

Materials Science and Engineering A 474 (2008) 236-242



www.elsevier.com/locate/msea

# Study of macrodroplet and growth mechanisms with and without ion etchings on the properties of TiN coatings deposited on HSS using cathodic arc physical vapour deposition technique

A. Mubarak<sup>a</sup>, E. Hamzah<sup>a,\*</sup>, M.R.M. Toff<sup>b</sup>

<sup>a</sup> Department of Materials Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia <sup>b</sup> Advanced Materials Research Center (AMREC), SIRIM Berhad, Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park, 09000 Kulim, Kedah, Malaysia

Received 26 February 2007; received in revised form 30 March 2007; accepted 8 April 2007

#### Abstract

In the present study, titanium nitride (TiN) films were deposited on high-speed steel (HSS) by using cathodic arc physical vapour deposition (CAPVD) technique. The main drawback of this technique, however, is the formation of macrodroplets (MDs) during deposition, resulting in films with rougher morphology. The presence of MDs in CAPVD process is a serious problem during practical tooling applications. The goal of this study was to examine the effect of ion etching with and without titanium (Ti) and chromium (Cr) on the properties of TiN coatings deposited on HSS. Various standard characterization techniques and equipment, such as electron microscopy, atomic force microscopy, hardness testing machine and surface roughness tester, were used to analyze and quantify the following properties and parameters: surface morphology, thickness, adhesion and hardness of the deposited coatings. The coatings deposited with Cr ion etching for 8 and 16 min show half the hardness compared to the samples etched with Ti for similar etching times. Both coating thickness and indentation loads influenced the hardness of the deposited coating. Cr ion etching significantly reduced the surface roughness and hardness compared to Ti ion etching. © 2007 Elsevier B.V. All rights reserved.

Keywords: Cathodic arc; Titanium nitride; Ion etching; Surface morphology; Hardness

# 1. Introduction

Surface coating techniques with surface pre-treatment offer the possibility of modifying the surface properties of a component, and thereby achieving improvements in both performance, and reliability. Most of the coating applications demand common requirement for acceptable performance of coated components and that is sufficient level of coating/substrate adhesion, an improvement in hardness with decreased surface roughness.

Titanium (Ti)-based hard coating is widely used in tools, dies and mechanical parts to enhance their lifetime and performance due to its attractive properties such as high hardness, high wear resistance and chemical stability. Among these coatings, titanium nitride (TiN) is widely used in tools and other hard surfaces.

It has been demonstrated that the metal ion bombardment favors local epitaxial film growth, which enhances adhesion

\* Corresponding author. *E-mail address:* esah@fkm.utm.my (E. Hamzah).

0921-5093/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.msea.2007.04.030 between coating and substrate [1]. Additionally, the Cr ion etching minimizes the surface roughness of the subsequent coatings [2]. Münz et al. [2] studied the effect of ion etching with target materials Al, Cu, TiAI, Ti, Zr, Cr, Nb and MO, and found that the number and size of droplets depend on the melting point of the metals used during ion etching.

Even though the effect of ion etching has been studied long time ago but to have a better understanding and in depth knowledge a critical study is important to analyze and measure the microstructure, surface morphology, surface roughness and hardness of the TiN coatings deposited on HSS substrates.

# 2. Experimental procedure

Titanium nitride films were deposited on HSS discs (diameter: 10 mm; thickness: 6 mm) using the Hauzer Techno Coating (HTC) 625/2 ARC coating system. The complete deposition procedure with metallography process has been described earlier [3]. A summary of the etching and deposition parameters can be seen in Tables 1a and 1b. During deposition process, one

Table Ta	
Parameters for ion	etching process

T-1.1. 1.

No.	Rotation speed (%)	Pre-bias (V)	Ar gas flow rate (sccm)	Arc current Ti cathode (A)	Arc current Cr cathode (A)	Ion etching time (min)
1	60	0	0	0	0	0
2	60	-1000	50	100	0	8
3	60	-1000	50	100	0	16
4	60	-1000	50	0	100	8
5	60	-1000	50	0	100	16

Table 1b Parameters for deposition process

No.	Rotation speed (%)	Substrate bias (V)	Nitrogen gas flow rate (sccm)	Arc current (A)	Substrate temperature (°C)	Deposition time (min)
1	60	-50	250	100	300	90
2	60	-50	250	100	300	90
3	60	-50	250	100	300	90
4	60	-50	250	100	300	90
5	60	-50	250	100	300	90

target was fully dedicated for etching and one for the coating process.

The aim of this work is to present the results of an investigation about the effect of metal ion etching on the properties of TiN coatings deposited on HSS using CAPVD technique (random arc). For this purpose, surface morphology and interface studies were done using field emission scanning electron microscope (FE-SEM; Model LEO-1525). The thickness and adhesion of the deposited coatings was measured using FE-SEM (crosssections). The elemental composition of coated and uncoated samples was analyzed using energy dispersive X-rays (EDX). The hardness of uncoated and coated samples was measured using a micro-Vickers hardness testing machine (Model-H31, Mitutoyo). The surface roughness of the samples was determined using a surface roughness tester (Model-Surftest SJ-301, Mitutoyo) and atomic force microscope (AFM) (Model: SPM-9500J2, Shimadzu Corporation).

# 3. Results and discussion

# *3.1. Scanning electron microscopy with energy dispersive X-rays*

SEM micrographs without and with Ti and Cr metals ion etching are shown in Fig. 1. From Fig. 1(a), it was observed that without metal ion etching, the surface occupies very few and small particles, which protrude through the growing film at the time of deposition. When the Ti ion etching increased to 16 min, a large amount of bigger size particles was observed, as shown in Fig. 1(b). These macro-sized particles produced during the etching phase. This could be said because Fig. 1(a and b) has the same deposition history, except metal ion etching, i.e. 0 and 16 min. In Fig. 1(c), the surface microstructure changed because of the Cr ion etching. In Fig. 1(c), the droplets size is smaller than in Fig. 1(b). It is because of the high melting temperature and vapour pressure of Cr target as compared to Ti target. Furthermore, Fig. 1(c) looks "Wax of Bee Web" with small particles distributed on the surface at various locations. The origin of that

shape was  $Ar^+$  bombardment during metal ion etching and could not be seen without ion etching (Fig. 1(a)). From the physical appearance of the coated samples, it was also observed that the coating deposited without and with 8 and 16 min Cr ion etching have golden colour, whereas the coating deposited with 8 and 16 min Ti ion etching have dark golden colour.

Cr ion etching could decrease significantly the surface roughness in TiN coatings. Fig. 1(c) show smooth surface compared with rough surfaces (in Fig. 1(b)) when Ti ion etching. The reason is that, Cr has smaller radii and higher vapour pressure compared to Ti atoms.

Münz et al. [2] suggested that the majority of MDs are produced during the etching stage and designated 'droplets', as shown in Fig. 1(b) and the part of the present work, whereas during the deposition process they are known, as 'growth defects' (shown in Fig. 1(a)). The dark light and hallow spot in Fig. 1 show some of the re-sputter particles and pitting defects on the coating surfaces, as considered detrimental features of CAPVD technique [4,5]. The density and average sizes of droplets and craters were lower in the steered-arc sample than in the random arc sample [6]. Mustapha and Howson showed that the TiN films examined by SEM deposited by reactive filtered arc evaporation, showed a fine crystalline structure with small grain size of 20-30 nm [7]. Moreover, Fig. 1 shows SEM photograph of spherical and non-spherical macroparticles. From the above discussion, the macroparticles might have their roots in the HSS substrate and lay through the TiN film. Because most of the MDs are apparently different in the case of metal ion etching as compared to droplets observed on the surface of the film during without metal ion etching.

A physical analysis of thickness of the deposited coating for 16 min Ti ion etching is shown in Fig. 2. The qualitative analysis of adhesion between the substrate and coating material can also be seen via cross-section in Fig. 2, which is dense, uniform, and well adhered with the base material. Fig. 3 represents SEM surface micrograph at higher magnification revealing that there is no vacant space to adjust the further atoms within the deposited coating, even for those particles having minimum size.





Fig. 1. SEM micrographs of TiN coating (a) without ion etching, (b) at Ti ion etching for 16 min and (c) at Cr ion etching for 16 min.

The macroparticles, evaporated from the source, become negatively charged by interacting with the electrons, as the latter are more mobile than the plasma ions. The repulsive force between the charged macroparticles and the negatively biased substrate, results in increased adatom mobility at the surface and a uniform deposition. Again, because of the negative bias, the plasma ions strike the substrate surface with higher energy, raising its temperature, smoothing out the film surface with the re-sputtering, from the non-uniform areas of the coating.

The use of the macrodroplet filter reduced the quantity and dimensions of titanium droplets in the TiN coatings deposited



Fig. 2. SEM cross-sectional image showing thickness and adhesion of TiN coating at Ti ion etching for 16 min.



Fig. 3. SEM micrograph at Ti ion etching for  $16 \min (\text{magnification} = 3000 \times)$ .

Table 2
Elemental composition of TiN coating via EDX

Ion etching (min)	Thickness (µm)	N (wt.%)	Ti (wt.%)	Cr (wt.%)	N (at.%)	Ti (at.%)	Cr (at.%)	Total
0	3.850	15.02	84.98	0	37.68	62.32	0	100
Ti for 8	4.109	13.98	86.02	0	35.72	64.28	0	100
Ti for 16	4.354	9.07	90.93	0	25.44	74.56	0	100
Cr for 8	3.903	14.22	84.50	1.28	36.21	62.91	0.88	100
Cr for 16	3.975	12.82	85.59	1.59	33.49	65.39	1.12	100

[8]. The quantity of the droplet phase in the TiN coatings decreased together with the increase in the nitrogen gas flow rate; as well as coatings roughness parameters [3,9]. Table 2 represents the elemental composition of various deposited coating by EDX. From Table 2, it can be concluded that by increasing Ti ion etching, atomic and weight percentages of Ti increased, whereas for coating deposited at Cr ion etching, a small amount of Cr is also observed, as an indication of Cr ion etching during etching phase. A line scan of Fig. 1(b) was also shown in Fig. 4(a), taken during EDX, representing the behaviour of coating composition between two points of deliberatively selected line, showing the trend of elemental composition behaviour in TiN coating.

#### 3.2. Hardness

Substrate hardness and coating hardness were measured using a micro-Vickers hardness testing machine and can be seen in Table 3. Microhardness of the uncoated HSS substrate was about 268  $HV_{0.05}$ . After being coated with TiN, the microhardness increased to about 1577  $HV_{0.05}$  (Ti ion etching for 16 min), which is about 600% of the hardness of the uncoated one. The coating deposited at Cr ion etching for 8 and 16 min showed half the hardness compared to the sample etched at Ti ion etching for 16 min (even less than the coating deposited at zero metal ion etching). The increase in hardness for titanium-etched coatings is mainly because of the formation of TiC phase, which is shown in Fig. 4(b). The effect of indenter load on hardness can be seen in Table 3, as the load increased from 50 to 100 g, the hardness of coating decreased about 100 in all coatings.

According to the Hall-Petch relationship [10], the microhardness varies linearly with the inverse square root of the grain diameter. The enlargement in the crystallite size may be interpreted because of increasing adatom mobility induced by increasing ion energy [8]. As the crystallite size decreases, the number of grain boundaries increases inversely; therefore

Table 3		
Surface roughness a	nd micro-Vickers	hardness



Fig. 4. (a) A line scan of Fig. 1(b) showing qualitative EDX analysis and (b) EDX analysis of TiN coating with carbon.

the dislocation motions by crystallite boundaries may cause an increase in the hardness of the films with smaller crystallite size. A SEM picture shown in Fig. 3, using In Lens Signal during SEM surface studies strengthens the above-mentioned statement.

When the indent load is decreased, the surface hardness of the coating assembly is significantly increased. In fact the measured hardness is not only associated with the substrate effect but also with the influence of the hard TiN coating [11].

No.	$R_a$ (ISO 97, Gauss) $\mu m$	$R_z$ (ISO 97, Gauss) $\mu m$	$R_q$ (ISO 97, Gauss) $\mu m$	HV <sub>0.05</sub> (gram)	HV <sub>0.1</sub> (gram)
1	0.02	0.23	0.03	268	305
2	0.14	3.06	0.29	1302	1198
3	0.25	3.29	0.40	1401	1300
4	0.30	3.69	0.46	1577	1475
5	0.19	2.78	0.32	795	685
6	0.19	2.64	0.30	780	674

Parameters	Metal ion etching (min)							
	0	Ti for 8 min	Ti for 16 min	Cr for 8 min	Cr for 16 min			
$\overline{R_{a}}$ (nm)	20.95	65.2	133.9	46.2	47.06			
$R_{\rm v}$ (nm)	403.03	594.1	911.0	541.7	537.96			
$R_{\rm z}$ (nm)	322.95	421.4	428.6	371.8	367.64			
$R_{\rm ms}$ (nm)	36.12	87.8	169.1	62.1	61.59			
$R_{\rm p}$ (nm)	290.73	378.9	523.8	348.4	310.23			
$R_{\rm v}$ (nm)	112.30	315.4	387.2	193.3	227.73			

Table 4 Surface parameter values of TiN-coated HSS at various metal ion etching

## 3.3. Surface roughness tester

The results of quantitative surface roughness test via surface roughness tester on uncoated and coated HSS coupons are given in Table 3. The roughness of TiN-coated HSS coupons defined by  $R_a$  parameter is within the 0.14–0.30 µm range and is significantly higher than in the case of the uncoated polished sample, i.e. 0.02 µm. The maximum  $R_a$  value was noted for coating where the Ti ion etching for 16 min. The surface roughness increase during etching and coating stages can be attributed to the following factors:

- 1. Occurrence of the characteristic MDs during etching stage (except zero ion etching and less in the case of Cr ion etching).
- 2. Deposition of the pure titanium droplets, bigger in both size and number in the case of Ti ion etching and increased by increasing Ti ion etching.



Fig. 5. Average roughness of uncoated and TiN-coated HSS coupons (a) without ion etching, (b) Ti ion etching for 16 min, and (c) Cr ion etching for 16 min.



Fig. 6. Surface profiles of TiN coating (EVA-L = 4 mm,  $\lambda_c$  = 0.8 mm × 5 mm).



Fig. 7. AFM images (a) without ion etching (b) at Ti ion etching for 16 min and (c) at Cr ion etching for 16 min.

- 3. Pits developing due to the titanium MDs, which dropping out from the substrate surface, immediately after finishing the coating process.
- 4. Growth defects originating probably during sputtering when the particles hit the substrate surface at the time of coating process.

Therefore, the surfaces of the coatings demonstrate inhomogeneities connected with shaped occurrences of the MDs, which re-sputtered during coating process, more pronounced for Ti ion etching.

Harris et al. [9] calculated the roughness of the TiN Coatings on HSS twist Drill, and found that it increased from 0.104 to 0.116  $\mu$ m as the chamber pressure decreased from 1.2 to 0.1 Pa. Golombek et al. [12] measured surface roughness  $R_a$ , parameter value 0.59  $\mu$ m, TiN-coated cement carbides using the CAE technique.

A line bar graph between surface roughness ( $R_a$ ) and metal ion etching can be seen in Fig. 5. A surface profile for sample uncoated and TiN-coated HSS can be seen in Fig. 6. Cr ion etching minimizes the surface roughness of the subsequent coatings [2] and similar results can be seen in term of surface roughness.

#### 3.4. Atomic force microscopy (AFM) studies

Prior to the investigations of TiN coatings, the excellent performance of the AFM was confirmed by imaging a standard sample for calibration provided by the manufacturer. We only selected typical AFM images consisting of well-defined scan area  $10 \,\mu m \times 10 \,\mu m$  morphology.

Fig. 7(a) shows the clear indication of reduction in MDs without metal ion etching. Fig. 7(b) shows large quantity of MDs, whereas Cr ion etching shows very small particles in both size and number. These figures clarify that Fig. 7(b) is about Ti ion etching, whereas Fig. 7(c) about Cr ion etching. It was noted from Table 4 that the minimum value of  $R_{\rm ms}$  was noted 36.12 nm, for the coating deposited at zero metal ion etching and the maximum value 169.1 nm for the coating deposited with Ti ion etching for 16 min with the surface roughness 20.95 nm and 133.9 nm respectively. A rough estimation about the surface roughness can also be made directly from Fig. 7, where Z-max = 300.09 nm (a), 826.72 nm (b), and 471.75 nm (c).

Ion bombardment effectively changes the film morphology, as shown in Fig. 7. One of the problems with ion bombardment is that if not properly controlled, a surface with inadequately removed impurities, and degraded surface morphology, due to the induced surface layer peeling, may develop. In our case, we observed that ion etching led to increased MDs concentration (Fig. 7(b)). Further investigations, of the raw substrate and the ion-bombarded substrate, by AFM revealed (Fig. 7(a and b)) that these microstructures are different from the film MDs in that these were non-spherical. With their origin in the substrate, they protruded out of the subsequently deposited film and appeared as MDs instead of microdroplets!

# 4. Conclusions

SEM analyses showed that all the films had dense structures with clearly defined substrate–film interfacial layers. From the physical appearance of the coatings, the coating colour change from golden for those deposited without and at Cr ion etching and to dark golden deposited at Ti ion etching. Cr ion etching decreases significantly the surface roughness as well as hardness whereas, for Ti ion etching, the behaviour is reversed. The substrate contribution to the hardness increases with decreasing coating thickness. The coatings deposited at Cr ion etching for 8 and 16 min show half the hardness compared to the samples etched at Ti ion etching for 8 and 16 min, less than the hardness for the coating deposited at without ion etching. Surface morphologies of the deposited coatings reveal that MDs produced during etching stage and lay through TiN coatings during deposition process.

#### Acknowledgments

Dr. Mubarak Ali would like to extend his cordial thanks to the Malaysian Government to award the scholarship for PhD study (MTCP 2004/2005), to Government of Pakistan for granting study leave, and to AMREC SIRIM Berhad for the facilities. Dr. Mubarak wishes to thank Dr. Parvez Akhter (Director General, PCRET) and Prof Manzar Abbas (Physics department, Comsats Institute of Information Technology-CIIT, Islamabad) Pakistan for their kind support and encouragement.

## References

- I. Petrov, P. Losbichler, D. Bergstrom, J.E. Greene, W.-D. Münz, T. Hurkmans, T. Trinh, Thin Solid Films 302 (1997) 179–192.
- [2] W.-D. Münz, I.J. Smith, D.B. Lewis, S. Creasey, Vacuum 48 (5) (1997) 473–481.
- [3] A. Mubarak, E. Hamzah, M.R.M. Toff, A.H. Hasim, Surf. Rev. Lett. 12 (4) (2005) 631–643.
- [4] A. Matthews, A.R. Lefkow, Thin Solid Films 126 (1985) 283-291.
- [5] G. Disatnik, R.L. Boxman, S. Goldsmith, IEEE Trans. Plasma Sci. PS-15 (1987) 520–523.
- [6] K. Miernik, J. Walkowicz, J. Bujak, Plasmas Ions 3 (2000) 41-51.
- [7] N.M. Mustapha, R.P. Howson, Vacuum 60 (2001) 361-368.
- [8] G. Håkansson, L. Hultman, J.-E. Sundgren, J.E. Greene, W.-D. Münz, Surf. Coat. Technol. 48 (1991) 51–67.
- [9] S.G. Harris, E.D. Doyle, Y.-C. Wong, P.R. Munroe, J.M. Cairney, J.M. Long, Surf. Coat. Technol. 183 (2004) 283–294.
- [10] N.J. Petch, Prog. Met. Phys. 5 (1954) 1–10.
- [11] P.J. Burnett, D.S. Rickerby, Thin Solid Films 148 (1) (1987) 41-50.
- [12] K. Golombek, L.A. Dobrzański, M. Soković, J. Mater. Process. Technol. 157/158 (2004) 341–347.