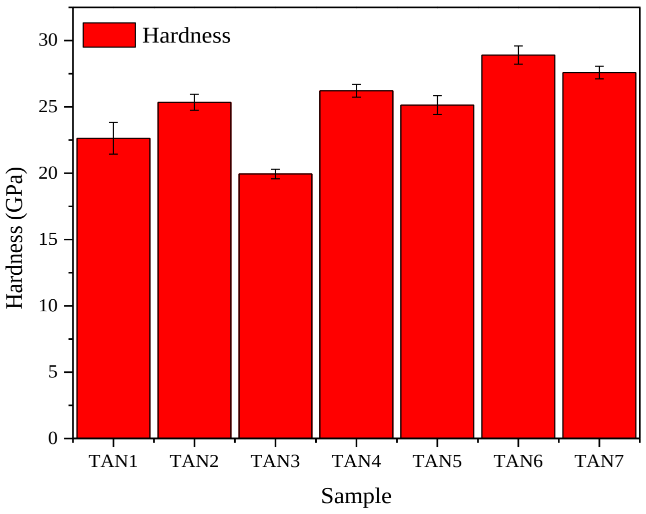

Figure 5. Hardness of TiAlN films deposited at various bias voltages, nitrogen gas flow rates, and substrate temperatures.

4. Conclusions

In this study, the structural and mechanical properties of TiAlN films prepared via reactive pulsed DC magnetron sputtering have been investigated by varying the substrate bias voltage, nitrogen gas flow rate, and substrate temperature. The results revealed that all TiAlN films exhibited a face-centered cubic structure with orientations in the (111), (200), and (220) crystallographic planes, with titanium aluminum and nitrogen as the elemental composition. The results of FE-SEM analysis showed that the film growth had a columnar morphology, and the increase in the bias voltage and nitrogen gas flow rate resulted in denser films. Increasing the substrate bias voltage and nitrogen gas flow rate decreased the film's thickness. Overall, the substrate bias voltage, nitrogen gas flow rate, and substrate temperature affected the crystallite size, surface morphology, and elemental composition of the TiAlN films, which consequently affected the films' hardness. TAN6 exhibited the highest hardness of approximately 28.9 GPa with reduced columnar structure and smallest crystallite size, and it exhibited a proportion of Al/(Al + Ti) close to 35%.

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