Table of Contents

1 INTRODUCTION 1 – FILMS AND MATERIALS 1

1.1 DIAMOND AND GRAPHITE 1

1.1.1 Introduction 1
1.1.2 Uses of Diamond 7
1.1.3 The Doping of Diamond 8

1.2 DIAMOND LIKE CARBON 9

1.2.1 Introduction 9
1.2.2 Uses of DLC 10
1.2.3 The Doping of DLC 11
1.2.4 The Deposition of DLC 13
1.2.4.1 Ion Beam Deposition Methods (Ion Deposition and Ion Assisted Sputtering) 16
1.2.4.2 Sputtering 17
1.2.4.3 Cathodic Vacuum Arc 18
1.2.4.4 Plasma Enhanced Deposition 18
1.2.4.5 Pulsed Laser Deposition 19

1.3 CARBON NITRIDE 20

1.3.1 The Properties of Carbon Nitride 20
1.3.2 Production of Carbon Nitride 22

1.4 CARBON PHOSPHIDE 24

1.4.1 Introduction 24
1.4.2 The Properties of Carbon Phosphide 24
1.4.3 Experimental Reports of Carbon Phosphide Materials 29

1.5 REFERENCES 32

2 INTRODUCTION 2 - DEPOSITION METHODS 39

2.1 RADIO FREQUENCY PLASMA ASSISTED CHEMICAL VAPOUR DEPOSITION (RF-CVD) 39

2.1.1 Striking and Maintenance of a Plasma 39
2.1.2 The Sheath Region 42
2.1.3 DC-Bias 43
2.1.4 The Average Ion Energy 45

2.2 PULSED LASER ABLATION AT THE SOLID-LIQUID INTERFACE 49

2.3 REFERENCES 54

3 EXPERIMENTAL METHODS *56*
3.1 DEPOSITION METHODS **56**
3.1.1 Radio Frequency Plasma Enhanced Chemical Vapour Deposition (RFCVD) 56
3.1.2 Pulsed laser ablation at the solid-liquid interface (LP-PLA) 61
3.1.2.1 Manufacture of Mixed Carbon/Phosphorus Targets for Laser Ablation at the Solid-Liquid Interface 64
3.2 PROCESSING METHODS **65**
3.2.1 Thermal Annealing 65
3.3 ANALYSIS METHODS **67**
3.3.1 X-ray photoelectron spectroscopy (XPS) 67
3.3.1.1 X-ray photoelectron spectroscopy at the Daresbury Laboratory Synchrotron Light Source. 71
3.3.2 Secondary Ion Mass Spectrometry (SIMS) 75
3.3.3 Auger Electron Spectroscopy (AES) and Energy Dispersive X-ray Spectroscopy (EDX) 80
3.3.4 Scanning Electron Microscopy (SEM) 82
3.3.5 Transmission Electron Microscopy (TEM) 84
3.3.6 Laser Raman Spectroscopy (LRS) 85
3.3.7 Ultraviolet / visible (UV/Vis) spectroscopy 87
3.3.8 Optical Emission Spectroscopy (OES) 88
3.3.9 X-ray Powder Diffraction (XRD 89
3.4 REFERENCES **91**

4 RESULTS AND DISCUSSION: RF PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION *92*
4.1 DLC AND AMORPHOUS CARBON THIN FILMS **92**
4.1.1 Aims 92
4.1.2 Growth and Analysis Parameters 93
4.1.3 Results and Discussion 95
4.2 ADDITION OF PH_3 TO THE PROCESS GAS MIXTURE **100**
4.2.1 Aims 100
4.2.2 Deposition and Analysis Parameters 100
4.2.3 Results and Discussion 101
4.3 VARIATION OF THE ION ENERGY AND ITS EFFECT ON THE DEPOSITION OF AMORPHOUS CARBON PHOSPHIDE THIN FILMS **120**
4.3.1 Aims 120
4.3.2 Deposition and Analysis Parameters 120
4.3.3 As-deposited films 121
4.3.4 Annealed films 124
4.3.5 XPS at the Synchrotron Radiation Light Source 126

4.3.6 Conclusion 128
4.4 THE EFFECT OF SUBSTRATE TEMPERATURE ON THE DEPOSITION OF CARBON PHOSPHIDE THIN FILMS 128
4.4.1 Aims 128
4.4.2 Deposition and analysis parameters 129
4.4.3 Results and discussion 129
4.4.4 Conclusions 135
4.5 REFERENCES 136

5 LASER ABLATION AT THE SOLID/LIQUID INTERFACE 138

5.1 GRAPHITE ABLATED UNDER OXYGEN AND CARBON CONTAINING LIQUIDS 138
5.1.1 Ablation of Graphite Under Water 139
5.1.2 Ablation of Graphite Under Cyclohexane 146
5.1.3 Optical Emission Spectra of the Ablation Plume 150
5.2 PHOSPHORUS ABLATED UNDER CARBON CONTAINING LIQUIDS 152
5.2.1 The Ablation of Phosphorus Under Cyclohexane 152
5.2.2 Ablation of Phosphorus Under Xylene 170
5.2.3 Ablation of mixed (red phosphorus/graphite) targets under cyclohexane. 171
5.3 REFERENCES 174

6 SUMMARY AND CONCLUSIONS 176

6.1 RF-DEPOSITION OF AMORPHOUS CARBON PHOSPHIDE 176
6.2 PULSED LASER ABLATION AT THE SOLID/LIQUID INTERFACE 177
6.3 FURTHER WORK 178
6.4 REFERENCES 178

A The Synthetic Route Towards Carbon Phosphide A1