DEPOSITION AND CHARACTERIZATION OF POLYCRYSTALLINE DIAMOND COATED ON SILICON NITRIDE AND TUNGSTEN CARBIDE USING MICROWAVE PLASMA ASSISTED CHEMICAL VAPOUR DEPOSITION TECHNIQUE

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To my beloved parents, teachers and family

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ABSTRACT

Diamond (*sp^3*) is a unique engineering material, due to its superior combination of physical, optical and chemical properties and thus it is possible to take advantage of these properties in many engineering applications for which high hardness, high resistance to corrosion and erosion is required. In the present study, deposition and characterization of polycrystalline diamond coated on silicon nitride (Si_3N_4) and tungsten carbide (WC) substrates using microwave plasma assisted chemical vapor deposition (MPACVD) technique were investigated. The pretreatment processes were conducted on the substrate materials to enhance adhesion and nucleation of diamond namely cleaning, chemical etching (for WC substrate to remove cobalt content from the substrate surface) and diamond seeding. Total gas flow rate and deposition time were kept constant at 200 sccm and for 7 hours respectively. Variable deposition parameters used were %CH_4 concentration, microwave power, and chamber pressure at 1 – 3%CH_4, 2.75 – 3.75kW, and 40 – 60 torr respectively. Microstructure, morphology and surface roughness were investigated by optical microscopy, scanning electron microscopy and atomic force microscopy. Phase analysis, residual stress and diamond quality were determined by X-ray diffraction and Raman spectra. Coating adhesion and wear resistance was determined using Rockwell hardness indenter and pin-on-disk tribometer. The results show that H_2O_2:HNO_3:H_2O reagent and 10 minutes etching time was found to be the optimum parameter on cobalt removal from WC substrate. It was also observed that increase in %CH_4 concentration enhance diamond nucleation and growth, increase diamond coating thickness and reduce surface roughness. Microwave power and chamber pressure increase the density of diamond, diamond quality and transform diamond facet from cauliflower to octahedral structure. Raman spectra results show that all residual stresses are compressive and pin-on-disk results indicate that octahedral diamond structure has better coating adhesion than cauliflower structure.

ABSTRAK

Intan (*sp*^{3}*)* adalah bahan kejuruteraan yang unik, disebabkan gabungan paling baik diantara sifat fizik, optik dan kimia. Oleh itu kelebihan sifat – sifat ini boleh digunakan dalam pelbagai aplikasi kejuruteraan dimana kekerasan yang tinggi, ketahanan terhadap kakisan dan hakisan diperlukan. Dalam kajian ini, pengenapan dan pencirian intan polihablur disalut keatas silikon nitrida (Si_3N_4) dan tungsten karbida (WC) dengan menggunakan teknik pengenapan wap kimia dibantu plasma gelombang mikro telah dikaji. Proses prarawatan dilakukan keatas bahan subtrat untuk meningkatkan rekatan dan penukleusan intan iaitu pembersihan, punaran kimia (bagi substrat WC untuk menyingkir kandungan kobalt daripada permukaan substrat) dan juga penyemaian intan. Jumlah kadar aliran gas dan masa pengenapan masing – masing ditetapkan pada 200 sccm dan selama 7 jam. Parameter pengenapan boleh ubah yang digunakan ialah kepekatan methana (%CH_4), kuasa gelombang mikro dan tekanan kebuk masing – masing pada 1 – 3%CH_4, 2.75 – 3.75kW dan 40 – 60 torr. Mikrostruktur, morfologi dan kekasaran permukaan intan polihablur dikaji dengan menggunakan mikroskop optik, mikroskop elektron imbasan dan mikroskop daya atom. Analisis fasa, tegasan baki dan kualiti intan ditentukan melalui pembelauan sinar-X dan spektrum Raman. Rekatan salutan dan ketahanan haus diperolehi dengan menggunakan pelekuk kekerasan Rockwell dan tribometer cekara-atas-cemat. Keputusan kajian menunjukkan bahawa larutan H_2O_2:HNO_3:H_2O dan masa punaran selama 10 minit adalah parameter optimum untuk menyingkir kobalt daripada substrat WC. Hasil kajian juga menunjukkan bahawa kepekatan methana %CH_4 meningkatkan penukleusan dan pertumbuhan intan, meningkatkan ketebalan salutan dan mengurangkan kekasaran permukaan. Kuasa gelombang mikro dan tekanan kebuk meningkatkan ketumpatan intan, kualiti intan dan mengubah muka intan daripada struktur kubis bunga kepada oktahedron. Keputusan spektrum Raman menunjukkan bahawa semua tegasan baki adalah tegasan mampatan dan keputusan cakera-atas-cemat menunjukkan bahawa struktur intan oktahedron mempunyai rekatan salutan lebih baik dari struktur kubis bunga.

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LIST OF ABBREVIATIONS

a.u	-	Arbitrary Unit
AFM	-	Atomic Force Microscopy
cBN	-	Cubic Boron Nitride
Cps	-	Count per second
CVD	-	Chemical Vapor Deposition
EDX	-	Energy Dispersive X-ray
FESEM	-	Field Emission Scanning Electron Microscopy
MPACVD	-	Microwave Plasma Assisted Chemical Vapor Deposition
PVD	-	Physical Vapor Deposition
Ra	-	Average surface roughness
Rms	-	Root-mean-square roughness of the profile
Rp	-	Maximum profile height
Rv	-	Maximum profile valley depth
Ry/Rt	-	Maximum height of profile/total roughness
Rz	-	Average maximum height of the roughness profile
sccm	-	Standard cubic per centimeter
SEM	-	Scanning Electron Microscopy
Si_3N_4	-	Silicon Nitride
WC	-	Tungsten Carbide
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

μ	-	Coefficient of Friction
λ	-	Wavelength
θ	-	Angle
α	-	Diamond growth parameter
μm	-	Micrometer, micron
$\AA$	-	Angstrom
υ_m	-	Raman shift mean
υ_o	-	Raman shift diamond
T_1	-	Room temperature
T_2	-	Deposition temperature
E	-	Elastic modulus
I_d	-	Maximum intensity Raman shift of diamond
I_g	-	Maximum intensity Raman shift of graphite
I_q	-	Diamond quality factor
σ	-	Residual stress
σ_{th}	-	Thermal stress
σ_i		Intrinsic stress

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CHAPTER 1

INTRODUCTION

1.1. Background of the Research

Diamond is, of course, not a new material. Many of the unique properties of naturally occurring diamond have been known for many years. The extreme hardness, high thermal conductivity, excellent infrared transparency, and remarkable semiconductor properties combine to make diamond one of the most technologically and scientifically valuable materials found in nature (Pierson, 1993). However, natural diamond is rare and only obtainable as gem stones in small sizes, scarcity and at great expense: these have motivated researchers to attempt to duplicate nature and synthesize diamond since it was discovered in 1797 that diamond is an allotrope of carbon.

Over the past 50 years a variety of techniques have evolved for the synthesis of diamond which include high pressure high-temperature (HPHT) processes, chemical vapor deposition (CVD), and physical vapor deposition (PVD). Schwartz (2002) reported the basic concept of HPHT method that these diamonds are produced from graphite at pressures from 5,512 to 12,402 MPa and temperatures from 1204 to 2427°C. A molten metal catalyst of chromium, cobalt, nickel, or other metal is used, which forms a thin film between the graphite and the growing diamond crystal. Without the catalyst much higher pressures and temperatures are needed. The shape of the crystal is controllable by the temperature. At the lower temperatures cubes predominate, and at the upper limits octahedral predominate; at the lower temperatures the diamonds tend to be black, whereas at higher temperatures they are yellow to white. The synthetic diamonds produced by the General Electric Co. are up to 0.01 carat in size, and are of industrial quality comparable with natural diamond powders.

This achievement has been made possible both by an improved scientific understanding of how diamond is formed and by a significant engineering development of chemical vapor deposition (CVD) systems designed specifically for the deposition of diamond. It has become widely recognized that polycrystalline and homoepitaxial diamond can be deposited using a variety of CVD techniques. Polycrystalline diamond films have been deposited on various non-diamond substrates, including insulators, semiconductors and metals, ranging from single crystals to amorphous materials (Liu and Dandy, 1995). And also, they conduct heat better than any known material five times better than copper making them useful as heat sinks to conduct heat away from electrical components (Schwartz, 2002).

In many cases, the properties of diamond are superlative. For example, it is reported to have the highest hardness of any material, the highest thermal conductivity, and the lowest compressibility. In other cases, the diamond material property is not necessarily the best, but diamond is still highly competitive with other materials. For example, the coefficient of friction is comparable to that of Teflon. In any case, diamond is properly considered to be a unique material because it exhibits an unusual constellation of highly attractive properties of interest for many applications.

Development of manufacture technology needs a high requirement on machining accuracy and surface quality. To fulfill these requirements attention must be paid to machine tool and production technology. Cutting tool materials have high contribution to improve machine tool quality. Coating is technology to improve cutting tool characterization. The combined properties of the chemical inertness along with the high hardness, high wear resistance, and high quality conductivity makes diamond thin films an ideal protective coating against corrosion and wear in cutting tool and metal working industries.

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