Effects of Substrate Surface Roughness and Energy using Pulse DC Substrate Bias during PVD Cleaning on Coating Adhesion

H. Hanizam[1], U. Al-Amani[1], and A.M.H. Effendi[1]

[1]Faculty of Engineering Technology, Universiti Teknikal Malaysia Melaka, Kampus Industri, Ayer Keroh, 75450 Melaka, Malaysia
Phone: +606-2346528, Fax: +606-2346526
Email: hanizam@utem.edu.my, umar@utem.edu.my, hairuleffendi@utem.edu.my

A.R. Md Nizam[2], N. Mohamad[2], and M.S. Salleh[2]

[2]Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Durian Tunggal, 76100 Melaka, Malaysia
Phone: +606-3316002, Fax: +606-3316411
Email: mdnizam@utem.edu.my, noraiham@utem.edu.my, shukor@utem.edu.my,

***Abstract*—The aims of this research are to compare the resultant substrate and coating characteristic between PDC and DC in situ cleaning techniques The in situ cleaning experimental runs for both DC and PDC substrate biases was performed at 500V for 3 hours on WC substrate prior to the deposition of TiN coating. Coating adhesion, substrate surface energy, surface roughnesses were inspected using CSEM scratch tester, wettability test and atomic force microscopy (AFM), respectively. The data was analyzed using Minitab and Excel software. Coating adhesion of samples treated by PDC was higher by 5.0% compared to that of cleaned using DC substrate bias. The analysis suggested that the improvement in adhesion was due to higher substrate surface energy and roughness.**

Keywords: PVD coatings, Pulse direct current, Surface roughness, Coating adhesion, Titanium nitride

I. INTRODUCTION

There are common hard coating materials available to coat machining tools such as TiN, TiC, CrN and ternary materials of TiAlN [1]. Coating with good adhesion often fails cohesively rather than adhesively and usually resulted in superior tool life [2]. Consequently, various processing methods had been developed to improve coating adhesion. For instance, in PVD process, the in situ sputtered cleaning sequence prior to coating help to improve coating adhesion [3]. Furthermore, substrate without bias application during in situ cleaning is hard to obtain good coating adhesion [4]. However, at higher potential different, the tendency of arcing to occur is very high as well and introduces drawbacks to the adhesion [5,6]. Arcing will not only causing problem to the in process substrate, but also to the subsequent substrates because arcing will contaminate the chamber of the machine. Hence, the adhesion quality will be degraded further until proper cleaning and maintenance is carried out [7]. Based on some previous researches, the arcing issue can be solved by having negative PDC bias instead of conventional DC bias applied to the substrate during in situ cleaning. However, there are still less focused and papers that have been published on PDC bias [8,9,10,11] compared to majority of researches using the conventional method of DC bias [12,13,14,15].

A good surface quality of cemented carbide, the critical load of TiN coating is more than 70N can be achieved. Whereas, if the coating is deposited on bad quality of cemented carbide surface, critical loads obtained may be very low, between 10 – 25N [16]. Besides, the PDC coating adhesion mean and median is expected to be higher and the variation to be lower, as compared to DC. Comparison of adhesion properties shall be analyzed using statistical tools, such as, Mann-Whitney test, Two-Sample T-test and F-test: Anova. There are many common statistical software packages available in the market that should be able to do the tests, for examples, Excel, SPSS, SAS, SYSTAT and Minitab [17].

There is still lack of study using PDC over DC substrate bias techniques to improve coating adhesion, especially on the analyses of substrate surface roughness and energy effects to coating adhesion. Therefore, the research objectives are to make direct comparison between the two techniques and to validate the results using common statistical analysis tools.

II. EXPERIMENT DETAILS

A. *Coatings Deposition Process*

The experiments were conducted using a magnetron sputtering Vactec, PVD 1000 system from Korea. The machine is equipped with an ENER5 pulse power supply that has a pulse direct current (PDC) substrate biasing up to 800V and frequency range between 0 – 100 kHz. The holder rotary speed was set at 2RPM throughout the deposition process. Titanium (Ti) and Tungsten carbide (WC) cutting tool inserts by Sumitomo were used as target and substrate materials, respectively. The substrates were soaked in ethanol solution using ultrasonic machine JAC Ultrasonic 1505 at 42ºC for 30minutes. Machine chamber was vacuum pumped down to $5.0x10^{-5}$mbar and process temperature was to 400ºC. When the vacuum chamber reached setting temperature, a 50sccm pure Ar gas with a purity of 99.999% was pumped into the chamber through an ion gun outlet power at a setting of 0.24kV/0.4A until the process pressure dropped to 3.0 x 10^{-3}mbar. Biases of substrates were set at similar voltage level of -500V for PDC at frequency of 50kHz (duty cycle 20%) and DC at constant voltage for 30minutes [18].

Deposition process was carried out for 3 hours at deposition rate of 3.90 x 10^{-3}µm/min. A 99.999% purity of reactive nitrogen gas was pumped at 0.5 x 10^{-3}mbar into the chamber at ratio 0.12:1 of N_2:Ar. Substrate bias set at -250V, target power of 6kW and temperature of 400ºC for 5 minutes for Ti interlayer and 180 minutes for TiN coating.

B. Testing on Coating Adhesion and Substrate Surface Properties

The coating adhesion tests were conducted using a scratch tester by CSEM, Revetest fitted with a Rockwell C diamond stylus (200µm tip radius; cone apex angle 120º). A progressive load from 0.9N to 200N was applied for total scratch length of 5.0mm. The loading rate and speed were constant at 382.67N/min and 9.61mm/min, respectively. The equipment is attached to an acoustic emission monitoring device within vicinity of 100 kHz for failure detection.

Surfaces of post in situ cleaning were inspected using non-contact mode AFM, Park System XE-100 model. The topography’s scanning area X-5µm x Y-5µm, and analyses were performed at scan rate of 0.5Hz.

Wettability test uses contact angle of a water drop to a surface as a measurement of surface energy level (Paital and Dahotre. *et al.*, 2009). The meniscus of contact angle between the surface and pure water was measured between 0 and 180º. The interfacial surface energy (γ) equation of a material surface in relation to a liquid as derived by Young as shown in (Equation 1) [19], as following:

$$\gamma_{lv} \cos\theta + \gamma_{sl} = \gamma_{sv} \qquad (1)$$

Where, γ_{lv} is liquid - vapor interfacial tension; γ_{sv} is substrate surface - vapor interfacial tension; γ_{sl} is liquid - surface interfacial tension; θ is contact angle. Hence, at lower θ value shall reflect higher substrate surface energy. The static contact angle was observed using a digital 800k USB 2.0 CCD DCAM and VIS ver7 (Professional Edition) software which allows auto calculations of the angles.

Finally, a Minitab software version 16 and Excel software were utilized to perform statistical analyses and validate the results of DC and PDC coating adhesions and substrate surface properties.

III. Results and Discussion

A. Coating Adhesions of DC and PDC Treated Samples

Results of TiN coating adhesions or critical loads obtained from the scratch tests are tabulated in Table 1.

TABLE I. : Coating Adhesion Values of DC and PDC Substrate Biases

Sample	**Critical Load (coating adhesion)/ Newton (N)**	
	DC -500V	PDC -500V
1	68.8	72.3
2	69.8	76.3
3	68.0	75.3
4	66.3	75.3
5	66.0	75.0
6	69.8	76.8
7	68.8	77.0
8	68.8	77.8
9	68.0	77.5
10	70.3	77.8
11	72.3	70.3
12	73.3	69.3
13	68.5	72.0
14	76.5	75.3
15	73.3	75.3
Mean	69.9	74.9
Range	10.5	8.5
Std Dev	2.849	2.698

The mean adhesion (critical load) values for DC and PDC were 69.9N and 74.9N respectively. Analysis of means using the Two-sample t-test had shown that the P-value is less than a critical factor value of 0.05. In other words, there is a significant difference between the two means, DC and PDC at -500V.

Fig. 1 shows the box plot with significant improvement on coating adhesion in means of about 7.0% comparing DC to PDC mean values of the experimental data. The data distribution of PDC shows a 5.0% improvement in term of their standard deviations and has more normal distributed data compared to DC, which indicates more predictable coating adhesion strength.

PDC substrate bias technique does have a positive impact to substrate readiness prior to coating deposition and increases coating adhesion properties [2]. In addition, PDC enhances ionization and electron density in a plasma environment compared to DC, which increases the sputtering rate during in situ cleaning. Moreover, it eliminates arcing that might damage substrate surface, and produces better consistency of cleaning capability. Finally, PDC leads to more uniform and higher coating adhesion compared to comparable DC working conditions [8].

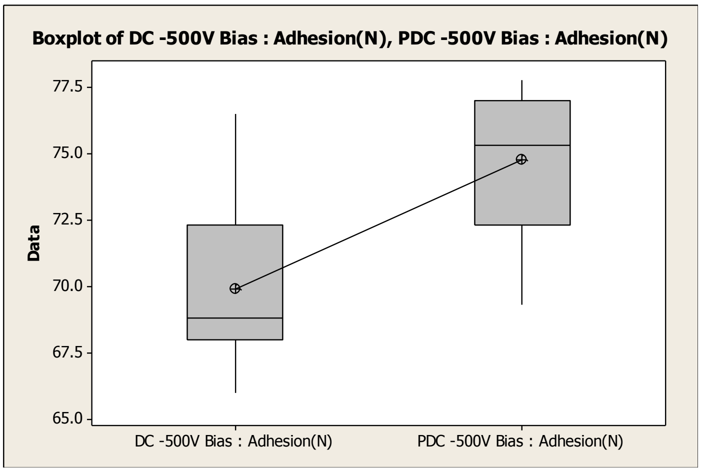


Fig. 1: A box plot of DC and PDC at -500 V Bias

The results of PDC coating adhesion samples are significantly higher and more consistent compared to DC. Therefore, this data analysis supports the conclusion being made that, PDC substrate bias is more effective to clean the substrate surface during in situ cleaning and leads to higher coating adhesion compared to DC.

B. Comparison of Substrate Surface Roughness between DC and PDC

Table 2 shows the AFM results of WC substrate surface roughness, R_a, for PDC and DC at -500 V substrate bias voltages during in situ cleaning.

TABLE II. : SUBSTRATE ROUGHNESS AND COATING ADHESION RESULTS BETWEEN DC AND PDC

Criteria	Substrate Bias Technique		Improvement % from DC to PDC
Bias (V)	DC -500	PDC -500	26.5%
R_a (nm)	63.197	45.882	

Based on the results, PDC shows reduction of about 26.5% in surface roughness if compared to DC. It was a direct indication of no excessive sputtering process taken place onto the substrate surface during cleaning process. In other words, pulse bias allows better control in term of sputtering rate with minimum unwanted arcing issues and helps to prevent the excessive bombardments effect [8, 11]. In addition, lower surface roughness increases surface area and minimize shadowing effect during the deposition process.

Surface of DC treated substrate as in Fig. 2a shows coarser surface grain compared to the PDC treated substrate in Fig. 2b. Hence, the observation is good agreement with surface roughness data obtained using the same AFM. Moreover the surface grain structure of PDC treated substrate in the form of globular or angular shape rather than spikes of peaks and valleys in DC treated substrate. Therefore, indicates that PDC not only produces finer surface grain but also improves its structure. The R_a observed in DC treated substrates depicts irregularity in its grain structure. It might due to arcing phenomenon during in situ cleaning process and resulted in severe adhesion defect. The result of coating adhesion decreases with increasing roughness of the substrate surface similar to previous observation [5].

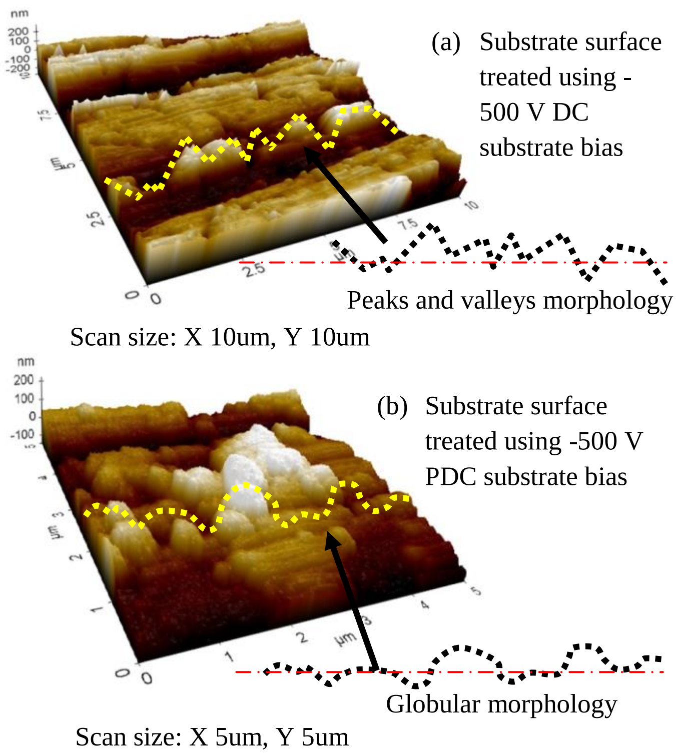


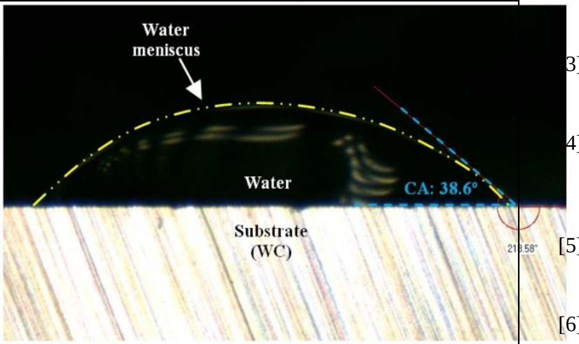
Fig.2: AFM three-dimensional images of WC substrate surface inspected area formerly treated by (a) DC and (b) PDC substrate biases

C. Comparison of Substrate Surface Energies

Fig. 3 shows the results of contact angles of PDC and DC treated substrate. By altering the substrate bias from conventional DC bias to PDC bias at -500V, the substrate experienced reduction in contact angle. Based on Young Equation (1), the surface energy (γ_{sv}) is inversely proportionate to contact angle ($\cos\theta$). So, it can be directly concluded that the utilization of PDC bias is efficient to increase the surface energy of substrate surface compared to DC bias by 5.6%.

Fine globular and homogenous grain microstructure produce better coating adhesion compared to peaks and valleys. Wider area shall provide higher surface energy that allows interactions via formation of Van der Waals bonding between substrate and coating materials for better adhesion [20].

<table>
<tr><th>In Situ/Contact Angle</th><th>Image : A drop of water on substrate</th></tr>
<tr><td>DC
-500 V

Contact Angle:
38.6 º</td><td>
</td></tr>
<tr><td>PDC
-500 V

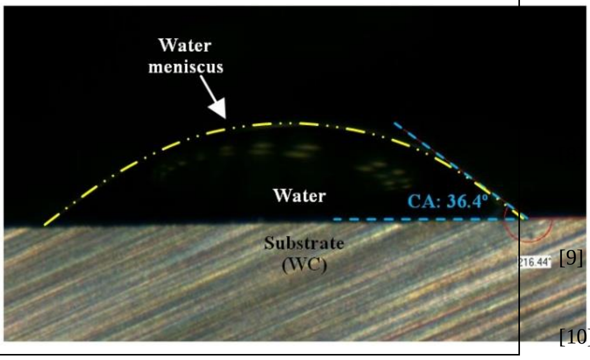
Contact Angle:
36.4 º</td><td>
</td></tr>
</table>

Fig. 3: Water drop wetting ability of WC substrate at DC -500 V and PDC -500 V

IV. Conclusion

These analyses conclude that PDC substrate bias is more effective to clean the substrate surface during in situ cleaning compared to DC substrate during in situ cleaning process. The coating adhesion strength improved by 7.0% and its variation reduced by 5.0% by applying PDC compared to DC at -500V of substrate bias during in situ cleaning. The improvement trends are contributed by the change on substrate surface morphology properties. The modifications of substrate surface morphology properties in terms of surface roughness reduction of 27.4% and surface energy increment of 5.6% and surface morphology patterns shifted from peaks and valleys to globular microstructures of PDC compared to DC bias techniques. The data was analyzed using statistical analysis of t-test and the results were significant.

Acknowledgment

Thanks to University Technical Malaysia Melaka (UTeM) and fellow researchers and especially to Dr. Md Nizam Abd Rahman, for his guidance and support throughout the studies.

References

[1] J. Patscheider, T. Zehnder, M. Diserens, (2001) Structure–Performance Relations in Nanocomposite Coatings. *Surface & Coatings Technology*, vol.147, pp.201-208.

[2] M, Lattemann, A.P. Ehiasarian, J. Bohlmark, P.A.O Persson, U. Helmersson, (2006) Investigation of High Power Impulsed Magnetron Sputtering Pretreated Interfaces for Adhesion Enhancement of Hard Coatings on Steel. *Surface and Coating Technology*, vol. 200, pp. 6495-6499.

[3] K. Koski, J. Holsa, J. Ernoult, A. Rouzaud, (1996) The Connection Between Sputter Cleaning and Adhesion of Thin Solid Films *Surface and Coating Technology*, vol.90, pp. 195-199.

[4] L.A. Dobrzański, and M. Staszuk, (2011) Surface Modification of Sialon Ceramics and Cemented Carbides by PVD Coating Deposition. *Journal of Achievements in Materials and Manufacturing Engineering*, vol. 49, pp. 158-165

[5] C. Mitterer, O. Heuz, V.H. Derttinger, (1997) Substrate and Coating Damage by Arcing During Sputtering. *Surface and Coatings Technology*, vol. 89, pp. 233-238.

[6] K. Sarakinos, J. Alami, S. Konstantinidis, (2010) High Power Pulsed Magnetron Sputtering: A Review on Scientific and Engineering State or the Art. *Surface and Coating Technology*, vol.204, pp. 1661-1684.

P. Panjan, M. Cekada, M. Panjan, D. Kek-Merl, F. Zupani, L. Curkovi, S. Paskvale, (2012) Surface Density of Growth Defects in Different PVD Hard Coatings Prepared by Sputtering. *Vacuum*, vol.86, pp. 794-798.

K.E. Cooke, J. Hamsphire, W. Southall, D.G. Teer, (2004) The Industrial Application of Pulsed DC Bias Power Supplies in Closed Field Unbalanced Magnetron Sputter Ion Plating. *Surface and Coating Technology*, vol. 177-178, pp. 789-794.

[9] Y. Wei, and C. Gong, (2011) Effects of Pulsed Bias Duty Ratio on Microstructure and Mechanical Properties of TiN/TiAlN Coatings *Applied Surface Science*, vol.257, pp. 7881-7886.

[10] E. Vogli, W. Tillmann, U. Selvadurai-Lassl, G. Fischer, J. Herper, (2011) Influence of Ti/TiAlN-Multilayer Designs on Their Residual Stresses and Mechanical Properties. *Applied Surface Science*, vol. 257, pp. 8550-8557.

[11] H. Tanoue, M. Kamiya, S. Oke, Y. Suda., H. Takikawa, Y. Hasegawa, M. Taki, M. Kumagai, M. Kano, T. Ishikawa, H. Yasui, H. (2009) Argon-dominated Plasma Beam Generated by Filtered Vacuum Arc and Its Substrate Etching. *Applied Surface Science*, vol.255, pp. 7780-7785.

[12] D. Yu, C. Wang, X. Cheng, F. Zhang, (2008) Optimization of Hybrid PVD Process of TiAlN Coatings by Taguchi Method. *Applied Surface Science*, vol.255, pp. 1865-1869.

[13] P.J. Kelly, T.V. Braucke, Z. Liu, R.D. Arnell, E.D. Doyle, (2007) Pulsed DC Titanium Nitride Coatings for Improved Tribological Performance and Tool Life. *Surface and Coating Technology*, vol.202, pp. 774-780.

[14] M. Audronis, P.J. Kelly, A. Leyland, A. Matthews, (2006) Microstructure of Direct Current and Pulse Magnetron Sputtered Cr-B Coatings. *Thin Solid Film*, vol. 515, pp. 1511-1516.

[15] C.H. Barshilia, and K.S Rajam, (2006) Reactive Sputtering on Hard Nitride Coatings Using Asymmetric-Bipolar Pulsed DC Generator. *Surface and Coating Technology*, vol. 201, pp. 1827-1835.

[16] [V. Braic, M. Balaceanu, I. Tudor, A. Popescu, M. Braic, G. Pavalescu, R. Zamfir, (2002) Properties of Titanium Based Hard Coatings Deposited by The Cathodic Arc Method. *Journal of Optoelectronics and Advanced Materials*, vol. 4, pp. 115-120.

[17] G.D. Ruxton, (2006) The unequal variance t-test is an underused alternative to Student's t-test and the Mann–Whitney U test. *International Society for Behavioral Ecology*. ark.016, pp. 688-690

[18] H. Hanizam, A.R. Mohd Soufhwee, A.R. Md Nizam, N. Mohamad, K.A. A Rahman, (2013) The Effect of Pulse DC and DC Substrate Bias during in situ Cleaning PVD Process on Surface Roughness Procedia Engineering 53, 562-568

[19] M. Cartier, M.T Neale, M.P. Polak, (Eds.) (2003). *Handbook of Surface Treatments and Coatings*.

[20] E. Lugscheider, and K. Bobzin, (2001) The Influence on Surface Free Energy of PVD-coatings. *Surface & Coatings Technology*, vol. 144, pp. 755-760.