A study on the microstructure and property development of d.c. magnetron cosputtered ternary titanium aluminium nitride coatings

Part III   *effect of substrate bias voltage and temperature*

R. WUHRER
Microstructural Analysis Unit, University of Technology, Sydney,
P.O. Box 123, Broadway NSW 2007, Australia
E-mail: Richard.Wuhrer@uts.edu.au

W. Y. YEUNG
Department of Chemistry, Materials and Forensic Sciences, University
of Technology, Sydney, P.O. Box 123, Broadway NSW 2007, Australia
E-mail: Wing.Yeung@uts.edu.au

Advanced ternary (Ti,Al)N coatings were produced by reactive magnetron co-sputtering technique with separate titanium and aluminium targets at a 30° magnetron configuration under various substrate bias voltages and temperatures. The effect of substrate bias and temperature on the microstructure and property development of the coatings was investigated. It was found that an increase in substrate bias and/or substrate temperature imposed no major effect on the composition and phase formation of the (Ti,Al)N coatings, but had significant influence on the development of their microstructure and surface morphology. As the substrate bias and/or temperature increased, the coating structure was densified with development of fine grain size and reduced surface roughness, resulting in a substantial increase of the coating hardness. However as the substrate bias increased over 200 volts, excessive residual stress was built up, causing a fracture of the coatings. It is believed that the microstructure and property enhancement is attributed to an increased translational kinetic energy of the depositing atoms and a greater thermal energy provided to the substrate and the coating material with increasing substrate bias and/or temperature. The adatom mobility and the surface diffusion of atoms are enhanced to reduce the detrimental effects induced by the statistical roughening and self-shadowing of a sputter deposition process. A densified zone T structure with low porosity and improved properties is produced. © *2002 Kluwer Academic Publishers*

1. Introduction

It is generally accepted that an application of a bias potential (usually negative) and/or a temperature to the substrate can enhance the deposition of the coatings in a sputtering deposition process. When a negative bias voltage is applied to a substrate the number of ionised molecules and atoms in the plasma increases. This effectively increases the ionisation within the plasma and increases the total number of ions impinging on the substrate. A number of researchers [1–6] have investigated the effect of substrate bias on the microstructure and properties of binary nitride coatings. An early work in 1983 by Sundgren *et al*. [1] found that an increase in substrate bias caused an increase in the nitrogen content of substoichiometric TiN films. Once a stoichiometric film of TiN was formed, then no further change in the composition occurred. Furthermore, the grain size of the TiN film increased with increasing bias voltage to

a maximum at −200 volts and then decreased at higher negative bias voltages. It was suggested that the structural changes that occurred when a substrate bias was applied, involved the processes of re-sputtering, ion-bombardment and enhanced diffusion of the atoms of the coatings. However, in deposition of TiC, a different trend of development was observed. With increasing bias voltage the grain size of the TiC coatings continuously decreased.

On the other hand, Sproul *et al*. [2–4] have reported that the substrate bias strongly influenced the crystallographic orientation of reactively sputtered TiN coatings. As the bias voltage was increased from 0 to −200 volts, the (111) orientations were depleted and the (220) component developed, resulting in an increase of the coatings hardness. Richter *et al*. [5] have also investigated the effect of bias voltage on the structure and properties of TiN films produced by dc magnetron

sputtering. It was found that the microstructure and properties of the films were strongly dependent on the impact of the energetic particles on the surface of the growing film. Films produced with negative bias voltage, which grew under the bombardment of highly energetic ions, had a smaller grain size, a higher mass density and higher hardness. Films produced with less negative bias voltage exhibited larger grains, high resistivity and low hardness. Research by Rickerby and Burnett [6] revealed that in TiN films, high bias levels resulted in coatings of higher internal strees and higher hardness. Furthermore, the type of substrate imposed a strong influence over grain size as it determined the availability of suitable heterogeneous nucleation sites on the substrate.

Research on the deposition of ternary nitride coatings under different bias voltages is rather scarce and the results reported are somewhat contradictory. Rohde et al. [7], using a dual unbalanced magnetron system for production of nitride coatings, have found that film stresses generally increased with increasing bias voltage. However, the films began to delaminate at a substrate bias of −185 volts, and virtually all of the films delaminated from the substrate at negative 200 volts due to internal stresses built-up in the films. It was also found that the surface of the films became rougher with increasing bias voltage, but the number and size of voids within the films decreased. On the other hand, Musil et al. [8] have reported contradictory results that increasing the substrate bias voltage resulted in smoothening of the film surface. Films produced below −200 volts were very rough with development of porous microstructure similar to zone 1 of Thornton's [9] structure zone model. At higher bias voltages, a dense and smoother microstructure similar to the zone T structure developed.

Freller and Haessler [10] and Coll et al. [11] also reported that in an arc sputtering process the Al : Ti ratio in the TiAlN films decreased as the substrate bias voltage increased. It was suggested that this demixing effect might be due to either (i) titanium and aluminium having different degrees of ionisation when they were evaporated or (ii) preferential re-sputtering of aluminium atoms at the higher bias voltages [11]. Roos [12] however reported that no bias effects were encountered on the Al : Ti ratio in deposition of titanium aluminium nitride coatings using magnetron sputtering. In respect to microstructure and texture development, Hakansson et al. [13] produced metastable single phase polycrystalline $Ti_{0.5}Al_{0.5}N$ coatings by dc magnetron sputtering from a TiAl target in mixed Ar-N_2 discharges. It was found that coatings produced below −80 volts had a columnar structure with a high intercolumnar/intragrain porosity. Increasing the bias voltage above −80 volts resulted in a rapid increase in both the lattice parameter and the width of the major (111) peaks. As the bias voltage increased, the grain size decreased and the microhardness of the coatings increased. A decrease in the void density and an increase in the dislocation densities at higher substrate biases were also evident.

There is less research work in relation to the substrate temperature for sputter deposition. In an investigation of deposition of metallic films, Thornton [9] reported

that the substrate temperature played a major role in the development of the coating microstructure. A structure zone model (SZM) incorporating the effect of temperature on coating microstructure was proposed to explain the structure development at different substrate temperatures. Musil et al. [8] further modified the SZM with a new system of coordinates of T/T_m incorporating the effects of formation energy of the films. It has been suggested that to give the adatoms on the growing films a sufficiently high thermal mobility the substrate temperature must exceed three tenths (0.3) of the melting temperature of the depositing material.

Combadiere and Machet [14, 15] have also investigated the effect of substrate temperature on the composition, morphology and mechanical properties of TiN coatings. It was found that for a give nitrogen pressure, the texture development was greatly affected by the substrate temperature. Increasing the substrate temperature caused the coatings to grow with their most dense planes parallel to the substrate surface. In other words, an increase in substrate temperature favoured a preferred growth on denser planes of the crystallographic structure. Combadiere and Machet [14, 15] also found that coatings produced at lower temperature showed a (111) texture, which were relatively hard but of poor wear resistance [15]. However, coatings produced at increased temperatures had a (200) texture with high hardness and good wear resistance. Similar observation was reported by Meng et al. [16] for TiO_2 films deposited on glass substrates. For ternary (Ti,Al)N coatings, Wang et al. [17] reported that the substrate temperature was one of the most important parameters affecting the mechanical properties of the coatings. With increasing substrate temperature, the microstructure of the (Ti,Al)N coatings became denser, which in turn improved the lattice and strengthened the interface, thus increasing the coating hardness.

In the present study, a detailed and systematic investigation of the effects of the substrate bias and temperature on the microstructure and property development of the d.c. magnetron cosputtered (Ti,Al)N coatings was performed. Analyses of the atomic force microscopy of the (Ti,Al)N coatings were conducted to achieve quantitative measures of the coating morphology. This paper reports the results obtained from the study. The overall effects of major deposition parameters including nitrogen pressure and magnetron discharge power on the coating development will also be discussed in this paper.

2. Experimental

The reactive magnetron co-sputtering technique, with separate titanium and aluminium targets was used to produce the titanium aluminium nitride coatings in the present study. (Ti,Al)N coatings were deposited with two slightly unbalanced, independently controlled magnetrons at a 30° magnetron arrangement. The target to substrate distance was set at 110 mm. The (Ti,Al)N coatings were deposited on glass slides 75 mm (length) × 25 mm (width) × 1.5 mm (thickness), which were thoroughly cleaned with ethanol and dried before being placed in the vacuum chamber.

The system used for coating was a Varian 3120 deposition unit equipped with Pirrani gauges and Tylan mass flow controllers to monitor the pressures and flow rates of nitrogen and argon gas respectively. With the deposition of (Ti,Al)N, the titanium magnetron current was set at 0.6 amp which corresponds to a discharge power of 9.0 W/cm^2 and the aluminium magnetron was set at 0.4 amps (6.0 W/cm^2). The nitrogen and argon gas pressures and flow rates were adjusted to suitable values. Before sputtering, the chamber was evacuated to a pressure below 2×10^{-6} Torr. Once a high vacuum of at least 2×10^{-6} Toor was reached, the sample holder was heated and maintainted at a predetermined temperature for the deposition. The targets were then sputter cleaned with argon for 10 minutes while the substrate were shielded by shutters over the magnetrons. Then a thin intermediate layer of titanium followed by a titanium aluminium layer were each deposited for 5 minutes respectively on the substrate with a preset substrate bias. After the titanium and titanium-aluminium interlayer films are deposited, reactive gas of high purity nitrogen was injected through an Alltech gas purifier filter into the deposition chamber to form titanium aluminium nitride. The coatings were deposited at a constant nitrogen pressure of 0.4 mTorr, which corresponded to gas flow rates of 10 standard cubic centimeters (sccm). The argon pressure was maintained constant at 2.4 mTorr during the deposition process. In studying the effect of substrate bias, the substrate temperature was set at a constant temperature of 240°C and the bias voltage was varied from 0 to −200 volts. In study of the substrate temperature effect, the bias was set at −100 volts and the substrate temperature was varied from 120 to 360°C. After completing a deposition for 60 minutes, 1.5 to 2.0 μm thick coatings developed on the substrate. The coating thickness was then determined using a Tencor Alphastep profilometer.

A number of characterisation techniques including scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffractometry (XRD) were used to study the microstructure and morphology of the coatings. The microstructure of the coatings was examined using a JEOL 6300F field emission SEM operated at an accelerating voltage of 8 kV. Composition of the coatings was determined using energy dispersive X-ray spectroscopy (EDS) at 8 kV and the $\Phi(\rho Z)$ quantitative analysis software. Aluminium and titanium standards of high purity (99.99%) were used in the EDS analysis to determine the contents of aluminium and titanium of the coatings and the nitrogen content was calculated as a difference of the element contents. Hardness of the coatings was measured at 2 and 10 g loads using a LECO M400-Hl microhardness tester with a Vickers indentor. The phase development and other crystallographic properties of the coatings were examined by XRD technique using a Siemens D5000 diffractometer with Cu K$_\alpha$ radiation at small scattering angles. AFM analysis was performed on a Park Scientific Instrument Autoprobe using ultralever tips. Region and line scans were conducted to determine the surface roughness and other topographical features of the coatings.
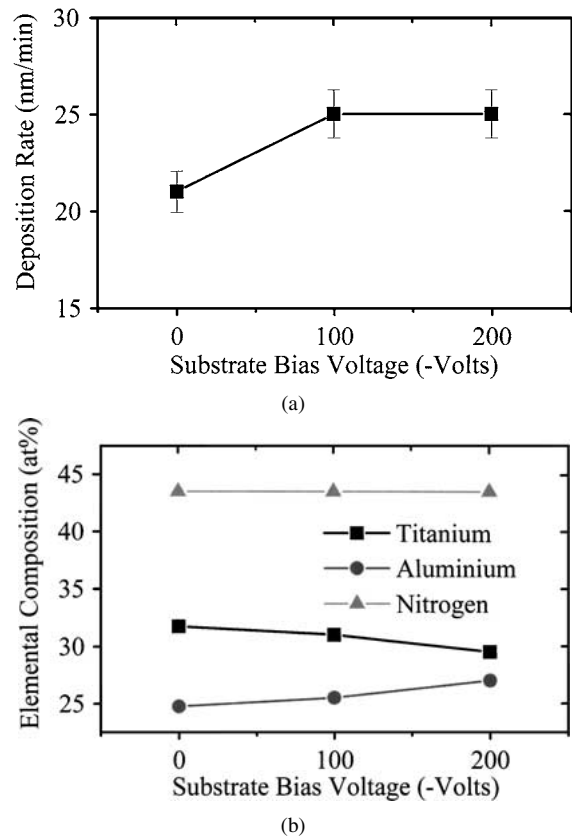

Figure 1 Effect of substrate bias voltage on (a) deposition rate and (b) elemental composition of the coatings.
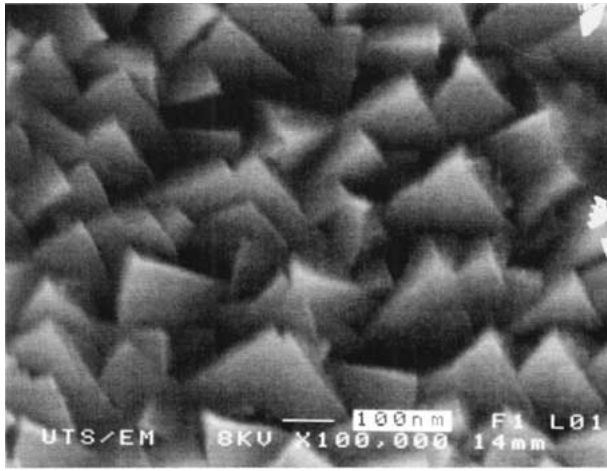
3. Results
3.1. Effect of substrate bias voltage
#### 3.1.1. Deposition rate and chemical composition
The deposition rates of (Ti,Al)N coatings at different substrate bias voltages are shown in Fig. 1a. The results showed that changes in the substrate bias voltage only slightly influenced the deposition rate of the coatings. With zero bias voltage, the coatings were deposited at a rate of 21 nm/min. As the bias voltage was increased to −200 volts, the deposition rate increased to 25 nm/min. An increase in substrate bias voltage also exhibited a small effect on the chemical composition of the coatings, Fig. 1b. The nitrogen content was found to remain constant at 43.5 at.% with increasing substrate bias voltage. On the other hand, the aluminium content increased slightly from 24.5 at.% to 27.5 at.% and the titanium content decreased from 32 at.% to 29.5 at.%.

3.1.2. Microstructure and surface morphology
SEM and AFM micrographs, which illustrate the microstructure and surface morphology of the (Ti,Al)N coatings deposited at different substrate bias voltages, are respectively shown in Figs 2 and 3. A porous tapered columnar structure similar to the microstructure of the zone 1 of the Thornton's [9] structure zone model developed at zero bias. As the bias voltage increased from 0 to −200 volts, the structure became densified, producing a very fine grain structure with features similar to the zone T structure of the Thornton's model.
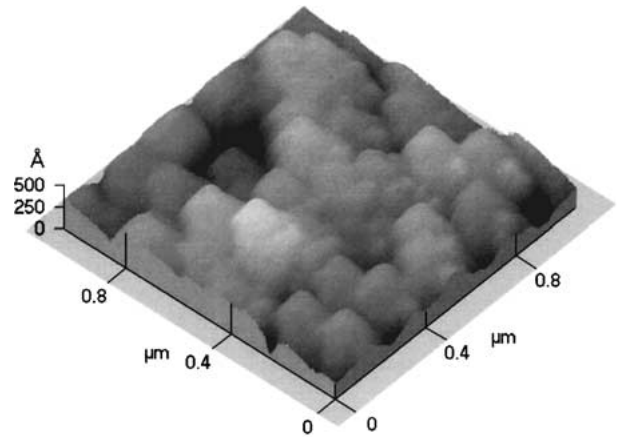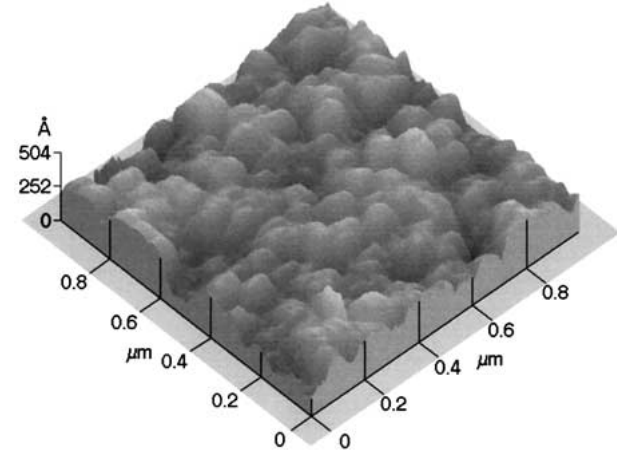
(a)
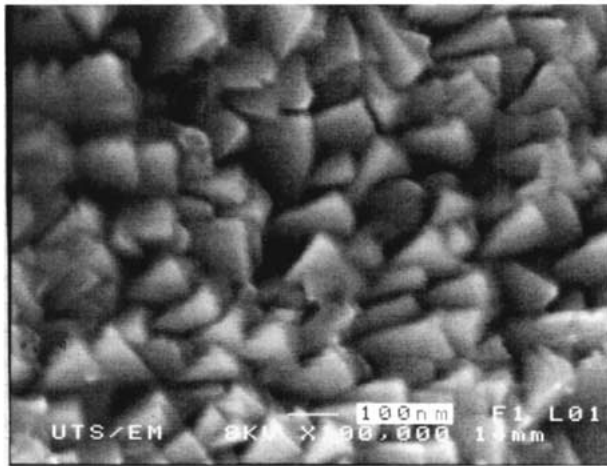
(b)
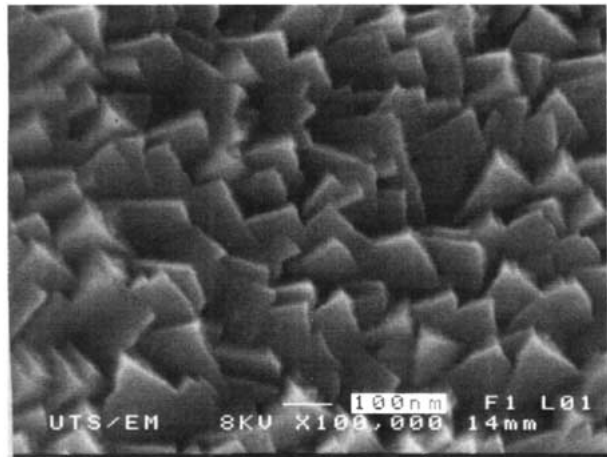
(c)

Figure 2 SEM micrographs of the coatings produced at different substrate bias voltages: (a) 0 Volts, (b) −100 Volts and (c) −200 Volts.

(a)

(b)

(c)

Figure 3 AFM images of the coatings produced at different substrate bias voltages: (a) 0 Volts, (b) −100 Volts and (c) −200 Volts.
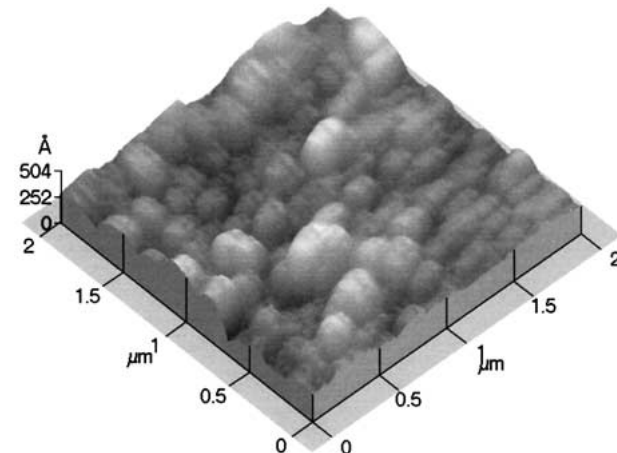
AFM region and line scan analyses were performed on the samples. The results showed that the coatings deposited at −100 volts generally exhibited the lowest surface roughness and grain height, Fig. 4a and b. It was found that as the substrate bias voltage increased from 0 to negative 100 volts, the average roughness of the coatings decreased from 5.4 nm to 2.6 nm. The roughness then increased to 3.8 nm at a bias of −200 volts. The rms roughness dropped from 6.8 nm to 3.2 nm and then increased to 4.3 nm. On the other hand, the mean height of the coating structure decreased from

41.7 nm at zero bias to 12.3 nm at −100 volts and then increased to 28 nm at −200 volts. The median height decreased from 42.3 nm to 12.6 nm and then increased to 28 nm. The line scan measurements showed similar topographical changes of the coating structure. The average grain size of the coatings determined by line scan measurements was found to decrease from 165 nm at zero bias to 90 nm at −100 volts but slightly increases to 130 nm at −200 volts, Fig. 4c. Deposition at higher bias voltages of −250 volts and −300 volts were also conducted. The coatings however fractured shortly after removal from the coating chamber possibly due to the excessive stress developed in the coatings.
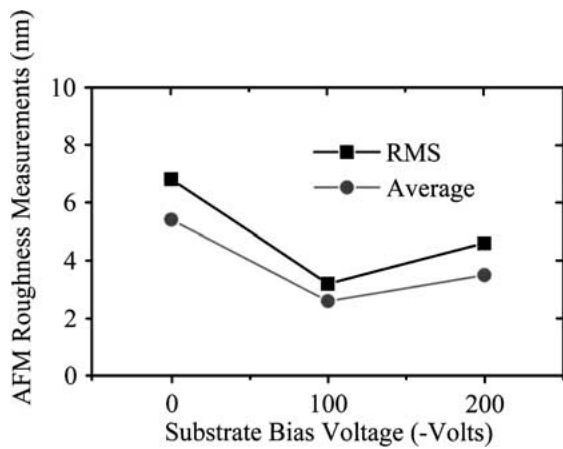
(a)
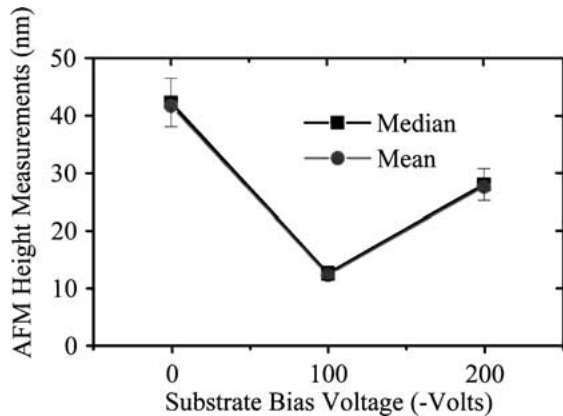
(b)
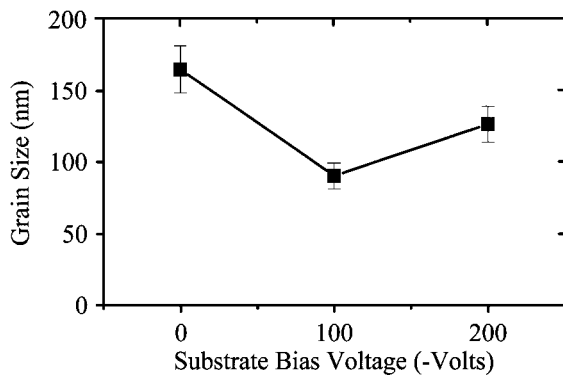
(c)

Figure 4 Effect of substrate bias voltage on (a) rms and average roughness, (b) mean and median height and (c) average grain size of the coatings.

3.1.3. Microhardness

Microhardness of the coatings deposited at different substrate bias voltages is shown in Fig. 5. As the bias voltage increased, the microhardness measured with a 2 g load increased from 1500 HV at zero bias to 2300 HV at −200 volts. The microhardness measured with a 10 g load also increased with increasing substrate bias voltage but at lower values due to the substrate effect.

3.1.4. Phase development and crystallographic properties

Typical XRD patterns measured of the (Ti,Al)N coatings produced at different substrate bias voltages are shown in Fig. 6. The standard 2θ positions for the (111)
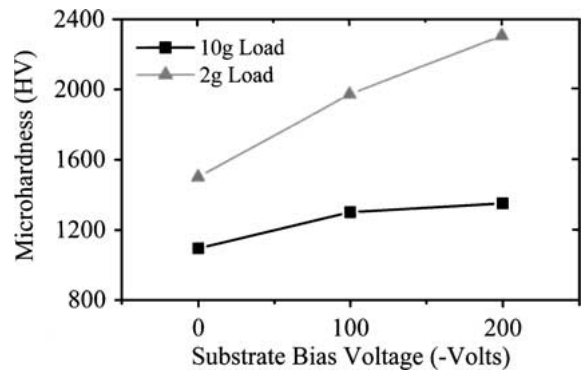

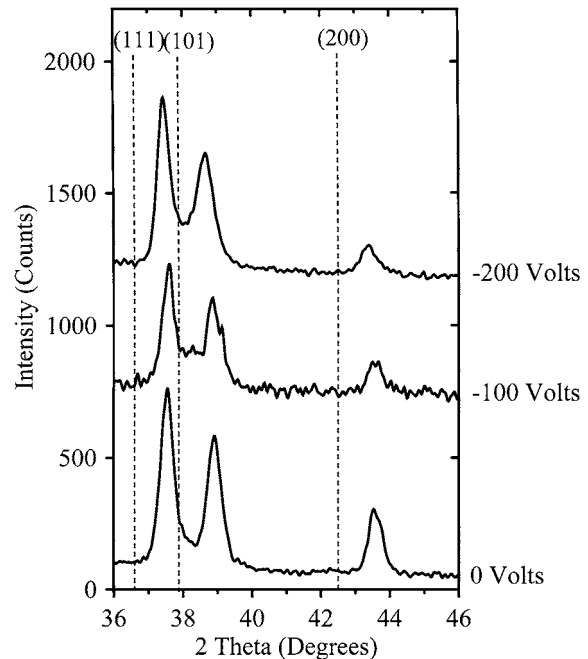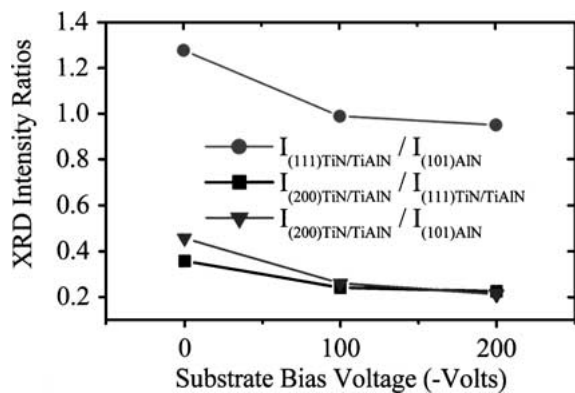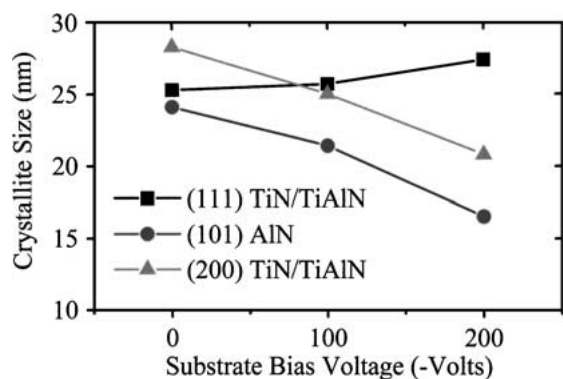*Figure 5* Effect of substrate bias voltage on the microhardness of the coatings.

Figure 6 XRD patterns for coatings produced at different substrate bias voltages. The dashed lines shown represent the standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure.

and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure are included in Fig. 6 for comparison purposes. As the substrate bias increased from 0 to −200 volts, the 2θ values for the (111) reflection of the TiN/TiAlN structure shifted slightly from 37.525° to 37.442°, suggesting a possible formation of coating structure with larger lattice parameters at higher bias voltages. Shifts of the 2θ values for the (200) reflection of the TiN/TiAlN structure from 43.555° to 43.369° and for the (101) reflection of the AlN structure from 38.880° to 38.604° were also evident.

Integrated intensity ratios for the major peaks of the (200) and (111) reflections of the TiN/TiAlN cubic structure and the (101) reflection of the hexagonal AlN structure are shown in Fig. 7a. It was found that as the substrate bias voltage increased from 0 to −200 volts, the intensity ratios of the (200) reflection to the (111) and (101) reflections both decreased, indicating the depletion of the TiN/TiAlN (200) component at higher bias voltages. On the other hand, an increase in

(a)

(b)
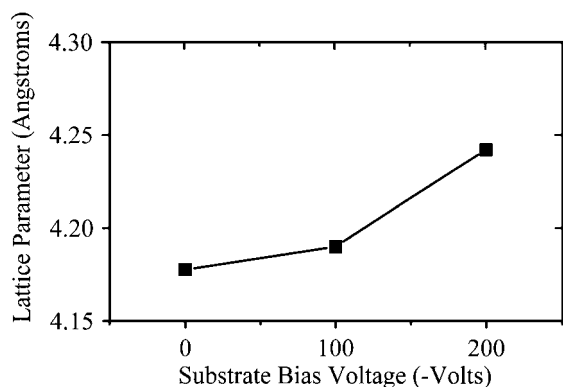
(c)

Figure 7 Effect of substrate bias voltage on the (a) integrated peak intensity ratios, (b) crystallite size and (c) lattice parameter of the coatings.

the substrate bias voltage enhanced the development of the AlN (101) components. As the substrate bias voltage increased from 0 to −200 volts, the ratio between $I_{(111)TiN/TiAlN}$ and $I_{(101)AlN}$ decreased from a value of 1.28 to 0.98.

Results for the calculated crystallite size and the lattice parameter of the coatings are shown in Fig. 7b and c. It was found that as the substrate bias voltage increased from 0 to −200 volts, the crystallite size calculated for the TiN/TiAlN (111) reflection slightly increased and for the TiN/TiAlN (200) and AlN (101) reflections decreased significantly, Fig. 7b and the lattice parameter of the coating structure increased from 4.1778 Å to 4.2420 Å, Fig. 7c.
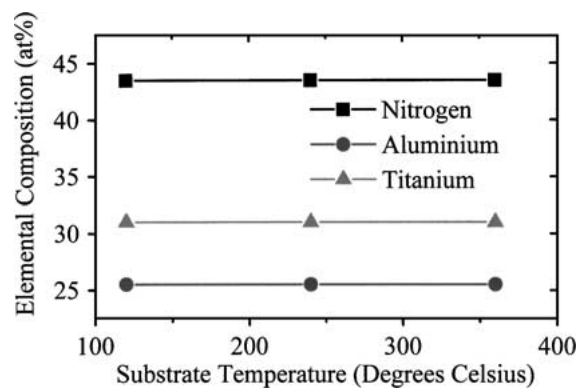
3.2. Effect of substrate temperature
3.2.1. Deposition rate and chemical composition
The deposition rates of (Ti,Al)N coatings at different substrate temperatures are shown in Fig. 8a. The re-
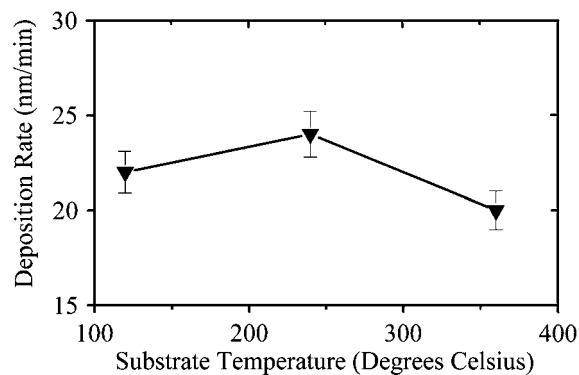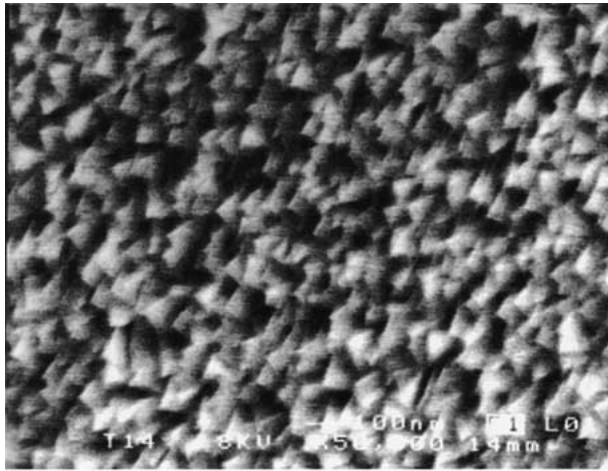

(a)

(b)

Figure 8 Effect of substrate temperature on (a) deposition rate and (b) elemental composition of the (Ti,Al)N coatings.
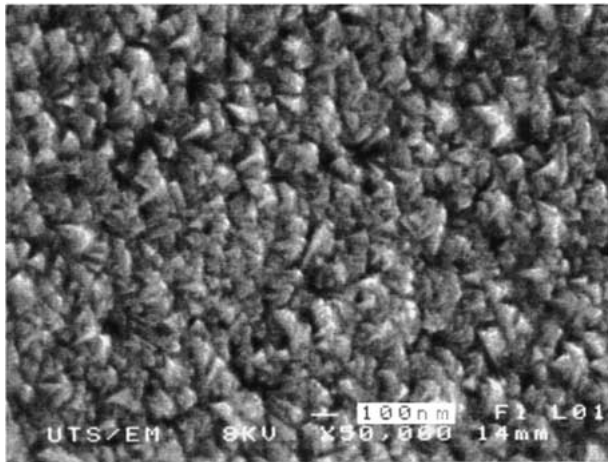
sults showed that the substrate temperature only imposed a slight effect on the deposition rate of the coatings. As the substrate temperature increased from 120°C to 240°C, the deposition rate increased slightly from 22 nm/min to 24 nm/min, and then decreased to 20 nm/min when the substrate temperature was raised to 360°C. An increase in temperature also showed no major change in the chemical composition of the coatings, Fig. 8b. The aluminium and titanium content of the coatings remained constant at 25.5 at.% and 31 at.% respectively. There was also no change in the nitrogen content of the coatings, which remained constant at 43.5 at.%.
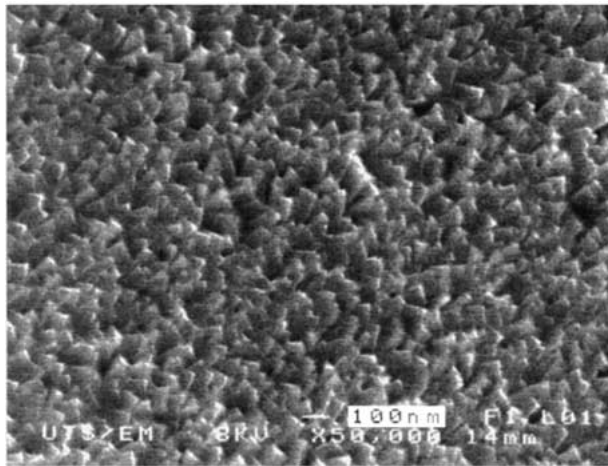
3.2.2. Microstructure and surface morphology
Micrographs of the (Ti,Al)N coatings deposited at different substrate temperatures, are shown in Fig. 9. At a temperature of 120°C, the coating showed faceted columns with a higher porosity. As the substrate temperature increased, the coating structure became densified with a finer grain size. On the other hand, results of AFM regional scans showed that increasing the substrate temperature caused the grain height, surface roughness and grain size to decrease, Fig. 10. As the substrate temperature increased from 120°C to 360°C, the average roughness of the coatings decreased from 8.2 nm to 2.6 nm and the rms roughness decreased from 10.1 nm to 3 nm, Fig. 10a. The mean height of the grain structure also decreased significantly from 44.1 nm to 12 nm, and the median grain height decreased from 44.5 nm to 12 nm, Fig. 10b, suggesting the formation

(a)

(b)

(c)

(a)

(b)

(c)

Figure 10 Effect of substrate temperature on (a) rms and average roughness, (b) mean and median height and (c) average grain size of the coatings.

Figure 9 SEM micrographs of the coatings produced at different substrate temperatures, (a) 120°C, (b) 240°C and (c) 360°C.

of a more densified structure at higher substrate temperatures. The average grain size of the coatings decreased from 100 nm to 70 nm as the substrate temperature increased from 120°C to 360°C, Fig. 10c.

3.2.3. Microhardness
The microhardness of the (Ti, Al)N coatings deposited at different substrate temperatures is shown in Fig. 11.

Figure 11 Effect of substrate temperature on the microhardness of the coatings.

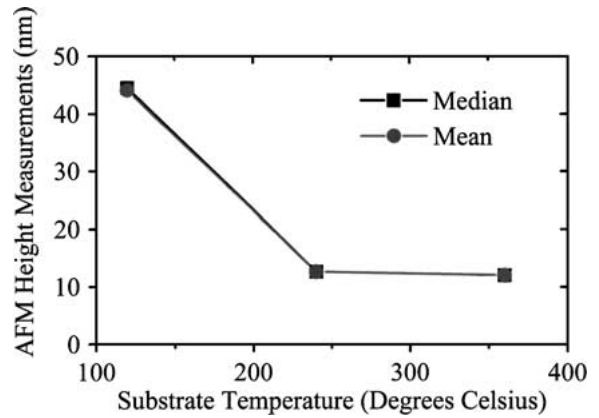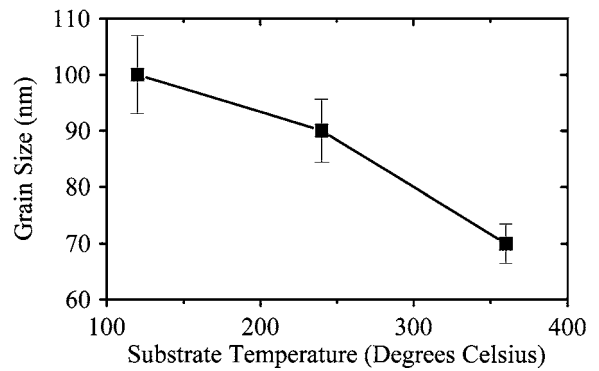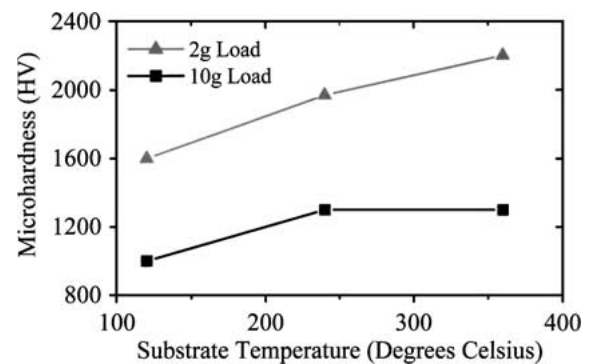The microhardness measured with a 2 g load was found to increase from 1600 HV to 2200 HV as the substrate temperature increased from 120°C to 360°C. The microhardness measured with a 10 g load also increased but at lower values as the substrate temperature was raised.

3.2.4. Phase development and crystallographic properties

XRD patterns measured on the (Ti,Al)N coatings deposited at different substrate temperatures are shown in Fig. 12. The standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure are included in Fig. 12 for comparison purposes. As the substrate temperature increased from 120°C to 240°C, the 2θ values for the (111) reflection of the TiN/TiAlN structure shifted from 37.420° to 37.459°. However, a further increase in temperature from 240°C to 360°C resulted in the shift back of the peak positions from 37.459° to 37.352°, suggesting a possible formation of a coating structure with larger lattice parameters. Similar shifts for the (200) reflection of the TiN/TiAlN and for the (101) reflection of the AlN structure were also evident. On the other hand, an extra peak reflection, between the TiN/TiAlN (111) and AlN (101) components, was observed to exist in the coatings deposited at 120°C and 360°C, Fig. 12. The peak reflection has been identified to be either Ti_3AlN (111) - JCPDS (37-1140), cubic AlN (311) - JCPDS (34-0679) or cubic AlN (111) - JCPDS (25-1495).

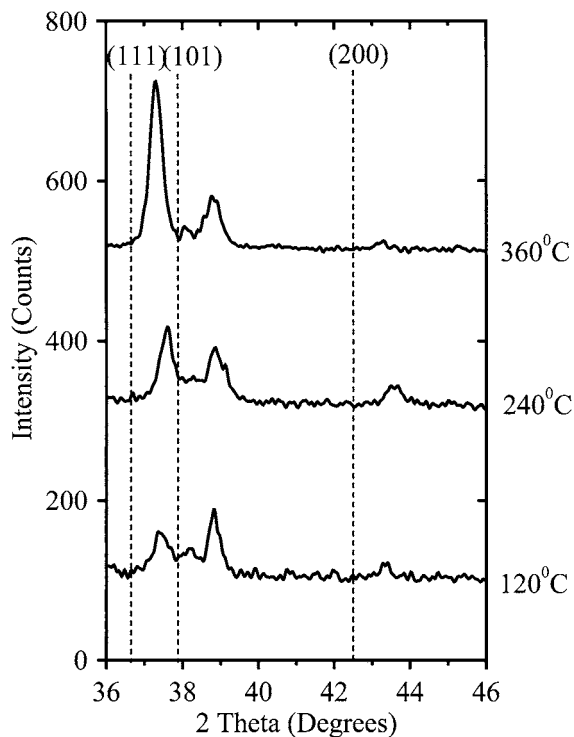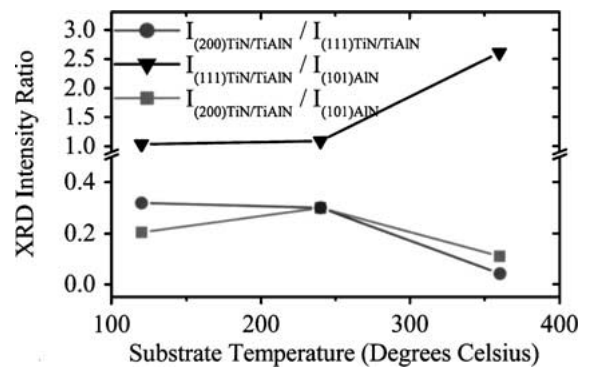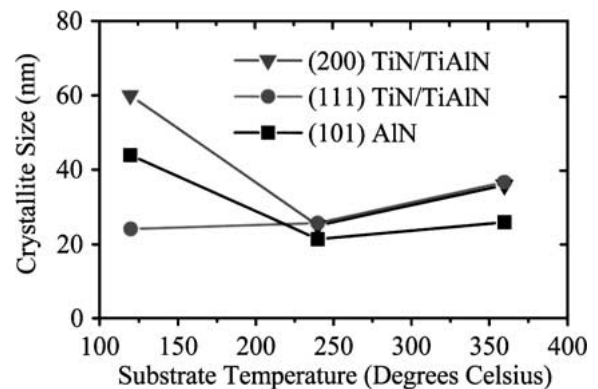Integrated intensity ratios for the major peaks of the (200) and (111) reflections of the TiN/TiAlN cu-

(a)

(b)

(c)

Figure 13 Effect of substrate temperature on (a) integrated peak intensity ratios, (b) crystallite size and (c) lattice parameter of the coatings.

bic structure and the (101) reflection of the hexagonal AlN structure are shown in Fig. 13a. It was found that as the substrate temperature increased from 120° to 360°, the intensity ratios of the (200) reflection to the (111) and (101) reflections both decreased, indicating the depletion of the TiN/TiAlN (200) component at higher substrate temperatures. Furthermore, an increase in the substrate temperature hindered the development of the AlN (101) components. As the substrate temperature increased from 120°C to 360°C, the ratio between $I_{(111)TiN/TiAlN}$ and $I_{(101)AlN}$ substantially increased with the TiN/TiAlN (111) becoming the major texture components of the coatings.

Results for the calculated crystallite size and the lattice parameter of the coatings are shown in Fig. 13b and c. It was found that as the substrate temperature increased from 120°C to 360°C, the crystallite size for the TiN/TiAlN (111) components slightly increased and those for the TiN/TiAlN (200) and AlN (101)
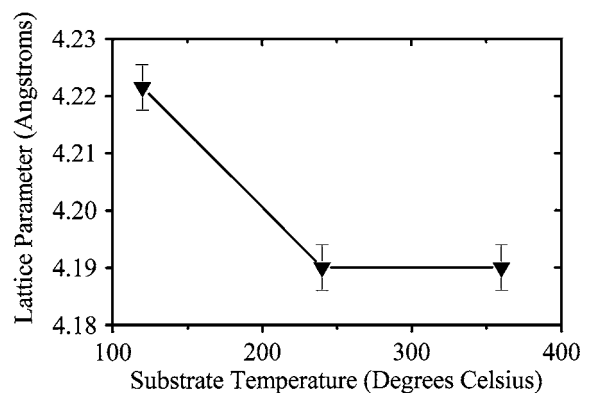

Figure 12 XRD patterns for coatings produced at different substrate temperatures. The dashed lines shown represent the standard 2θ positions for the (111) and (200) reflections of the cubic TiN structure and the (101) reflection of the hexagonal AlN structure.
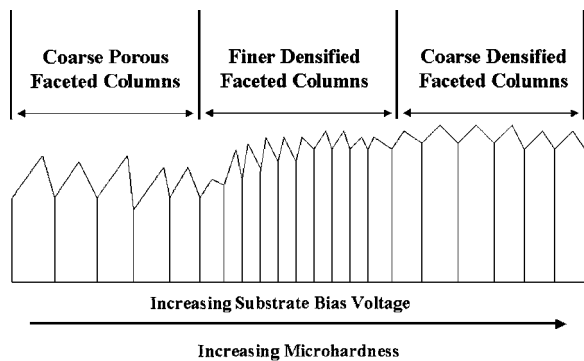
Figure 14 A two dimensional schematic structure zone model showing the effect of substrate bias voltage on the microstructure and property development of (Ti,Al)N coatings deposited with a 30° magnetron configuration.

components decreased. As the substrate temperature increased from 120°C to 240°C, the lattice parameter of the coating structure decreased from 4.222 to 4.190 Angstroms, Fig. 13c. A further increase in temperature to 360°C caused no further change in the lattice parameter of the coatings.

4. Discussion
4.1. Effect of substrate bias voltage
The application of a bias voltage to the substrate demonstrates the significance of the kinetics of the substrate bombarding particles in deposition of sputtered coatings. A summary of the effects is illustrated in Fig. 14. Although the composition of the coatings only varied slightly under the different bias voltages investigated, a densified structure with finer grain size and improved surface morphology developed as the bias voltage increased. A hardness enhancement of the coatings from 1500 HV to 2300 HV was achieved. This strength enhancement is believed to be related to the densified coating structure and improved surface morphology. In previous studies of magnetron sputtering process, Messier *et al.* [18, 19] reported that increasing the negative bias could result in a transition of the zone 1 to zone T microstructure of the Thornton's model [9] of sputtered coatings. Hakansson *et al.* [13, 20] also reported that as the substrate bias increased, the open porous columnar structure of the $Ti_{0.5}Al_{0.5}N$ coatings was suppressed with a substantial hardness enhancement. Results of the present study are consistent with these findings.

The effects of the bias voltage on the textural development of the coatings were also examined in this study, but found to be insignificant. A shift of the major reflection peaks from the standard 2θ position was evident, but remained almost constant as the bias voltage increased, suggesting that (Ti,Al)N formed in the coatings but the phase development had not been significantly affected by a change of the bias voltage. Furthermore, analysis of the XRD results showed that as the bias voltage increased, the TiN/TiAlN (200) component was moderately suppressed in favour of the development of the AlN (101) orientations.

It is understood that when the substrate bias is increased, the coatings are exposed to ion bombardment

with higher energy of the ions, thus creating preferential nucleation sites and enhancing atom mobility, which in turn reduces void formation and creates a fine grain structure. Results of the present study, however, showed the existence of a critical bias voltage for producing an optimum structure for the coatings, which had not been emphasised in recent studies of sputtered coatings. It was found that as the bias voltage increased from −100 volts to −200 volts, while the deposition rate remained constant, coatings with large grain size and rougher surface morphology developed, indicating that re-sputtering of the depositing atoms might have occurred. Therefore excessive energy of the depositing atoms may indeed cause a damaging effect to the coating structure and create significant residual stresses in the coating. Grain growth also becomes more significant and lead to the development of a coarse grain structure. Depositions at even higher bias voltages of −250 Volts and −300 Volts had also been attempted in the study, but the coatings fractured shortly after removal from the coating chamber, possibly due to excessive residual stress developed in the films. The results suggested that in the present study of sputter deposition of (Ti,Al)N coatings using a 30° magnetron arrangement, an application of a bias voltage of −100 to −200 Volts is probably the optimum voltage range that would produce coatings with quality structure and properties.

4.2. Effect of substrate temperature
The substrate temperature is an important parameter in a sputter deposition process, which has pronounced effects on refining the structure of the coatings and their interfaces with the substrate. A summary of the structural development of the coatings deposited at 120°C to 360°C is illustrated in Fig. 15. It was found that an increase in the substrate temperature from 120°C to 360°C resulted in the microstructure changing from a porous columnar structure to a much densified structure with finer grain size, showing a microstructure transition from the zone 1 to zone T of the Thornton's structure zone model [9]. On the other hand, increasing the temperature also improved the surface morphology of the coating with a significantly reduced roughness. The results are in agreement to those reported by
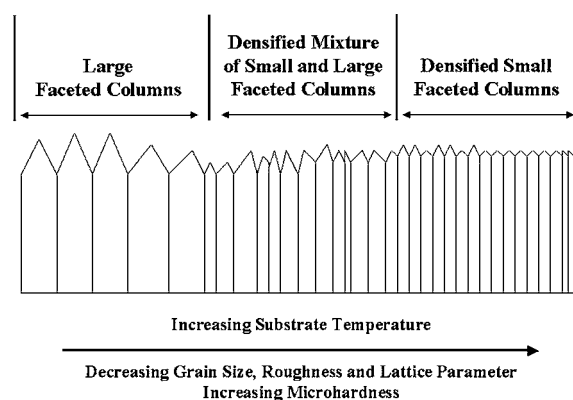

Figure 15 A schematic two dimensional structure zone model showing the effect of substrate temperature on the microstructure and property development of (Ti,Al)N coatings deposited with a 30° magnetron configuration.

Wang *et al.* [17] on TiAlN coatings. Wang *et al.* [17] reported that when the substrate temperature was increased from 400 to 480°C, the coating microstructure became denser, which improved the lattice and strengthened the interface. The present results showed a similar structure development in spite of the coatings were produced at lower substrate temperatures. Despite the absence of major changes in the deposition rate and composition, the microhardness of the coatings increased from 1600 HV to 2200 HV as the substrate temperature increased from 120°C to 360°C.

Analysis of the XRD results reflected the effect of substrate temperature on the texture development of the coatings. The results showed a shift of the major reflection peaks from the standard 2θ positions, but unlike those deposited at various nitrogen pressures, a shift back of the peak positions was not so significant at higher substrate temperatures. This suggested there was no major changes in phase formation as the substrate temperature increased. Further analysis of the XRD results however indicated the substrate temperature indeed caused different effects on the development of different texture orientations. It was found that the TiN/TiAlN (111) orientation strongly developed as the substrate temperature increased, suggesting a promotion of the (111) texture component at higher substrate temperatures. It is believed that the fcc (111) planes generally have a lower surface energy than the other faces as the exposed (111) face of an fcc crystal has fewer unsatisfied bonds sticking out of the surface [21]. As the substrate temperature increases, the atom mobility of the coatings will be enhanced and development of the (111) orientations will be promoted because of its lower surface energy.

As a whole, results of the present study indicate that an increase of the substrate temperature imposed significant effects on the microstructure, morphology and texture development of the coatings. The effect on the phase formation of the coatings is however very small. As the substrate temperature continues to increase, the coating structure will be more densified with reduced porosity and grain size, which results in an enhancement of the hardness of the coatings. However, in practice an increase of the substrate temperature will inevitably lower the strength of the substrate, which restricts the substrate temperature in the deposition of hard coatings. A selection of appropriate substrate temperature is therefore required to ensure whilst the property of the coating is enhanced, the strength of the substrate can be maintained.

4.3. Major effects of deposition parameters

Effects of the four important process parameters, namely nitrogen deposition pressure, target discharge power, substrate bias voltage and substrate temperature on the microstructure, morphology, texture and property development of (Ti,Al)N coatings produced under a 30° magnetron co-sputtering arrangement have been studied and presented in these three papers. It was found that the effects of the process conditions generally fell into 2 categories. An increase of the nitrogen deposition pressure and/or the target discharge power caused direct changes on both the composition and phase formation of the coatings and their microstructure and morphology. On the other hand, an increase of the substrate bias voltage and/or the substrate temperature caused significant effects on the microstructure and morphology, but only imposed minimal effect on the composition and phase formation of the coatings. As the deposition parameters worked into the optimum conditions, a transition of the porous zone 1 into the densified zone T structure of the Thornton's structural model [9] was identified, resulting in a significant increase of the hardness of the coatings. Results of the study further confirmed that property enhancement such as hardness of the coatings was usually associated with the formation of a smooth, fine grained, densified structure and an increase in aluminium content. The hardness could be increased substantially with a densified structure even though there was no associated change in composition and phase changes of the coatings, suggesting that the structural and morphological changes of the coatings might play a more dominant role in determining the mechanical properties of the films.

It is understood that when the depositing atoms arrive the substrate surface, two phenomena, namely statistical roughening and self-shadowing which affect the microstructure and morphology development of the coatings may occur. Statistical roughening arises because of the statistical fluctuation in the vapour arrival flux. A model has been established to demonstrate this situation, which confirmed that the roughness would be induced as the thickness of the coatings increased [21]. The surface roughening of the coatings, however, could be smoothed out by the enhanced surface diffusion of the atoms of the coatings under some energy enhanced processes, which will be discussed in the later section.

Self-shadowing is the second factor that may destabilise surface smoothness during the coating deposition process and is claimed to be the cause of characteristic zone 1 porous columnar structure. It has been suggested [21] that when the depositing atoms arrive at the substrate surface, the atoms generally cannot perch on top of each other, but rather settle sideways into the nearest cradle position in which they establish relaxed bond strengths to their nearest neighbours, creating a rough structure with void formation. When the depositing atoms arrive obliquely at angles to the substrate surface, self-shadowing increases and results in an increased formation of the zone 1 structure.

It is known that the zone 1 structure is undesirable in a hard coating because of its less densified structure with a high porosity and low strength. It is therefore necessary to reduce void formation and to transform the coatings into the densified zone T structure by employing the energy enhanced processes at a workable temperature of the sputter deposition. Muller [22, 23] has conducted a molecular dynamics computer modelling in thin film deposition by considering the vibratory motion of atoms and formation and breakage of bonds and proposed the following mechanisms, which might provide enough energy and momentum transfer for the structural transition.

The four mechanisms are:

1. Local heating due to the thermal spike produced upon impact, resulting in local surface diffusion.
2. Less trajectory curvature due to the higher approach velocity.
3. Higher impact mobility of the adatoms so that they can move down into the voids.
4. Forward sputtering of other adatoms into the voids.

The process controls adopted in the present study have demonstrated the effects of these four mechanisms, which will be discussed in the following sections. Increasing the substrate temperature generally provides greater thermal energy to the substrate and the coating material. Surface diffusion will then be enhanced at higher substrate temperatures and the diffusing adatoms will fill the voids in the films, thus producing a densified zone T structure with low porosity. In principle, a continuous increase of the substrate temperature will constantly densify the structure of the ternary nitride hard coatings and improve their strength. However as suggested by the present results, there are at least two areas of restrictions in an application of higher substrate temperatures. Firstly, as the substrate temperature increases, the strength of the substrate may drop. Secondly, the grain growth of the coating materials will be significant at higher substrate temperatures, excessive grain growth then occurs, resulting in development of a coarse grain sized structure with lower hardness. A suitable selection of the substrate temperature is therefore required to optimise the structure and properties of the coatings. According to the results obtained in the present study, substrate temperatures around 240°C are considered to be a lower end of the working temperatures, which can produce quality ternary (Ti,Al)N coatings in a magnetron co-sputtering deposition.

Increasing the substrate bias voltage will increase the translational kinetic energy [24] carried by the depositing atoms, which then involve most of the above four mechanisms to enhance the structure and properties of the coatings. A high impact mobility of the adatoms will create a high surface diffusion rate and the momentum transfer from the arriving atoms to the adatom will cause the latter to sputter forward and fill the voids. As a consequence, these energy enhanced processes will significantly reduce the voids in a film, and a densified zone T coating structure is formed. In principle, a continuous increase of the bias voltage will constantly improve the microstructure and properties of the coatings. However, in practice, according to the results obtained in the present investigation, surface damage and excessive residual stress will develop in the films when the bias voltage is raised too high, resulting in fracture of the coatings. An application of a substrate bias of −100 V to −200 V is identified to be the cut-off voltage for an optimum sputter deposition of the ternary (Ti,Al)N coatings.

Increasing the aluminium target discharge power aims at raising the sputter yield of aluminium atoms,

promoting the formation of (Ti,Al)N phase. The composition and x-ray diffraction results of the present study showed that the above purpose could be achieved, with an enhanced formation of the (Ti,Al)N structure in the coatings and a continuos increase of the hardness of the films. As the aluminium discharge power increased, the coating structure was also densified with a much smoother surface and a finer grain size. This structural improvement, is believed to be attributed to a high density of depositing atoms arriving at the substrate, filling the voids and creating a higher nucleation rate in the films. According to the results obtained in the present study, a aluminium discharge power between 4.5 to 6.0 W/cm^2 has been identified to be suitable for providing coatings with optimum structure and hardness.

Increasing the nitrogen deposition pressure induces a complicated situation to the sputter deposition process. As the nitrogen deposition pressure increases, formation of ternary nitrides is expected to be enhanced because of the higher concentration of nitrogen gas inside the deposition chamber. Experimental results however showed the replacement of the titanium atoms by the aluminium atoms in the lattice becoming less effective as the nitrogen pressure was raised beyond 0.4 mTorr. The microstructure was also transformed from a densified zone T structure at low nitrogen pressures into a porous zone 1 structure as the nitrogen pressure increased, resulting in an abrupt decrease of the coating hardness. It is believed that these compositional and microstructural changes of the coatings are related to a) the different formation energies of the different phases in the coatings and b) the energy reduction of the depositing atoms approaching the substrate surface due to an increased collision of the sputtered atoms and the nitrogen gas molecules. The free energy of formation for TiN is lower than that of AlN, the nitrogen will therefore react more readily with the titanium atoms during the deposition process. An increase of nitrogen amount in the process will enhance this trend. On the other hand, as the amount of the nitrogen gas increases in the chamber, collision between the sputtered atoms and the gas molecules will become more frequent. This will reduce the translational kinetic energy of the depositing atoms and scatter the atoms into more oblique incident angles when they approach the substrate surface. As a consequence, at higher nitrogen deposition pressures, the adatom mobility will reduce and the self-shadowing effect will increase. Void formation with rough coating surface will then be induced as evident in the present investigation. It has been confirmed in this study that a nitrogen pressure of 0.4 mTorr is the deposition pressure for producing optimum structure and properties of the ternary (Ti,Al)N coatings under a 30° magnetron co-sputtering deposition arrangement.

5. Conclusions

The effect of substrate bias voltage and substrate temperature on the microstructure and property development of magnetron co-sputtered ternary (Ti,Al)N coatings was investigated. It was found that an increase in

substrate bias and/or substrate temperature imposed no major effect on the composition and phase formation of the (Ti,Al)N coatings, but had significant influence on the development of their microstructure and surface morphology. As the substrate bias and/or temperature increased, the coating structure was densified with development of fine grain size and reduced surface roughness, resulting in a substantial increase of the coating hardness. It is believed that the microstructure and property enhancement is attributed to an increased translational kinetic energy of the depositing atoms and a greater thermal energy provided to the substrate and the coating material with increasing substrate bias and/or temperature. The adatom mobility and the surface diffusion of atoms are enhanced, producing a densified zone T structure with low porosity.

Acknowledgements

References

1. J. E. SUNDGREN, B. O. JOHANSSON, H. T. G. HENTZELL and S. E. KARLSSON, *Thin Solid Films* **105** (1983) 385.
2. W. D. SPROUL, P. J. RUDNIK, C. A. GOGOL and R. A. MUELLER, *Surf. Coat. Technol.* **39/40** (1989) 499.
3. W. D. SPROUL, P. J. RUDNIK and M. E. GRAHAM, *ibid.* **39/40** (1989) 355.
4. W. D. SPROUL, P. J. RUDNIK, M. E. GRAHAM and S. L. ROHDE, *ibid.* **43/44** (1990) 270.
5. F. RICHTER, H. KUPFER, H. GEIGENGACK, G. SCHAARSCHMIDT, F. SCHOLZE, F. ELSTNER and G. HECHT, *ibid.* **54/55** (1992) 338.
6. D. S. RICKERBY and P. J. BURNETT, *Thin Solid Films* **157** (1988) 195.
7. S. L. ROHDE, W. D. SPROUL and J. R. ROHDE, *J. Vac. Sci. Technol.* **A9** (1991) 1178.
8. J. MUSIL, V. POULEK, V. VALVODA, R. JR. KUZEL, H. A. JEHN and M. E. BAUMGARTNER, *Surf. Coat. Technol.* **60** (1993) 484.
9. J. A. THORNTON, *J. Vac. Sci. Technol.* **11** (1974) 666.
10. H. FRELLER and H. HASSLER, *Surf. Coat. Technol.* **36** (1988) 219.
11. B. F. COLL, P. SATHRUM, R. FONTANA, J. P. PEYRE, D. DUCHATEAU and M. BENMALEK, *ibid.* **52** (1992) 57.
12. J. R. ROOS, J. P. CELIS, E. VANCOILLE, H. VELTROP, S. BOELENS, F. JUNGBLUT, J. EBBERINK and H. HOMBERG, *Thin Solid Films* **193/194** (1990) 547.
13. G. HAKANSSON, J. E. SUNDGREN, D. MCINTYRE, J. E. GREEN and W. D. MUNZ, *ibid.* **153** (1987) 55.
14. L. COMBADIERE and J. MACHET, *Surf. Coat. Technol.* **88** (1996) 17.
15. *Idem., ibid.* **88** (1996) 28.
16. L. MENG, M. ANDRITSCHKY and M. P. DOS SANTOS, *Thin Solid Films* **223** (1993) 242.
17. Y. K. WANG, X. Y. CHENG, W. M. WANG, X. H. GU, L. F. XIA, T. C. LEI and W. H. LUI, *Surf. Coat. Technol.* **72** (1995) 71.
18. R. MESSIER, A. P. GIRI and R. A. ROY, *J. Vac. Sci. Technol.* **A2** (1984) 500.
19. R. MESSIER, *ibid.* **A4** (1986) 490.
20. G. HAKANSSON, L. HULTMAN, J. E. SUNDGREN, J. E. GREEN and W. D. MUNZ, *Surf. Coat. Technol.* **48** (1991) 51.
21. D. L. SMITH, in "Thin-Film Deposition: Principles and Practice" (McGraw-Hill, New York, 1995) p. 162.
22. K. H. MULLER, *Phys. Rev.* **35** (1987) 7906.
23. *Idem., J. Appl. Phys.* **62** (1987) 1796.
24. O. KNOTEK, R. ELSING, G. KRAMER and F. JUNGBLUT, *Surf. Coat. Technol.* **46** (1991) 265.