PROJECT COMPLETION REPORT

FOR

SHORT TERM RESEARCH GRANT

DEPOSITION AND CHARACTERIZATION OF TIN COATED PVD SPUTTERING OF MAGNETIZED SUBSTRATE

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ABSTRACT

External magnetic fields are applied by mounting permanent magnets on the substrate holder in the Physical Vapor Deposition (PVD) magnetron sputtering machine. Three experiments are performed including the transverse permanent magnet, the parallel permanent magnet and without permanent magnet. The materials investigated are Tungsten Carbide inserted with cobalt contents of 3.09, 6.58 and 7.60 wt.%. The objectives of the study are to develop a systematic method to create a magnetic field at the vicinity of substrate surface, to assess the impact of substrate magnetic field on the deposited coating (TiN) properties using DOE approach and to characterize and evaluate the coating performance that includes hardness, thickness, crystallographic and coating adhesion. The coating thickness is obtained by using Field Emission Scanning Electron Microscopy (FESEM) while the coating structure and morphology are obtained by using X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM), respectively. The coating hardness and adhesion are obtained by using micro-hardness test and indentation test. Analysis of the coating thickness shows that generally the coating thickness increases when transverse permanent magnet at the substrate holder is used. At 7.60 wt. % cobalt content, the thick coating (~800 nm) is achieved by using the transverse permanent magnet due to high ions density around the substrate for the bombardment of growing film. The coating hardness, structure and morphology are significantly influenced by using transverse permanent magnet at the substrate holder while the interaction of cobalt content and transverse permanent magnet significantly influences the adhesion strength due to the coating densification or re-sputtering of deposited atom. This indicates that applying external magnetic fields by mounting transverse permanent magnets on the substrate holder has an ability to change the quality of the TiN coating.

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ABSTRAK

Medan magnet luar digunakan dengan memasang magnet kekal di pemegang substrat dalam mesin deposisi wap fizikal (PVD). Tiga eksperimen dilakukan termasuk magnet kekal melintang, magnet kekal selari dan tanpa magnet kekal. Bahan-bahan yang disiasat adalah tungsten karbida dengan kandungan kobalt 3.09, 6.58 dan 7.60 wt.%. Objektif kajian ini adalah untuk membangunkan satu kaedah yang sistematik untuk mewujudkan medan magnet di sekitar permukaan substrat, untuk mengesan pengaruh medan magnet terhadap lapisan (TiN) menggunakan rekabentuk eksperimen (DOE) dan untuk mencirikan dan menilai prestasi lapisan termasuk kekerasan, ketebalan, kristalografi dan lapisan lekatan. Ketebalan lapisan diperolehi dengan menggunakan pelepasan field mengimbas mikroskop elektron (FESEM). Struktur lapisan dan morfologi diperolehi dengan menggunakan pembelauan x-ray (XRD) dan mikroskop daya atom (AFM). Kekerasan dan lekatan salutan diperolehi dengan menggunakan ujian kekerasan dan ujian lekukan. Analisis ketebalan lapisan menunjukkan bahawa umumnya ketebalan salutan itu meningkat apabila magnet melintang digunakan. Pada 7.60 % kandungan kobalt, salutan tebal (~ 800 nm) dicapai dengan menggunakan magnet kekal melintang disebabkan kepadatan ion yang tinggi di sekeliling substrat untuk pengeboman filem yang semakin meningkat. Kekerasan salutan, struktur dan morfologi yang ketara dipengaruhi oleh penggunaan magnet kekal melintang manakala interaksi kandungan kobalt dan penggunaan magnet kekal melintang mempengaruhi lekatan lapisan. Ini menunjukkan bahawa penggunaan medan magnet luaran secara melintang mempunyai keupayaan untuk mengubah kualiti lapisan TiN.

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DEDICATION

To Abang Mef'at,

without you I could not have completed this dissertation.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ANOVA	Analysis of Variance
DOE	Design of Experiment
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
PVD	Physical Vapor Deposition
RMS	Root Mean Square
TiN	Titanium Nitride
VSM	Vertical Sample Magnetometer
WC	Tungsten Carbide
XRD	X-Ray diffraction

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LIST OF SYMBOLS

A	-	Ampere
Al	-	Aluminium
Ar	-	Argon
B	-	Magnetic field
C	-	Carbide
°C	-	Celsius degree
d	-	Crystal plane spacing
D	-	Crystal size
D	-	Indentation depth
e^-	-	Electron
E	-	Electric field
H	-	Strength magnetic field
I	-	Current
kgf	-	Kilogram-force
λ	-	Wave length
m	-	Meter
M	-	Magnetization
N, N_2	-	Nitrogen
N	-	Newton
N	-	North
nm	-	Nanometer (10^{-9} meter)
P	-	Pressure
Pa	-	Pascal
R_a	-	Average surface roughness
S	-	South

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s	-	Second
sccm	-	Standard centimetre per cubic
T	-	Temperature
Ti	-	Titanium
T_m	-	Melting temperature
T_s	-	Substrate temperature
μ	-	Micron
θ	-	Diffraction angle
V	-	Volt
V_b	-	Substrate bias
x	-	Magnetic susceptibility

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LIST OF PUBLICATIONS

Razali, M. M., Mazliah, M., Nizam, A. R. M., Izani, M. Z. K., 2012. Correlation between Cobalt Content and Magnetic Properties of Tungsten Carbide (WC) Inserts. Proceeding of International Conference on Design and Concurrent Engineering (iDECON 2012). October 15-16. Melaka: Universiti Teknikal Malaysia Melaka (UTeM).

Razali, M. M., Mazliah, M., Nizam, A. R. M., Izani, M. Z. K., 2012. Deposition and Characterization of TiN Coated PVD Sputtering of Magnetized Substrate. Proceeding of The 5th International Conference On Postgraduate Education (ICPE-5 2012). December 18-19. Johor: Universiti Teknologi Mara (UTM).

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CHAPTER 1

INTRODUCTION

1.0 Background

Surface engineering includes modifying the properties and characteristic of the surface in attractive ways (Gangopadhayay *et. al*., 2009). Surface engineering can also engage an overlay process or a surface alteration process. In overlay process, a material is added to the surface and the underlying material (substrate) is secured and not discernible on the surface. A surface alteration process changes the properties and characteristic of the surface without affecting the substrate material (Mattox, 2010). Every process has its favourable circumstances and weaknesses and also additionally requisitions. In a few cases surface alteration process could be utilized to adjust the substrate surface prior to depositing a film or coating.

Deposition coating applications has been used extensively in many industrial sectors since the beginning of 1980s, including for hard coating on cutting tools (Sproul, 1996). Consequently, these applications are critical to enhance cutting tool exhibition by upgrading the surface properties of the tool. Thus, the enhanced exhibition of coated cutting tools has been demonstrated and documented from many studies (i.e, Byrne and Scholta, 1993; Laing *et. al*., 1999; Gekonde and Subramanian, 2002; Tuffy *et. al.*, 2004; Razali *et. al*., 2009; Syukor *et. al*., 2012. Moreover, Musil (2000) claimed that the coated cutting tool was able to increase the lifetime of an uncoated tool for more than three times.

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Nevertheless, a coated cutting tool performance also depends on the material of coating used.

One of the materials used for coatings deposition is Titanium Nitride (TiN). The TiN coating on cutting tool is an excellent coating because of its high level of hardness at elevated temperatures (Ma *et. al*., 2007). The coating also has low coefficient of friction as well as wear resistance, oxidation and corrosion (Hultman, 2000; PalDey and Deevi, 2003). This notion is supported by Upadhyaya, (2001) who reports that TiN has a superior resistance to diffusion and combination with the lower coefficient of friction which results in better crater wear resistance.

Other than material used for coating, technique used can also change the properties and characteristics of the coating deposition. One of the common techniques used is PVD magnetron sputtering because this technique has a wide range of applications both in industry and research (Mubarak *et. al*., 2005). Extensive studies have been carried out on the PVD magnetron sputtering which improves the properties and characteristic of the coating deposition (i.e, Musil and Vlček, 1998; Barshilia *et. al*., 2007; Kim *et. al*., 2003; Gangopadhyay *et. al*., 2009). Furthermore, PVD coating has been proven to improve the cutting tool life significantly (Byrne and Scholta, 1993; Laing *et. al*., 1999; Gekonde and Subramanian, 2002; Tuffy *et. al*., 2004).

In addition, this technique has attracted the interests of both researcher and practitioners from industry, primarily because the major increase in deposition rate connected with the magnetic confinement of electrons. So as to acquire more independent control of the substrate surface ion bombardment, the additional anode might be utilized,

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while the magnetic field configurations might be adjusted by method of cells with permanent magnets. Various configurations of magnetic deposition systems have been discussed (Matthews *et .al.*, 1993; Mattox, 1998a; Zlatanović *et. al.*, 1998a; Zlatanović *et. al.*, 1998b; Laing *et. al.*, 1999; Mubarak *et. al.*, 2005; Mattox, 2010). The deposited coating characteristics are, in turn, greatly influenced by the particle bombardment of the growing film (Musil and Vlček, 1998; Mayrhofer *et. al.*, 2006).

The particle bombardment on the growing film can be of atoms or ions. If the particles are ions, the substrate bias can be utilized to influence the energy of ion bombardment (Petrov e*t. al.*, 2003). In the PVD magnetron sputtering, most of the sputtered particles are atoms, ranging from 95% to 99% (Lungscheider, 1996; Mubarak *et. al.*, 2005). In order to increase the percentage of ionization, the PVD magnetron sputtering technique has to be modified, whereby the magnetic field is applied at the vicinity of the substrate. Adopting the principle of applying a magnetic field at the target, it is postulated that the magnetic field at the vicinity of the substrate would also increase the ion density around the substrate for the bombardment of growing film. The outcome of this research would improve the understanding of the magnetron sputtering process, particularly, the effects of substrate magnetic field on the coating characteristics.

1.1 Research problem

The challenges in PVD magnetron sputtering process are to increase the coating characteristics and produce a high quality coated cutting tool. Previously, researchers solve the problem by applying various strategies such as developing process modelling and manipulating the magnetic field in the system of PVD magnetron sputtering. The common

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function of a magnetic field in PVD magnetron sputtering is to trap electrons close to the target surface. The high electron density increases the probability of sputtering gas to be ionized upon colliding with the electrons. These ions bombard and vaporize target materials to be deposited onto the substrate. Hence, the deposited coating characteristics are greatly influenced by the particle bombardment of the growing film. Matox *et. al.*, (2005) claim that the sputtered coating generally has a columnar structure and a smooth coating surface. In this regards, it would be highly desirable to control the properties of the coating, which consist of electrons, atoms, and ions. Among these, energetic ions are, in general, most important species to produce high quality coatings. As the coating consists of ions and electrons, magnetic field plays certain roles on the coating process. However, in PVD magnetron sputtering process, only about 5% of ejected particles from the targets are ions (Lungscheider, 1996; Mubarak *et. al.*, 2005). The ability to increase the number of ions to bombard the deposited coating on the substrate would greatly facilitate the ability to dictate the coating characteristics through substrate bias optimization. Adopting the principal of applying magnetic field at the target, it can be postulated that the magnetic field at the vicinity of the substrate would also increase the ion density around the substrate for the bombardment of growing film. Thus, this study plays a significant role to investigate the potentials of the magnetic field at the vicinity of the substrate in PVD system to produce high quality coating.

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1.2 Objectives

The purpose of this study is to develop a systematic method that can create a magnetic field at the vicinity of the substrate surface in the PVD magnetron sputtering.

Specific objectives of this study are:

(a) To develop a systematic method to create magnetic field at the vicinity of substrate surface.

(b) To assess the impact of substrate magnetic field, on the deposited coating (TiN) using DOE approach.

(c) To characterize and evaluate the coating performances that includes hardness, surface morphology, thickness, crystallographic and coating adhesion.

1.3 Significance of research

PVD magnetron sputtering has been developed rapidly in the course of the most recent decade to the focus where it is established as the process of decision for the deposition of a wide range of industrially important coatings (Hultman, 2000). The driving constrain behind this advancement has been the expanding interest for great utilitarian coatings in numerous assorted industry sector divisions. Hence, many studies have been geared on the PVD magnetron sputtering to increase the quality of the coating by applying a magnetic field on the substrate surface during coating deposition.

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1.4 Scope

The scope of this research is to develop a systematic method that can create a magnetic field at the vicinity of the substrate surface in the PVD magnetron sputtering of TiN coating onto the tungsten carbide insert. A magnetic field is produced by permanent magnet that is capable of withstanding the demagnetizing. Permanent magnet is an improved determination as it gives steady magnetic fields without nonstop consumption of electric current and heat generation. The TiN coating is selected for this study due to the fact that it is one of the widely used coatings and has a high level of hardness at elevated temperature (Ma *et. al.*, 2007). The General Factorial analysis is carried out using Design Expert 7.0.0 software.

1.5 Structure of thesis

This thesis is divided into five chapters. The first chapter is an introduction to the study which consists of problem statements, objectives, the significance of the study and scope. Chapter Two presents the literature review that relates to the theories on magnetron sputtering process and previous investigation on magnetic field applied to the PVD magnetron sputtering. The important element included in this chapter is about the magnetic field and also related experimental testing. Chapter Three details the methodology used for overall research work, raw materials, procedure and characteristic analysis. In Chapter Four, the results of the characterization and discussions are discussed. The final chapter provides the conclusion to the work. The recommendations for future project are presented.

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CHAPTER 2

LITERATURE REVIEW

2.1 Coating Technology

A coating is a layer that is applied on the surface of the object known as the substrate. In many cases, coatings are applied to enhance surface properties of the substrate, for example adhesion, wears resistance, corrosion resistance, and scratch resistance (Abdelouahdi *et. al.*, 2006; Gangopadhayay *et. al.*, 2009). Wolfe and Singh (2000) claim that the coating technology is commonly applied in the manufacturing industrial, optical, automotive and aerospace industries. For example 75% of aircraft engine components is coated by metallic or ceramic coatings to enhance performance and reliability (Wolfe and Singh, 2000; Tracton, 2006). Some examples of coatings are Titanium Nitride (TiN), Titanium Aluminium Nitride (TiAlN), and Titanium Carbide (TiC). Among them, TiN coating is the most explored hard coating due to its excellent properties (Holmberg and Mattews, 1998; Barshilia, 2006).

The TiN coating had been studied extensively since 1980s (Barshilia *et. al.*, 2007) and widely used in industry due to its attractive mechanical and tribological properties. It typically possesses hardness of 21-28 GPa (Musil, 2000), and is able to increase the lifetime of uncoated tool for more than three times. It is usually used on high speed steel tools for metal cutting processes such as milling and turning. The method used to deposit TiN coating is mainly by physical vapor deposition (PVD) process.

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