

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

AGUNG PURNIAWAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Mechanical Engineering)

Faculty of Mechanical Engineering
Universiti Teknologi Malaysia

FEBRUARY 2008

To my beloved parents, teachers and family

ACKNOWLEDGEMENTS

On this occasion, firstly, we praise our thanks to the presence of Allah, the Great Unity for showering us with blessing, so in this moment I can complete my thesis. Secondly, my appreciation to Professor Dr. Esah Hamzah, my main Supervisor who has given me the opportunity to join her research group. I also would like to thank her for the time, exceptional guidance, motivation and effort toward me throughout my study. I would like to also thank my co-supervisor Dr. Mohd Radzi Mohd.Toff (AMREC, SIRIM Berhad) for his guidance, assistance and constructive suggestion on my experimental works.

I would like to express my appreciation to the Ministry of Science, Technology and Innovation of Malaysia (MOSTI) under the Intensification of Research in Priority Areas (IRPA) [03 – 02 – 14 – 0001 PR 0074/ 03 – 02] for the research grant and also the author gratefully acknowledge the technical support provided by Advanced Material Research Center (AMREC), SIRIM Berhad. I also would like to thank my colleagues Mohd. Hazri Othman, Zakuan, Zuber Me, Abdul Hakim, Sudirman, Lokman, En Zahidan, Nizam, Bakri from AMREC and also En Ayub, Jefri, Azri and adnan from Materials Science Laboratory FKM-UTM, for their assistance and support during my experimental works.

Special thanks are due to my dearest mother Ibu Tasmia and Almarhum Bapak Jahman Harjono for their unselfish love and understanding and also to my family especially for my beloved wife Dewi Libiawati SSi, Apt. for her encouragement, and my lover daughters Affifah Rahma Adila, Izzah Naufalia Adila and Irdin Nafiati Ilmi who always cheer up my days. Without them, I could never have reached this point. Finally, I would like to thank everyone for their unending support, encouragement and motivation throughout my studies in Universiti Teknologi Malaysia (UTM).

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 substrat 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 cekera-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.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xiii
	LIST OF ABBREVIATIONS	xxi
	LIST OF SYMBOLS	xxii
	LIST OF APPENDICES	xxiii
1	INTRODUCTION	1
	1.1. Background of the Research	1
	1.2. Problem Statement	3
	1.3. Objectives of the Research	3
	1.4. Scope of the Research	4
	1.5. Significance of the Research	4
2	LITERATURE REVIEW	5
	2.1. Introduction	5
	2.2. An Overview on Cutting Tools	7
	2.2.1. Uncoated Tools Materials	9
	2.2.1.1 High Speed Steel	9
	2.2.1.2 Cemented Carbide	9

2.2.1.3	Ceramics	11
2.2.2.	Coated Tools Materials	12
2.2.2.1	Coating material: Titanium Based Materials	12
2.2.2.2	Coating material: Cubic boron nitride (c-BN)	15
2.2.2.3	Coating material: Diamond	16
2.2.3.	Effect of cobalt on polycrystalline Diamond Coated on Tungsten Carbide (WC)	18
2.2.4.	Application of Cutting Tool	20
2.3.	An overview on Diamond as Coating Material	21
2.3.1.	Structure and Properties of Diamond	21
2.3.2.	Nucleation and Growth of Polycrystalline Diamond	26
2.3.3.	Diamond Nucleation on Metal Carbide	32
2.4.	Deposition Technique of polycrystalline diamond	33
2.4.1.	Introduction	33
2.4.2.	Chemical Vapor Deposition (CVD)	34
2.5.	Characterization Technique of Polycrystalline Diamond	41
2.6.	Contribution and Perspective of Diamond Coating Technology	54
3	EXPERIMENTAL PROCEDURE	57
3.1.	Introduction	57
3.2.	Sample Preparation and Pretreatments	57
3.2.1.	Substrate Material	57
3.2.2.	Coating Material	58
3.2.3.	Pretreatments	58
3.3.	Polycrystalline Diamond Deposition by Chemical Vapor Deposition Method	62

3.4.	Micro-structural Characterization	63
3.4.1.	Morphology by Scanning Electron Microscopy	63
3.4.2.	Topography and Surface Roughness by Atomic Force Microscopy	64
3.4.3.	Phase Analysis by X-ray Diffraction	65
3.4.4.	Diamond Quality and Residual Stress by Raman Spectroscopy	66
3.5.	Mechanical Characterization	67
3.5.1.	Adhesion Properties	67
3.5.2.	Wear Properties	68
4	RESULTS AND DISCUSSION	70
4.1.	Introduction	70
4.2.	Materials	70
4.3.	Pretreatments Analysis	75
4.3.1	Chemical Etching on Tungsten Carbide	75
4.3.2	Diamond Seeding on Silicon Nitride	82
4.4.	The Effect of Deposition Parameters on Microstructural of Polycrystalline Diamond	85
4.4.1	Polycrystalline Diamond Morphology	85
4.4.1.1	Effect of CH ₄ Concentration	85
4.4.1.2	Effect of Microwave Power	87
4.4.1.3	Effect of Chamber Pressure	89
4.4.2	Polycrystalline Diamond Thin Film Thickness	92
4.4.3	Topography and Surface Roughness	99
4.4.4	Diamond Quality and Residual Stress	111
4.4.5	Phase and Growth Rate Parameter Analysis	120
4.4.4.1.	Phase identification	120

4.4.4.2. Determination of Growth Rate	
Parameter	122
4.5. Mechanical Properties Analysis	126
4.5.1. Adhesion	126
4.5.2. Wear Resistance	130
5	
CONCLUSIONS	139
5.1. Conclusions	139
5.2. Recommendations for Future Work	141
REFERENCES	142
Appendices A-D	153 - 193

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	The properties and application of commercial cutting tool materials.	8
2.2	List of various tungsten carbide cutting tools based on %Co content	10
2.3	Properties of tungsten carbide	10
2.4	Properties of silicon nitride	11
2.5	Methods to improve coating quality of titanium based material coated cutting tools	14
2.6	Previous research work have been conducted to enhanced diamond coating quality coated on tungsten carbide	17
2.7	Previous research by other researchers conducted to enhance diamond coating quality coated on silicon nitride	18
2.8	Diamond reactivity with temperature	24
2.9	Properties comparison of single-crystalline and polycrystalline diamond	25
2.10	A general comparison of CVD and PVD technique with respect to the coating of cutting tools	34
2.11	Characteristics of plasma on CVD	38
2.12	Technical data and characteristics of CVD diamond techniques	40
2.13	The perspective of hard coating application on cemented carbide tools	55
2.14	Actual and suggested applications of diamond and diamond-like films	56

3.1	Deposition and characterization experiments of polycrystalline diamond coated on silicon nitride	60
3.2	Deposition and characterization experiments of polycrystalline diamond coated on tungsten carbide	61
3.3	Design of experiment to remove cobalt content on substrate surface	62
3.4	Parameters of XRD diffraction	66
3.5	Parameter of Raman spectra analysis	67
3.6	Wear test parameter using Pin-on-Disk Tribometer	69
4.1	XRD analysis results of as-received silicon nitride (Si_3N_4)	74
4.2	XRD analysis results of as-received tungsten carbide (WC)	74
4.3	The amount % cobalt on the surfaces after chemical etching in various etching reagents and etching time	80
4.4	Thickness of polycrystalline diamond coating on sample substrate	97
4.5	Surface roughness of polycrystalline diamond coated on silicon nitride (Si_3N_4) and tungsten carbide (WC)	104
4.6	Summary of atomic force microscope (AFM) profile analysis	110
4.7	A summary of thermal stress analysis	113
4.8	A summary of Raman spectra data and analysis	114
4.9	Growth parameter was calculated from X-ray Diffraction results of polycrystalline diamond coated silicon nitride and tungsten carbide	123
4.10	Pin volume loss during wear resistant test	138

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Phase diagram for carbon	6
2.2	Phase diagram of the Co-C system	19
2.3	Schematic of graphite hexagonal crystal structures	22
2.4	Schematic of diamond tetrahedral crystal structures	22
2.5	Idiomorphic crystal shapes of diamond for different value of the growth parameter α ($\alpha = v_{100}/v_{111} x\sqrt{3}$); the arrows on the crystals indicate the direction of fastest growth	23
2.6	Hardness of diamond and other hard materials	26
2.7	Schematic of the physical and chemical processes occurring in production of CVD diamond	27
2.8	Simplified form of the Bachmann triangle C–H–O composition diagram	28
2.9	Schematic of the reaction process occurring at the diamond surface leading to stepwise addition of CH ₃ species and diamond growth	30
2.10	Diamond growth on a non-diamond substrate occurs by sequential steps: (a) nucleation of individual crystallites; (b, c) termination of nucleation followed by growth of individual crystallites; (d) faceting and coalescence of crystallites; (e, f) competition between growing crystallites and eventual overgrowth to form continuous film	31
2.11	Schematic diagram showing the proposed nucleation mechanism of diamond nuclei form on a carbide interlayer on carbide forming refractory metal substrate	33
2.12	Schematic diagram of External heating methods (Hot Filament CVD)	35
2.13	Schematic diagram of combination of thermal and chemical activation methods (Flame CVD)	36

2.14	Schematic diagram of microwave plasma assisted CVD (MPACVD)	36
2.15	Schematic diagram of Radio Frequency CVD (RFCVD)	37
2.16	Schematic diagram of Direct Current Plasma – Assisted CVD (DCPACVD)	37
2.17	Schematic diagram of Cyclotron Electron Cyclotron Resonance Microwave – Assisted CVD (ECRMWCVD)	38
2.18	Typical growth rate versus gas phase temperatures in various diamond CVD process, illustrating the importance of gas phase temperature for high rate diamond synthesis	41
2.19	Schematic diagram of Scanning electron microscopy (SEM)	42
2.20	Schematic diagram of Atomic force microscopy (AFM)	43
2.21	Schematic diagram of Bragg’s Law X-ray Diffraction where d is distance between atomic and certain θ is incidence angles	44
2.22	Energy level diagram for Raman scattering; (a) Stokes Raman Scattering (b) Anti – Stokes Raman Scattering	46
2.23	Schematic diagram of Pin-on Disk Tribometer	53
3.1	Flow chart of Research Methodology	59
3.2	Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD)	63
3.3	Field Emission Scanning Electron Microscopy (FESEM)	64
3.4	Atomic force microscopy (AFM)	65
3.5	X-ray Diffraction (XRD) equipment	65
3.6	Raman spectra equipment	67
3.7	Rockwell hardness tester	68
3.8	Pin-on disk tribometer	69
4.1	The EDX spectrum of as received material (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	71

4.2	Scanning electron micrograph of as received sample (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	72
4.3	The X-ray diffraction patterns of as-received material (a) silicon nitride (Si_3N_4), (b) tungsten carbide (WC)	73
4.4	Scanning electron micrographs of tungsten carbide (a) before and (b) after etching using $\text{H}_2\text{O}_2:\text{HNO}_3:\text{H}_2\text{O}$	76
4.5	EDX spectrum of etched tungsten carbide substrate in pure peroxide (H_2O_2) solution at various etching time (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 20 minutes and (d) 25 minutes.	77
4.6	EDX spectrum of etched tungsten carbide in $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ solution at various etching time (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 20 minutes and (e) 25 minutes.	78
4.7	EDX spectrum of etched tungsten carbide in $\text{H}_2\text{O}_2:\text{HNO}_3:\text{H}_2\text{O}$ solution at various etching time (a) 5 minutes (b) 10 minutes (c) 15 minutes (d) 20 minutes and (d) 25 minutes.	79
4.8	The effect of various etching solutions and time on wt% residual Co on tungsten carbide substrate surface	81
4.9	Cobalt removal mechanisms on WC-Co surface by etching process (a) early etching, (b) Co – Acid reaction on the surface (c) early stage over etching (d) over etching	82
4.10	Scanning electron micrograph of polycrystalline diamond coated on silicon nitride (Si_3N_4) (a) unseeded substrate and (b) seeded substrate	83
4.11	X-ray Diffractographs of polycrystalline diamond coated on (a) unseeded silicon nitride and (b) seeded silicon nitride	83
4.12	Scanning electron micrographs of polycrystalline diamond coated on silicon nitride at constant microwave power (3.75kW) and chamber pressure (60torr) with various % CH_4 concentration (a) 1%, (b) 2% and (c) 3%	86
4.13	Scanning electron micrographs of polycrystalline diamond coated on tungsten carbide at constant microwave power (2.75kW) and chamber pressure (50torr) with various % CH_4 concentration (a) 1%, (b) 2% and (c) 3%	87

- 4.14 Scanning electron micrographs of polycrystalline diamond coated on silicon nitride at constant %CH₄ concentration (2%CH₄) and chamber pressure (40torr) with various microwave power (a) 2.75kW, (b) 3.25kW and (c) 3.75Kw 88
- 4.15 Scanning electron micrographs of polycrystalline diamond coated on tungsten carbide at constant %CH₄ concentration (2%CH₄) and chamber pressure (40torr) with various microwave power (a) 2.75kW, (b) 3.25kW and (c) 3.75kW 88
- 4.16 Scanning electron micrographs of polycrystalline diamond coated on silicon nitride at constant %CH₄ concentration (3%CH₄) and microwave power (3.75Kw) with various chamber pressure (a) 40 torr, (b) 50 torr and (c) 60 torr. 89
- 4.17 Scanning electron micrographs of polycrystalline diamond coated on tungsten carbide at constant %CH₄ concentration (2%CH₄) and microwave power (3.75Kw) with various chamber pressure (a) 40 torr, (b) 50 torr and (c) 60 torr. 90
- 4.18 Scanning electron micrographs of the cross section view of polycrystalline diamond coating on silicon nitride (Si₃N₄) at constant microwave power (3.75kW) and chamber pressure (40 torr) and variable %CH₄ concentration (a) 1%, (b) 2% and (c) 3%. 92
- 4.19 Scanning electron micrographs of the cross section view of polycrystalline diamond coating on tungsten carbide (WC) at constant microwave power (3.75kW) and chamber pressure (40 torr) and variable %CH₄ concentration (a) 1%, (b) 2% and (c) 3%. 93
- 4.20 Scanning electron micrographs of the cross section view of polycrystalline diamond coating on silicon nitride (Si₃N₄) at constant %CH₄ concentration(1%) and chamber pressure (40 torr) and variable microwave power (a) 2.75 kW (b) 3.25kW and (c) 3.75kW 93
- 4.21 Scanning electron micrographs of the cross section view of polycrystalline diamond coating on tungsten carbide (WC) at constant %CH₄ concentration(1%) and chamber pressure (40 torr) and variable microwave power (a) 2.75 kW (b) 3.25kW and (c) 3.75kW 94
- 4.22 Scanning electron micrographs of the cross section view of polycrystalline diamond coating on silicon nitride (Si₃N₄) at constant %CH₄ concentration(1%) and microwave power (3.25 kW) and variable chamber pressure (a) 40 torr (b) 50 torr and (c) 60 torr 95

4.23	Scanning electron micrographs of the cross sectional view of polycrystalline diamond coating on tungsten carbide (WC) at constant %CH ₄ concentration(1%) and microwave power (3.25 kW) and variable chamber pressure (a) 40 torr (b) 50 torr and (c) 60 torr	95
4.24	The effect of deposition parameters with various levels on polycrystalline diamond coating thickness coated on (a) silicon nitride (Si ₃ N ₄) and (b) tungsten carbide (WC)	98
4.25	AFM topography of polycrystalline diamond coated on silicon nitride (Si ₃ N ₄) at constant microwave power (3.75kW) and chamber pressure (60 torr) and various %CH ₄ concentration (a) 1%, (b) 2%) and (c) 3%.	99
4.26	AFM topography of polycrystalline diamond coated on tungsten carbide (WC) at constant microwave power (2.75kW) and chamber pressure (60 torr) and various %CH ₄ concentration (a) 1%, (b) 2%) and (c) 3%.	100
4.27	AFM topography of polycrystalline diamond coated on silicon nitride (Si ₃ N ₄) at constant %CH ₄ concentration (3%) and chamber pressure (60 torr) and various microwave power (a) 2.75 kW (b) 3.25kW and (c) 3.75kW	100
4.28	AFM topography of polycrystalline diamond coated on tungsten carbide (WC) at constant %CH ₄ concentration (3%) and chamber pressure (60 torr) and various microwave power (a) 2.75 kW (b) 3.25kW and (c) 3.75kW	101
4.29	AFM topography of polycrystalline diamond coated on silicon nitride (Si ₃ N ₄) at constant %CH ₄ concentration (3%) and microwave power (3.25kW) and various chamber pressure (a) 40 torr (b) 50 torr and (c) 60 torr	102
4.30	AFM topography of polycrystalline diamond coated on tungsten carbide (WC) at constant %CH ₄ concentration (3%) and microwave power (3.25kW) and various chamber pressures (a) 40 torr (b) 50 torr and (c) 60 torr	102
4.31	The effect of deposition parameters on surface roughness (a) %CH ₄ concentration (b) microwave power (c) chamber pressure	105
4.32	AFM image analysis of large grain polycrystalline diamond coated on tungsten carbide at deposition parameters %CH ₄ concentration (3%), microwave power (3.75kW) and chamber pressure (60torr) (a) top view (b) three dimension (3D) image (c) surface roughness along A-B line and (d) grain size analysis	107

4.33	AFM image analysis of small grain polycrystalline diamond coated on silicon nitride (Si_3N_4) under deposition parameters % CH_4 concentration (3%), microwave power (3.25kW) and chamber pressure (40torr) (a) top view (b) three dimension image (c) surface roughness along A-B line and (d) grain size analysis	108
4.34	AFM image analysis of cauliflower/ball like structure of polycrystalline diamond coated on tungsten carbide (WC) at deposition parameters % CH_4 concentration (3%), microwave power (2.75kW) and chamber pressure (60torr) (a) top view (b) three dimension image (c) surface roughness along A-B line and (d) grain size analysis	109
4.35	Raman spectra of polycrystalline diamond between 1000 to 2000 cm^{-1} at various % CH_4 concentration coated on (a) silicon nitride (Si_3N_4) at 3.75kW:60 torr (b) tungsten carbide (WC) at 3.25kW:50 torr.	111
4.36	Raman spectra of polycrystalline diamond between 1000 to 2000 cm^{-1} on various microwave power coated on (a) silicon nitride (Si_3N_4) at 1% CH_4 :40 torr (b) tungsten carbide (WC) at 3% CH_4 :60 torr.	112
4.37	Raman spectra of polycrystalline diamond between 1000 to 2000 cm^{-1} on various chamber pressure coated on (a) silicon nitride (Si_3N_4) at 3% CH_4 :3.25kW (b) tungsten carbide (WC) at 3% CH_4 :3.75kW	112
4.38	The effect of deposition parameters on full width half maximum (FWHM) of polycrystalline diamond coated on (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	116
4.39	The effect of deposition parameters on quality factor of polycrystalline diamond coated on (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	117
4.40	The effect of deposition parameters on residual stress of polycrystalline diamond coated on (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	117
4.41	The effect of deposition parameters on intrinsic stress of polycrystalline diamond coated on (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	118
4.42	X-ray Diffraction pattern of polycrystalline diamond coated on silicon nitride (Si_3N_4) with deposition parameters 1% CH_4 concentration, microwave power (3.25kW) and chamber pressure (50torr).	121

4.43	Maximum intensity with various deposition parameters of polycrystalline diamond (111) coated on (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	122
4.44	Growth parameter with various deposition parameters of polycrystalline diamond coated (a) silicon nitride (Si_3N_4) and (b) tungsten carbide (WC)	124
4.45	Scanning electron micrographs of micro crack without peel off of cubic diamond structure coated on Si_3N_4 with deposition parameter % CH_4 concentration (3%), microwave power (2.75kW) and chamber pressure (50torr)	126
4.46	Scanning electron micrographs of crack-type of cubic diamond structure coated on silicon nitride (Si_3N_4) with deposition parameters % CH_4 concentration (3%), microwave power (3.25kW) and chamber pressure (40torr)	126
4.47	Scanning electron micrographs of Crack and facet damage without peel off of octahedral diamond structure coated on silicon nitride (Si_3N_4) with deposition parameters % CH_4 concentration (3%), microwave power (3.75kW) and chamber pressure (60torr)	127
4.48	Scanning electron micrographs of facet damage and peel off without crack of cauliflower diamond structure coated on tungsten carbide (WC) at deposition parameters % CH_4 concentration (3%), microwave power (3.25kW) and chamber pressure (50torr)	127
4.49	Scanning electron micrographs of Peel off and crack of cubic diamond structure coated on tungsten carbide (WC) at deposition parameters % CH_4 concentration (3%), microwave power (3.75kW) and chamber pressure (50torr)	128
4.50	Scanning electron micrographs of facet damage and peel off without crack of cauliflower diamond structure coated on tungsten carbide (WC) at deposition parameters % CH_4 concentration (3%), microwave power (2.75kW) and chamber pressure (50torr)	128
4.51	Pin-on-disk test result of uncoated silicon nitride (Si_3N_4)	131
4.52	Pin-on-disk test result of uncoated tungsten carbide (WC)	131
4.53	Pin-on-disk test result of cauliflower structure polycrystalline diamond coated on silicon nitride (Si_3N_4) at % CH_4 concentration (2% CH_4), microwave power (2.75kW) and chamber pressure (40torr)	132

- 4.54 Pin-on-disk test result of cauliflower structure polycrystalline diamond coated on tungsten carbide (WC) at %CH₄ concentration (3%CH₄), microwave power (3.25kW) and chamber pressure (50torr) 132
- 4.55 Pin-on-disk test result of octahedral structure polycrystalline diamond coated on silicon nitride (Si₃N₄) at %CH₄ concentration (3%CH₄), microwave power (3.75kW) and chamber pressure (60torr) 133
- 4.56 Pin-on-disk test results of octahedral structure polycrystalline diamond coated on tungsten carbide (WC) at %CH₄ concentration (3%CH₄), microwave power (3.75kW) and chamber pressure (60torr) 133
- 4.57 Scanning electron micrograph of wear track of the samples after wear resistance test on uncoated substrate (a) silicon nitride (Si₃N₄) (b) tungsten carbide (WC) 134
- 4.58 Scanning electron micrograph of wear track of the samples after wear resistance test on coated (a) silicon nitride (Si₃N₄) at 2%CH₄:2.755kW:40torr and (b) tungsten carbide (WC) at 3%CH₄:3.25kW:50torr 135
- 4.59 Pin-on-disk test results (a) uncoated substrate and (b) coated substrate using polycrystalline diamond. 135
- 4.60 Optical micrographs of wear track diameter pin with magnifications X50 for (a) uncoated silicon nitride (Si₃N₄) (b) cauliflower diamond coated on silicon nitride (Si₃N₄) (c) octahedral diamond coated on silicon nitride (Si₃N₄) 137
- 4.61 Optical micrographs of wear track diameter pin with magnifications X50 for (a) uncoated tungsten carbide (WC), (b) cauliflower diamond coated on tungsten carbide (WC) and (c) octahedral diamond coated on tungsten carbide (WC). 137

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 ₃ N 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
ν_m	-	Raman shift mean
ν_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

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	List of Publications	153
B	Raman Spectra Analysis	165
C	Profile Analysis of Polycrystalline Diamond Coated on Si ₃ N ₄ by using Atomic Force Microscopy	168
D	X – ray Diffraction Analysis	176

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.

REFERENCES

- Abdellaoui A., Bath A., Bouchikhi B., Baehr O. (1997). Structure and optical properties of boron nitride thin films prepared by PECVD. *Materials Science and Engineering*, B47. 257-262
- Ager J.W, Drory M.D. (1993). Quantitative measurement of residual biaxial stress by Raman spectroscopy in diamond grown on a Ti alloy by chemical vapor deposition. *Physical Review*, B48: 2601.
- Ahmed W, Sein H., Ali N., Gracio J., Woodward R.. (2003). Diamond films grown on cemented WC-Co dental burs using an improved CVD method. *Diamond and Related Materials*. 12: 1300-1306
- Ali N, Cabral G., Lopes A.B., Gracio J., (2004b). Time-modulated CVD on 0.8 μm -WC-10%-Co hardmetals: study on diamond nucleation and coating adhesion. *Diamond and Related Materials*, 13: 495-502
- Ali N., Cabral G., Titus E., Ogwu A. A. and Gracio J. (2004a). Characterization of diamond adhesion on micro-grain WC-Co substrates using Brinell indentations and micro-Raman spectroscopy. *J. Phys: Condens. Matter*, 16: 6661-6674.
- Amaral M., Mohasseb F., Oliveira F.J., Benedic F., Silva R.F., Gicquel A. (2005). Nanocrystalline diamond coating of silicon nitride ceramics by microwave plasma-assisted CVD. *Thin Solid Films*, 428: 232 - 236.
- Amirhaghia S., Reehala H.S.U., Woodb R.J.K., Wheeler D.W. (2001). Diamond coatings on tungsten carbide and their erosive wear Properties. *Surface and Coatings Technology*, 135: 126 - 138
- ASM Hand book. (1997). *Alloy Phase Diagrams*. Ohio, USA. Hugh Baker, editor, ASM International, second printing Volume 3, Metal Park,
- Asmussen J., Reinhard D. K.. (2002). *Diamond Films Handbook*. USA. Marcel Dekker, Inc.
- Badzian A., and Teresa Badzian. (1996). Defects in CVD diamonds, *Ceramics International*. 22: 223-228

- Baron C., Ghodbane S., Deneuille A., Bustarret T, E., Ortega L., Jomard F. (2005). Detection of CH_x bonds and sp² phases in polycrystalline and ta-C:H films from Raman spectra excited at 325 nm. *Diamond and Related Materials*, 14: 949-953.
- Belmonte M. (2005). Diamond coating of coloured Si₃N₄ ceramics. *Diamond and Related Materials*, 14: 54- 59.
- Bruno P., Be'ne'dic F., Tallaire A., Silva F., Oliveira F.J., Amaral M., Fernandes A.J.S, Cicala G., Silva R.F. (2005). Deposition of nanocrystalline diamond films on silicon nitride ceramic substrates using pulsed microwave discharges in Ar/H₂/CH₄ gas mixture. *Diamond and Related Materials*, 14: 432- 436.
- Bundy FP., Hall H.T., Strong H.M., Wentorf R.H. (1955). Man - Made Diamonds, *Nature*, 176:51-55.
- Burstein E. (2003). A major milestone in nanoscale material science: the 2002 Benjamin Franklin Medal in Physics presented to Sumio Iijima. *Journal of The Franklin Institute*. 340 (3-4): 221-42.
- Callister, W.D., (2003). *Materials Science and Engineering an Introduction*. 6th edition. New York. John Willey and Sons.
- Cappelli E., Orlando S., Mattei G., Armigliato A. (2004). Boron nitride thin films deposited by RF plasma reactive pulsed laser ablation as interlayer between WC-Co hard metals and CVD diamond films. *Surface and Coatings Technology*. 180 -181: 184-189
- Cappelli E., Orlando S., Pinzari F., Napoli A., Kaciulis S. (1999). WC-Co cutting tool surface modifications induced by pulsed laser treatment. *Applied Surface Science*. 138-139: 376-382.
- Cappelli E., Pinzari F., Ascarelli P., Righini G. (1996). Diamond nucleation and growth on different cutting tool materials: influence of substrate pre-treatments, *Diamond and Related Materials*. 5: 292-298.
- Cardinale G.F., Howitt D.G., Mc.Carty K.F., Medlin D.L., Mirkarimi P.B. and Moody N.R. (1996). Analysis of residual stress in cubic boron nitride thin films using micromachined cantilever beams *Diamond and Related Materials* 5: 1295 – 1302
- Childs T.H.C, Maekawa K., Obikawa T., and Yamame T. (2000). *Metal Machining Theory and Application*, New York: John Willey and Sons. Inc.

- Chowdhury S.E., De Barra, Laugier M.T. (2005). Hardness measurement of CVD diamond coatings on SiC substrates. *Surface & Coatings Technology*, 193, 200–205
- Collazo-Davila C., Bengu E., Marks L.D., Kirk M. (1999). Nucleation of cubic boron nitride thin films. *Diamond and Related Materials*. 8: 1091–1100
- Cullity, B.D. (1978). *Element of X-Ray Diffraction*. 2nd.ed. New York: Mc Graw-Hill
- Davis R.F. (1993). *Diamond Films and Coating*. New Jersey: Noyes Publications.
- De Barros M.I., Vandenbulcke L., Chinsky L., Rats D., Von Stebut J. (2001). Smooth fine-grained diamond coatings on titanium alloy for mechanical applications. *Diamond and Related Materials*, 10, 337 - 341
- Deuerler F., O. Lemmer, M. Frank, M. Pohl, C. Heßing. (2002). Diamond films for wear protection of hardmetal tools, *International Journal of Refractory Metals & Hard Materials*. 20: 115-120
- Deurler F., H.Van den Berg, R.Tabersky, Freundlieb A., Pies M., Buck V. (1996). Pretreatment of substrate surface for improved adhesion of diamond films on hard metal cutting tools, *Diamond and Related Material*. 5: 1478 - 1489.
- Dobrzański L.A.Mikuła., J. (2005). Structure and properties of PVD and CVD coated Al₂O₃ + TiC mixed oxide tool ceramics for dry on high speed cutting processes. *Journal of Materials Processing Technology*. 164–165: 822–831
- Dongping Liu, Gunther Benstetter, Edgar Lodermeier, Xi Chen, Jianning Ding, Yanhong Liu, Jiaaliang Zhang, Tengcai Ma. (2003). Surface and structural properties of ultra thin diamond-like carbon coating. *Diamond and Related Materials*. 12: 1594 - 1600.
- Endler I., Leonhardt A., Scheibe H-J, Born R. (1996). Interlayer for diamond deposition on tool materials. *Diamond and Related Materials*. 5: 299 - 303.
- Evans A.G., Hutchingson J.W., He M.Y. (1999). Micromechanics model for the detachment of residually compressed brittle films and coatings. *Acta Material*. 47: 1513-1522.
- Fantoni, E. Borsella, Piccirillo S. and Ceccato E.S.. (1990). Laser synthesis and crystallographic characterization of ultra-fine SiC powder. *Journal Material Research*. 5:1
- Faure C, W. Hanni, Julia Schmutz C., Gervanoni M.. (1999). Diamond-coated tools. *Diamond and Related Materials*. 8: 830-833.
- Fernandes A.J.S., Salgueiredo E., Oliveira F.J., Silva R., Costa F.M., (2005),

- Directly MPCVD diamond-coated Si₃N₄ disks for dental applications. *Diamond and Related Materials*. 14: 626- 630
- Gheeraert, E. Deneuille A. and Bonnot A. M. (1992), Defects and stress analysis of the Raman spectrum of diamond films, *Diamond and Related Materials*, 1: 525 - 528.
- Goodwin, D. G. and Butler, J. E., (1997), In *Handbook of industrial diamonds and diamond films* (ed. M. A. Prelas, G. Popovici & L. K. Bigelow), ch. 11. New York: Marcel Dekker.
- Gottardi G., N. Laidani, Bartali R., Filippi M, L. Calliari, Brusa R.S., Mariazzi S., Macchi C., Anderle M.. (2005). Amorphous carbon films PACVD in CH₄-CO₂ under pulsed and continuous substrate bias conditions. *Diamond & Related Materials* 14: 1031-1035.
- Gunnar J, Alahelisten A. (1996). Thermal stresses in diamond coatings and their influence on coating wear and failure. *Surface Coating Technology*. 80: 303-312.
- Halling J. (1983).The tribology of surface films. *Thin Solid Films*. : 108: 103 – 115
- Harbeur R. and Lux B.. (1996).On the formation of diamond coatings on WC/Co hard metal tools. *Int. J. Refract. Metal Hard Material*. 5: 111 - 118
- Hassouni, K. Grotjhon T. A. and Gicquel A. (1999). Self-consistent microwave field and plasma discharge simulations for a moderate pressure hydrogen discharge reactor. *Journal of Applied Physics*. 86: 134 – 151.
- Hideaki Itoh, Sung-Soo Lee, Kazuyoshi Sugiyama, Hiroyasu Iwahara, Takahiro Tsutsumoto. (1999). Adhesion improvement of diamond coating on silicon nitride substrate. *Surface and Coatings Technology*. 112: 199-203.
- Hirai, H., Fukunaga O., Odawara O. (1991). Effect of Microwave Power on Hydrogen Content in Chemically Vapor Deposited Diamond Films. *Journal of American Ceramic Society*. 74: 1715.
- Hsieh J.H., Liang C., Yu C.H., Wu W. (1998). Deposition and characterization of TiAlN and multi-layered TiN/TiAlN coatings using unbalanced magnetron sputtering. *Surface and Coatings Technology*. 108–109: 132–137
- Huang, T.C. In; Barret; C.S. (1990). *Advances in X-Ray Analysis*. New York: Plenum
- Hunn, J. D., Withrow, S. P., White, C. W., Clausing, R. E., Heatherly, L. & Christensen, C. P. (1994). . *Appl. Phys. Lett*. 65: 3072.
- Inderjeet, K., Ramesh S., Chakrabarty, C. K. (1999). Nucleation and growth of polycrystalline diamond particles on ceramic substrates by microwave plasma

- CVD. *Surface Modification Technologies (SMT XIII)*, ASM International, 13, 83 – 90.
- Jian X.G, L.D. Shi, Chen M., Sun F.H. (2006). Tribological studies on ultra-fine diamond composite coatings deposited on tungsten carbide. *Diamond & Related Materials* 15: 313 - 316
- Kikuchi N and Komatsu T., Yoshimura H.. (1988). Characteristics of thin film growth in the synthesis of diamond by chemical vapour deposition and application of the thin film synthesis technology for tool. *Materials Science and Engineering*. 105: 525-534
- Li X, James Perkins, Ramon Collazo, Robert J. Nemanich, Zlatko Sitar. (2006). Investigation of the effect of the total pressure and methane concentration on the growth rate and quality of diamond thin films grown by MPCVD. *Diamond & Related Materials*. 15: 1784-1788.
- Lin C R, Cheng Tzuo Kuo, Ruey Ming Chang. (1998). Improvement in adhesion of diamond films on cemented WC substrate with Ti-Si interlayers. *Diamond and Related Materials*. 7: 1628-1632
- Lin C.R, Su C.H., Hung C.H., Chang C.Y., Shi-Hao Yan. (2005). The effect of the substrate position on microwave plasma chemical vapor deposition of diamond films. *Surface and Coatings Technology*.
- Liu H., D.S. Dandy. (1995). *Diamond Chemical Vapor Deposition: Nucleation and Early Growth Stages*. New Jersey. Noyes Publications.
- Liu Z.J, Zi-Kui Liu, Charles McNerny, Pankaj Mehrotra, Aharon Inspektor. (2005). Investigations of the bonding layer in commercial CVD coated cemented carbide inserts. *Surface and Coatings Technology*. 198: 161- 164.
- Lugscheider E., Knotek O., Zimmermann H., Hellmann S.. (1999). Investigation of the mechanical and structural properties of Ti–Hf–C–N arc PVD coatings. *Surface and Coatings Technology*. 116–119: 239–243
- Lux B and Haubner R. (1994). Diamond substrate interactions and the adhesion of diamond coatings. *Pure and Appl. Chem*. 66: 1783 -1788
- Maeda H., Sumihisa Masuda, Katsuki Kusakabe and Shigeharu Morooka (1992). Nucleation and growth of diamond in a microwave plasma on substrate pretreated with non-oxide ceramic particles. *Journal of Crystal Growth*. 121(3): 507-515
- Malcher V, Mrska A., Kromka A., Satka A., anik J. J. (2002). Diamond film coated

- on WC/Co tools by double bias-assisted hot filament CVD. *Current Applied Physics*. 2: 201-204
- Mallika K., Komanduri R. (2001). Low pressure microwave plasma assisted chemical vapor deposition (MPCVD) of diamond coatings on silicon nitride cutting tools. *J. Thin Solid Films* 396: 145-165
- May P.W. (2000). Diamond Thin Film: a 21st-Century Material. *Phil. Trans. R. Soc. Lond. A*. 358: 473 - 495
- Miyahara K., Nagashima N., Ohmura T., and Matsuoka S.. (1999). Evaluation of mechanical properties in nanometer scale using AFM-based nanoindentation tester. *Nanostructured Materials*. 12: 1049-1052
- Miyoshi K. (1999). *Surface Diagnostics in Tribology Technology and Advanced Coatings Development*. Glenn Research Center. Cleveland. Ohio. NASA/TM-1999-208527.
- Miyoshi K. (2002). *Surface Characterization Techniques: An Overview*, NASA/TM - 2002 - 211497, Glenn Research Center, Cleveland, Ohio
- Mohrbacher H, K. Van Acker, Blanpain B., Van Houtte P., Celis J.P.. (1996). Comparative measurement of residual stress in diamond coatings by low-incident-beam-angle-diffraction and micro-Raman spectroscopy. *Journal of materials research*. 11: 1776 - 1782
- Murayama M., Kojima S., Uchida K. (1991). Uniform deposition of diamond films using a flat flame stabilized in the stagnation-point flow. *Journal of Applied Physics*. 69, 7924-7926.
- Ohring M. (1992). *The material sciences of thin films*. Hoboken. New Jersey. Academic press.
- Olszyna A., Smolik J. (2004). Nanocrystalline diamond-like carbon coatings produced on the Si₃N₄ -TiC composites intended for the edges of cutting tools. *Thin Solid Films*. 459: 224-227
- Pandey M., D. Bhattacharyya , D.S. Patil , Ramachandran K., Venkatramani N. (2004). Diamond-like carbon coatings: AFM and ellipsometric studies. *Surface and Coatings Technology*. 182: 24-34
- Park J.K, Dae-Hoon Kim, Wook-Seong Lee, Dae-Soon Lim, Young-Joon Baik. (2005). Adhesion improvement of the diamond film in diamond-coated WC-Co insert prepared with AC substrate bias. *Surface and Coatings Technology*. 193: 234 - 238.

- Peng X.L, H.F. Liu, Z.P. Gan, H.Q. Li, H.D. Li. (1995). Characterization and adhesion strength of diamond films deposited on silicon nitride inserts by d.c. plasma jet chemical vapour deposition. *Diamond and Related Materials*. 4: 1260 – 1266.
- Pierson H.O. (1993). *Handbook of Carbon, Graphite, Diamond, and Fullerenes*. New Jersey, USA. Noyes Publications.
- Pierson H.O. (1999). *Handbook of Chemical Vapor Deposition: Principles, Technology and Applications, 2nd edition*. New York, USA. Noyes Publications.
- Piscanec S, Mauri F., Ferrari A.C., Lazzeri M., Robertson J.. (2005). Ab initio resonant Raman spectra of diamond-like carbons. *Diamond and Related Materials*. 14: 1078- 1083
- Polini R, Fabrizio Casadei , Pierangelo D'Antonio , Enrico Traversa. (2003a). Dry turning of alumina/aluminum composites with CVD diamond coated Co-cemented tungsten carbide tools. *Surface and Coatings Technology*. 166:127-134.
- Polini R, Pierangelo D'Antonio, Enrico Traversa. (2003b). Diamond nucleation from the gas phase onto cold-worked Co-cemented tungsten carbide. *Diamond and Related Materials*. 12: 340-345
- Polini R., Fabio Pighetti Mantini, Massimiliano Barletta, Roberta Valle, Fabrizio Casadei. (2006). hot filament chemical vapor deposition and wear resistance of diamond films on WC-Co substrates coated using PVD-arc deposition technique. *Diamond and Related Materials*. 15: 1284 - 1291.
- Quinto D. T. (1996). Technology perspective on CVD and PVD coated metal-cutting tools. *Int. J. of Refractory Metals & Hard Materials*. 14: 7-20.
- Raghuveer M. S, S.N. Yoganand, K. Jagannadham, R.L. Lemaster, J. Bailey. (2002). Improved CVD diamond coatings on WC-Co tool substrates. *Wear*. 253: 1194-1206.
- Rahaman M. N. (2003). *Ceramic Processing and Sintering, 2nd edition*. New York. Marcel Dekker Inc.
- Ralchenko V.G., Smolin A.A., Pereverzev V.G., Obraztsova E.D., Korotoushenko K.G, Konov V.I., Lakhokin Yu V and Loubnin E.N. (1995). *Diamond Related Material*. 4: 754.
- Rats D, Vandenbulcke L., Herbin R., Bou P. and Beny C. (1995). Pressure influence on the diamond deposition domain from various C---H---O (-Ar)-containing

- gaseous mixtures. *Diamond and Related Materials*. 4: 207-215.
- Raymond B. Corvin, Joseph G. Harrison, Shane A. Catledge, and Yogesh K. Vohra. (2002). Gas-phase thermodynamic models of nitrogen-induced nanocrystallinity in chemical vapor-deposited diamond. *Applied Physics Letters*. 80(4): 2550 - 2552
- Rie K.T., A. Gebauer, J. Wohle, H.K. Tonshoff, C. Blawit. (1995). Synthesis of TiN/TiCN/TiC layer systems on steel and cermet substrates by PACVD. *Surface and Coatings Technology*. 74 -75: 375-381
- Risti G.S, Zarko D. Bogdanov, Slavica Zec, Nebojša Romcevic, Zorana Dohcevic-Mitrovic, Šćepan S. Miljanic. (2003). Effect of the substrate material on diamond CVD coating properties. *J. Materials Chemistry and Physics*. 80: 529-536.
- Ristic G S, Zarko D. Bogdanov, Slavica Zec, Nebojsa Romcevic, Zorana Dohcevic-Mitrovic, Scepan S. Miljanic. (2003). Effect of the substrate material on diamond CVD coating properties. *J. Materials Chemistry and Physics*. 80: 529-536
- Roberts, G.A. and Cory, R.A. (1980). *Tools steels*. 4th ed. Metals Park Ohio. American Society for Metals.
- Sangeeta D. (1997). *Inorganic Materials Chemistry Desk References and Index*. Florida. CRC Press LCC.
- Schwartz M. (2002). *Encyclopedia of materials, parts, and finishes*. 2rd ed. Florida. CRC Press LLC.
- Seidel F., H. R. Stock, P. Mayr. (1998). Carbon, nitrogen and oxygen implantation into TiN coatings. *Surface and Coatings Technology*. 108–109: 271–275
- Sein H, Waqar Ahmed, Mark Jackson , Robert Woodward , Riccardo Polini. (2004). Performance and characterization of CVD diamond coated, sintered diamond and WC-Co cutting tools for dental and micromachining applications. *Thin Solid Films*. 447 - 448: 455-461
- Sein H., W Ahmed, C A Rego, A N Jones, M Amar, M Jackson and R Polini. (2003b). Chemical vapor deposition diamond coating on tungsten carbide dental cutting tools. *J. Phys.: Condens. Matter*. 15: S2961-S2967.
- Sein H., W. Ahmed , M. Jackson , R. Polini , I. Hassan , M. Amar , C. Rego. (2004). Enhancing nucleation density and adhesion of polycrystalline diamond films deposited by HFCVD using surface treatments on Co cemented tungsten carbide. *Diamond and Related Materials*. 13: 610-615.

- Sein H., W. Ahmed, M. Jackson, N. Ali, J. Gracio. (2003a). Stress distribution in diamond films grown on cemented WC-Co dental burs using modified hot-filament CVD. *Surface and Coatings Technology*. 163 -164: 196-202
- Shinha A. K. (2003). *Physical Metallurgy Handbook*. USA. Mc. Graw Hill.
- Silva F., Benedic F., Bruno P., Gicquel A. (2005). Formation of {110} texture during nanocrystalline diamond growth: an X-ray diffraction study. *Diamond & Related Materials*. 14: 398- 403
- Silva F., Gicquel A., Tardieu A., Cledat P. and Chauveau Th. (1996). Control of an MPACVD reactor for polycrystalline textured diamond films synthesis: role of microwave power density. *Diamond and Related Material*. 5: 338 - 344.
- Silva V.A, Corat E.J., Silva C.R.M.. (2001). Influence of CF₄ addition for HFCVD diamond growth on silicon nitride substrates. *Diamond and Related Materials*. 10: 2002 - 2009.
- Silva V.A., Costa F.M., Fernandes A.J.S, Nazare M.H., Silva R.F.. (2000). Influence of SiC particle addition on the nucleation density and adhesion strength of MPCVD diamond coatings on Si₃N₄ substrates. *Diamond and Related Materials*. 9: 483-488
- Straffelini G., Scardi P., Molinari A., Polini R. (2001). Characterization and sliding behavior of HFCVD diamond coatings on WC-Co. *Wear*. 249: 461-472.
- Strawbridge A., Evans H.E. (1995). Mechanical failure of thin brittle coatings. *Engineering Failure Analysis*. 22: 85-103.
- Sun F.H., Zhang Z.M., Chen M., Shen H.S. (2003). Improvement of adhesive strength and surface roughness of diamond films on Co-cemented tungsten carbide tools. *Diamond and Related Materials*. 12: 711-718.
- Takeuchi S, Kojima M., Murakawa M. (2003). Evaluation of mechanical properties of high-toughness multilayered diamond films. *Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference (ADC/FCT 2003)*. August 18-21. Tsukuba. Japan. NASA Glenn Research Center. 197 - 200.
- Tallaire A., Silva V.A., Fernandes A.J.S., Costa F.M., Silva R.F. (2002). Effect of intergranular phase of Si₃N₄ substrates on MPCVD diamond deposition. *Surface and Coatings Technology*. 151 -152: 521-525
- Tang W, Wang Q., Wang S., Lu F. (2001). Adherent diamond coating on cemented carbide substrates with different cobalt contents. *Diamond and Related*

- Materials*. 10: 1700 - 1704
- Tang W, Wang Q., Wang S., Lu F. (2002). A comparison in performance of diamond coated cemented carbide cutting tools with and without a boride interlayer. *Surface and Coatings Technology*. 153: 298-303
- Tang W, Wang S., Lu F. (2000). Preparation and performance of diamond coatings on cemented carbide inserts with cobalt boride interlayers. *Diamond and Related Materials*. 9: 1744 - 1748
- Ternyak, O., Akhvlediani R., Hoffman A. (2005). Study on diamond films with ultra high nucleation density deposited onto alumina, sapphire and quartz. *Diamond and Related Materials*. 14: 323-327
- Tonshoff H.K., Blawit C. (1997). Development and evaluation of PACVD coated cermet tools. *Surface and Coatings Technology*. 93: 119-127
- Tonshoff H.K., Mohlfeld A., Gey C., Winkler J. (1998). Surface modification of cemented carbide cutting tools for improved adhesion of diamond coatings. *Surface and Coatings Technology*. 108-109:543-550
- Tsubota T, Shintaro Ida , Naoki Okada , Masanori Nagata , Yasumichi Matsumoto, Nobumitsu Yatsushiro. (2003). CVD diamond coating on WC-Co cutting tool using ECR MPCVD apparatus via electrophoretic seeding pretreatment, *Surface and Coatings Technology*. 169 -170: 262-265
- Uhlmann E., Brücher M. (2003). Tribological behavior of CVD diamond tools, *Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference (ADC/FCT 2003)*. August 18-21. Tsukuba, Japan. NASA Glenn Research Center. 191 - 196.
- Vandierendonck K., Nesladek M., Kadlec S., Quaeysaegens M., Van Stappen M., Stals L.M.M. (1998). W/WC diffusion barrier layer for CVD diamond coatings deposited on WC-Co: microstructure and properties. *Surface and Coating Technology*. 98: 1060 - 1065
- Vojs M.,T, Vesely M., Redhammer R., Janík J., Kadlec'kova M., Danisa T., Marton M., Michalka M., Sutta P. (2005). Double bias HF CVD multilayer diamond films on WC-Co cutting tools. *Diamond & Related Materials*. 14: 613-616.
- Windischmann H, Epps G.F., Cong Y., Collins R.W. (1991). Intrinsic stress in diamond films prepared by microwave plasma CVD. *Journal Applied of Physics*. 69: 2231 – 2237.
- Wong M.S, Meilunas R., Ong T.P., Chang R.P.H. (1989). Tribological properties of

- diamond films grown by plasma-enhanced chemical vapor deposition. *Applied Physics Letter*. 54: 2006-2008.
- Yap Y. K., Aoyama T., Wada Y., Yoshimura M., Mori Y. and Sasaki T. (2000) Growth of adhesive c-BN films on a tensile BN buffer layer. *Diamond and Related Materials*. 9: 592-595
- Yongqing Fu, Chang Q. Sun, Hejun Du , Bibo Yan. (2002). From diamond to crystalline silicon carbonitride: effect of introduction of nitrogen in CH₄/H₂ gas mixture using MW-PECVD. *Surface and Coatings Technology*. 160: 165-172.
- Zalavutdinov R.K, Gorodetsky A.E., Zakharov A.P., Lakhotkin Y.V., Ralchenko V.G., Samakhvalov N.V., Anikin V.N., Pjyanov A.I.. (1998). Diamond-coated cemented carbide cutting insets. *Diamond and Related Materials*. 7: 1014 - 1016.
- Zhihai Cai, Ping Zhang, Jun Tan (2007). Adhesion improvement of cubic boron nitride film on high speed steel substrate by BN_x implanted buffer interlayer. *Surface & Coatings Technology*. 201: 6723–6725
- Zhu W, Badzian A. R. and Messier. R. (1990). Morphological Phenomena of CVD Diamond (Part I). *Proc. SPIE (Diamond Optics III)*. 1325: 187-201