View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Sydney eScholarship

Metal plasma immersion ion implantation and deposition using polymer substrates

By
Thomas William Henry Oates

A thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy

School of Physics
University of Sydney
Sydney Australia

September 2003

Contents

Abstract v
Acknowledgements vii
Author's contributions viii
Author's publications relating to this work ix
List of figures and tables xi

1. Introduction 1

2. Review of Ion Implantation 4
- **2.1. Ion implantation of polymers 4**
  - 2.1.1. Polymer structure 4
  - 2.1.2. Ion-polymer interactions 7
  - 2.1.3. Thermal considerations 12
  - 2.1.4. Examples in the literature 16
- **2.2. Plasma Immersion Ion Implantation 20**
  - 2.2.1. Introduction 20
  - 2.2.2. The physics of plasma sheaths 22
  - 2.2.3. Metal plasma immersion ion implantation and deposition 30
  - 2.2.4. Plasma immersion ion implantation of insulators 33
- **2.3. References 35**

3. Cathodic Vacuum Arcs 39
- **3.1. Introduction 39**
  - 3.1.1. Historical overview 39
  - 3.1.2. Arc thin film deposition 40
  - 3.1.3. Arc ion source 41
- **3.2. General considerations 42**
  - 3.2.1. Cathodic arc components 42
  - 3.2.2. The arc discharge 43
  - 3.2.3. Pulsed vs continuous 44
- **3.3. Cathode spots 45**
  - 3.3.1. Current per spot 46
  - 3.3.2. Current density 46
  - 3.3.3. Ion velocities 47
  - 3.3.4. Ion charge states 48
  - 3.3.5. Spot types 49
  - 3.3.6. Retrograde motion 49
- **3.4. DC arc applications 51**
  - 3.4.1. DC arc design 52
  - 3.4.2. Plasma properties 54
    - 3.4.2.1. Plasma density 54
    - 3.4.2.2. Ion energies 56
  - 3.4.3. Film adhesion 57
  - 3.4.4. Ceramic films 59
  - 3.4.5. Polymer PIII 60

3.5. References **63**

4. Thin Conductive Film Method **66**

4.1. *Plasma immersion ion implantation using polymeric substrates with a sacrificial conductive surface layer*,
Published in Surface and Coatings Technology
Volume 156, pages 332-337, 2002 67

4.2. *Insulator surface charging and dissipation during plasma immersion ion implantation using a thin conductive surface film*,
Published in Journal of Applied Physics
Volume 92, number 6, pages 2980-2983, Sept. 2002. 73

5. Pulsed Cathodic Vacuum Arc **77**

5.1. Introduction **77**
5.2. System design **79**
5.2.1. Arc triggering 80
5.2.2. Anode design 82
5.2.3. Power supply 85
5.3. Cathode spots in a high current pulsed arc **92**
5.3.1. Retrograde motion and spot velocities 92
5.3.2. Spot types 97
5.4. Operational performance **102**
5.5. Conclusion **104**
5.6. References **105**

6. Sheath measurements **108**

6.1. *Electric probe measurements of high voltage sheath collapse in cathodic arc plasmas due to surface charging of insulators*,
Published in IEEE transactions on plasma science
Volume 31, number 3, pages 438-443, June 2003. 109

7. Ultra-thin films **115**

7.1. Introduction **115**
7.2. Film growth **116**
7.2.1. Growth modes 116
7.2.2. Thermodynamic considerations 117
7.2.3. Island nucleation and growth 119
7.2.4. Particle mobility 120
7.2.5. Bulk film properties 121
7.3. Percolation Theory and Experiments **123**
7.3.1. *In-situ* resistivity measurements 125
7.3.2. Influence of the substrate and deposition parameters 128
7.4. Post-deposition resistance changes **130**
7.4.1. Observations 130

7.4.2. Negative Temperature Coefficient of Resistance 133
7.5. Conclusions 138
7.6. References 139

8. Spectroscopic Ellipsometry 142
8.1. Introduction 142
8.2. Fundamentals of Ellipsometry 142
8.2.1. Data representation 143
8.2.2. Modelling 144
8.2.3. Uncertainties 145
8.3. Ellipsometer Hardware 147
8.4. Experiments 148
8.4.1. Variable-angle *ex-situ* spectroscopic ellipsometry 148
8.4.2. *In-situ* spectroscopic ellipsometry 151
8.4.2.1. Pulsed cathodic vacuum arc deposition of titanium 151
8.4.2.2. Modelling using the method of Arwin and Aspnes 154
8.4.2.3. Discussion 156
8.5. Effective Medium Approximations 162
8.5.1. Theories 162
8.5.2. Analysis 164
8.6. Real-time *in-situ* spectroscopic ellipsometric study of post deposition morphological changes 168
8.6.1. Experimental 169
8.6.2. Results 169
8.6.3. Discussion 171
8.7. Conclusions 173
8.8. References 174

9. Conclusions 176

Appendix 1: Matlab code
Appendix 2: Third year lab experiment.

Abstract

This thesis investigates the application of plasma immersion ion implantation (PIII) to polymers. PIII requires that a high negative potential be applied to the surface of the material while it is immersed in a plasma. This presents a problem for insulating materials such as polymers, since the implanting ions carry charge to the surface, resulting in a charge accumulation that effectively neutralises the applied potential. This causes the plasma sheath at the surface to collapse a short time after the potential is applied.

Measurements of the sheath dynamics, including the collapsing sheath, are performed using an electric probe. The results are compared to theoretical models of the plasma sheath based on the Child-Langmuir law for high voltage sheaths. The theoretical model predicts well the sheath dynamics for conductive substrates. For insulating substrates the model can account for the experimental observations if the secondary electron coefficient is modified, justified on the basis of the poly-energetic nature of the implanting ions.

If a conductive film is applied to the insulator surface the problem of charge accumulation can be avoided without compromising the effectiveness of PIII. The requirement for the film is that it be conductive, yet transparent to the incident ions. Experimental results are presented which confirm the effectiveness of the method. Theoretical estimates of the surface potential show that a film of the order of 5nm thickness can effectively circumvent the charge accumulation problem. Efforts to produce and characterise such a film form the final two chapters of this thesis. The optimal thickness is determined to be near the percolation threshold, where a marked increase in conductivity occurs. Spectroscopic ellipsometry is shown to be an excellent method to determine the film thickness and percolation threshold non-invasively.

Throughout this work cathodic vacuum arcs are used to deposit thin films and as a source of metal plasmas. The design and construction of a pulsed cathodic vacuum arc forms a significant part of this thesis. Investigations of the cathode spots and power supply requirements are presented.

“When the conjunctions of matter are in your favour a moment
Go and live happily, you did not choose your lot;
Keep company with men of science since your bodily properties
Are a speck of dust joined with a puff of air, a mote with a gasp of breath.”

Omar Khayyam

Acknowledgements:

Thanks to my supervisors Marcela Bilek and David McKenzie, who have provided guidance and encouragement throughout this project. The examples they have provided me by setting high standards of scientific integrity and demonstrating a diligent work ethic have been invaluable.

Early in this project it became clear to me that there was a lot to learn from a man named John Pigott. With over 40 years experience in the plasma physics department, he is a wealth of knowledge, and I unabashedly stuck to him like glue for a large portion of this project. The construction of the pulsed vacuum arc must be largely attributed to him. His contribution to many other facets of this thesis is also gratefully acknowledged.

The two months spent as a visiting research student with André Anders in Berkeley, California, had a profound impact on the direction and outcomes of this work. I thank him firstly for the opportunity, but also for the patience and hospitality he afforded me during my stay.

Special thanks also to Richard Tarrant, Terry Pfieffer, Mick Paterson, Graham Mannes and Leanne Howie for technical and administrative assistance and support.

Thanks to Damo, Chris, Joce, Kerrie, Bee, Manni, Bosi and Michael; fellow PhD students and postdocs, who know what its like…

Finally thanks to Mum, Dad, Heidi, Rose, Big Dave, Poss, Ronnie, Lizzy, Daisy, Bob, Matt, Taus, Cheetah, Mr Mikey, Chad, Jug, Rosco, Rombo, Podders and Savvy…

“How long boy will you chatter about the five senses and the four elements?
What matter if the puzzles be one or a hundred thousand?
We are dust, strum the harp boy.
We are air, boy, bring out the wine.”

Omar Khayyam, b.1048-d.1131
Astronomer and Mathematician

Author’s contributions

Chapter 1 is an introductory chapter. Chapter 2 is a review chapter and contains no original results apart from figure 2.1, which was produced by the author using the computer program TRIM, and figure 2.3, which was produced using MATLAB with code written by the author from published theory.

The first half of chapter 3 is a review. The second half contains results from experiments performed by the author. Dr Richard Tarrant provided figure 3.3. An undergraduate student, Paul Thompson, produced the data for figure 3.4, under supervision of the author.

The results presented in chapters 5, 7 and 8 are the work of the author. John Pigott provided the photographs in figure 5.1. Phil Dennis provided figure 5.4. Dr Eungsun Byon produced half of the data in figure 7.5.

Chapters 4 and 6 comprise published work. Contributions by the co-authors are stated on the following page.

Author's publications relating to this work

Refereed Journals:

T.W.H. Oates, M.M.M. Bilek, D.R. McKenzie, *Plasma immersion ion implantation using polymeric substrates with a sacrificial conductive surface layer*, Surface and Coatings Technology, **156** p.332-337 (2002).

R.N. Tarrant, M.M.M. Bilek, T.W.H. Oates, J. Pigott, D.R. McKenzie, *Influence of gas flow rate and entry point on ion charge, ion counts and ion energy distribution in a filtered cathodic arc,* Surface and Coatings Technology, **156** p.110 –114 (2002).

T.W.H. Oates, M.M.M. Bilek, *Insulator surface charging and dissipation during plasma immersion ion implantation using a thin conductive surface film*, Journal of Applied Physics, **92**(6) p. 2980-2983 (2002).

E. Byon, T.W.H. Oates, A. Anders, *Coalescence of nanometer silver islands on oxides grown by filtered cathodic arc deposition.* Applied Physics Letters, **82**(10) p. 1634-1636 (2003)

T.W.H. Oates, J. Pigott, D.R. McKenzie, M.M.M. Bilek, *Electric probe measurements of high voltage sheath collapse in cathodic arc plasmas due to surface charging of insulators*, IEEE transactions on plasma science, **31**(3) p. 438-443 (2003).

T.W.H. Oates, J. Pigott, D.R. McKenzie, M.M.M. Bilek, *A high-current pulsed cathodic vacuum arc plasma source,* Review of Scientific Instruments, **74** (11) p.4750-4 (2003).

D.T.K. Kwok, T.W.H. Oates, D.R. McKenzie, M.M.M. Bilek. *Determination of the equilibrium ion sheath in the drifting plasma by numerical simulation,* IEEE transactions on plasma science, **31**(5) pt.2, p.1044-51, (2003).

M.M.M. Bilek, D. R. McKenzie, R.N. Tarrant, T. W. H. Oates, P. Ruch, K. Newton-McGee, Yang Shi, D. Thompsett, H.C Nyugen, and D. T. Kwok *Practical plasma immersion ion implantation for stress regulation, treatment of insulators and complex shapes,* submitted to Contributions to Plasma Physics.

Conference papers:

T.W.H. Oates, M.M.M. Bilek, D.R. McKenzie, *Plasma immersion ion implantation of polymers using a sacrificial conductive surface layer*, International conference on Plasma Based Ion Implantation (PBII), Grenoble, France, July 2001

T.W.H. Oates, M.M.M. Bilek, D.R. McKenzie, *Insulator Surface Charging and Dissipation During Plasma Immersion Ion Implantation*. International Gaseous Electronics Meeting (GEM), Murramurrang, Australia, February 2002.

T.W.H. Oates, J. Pigott, P. Denniss, D.R. Mckenzie, M.M.M. Bilek. *Investigations of a pulsed cathodic vacuum arc,* International Conference on Plasma Physics (ICPP), Manly, Australia, July 2002.

M.M.M. Bilek, D.R. McKenzie, T.W.H. Oates, J. Pigott, P. Denniss and J. Vlcek *Deposition of nanoscale multilayered structures using filtered cathodic vacuum arc plasma beams.* NATO Advanced Research Workshop - Emerging Applications of Vacuum-Arc-Produced Plasma, Ion and Electron Beams, Baikal, Siberia, Russia, 2002.

T.W.H. Oates, D.T. Kwok, D.R. Mckenzie, M.M.M. Bilek *High voltage sheath boundary location and range in cathodic arc plasma*, International Conference on Phenomena in Ionised Gases (ICPIG), Greifswald, Germany, July 2003

List of Figures and Tables

Page

Chapter 2

6 Table 2.1: Some common polymers, their repeating units, chemical structure and glass transition temperatures

10 Figure 2.1: TRIM simulation of 10kV Argon ion implantation into PMMA showing the relative contributions to LET from nuclear and electronic stopping.

11 Figure 2.2: Schematic of energetic-ion induced cross-linking and scission.

15 Figure 2.3: Temperature rise at the surface of substrates with widely varying thermal conductivities during a 10kV, 10μs, plasma immersion ion implantation pulse.

21 Figure 2.4: Schematic showing the concept of PIII.

26 Figure 2.5: Child-law sheath evolution

Chapter 3

42 Figure 3.1: Schematic showing the essential components of a cathodic vacuum arc.

46 Table 3.1: Cathodic arc characteristic parameters

50 Figure 3.2: Images of plasma jets bursting toward the retrograde side of the arc spots.

52 Figure 3.3: Schematic of DC cathodic arcs within the school of physics.

55 Table 3.2: Arc currents for low, medium and high density plasma settings.

56 Figure 3.4: Plasma density at the substrate as a function of location relative to the centre of the duct

58 Figure 3.5: Adhesion enhancement of copper films to polycarbonate substrates

60 Figure 3.6: Titanium nitride colour changes caused by ion implantation by PIII.

62 Figure 3.7: Optical micrograph of a scratch made in the surface of polycarbonate subjected to PIII.

Chapter 4

68 Figure 4.1: TRIM calculations showing the percentage of ions transmitted through copper films of different thickness. Also shown for comparison is the conductivity as a function of copper film thickness.

69 Figure 4.2: Cross-sectional TEM micrograph of carbon implanted polycarbonate showing the 10 nm conductive copper film on the surface.

70 Figure 4.3: Cross-sectional TEM micrograph of titanium implanted polycarbonate. The conductive copper film has been removed by acid etching.

71 Figure 4.4: Surface resistivity dependence on PI^3 processing time for titanium implanted polycarbonate for 20 and 50 μs pulse lengths.

75 Figure 4.5: Sheath voltage as a function of time for a planar dielectric insulator with a conductive surface film in a streaming plasma, in an isotropic plasma and in a streaming plasma.

75 Figure 4.6: Sheath width as a function of time for a planar dielectric insulator. (a) in a streaming plasma; (b) in a streaming plasma with a conductive surface film; (c) in an isotropic plasma; and (d) in an isotropic plasma with a conductive surface film.

Chapter 5

80 Figure 5.1: Schematic and photographs of pulse cathodic arc

84 Figure 5.2: Comparison of anode currents for different anode lengths.

86 Figure 5.3: Comparison of current profiles for the two power supplies tested;

87 Figure 5.4: Circuit diagram of the resonant LC circuit power supply used to drive the arc current.

89 Figure 5.5: CCD images of an aluminium cathode.

91 Figure 5.6: CCD images of arc spots on an aluminium cathode taken during an arc pulse.

92 Figure 5.7. Arcing between cathode and anode

93 Figure 5.8: CCD image of a typical arc trace on an aluminium cathode

94 Figure 5.9: 1μs exposures of arcs on aluminium, carbon and titanium cathodes.

95 Table 5.1: Number of cathode spots and current per spot for three different cathode materials at 600μs.

96 Figure 5.10. Arc spot radii vs time for different cathodes.

99 Figure 5.11. CCD images of an aluminium cathode showing transition from type I spot mode to type II mode.

101 Figure 5.12. Mass-spectrometer trace.

Chapter 6

110 Figure 6.1: Schematic of experimental arrangement.

110 Figure 6.2: Example of experimental data.

111 Figure 6.3: The measured width of the high voltage sheath near a conductive substrate as a function of the voltage applied to the substrate, compared with theoretical predictions made using the Child-Langmuir equation.

111 Figure 6.4: Electron current drawn by an electric probe as a percentage of the maximum current drawn when the probe is immersed in the plasma region, demonstrating the non-abrupt nature of the sheath-plasma boundary.

112 Figure 6.5: Example of the collapse of a high voltage sheath near an insulating substrate.

112 Figure 6.6: Observation of the reduction in collapse time of the sheath for an insulating substrate with increasing plasma density.

112 Figure 6.7: Observation of the increase in collapse time of the sheath for an insulating substrate with increased applied substrate voltage.

113 Figure 6.8: Simulation of the propagation of the sheath boundary as a function of time.

113 Figure 6.9: The collapse time of the high voltage sheath as a function of the high voltage applied to the substrate holder.

Chapter 7

117 Figure 7.1: Film growth modes

118 Figure 7.2: Angle the island makes with the surface.

124 Figure 7.3: Experimental arrangement of *in-situ* thin film conductivity measurements.

126 Figure 7.4: Gold film resistivity as a function of film thickness.

129 Figure 7.5: Sheet resistance as a function of film thickness for silver films on glass and zinc-oxide coated glass

131 Figure 7.6: Silver film resistance as a function of time.

134 Figure 7.7: Temperature coefficient of resistance as a function of the initial film resistance.

135 Figure 7.8: Resistance as a function of time for two silver films with different initial resistance values.

137 Figure 7.9: Temperature rise on the substrate surface during a cathodic arc pulse for substrate materials with different thermal properties.

Chapter 8

144 Figure 8.1: Schematic detailing ellipsometric measurements.

149 Figure 8.2: Ψ as a function of wavelength for four incident angles

150 Figure 8.3: Comparison of thickness measurements by profilometer and variable angle spectroscopic ellipsometry.

153 Figure 8.4. Δ and Ψ values for pulsed FCVA titanium deposited on SiO_2/Si in increments of 50 arc pulses.

155 Figure 8.5: Pseudodielectric functions determined for different guesses of film thickness.

156 Figure 8.6. Film thickness as a function of number of arc pulses.

158 Figure 8.7: Pseudodielectric functions for thin titanium films

160 Figure 8.8. Film resistivity vs film thickness for arc deposited titanium

161 Figure 8.9: Rt^2 as a function of film thickness

165 Figure 8.10: Titanium volume fraction as a function of film thickness using three different effective medium theories.

166 Figure 8.11: Mean squared error for the regression fits to the ellipsometric data from figure 7.5 for three different EMA's.

167 Figure 8.12: Film thickness from figure 7.7 scaled with the volume fraction from figure 7.11 to represent the total material deposited as a function of the number of arc pulses.

170 Figure 8.13: Silver film thickness as a function of the number of arc pulses. After 240 pulses the growth rate still has not reached a constant value.

171 Figure 8.14: Changes in the interference peak height and peak location in the tanΨ ellipsometric data.