AN EMPIRICAL RELATIONSHIP BETWEEN NITROGEN DEPOSITION PRESSURE AND HARDNESS OF MAGNETRON CO-SPUTTERED TERNARY NITRIDE COATINGS

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ABSTRACT

An empirical equation of the hardness of ternary nitride coatings and the nitrogen deposition pressure was formulated in the present study. A linear relationship was established between the coating hardness and the reciprocal of the square root of nitrogen pressure. The primary sputter yield of the coating materials was found to contain a linear relationship with the minimum hardness value, H_o, of the empirical equation but showed no effect on the rate of hardness increase, m_H. With defined discharge conditions and sputter yields of the target materials, the values of m_H and H_o can be calculated and the hardness of a coating produced at a specified nitrogen deposition pressure can be theoretically determined.

KEYWORDS

Ternary nitride coatings, magnetron sputtering, nitrogen deposition pressure.

INTRODUCTION

Development of complex ternary nitride coatings has attracted substantial interest in the last 15 years [1-10]. Despite the extensive studies on the microstructures and properties of the sputtered coatings, a generalised model of the nitrogen pressure effect on the mechanical properties of the ternary nitride coatings is lacking. In reactive magnetron co-sputter deposition of ternary nitrides, nitrogen pressure is generally used as a major controlling parameter of the deposition process. As the nitrogen pressure varies, the deposition rate and composition of the coatings change in accordance with the variation of nitrogen pressure, which then affect the microstructural development and mechanical properties of the coatings [11,12]. In a review of the sputtering process, Smith [13] has concluded that the microstructure development of the coatings is generally governed by the composition of the coatings, the deposition rate and the energy of the depositing atoms arriving at the substrate. While the composition affects the structure development in the coatings, the deposition rate and energy of the depositing atoms determine the nucleation and grain growth of the microstructure. The mechanical properties are then determined by the combined effect of both the composition and grain size development of the coatings. In the present study, by incorporating the experimental results obtained from the recent studies of (Ti,Al)N, (Ti,V)N and (Cr,V)N thin films [11,12], simulation of an empirical relationship between the nitrogen pressure and the hardness of the coatings is attempted. The study aims to investigate if an empirical relationship exists between the strength of the coatings and a measurable deposition parameter of the process, and if it exists, to determine the relationship. It is expected that the relationship between the property (hardness) of the coatings and a measurable deposition parameter (nitrogen pressure) will generate important information for production and application of these high-valued ternary coatings as the strength of the coatings can be established with appropriate deposition conditions to meet specified requirements.

METHODS AND PROCEDURES

Reactive magnetron co-sputtering, with separate magnetron targets, was used to produce titanium aluminium nitride, titanium vanadium nitride and chromium aluminium nitride coatings at various nitrogen deposition pressures. The coatings were deposited with two unbalanced, independently controlled d.c. magnetrons at a target-substrate working distance (W.D.) of 65 mm and at an angle of 45° to the substrate. A constant d.c. bias of negative 100 volts was applied between the substrate and the targets. The substrate holder was maintained at a temperature of 240°C for the formation of densified coatings [14]. Reactive gas of nitrogen with a high purity (99.99%) was injected through an Alltech gas purifier filter into the deposition chamber to form the ternary nitrides. Pirrani gauges and Tylan mass flow controllers were used to monitor the pressures and flow rates of reactive gas through the deposition process. The coatings were deposited to a thickness of 1.5 – 2.0 µm at nitrogen pressures varying from 0.027 – 0.320 Pa (0.2 – 2.4 mTorr). The argon pressure was maintained constant at 0.32 Pa (2.4 mTorr) in deposition of the coatings. Hardness of the coatings was measured at a 2g load to minimise the substrate effect. A LECO M400-H1 microhardness tester with a Vickers indenter was used for the microhardness measurements.

EMPIRICAL ANALYSIS OF EXPERIMENTAL RESULTS

Hardness Relationship

The microhardness of the coatings was measured at a low load of 2g. Experimental results of the microhardness of the coatings with increasing nitrogen pressure are shown in Figure 1.

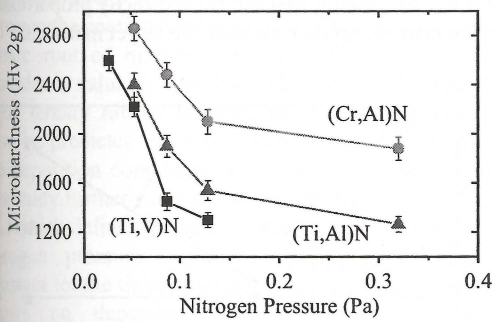

Figure 1: Variation of microhardness of the (Ti,Al)N, (Cr,Al)N and (Ti,V)N coatings with nitrogen deposition pressure.

A consistent relationship was observed between the nitrogen deposition pressure and the hardness of the three ternary nitride coatings. As the nitrogen pressure increased from 0.053 to 0.320 Pa, the microhardness of (Ti,Al)N decreased from 2400 HV to 1300 HV and that of (Cr,Al)N decreased from 2850 to 1900 HV. On the other hand, as the nitrogen pressure increased from 0.027 to 0.128 Pa, the microhardness of the (Ti,V)N decreased from 2600 HV to 1300 HV. Using the results of Figure 1, the data was re-plotted as the microhardness *vs* the reciprocal of the square root of nitrogen pressure as shown in Figure 2. A linear relationship was successfully established for all the three coatings, suggesting that the microhardness is inversely proportional to the square root of the nitrogen deposition pressure. The relationship between the microhardness and the nitrogen deposition pressure can then be described as follows:

$$H_V = \frac{m_H}{\sqrt{P_N}} + H_o \qquad (1)$$

where:

m_H = equation constant (reflecting rate of hardness change w.r.t. nitrogen pressure)

H_v = hardness of the coating

H_o = (minimum) hardness of the coating at large nitrogen pressure

P_N = nitrogen pressure (Pa)

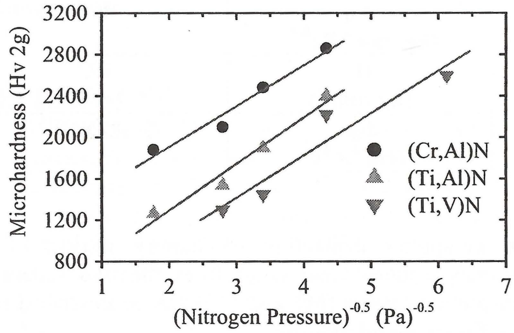

Figure 2: Graphs of microhardness versus reciprocal of square root of the nitrogen pressure for the (Ti,Al)N, (Cr,Al)N and (Ti,V)N coatings.

The calculated results of m_H and H_o for the three ternary nitride coatings are listed in Table 1.

Justification of m_H and H_o

In the equation (1), m_H can be interpreted as the rate of hardness increase with respect to the pressure change and H_o is the minimum hardness of the coatings developed at very high nitrogen pressures. Both m_H and H_o are of great industrial significance as they suggest the value of hardness increase and the minimum hardness of the coatings that can be achieved in the deposition process. Surprisingly the values of m_H were found to be almost the same for the three different ternary coatings, suggesting that m_H may be independent of the species of the coating materials. On other hand, the values of H_o showed a strong dependence upon the material characteristic. In the present study, with the same substrate temperature, substrate bias voltage and target to substrate distance, the only difference remained for the deposition rate at a specified nitrogen pressure is the discharge powers of the metallic targets. The discharge power of the individual target changes the sputter yield and the deposition flux of the metallic element, which in turn determine the composition and the grain size of the coating. An analysis for the relationship between m_H and H_o and the primary sputtering yield of the target materials under given deposition conditions was therefore pursued.

Table 1: Sputter characteristics and equation constants of the ternary nitride coatings.

Constants	(Ti,V)N	(Ti,Al)N	(Cr,Al)N
Magnetron Discharge Power (Watts/cm²)	9 for Ti 6 for V	9 for Ti 6 for Al	9 for Cr 6 for Al
Metal Sputtering Yield (atoms/ion)	0.51 for Ti 0.65 for V	0.51 for Ti 1.05 for Al	1.18 for Cr 1.05 for Al
m_H ($kg.mm^{-2}.Pa^{0.5}$)	408	413	395
H_o ($kg.mm^{-2}$)	193	482	1118
J_{MP} ($cm^{-2}.s^{-1}$)	$3.323X10^{16}$	$4.262X10^{16}$	$6.622X10^{16}$

In co-sputter deposition of ternary nitrides, the primary sputter yield (J_{MP}) from the two separate magnetron targets (M1 and M2) can be described by the following relationship:

$$J_{MP} = (S_M J_{Ar+})_{M1} + (S_M J_{Ar+})_{M2} \qquad (2)$$

where:
J_{Ar+}= ion current density at the target ionised by argon ($A.cm^{-2}$)
S_M= sputtering yield of the metal (atoms/ion)

The ion current density at the target (J_{Ar+}) is dependent upon the magnetron power and is generally determined by the following expression:

$$J_{Ar+} = \frac{i_T}{A_T e(1+\gamma)} \qquad (3)$$

where:
A_T = area of target (cm^2)
e = elementary charge of an electron (1.602×10^{-19} C)
γ = secondary electron yield = 0.1
i_T = magnetron current (Amps)

With the sputter characteristics of the target materials used in this study, the values of J_{MP} can be calculated. The results are given in Table 1, and the relationship of m_H and H_o against J_{MP} is plotted in Figure 3. It was found that m_H remained constant with increasing J_{MP} indicating that the sputter characteristics of the target materials play no effect on the rate of hardness increase of the coatings. However, a linear relationship was reasonably established between H_o and J_{MP}, suggesting that the H_o is directly proportional to the primary sputter yield of the target materials.

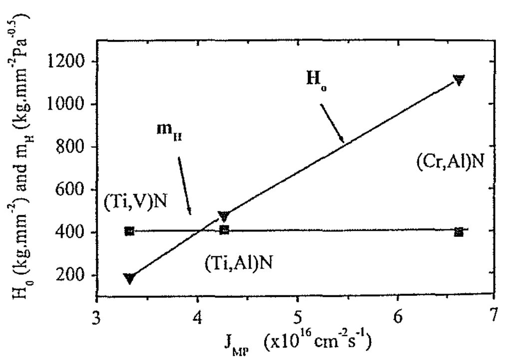

Figure 3: Graphs of and m_H and H_o versus J_{MP} of the (Ti,Al)N, (Cr,Al)N and (Ti,V)N coatings.

DISCUSSION

Reactive magnetron co-sputter deposition of ternary nitrides is a complex process in which the process parameters such as nitrogen pressure, sputtering power and magnetron configuration all play a crucial role in determining the microstructure and strength of the coatings. In recent studies of the authors, it has been found that as the nitrogen pressure increases, the deposition rate of the ternary coatings decreases significantly [11,12]. Adopting the analytical approach proposed by Hofmann [15] for binary nitride deposition, modelling on the deposition behaviour of the ternary coatings has been established and agreed well with the experimental results [11]. The model has considered the effects of the sputtering reactions and nitriding at the target surfaces, the transfer of sputtered atoms to the substrate and the reactions at the substrate surface. It has been further confirmed that as the deposition rate increases, grain refinement of the coating structure occurs, leading to the development of a nanograin size of ~80 nm [12]. On the other hand, the strength of the coatings has been investigated in an earlier study and the relationship between the hardness of the ternary nitride coatings and their grain size and composition has been established [16].

In the above relationship, the grain size and composition of the coatings have to be determined before the hardness can be worked out. For industrial production, a simpler approach is preferable. The present study aims to investigate if an empirical relationship exists between the hardness of the coatings and the measurable deposition parameter of nitrogen deposition pressure, and if it exists, to determine the relationship. The current results show that with defined magnetron configuration and discharge power, a linear relationship is identified between the coating hardness and the reciprocal of the square root of nitrogen pressure. The relationship provides a valuable tool for industrial production of these ternary nitride coatings as their strengths can now be predicted once the equation parameters and the deposition conditions are defined. The results of this study further suggest that the equation parameter, m_H, which defines the rate of change in the hardness – nitrogen pressure equation, surprisingly remains constant for the three coatings under investigation and shows no dependence with the sputter yield characteristics of the target materials. The results suggest that the nitrogen pressure may have imposed counter effects on the microstructure and composition of the coatings respectively. Further analysis on these relationships is being pursued. With the relationships defined in the Equations (1) and (2), once the discharge conditions and the sputter yield of the target materials are known, the values of m_H and H_o can be defined and the hardness of the coating produced at a specified nitrogen deposition pressure can be theoretically determined. It should be noted that with the above relationship, the hardness of the coatings would continuously increase as the nitrogen partial pressure decreases. However, in reality, as the nitrogen pressure goes to very large or very small values, the structure and composition of the coatings become non-uniform, leading to large variations of the hardness values. The nitrogen pressures adopted in the present study have provided very consistent hardness values for the three ternary coatings.

CONCLUSIONS

An empirical equation of the hardness of ternary nitride coatings and the nitrogen deposition pressure was formulated in the present study. A linear relationship was established between the coating hardness and the reciprocal of the square root of nitrogen pressure. The primary sputter yield of the coating materials was found to contain a linear relationship with the minimum hardness value, H_o, of the empirical equation but showed no effect on the rate of hardness increase, m_H.

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