UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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EFFECT OF IN SITU DC AND PDC SUBSTRATE BIAS CLEANING PROCESS ON TiN COATING ADHESION IN PVD SYSTEM

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ABSTRACT

This research compared the effect of PDC and DC substrate biases applications at -500V and study the effect of PDC voltage variations (0V, -200V, -500V, -800V) during substrate cleaning on coating adhesion. The substrate and coating materials used were tungsten carbide (WC) and titanium nitride (TiN), respectively. Aside from adhesion, data on surface roughness, surface energy, crystallite size and crystal orientation were also collected to further explain the experimental results. Statistical analyses such T-Test, ANOVA, and Regressions Analysis were conducted on the collected data using Minitab and EXCEL software. The results of this research indicated that coating adhesion on specimen using PDC as substrate bias exhibited significantly higher coating adhesion (7%) compared to that of the DC substrate specimen. In addition, substrate's surface roughness reduced by 38%, crystallite size reduced by 10% and surface energy increased by 5.7% that lead to the adhesion improvement trend from DC to PDC. The study also indicated that as PDC voltage increased, coating adhesion also increased linearly and the coefficient of determination R^2 value of 0.961 between the two indicates a strong correlation. The results of PDC substrate bias also indicated linear correlations between surface roughness and surface energy to coating adhesion with R^2 values of 0.982 and 0.903, respectively.

ABSTRAK

Kajian ini membandingkan kesan DC di substratum pada voltan -500V dan PDC voltan berbeza (0V, -200V, -500V, -800V) semasa pembersihan didalam kebuk keatas daya lekatan salutan. Bahan substratum yang digunakan adalah tungsten carbide (WC) dan bahan salutan adalah titanium nitride (TiN). Selain daya lekatan, data kekasaran permukaan, daya permukaan, saiz kristal dan orientasi kristal juga dikumpul untuk menerangkan hasil-hasil daripada ekperimen yang dijalankan. Analisa statistik seperti T-Test, ANOVA, dan Regression Analysis juga dijalankan menggunakan sofware Minitab dan Excel. Keputusan hasil daripada kajian ini menunjukkan daya lekatan salutan keatas substratum menggunakan PDC adalah 7% lebih tinggi berbanding DC. Selain itu, kekasaran permukaan substratum juga berkurangan sebanyak 38%, saiz kristal sebanyak 10% dan daya permukaan meningkat sebanyak 5.7% menyebabkan daya lekatan salutan bertambah daripada DC kepada PDC. Disamping itu juga, apabila voltan PDC yang meningkat, daya lekatan salutan juga akan meningkat sejajar dengan peningkatan voltan yang nilai R^2 adalah 0.961. Hasil daripada aplikasi PDC juga menunjukkan hubungan sejajar diantara kekasaran permukaan dan daya permukaan kepada daya lekatan salutan dengan nilai R^2 adalah 0.982 dan 0.903.

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DECLARATION

I hereby declared this report entitled "Effect of in situ DC and PDC substrate bias cleaning process on TiN coating adhesion in PVD system" is the results of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : HANIZAM BIN HASHIM

Date : 13 SEPTEMBER 2013

DEDICATION

Dedicated to my beloved family and friends

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LIST OF ABBREVIATIONS

PVD	-	Physical Vapor Deposition
CVD	-	Chemical Vapor Deposition
DC	-	Direct Current
PDC	-	Pulse Direct Current
XRD	-	X-ray Diffraction
SEM	-	Scanning Electron Microscope
EDX	-	Energy-dispersive X-ray Spectroscopy
AFM	-	Atomic Force Microscope
RPM	-	Revolution per Minute
SCCM	-	Standard Cubic Centimeters per Minute
CCD	-	Charge-couple Device
DCAM	-	Digital Camera
R^2	-	Coefficient of Determination

LIST OF SYMBOLS

Ar	-	Argon
N_2	-	Nitrogen
O_2	-	Oxygen
CO_2	-	Carbon dioxide
WC	-	Tungsten Carbide
TiN	-	Titanium Nitride
TiC	-	Titanium Carbide
CrN	-	Chromium Nitride
ZrN	-	Zink Nitride
TiAlN	-	Titanium Aluminum Nitride
Mo	-	Molybdenum
Nb	-	Niobium
Co-Cr	-	Cobalt Chromium
UV	-	Ultra violet
AC	-	Alternating Current

LIST OF PUBLICATIONS

Journal

1. Hanizam. H, A.R. Md Nizam, N.Mohamad, Soufhwee. A.R. and K.Anuar A.R. (2012) The Effect of Pulse DC and DC Substrate Bias during In Situ Cleaning PVD Process on Surface Roughness. *Procedia Engineering 53 (2013) pp 562 – 568.*

2. Hanizam. H, A.R. Md Nizam, N.Mohamad and Soufhwee. A.R. (2012). Surface Energy and Crystallite Size Comparisons by Applying Direct Current on Substrate Bias in PVD Process. *Applied Mechanics and Materials Vol. 315 (2013) pp 98-102.*

Proceeding

1. Hanizam. H, A.R. Md Nizam, N.Mohamad and Soufhwee. A.R. (2012). Surface Energy and Crystallite Size Comparisons by Applying Direct Current on Substrate Bias in PVD Process. *Proceeding of 3rd International Conference on Mechanical and Manufacturing Engineering 2012.* 20 – 21st November 2012. Johor, Malaysia.

2. Hanizam. H, A.R. Md Nizam, N.Mohamad, Soufhwee. A.R. and K.Anuar A.R. (2012) The Effect of Pulse DC and DC Substrate Bias during In Situ Cleaning PVD Process on Surface Roughness. *Malaysian Technical Universities Conference on Engineering and Technology 2012.* 20 - 21st November 2012 Perlis, Malaysia.

3. Hanizam. H, A.R. Md Nizam, N.Mohamad, Soufhwee. A.R. and Hassan, A. (2012) Nitrogen Gas Partial Control Effects on Titanium Nitride Coating's Thickness and Color over Tungsten Carbide Substrate using PVD. *Proceeding of 2nd International Conference on Conference on Design and Concurrent Engineering and Concurrent Engineering 2010.* 15 -16th October 2012 Melaka, Malaysia.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Physical Vapor Deposition (PVD) thin film coating process has been extensively used by manufacturers in many thin film coating applications. PVD is more environmental friendly process compared to other coating techniques such as Chemical Vapor Deposition (CVD) (Navinsek *et al.*, 1999). Common applications of PVD thin film coating are tinted glasses, jewelries, watches, molds, decorative parts, sliding parts and cutting tools (Tanoue *et al.*, 2009). Furthermore, additional micro layer coating will not only increase the value and better appearance, but also will prolong the life of the base products (Bobzin *et al.*, 2005; Santos *et al.*, 2004). In addition, coating helps to prevent corrosion to the product (Fenker *et al.*, 2002).

In cutting tool technology, having additional hard thin film coating over a cutting tool will prolong the tool life significantly (Laing *et al.*, 1999; Gekonde and Subramanian, 2002; Bouzakis *et al.*, 2010). Furthermore, good coating quality will boost up productivity, reduce production costs, remains competitive and more profitable (Mubarak *et al.*, 2005; Sahoo and Sahoo, 2011). According to Dowey and Matthews (1998), the 25% increase in cost of cutting tool due to coating process of the uncoated tools is overcome by 40% reduction in the relative lost of quality. This benefit is the main driving factor to explore for better solutions and optimizations of PVD coating process.

A typical PVD coating process consists of three process sequences, external cleaning, in situ cleaning and coating deposition (Mattox, 2010). Currently, research on new methods, discoveries and implementation activities of each process are still actively evolved. There were many studies carried out and published on each segment for the last few decades. For instance, in external cleaning process, there were numerous alcohol (Vogli *et al.*, 2011; Yu *et al.*, 2008; Kelly *et al.*, 2007; Lattemann *et al.*, 2006) and alkaline (Hofmann et al. 1996) based chemicals used to clean the substrate surface using an ultrasonic machine itself. The selection of chemicals used normally based on types of material surface. Some rough and oxidized surface may require mechanical abrasion, sand blasting, or other cleaning methods prior to ultrasonic cleaning.

Similarly, studies on in situ cleaning parameter optimization are constantly being conducted. Some of the parameters evaluated are gas pressure, temperature, power and bias voltage (Cooke *et al.*, 2004). In situ cleaning process is essential since substrate external cleaning process usually is not able to clean the surface completely (Hofmann *et al.*, 1996). A poor in situ cleaning process will lead to low coating adhesion and unexpected failure during machining (Mattox, 2010). According to Braic *et al.* (2002), a good surface quality of cemented carbide (WC), critical load of TiN coating is more than 70 N can be achieved. Hence, in situ process is the main focus of the study.

PVD coating deposition method is still facing rapid improvement trend activities for various types of materials and applications. One of the significant improvements made to the process is by changing from conventional DC bias on the substrate to PDC bias. According to Kelly *et al.* (2007), the deposition of TiN coating over high speed steel (HSS) using PDC substrate bias enhances physical and tribological properties of the coating compared to DC substrate bias.

Summary of available results and findings from previous research works shows that there is still gap to be explored in applying PDC biasing concepts to a substrate during in situ cleaning process to ensure better surface readiness prior to film coating (Lattemann, *et al.,* 2006). In addition, sudden drop in negative potential of the PDC bias substrate allows higher biasing without arcing (Mattox, 2010; Gangopadhyay *et al.*, 2010). Problem of arcing is a very common issue when high bias voltage is applied to the substrate. Subsequently, at higher potential, inert gas ions gained more energy and moved at a faster speed to give in greater impact and bombardment to the substrate surface. As a result, not only more contaminants, but also more atoms in the outer layer will be expelled out from the substrate surface. This enables modification of substrate surface properties for superior adhesion between coating and substrate surface.

1.2 Problem Statement

Application of PDC substrate bias during deposition process had shown some improvements on mechanical properties of the film coating, for examples, higher hardness and wear rate compared to DC substrate bias (Kelly *et al.*, 2007). However, studies on the effect of PDC technique during in situ cleaning is still lacking. Based on literature reviews, works of PDC technique during in situ cleaning are limited to surface roughness, pulse frequency and adhesion values and without direct comparison to DC. Including, the contributory factors for the results and the effects over a range of PDC substrate bias voltages. In other words, correlations between substrate morphology properties, coating adhesions and PDC voltages are still unclear.

1.3 Research Objectives

The aims of the research are to assess and compare the coating adhesions of coated samples that have been subjected to PDC and DC substrate biases during PVD in situ cleaning process. In addition, the correlation between the coating adhesions and PDC substrate bias voltage variations is also explored. The specific objectives of the research are listed below;

- To investigate the substrate surface morphology and crystallite size differences at post PDC and DC in situ cleaning process.
- To analyze the substrate surface energy differences at post PDC and DC in situ cleaning process.
- To correlate the effects between PDC substrate bias voltage variations and coating adhesions.
- To study the effects of PDC and DC substrate biases on coating adhesion.

1.3 Scope of Study

The research was carried out using an unbalanced magnetron PVD system with tungsten carbide (WC) and titanium nitride (TiN) as a substrate and coating materials, respectively. The TiN coating was reactively synthesized using Ti target and nitrogen gas (N_2). Inert argon (Ar) gas was utilized as a sputtering agent during in situ cleaning and deposition processes. Common inspection tools were used to study the effects of substrate surface morphology, crystallite size and surface energy such as a profiler, XRD and wettability test, respectively. Whereas, coating adhesion and thickness were inspected using scratch test and SEM/EDX. Data of coating adhesions and substrate surface properties were analyzed using Minitab statistical and Excel software.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This section covers the overviews of PVD processes, reviews on results and findings from published works related to this research topic. Besides that, the reasoning for selecting materials, processes, critical parameters, characterization methods and statistical analysis of this research are also discussed.

2.1 Physical Vapor Deposition (PVD)

In general, there are two common thin film deposition techniques of carbide cutting tools, namely a chemical vapor deposition (CVD) and physical vapor deposition (PVD) (Prengel *et al.*, 2001). In CVD technique, the source of coating materials comes from either gaseous of chemical decomposition, displacement or reduction. The materials are breakdown from one phase into two or more phases or simpler compounds through electrons transfer between species (Cartier *et al.*, 2003). Whereas in PVD, the source of coating is from excitation of solid surface material and transfer through the vapor phase to another solid surface (Carter and Norton, 2007). Some advantages of PVD over other techniques are its versatility to deposit various compositions of coating materials with high purity to any metal or alloy and able to produce an excellent coating over a wide range of process temperature. Another desirable impact of PVD is its effectiveness and less harmful to the environment (Navinsek *et al.*, 1999). Overall, PVD processes can be divided into three sections as illustrated in Figure 2.1.

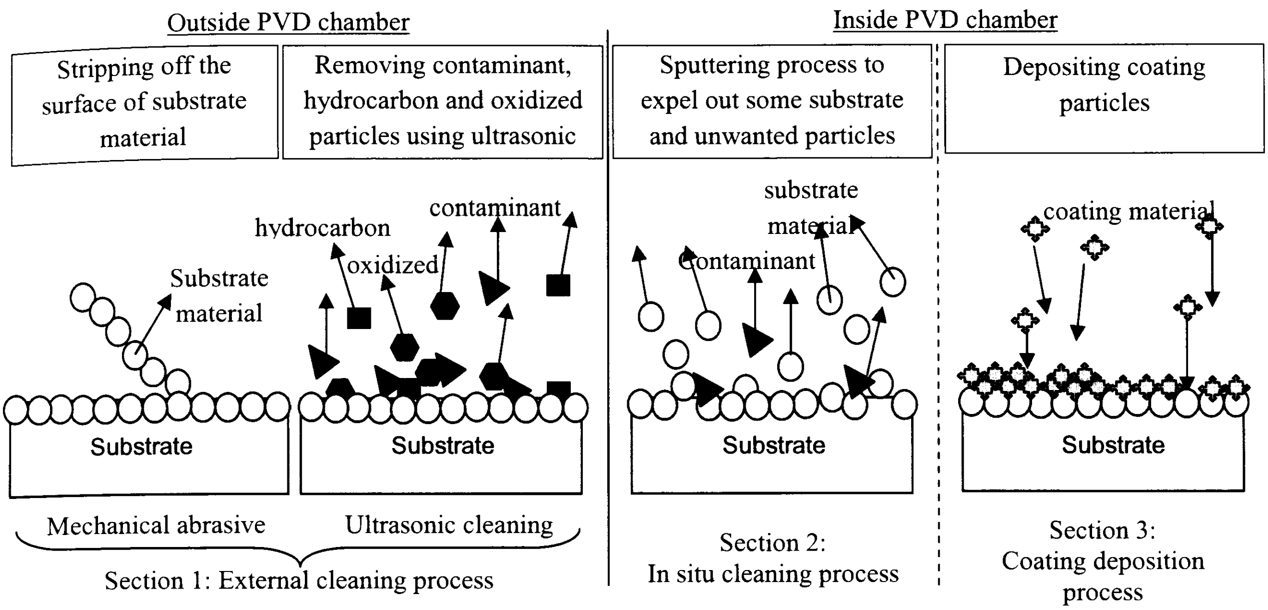

Figure 2.1: Illustration of external cleaning, in situ cleaning and coating deposition of PVD processes

Each section must be optimized in order to obtain optimum coating performance. There are many papers published on parameter optimizations, alternative and improvement of processes start from external cleaning up to the post deposition processes as mentioned in Table 2.1. Some of PVD critical process parameters are substrate bias methods, substrate temperature, inert to reactive gas ratio and sputtering power (Nizam *et al.*, 2010). The inert gas such as argon and krypton do not react with other materials. Unlike, the reactive gas is chemically reactive to other substances. Bouzakis *et al.* (2007) discovered that prolong inert gas ions bombardment after deposition process leads to denser film coating and extend tool life. The positive argon ions (Ar^+) will accelerate and bombard the negatively charged coated substrate and harden the coating. Some of the previous works of techniques carried out in the past to improve TiN coating are tabulated in Table 2.1.

Table 2.1: Examples of deposition techniques to improve TiN coating properties

Reference	Focus area	Substrate /Bias /Temperature/ gas ratio/	Related to process: Conclusions
(Jones. *et al.*, 2000)	TiN coating on different substrate surface preparations; wet grinding papers of 400, 800, 1200 and 4000 grits.	Titanium disc/ not available/ 200°C/ 85:15	Pre deposition process: TiN coating quality is partly dependent on the nature of underlying substrate
(Chun, 2010)	TiN coating using different substrate bias voltages DC - 0V, -100V, -500V and - 900V.	Silicon/ -0 to - 900V/ 300°C/ 10:3	Substrate Bias: TiN texture changed from 111 to 200, from a higher to a lower substrate bias voltage.
(Wei *et al.*, 2002)	TiN coating at different deposition temperatures between 380°C to 520°C.	Stainless Steel/ DC - 200V/ 380°-520°C/ 80:20	Process temperature: Optimum temperature during deposition between 460-480°C for highest micro hardness.
(Vaz *et al.*, 2005)	The influence of nitrogen content on TiN coating properties.	High Speed Steel/ DC - 70V/ 250°C/ 0Pa to $3x10^{-2}$ Pa	Gas mixture: Nitrogen content in TiN coating decreases with increase nitrogen gas ratio during deposition.
(Gerth and Wiklund, 2008)	The influence of interlayers, tungsten (W), Molybdenum (Mo), Niobium (Nb), Chromium (Cr) on TiN coating adhesion.	High Speed Steel/ DC - 110°C/ 300°C-400°C/ 2.5:1.5	In process: Additional interlayer of Mo or Nb showed better coating adhesion over W and Cr.
(Rubiniec *et al.*, 2010)	The influence of duplex coatings compared with single layer coating to TiN coating adhesion.	Hot Work Steel/ not available/ 450°C/ not available	Post process: Duplex coating improves coating adhesion

2.1.1 Sputtering Deposition Process

In general, PVD coating deposition of TiN thin film coating steps are illustrated in Figure 2.2. The vacuum pump extracts the air from coating chamber to achieve process pressure in the range of 10^{-5} to 10^{-7} mbar. Low pressure condition allows