ELECTRODEPOSITION OF THIN FILMS BY ELECTROCHEMICAL – ATOMIC LAYER DEPOSITION (ALD)

by

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(Under the Direction of JOHN L. STICKNEY)

ABSTRACT

The formation of metal nanofilms using Electrochemical ALD is discussed. Surface Limited Redox Reactions (SLRR) were used to form thin film deposits by ALD. The SLRR involves the underpotential deposition of an atomic layer of a less noble metal (sacrificial metal). This is then replaced in a solution of cations of the desired element, a more noble element. Lead was used as a sacrificial metal in the present studies. Cyclic Voltammetry was used to investigate the optimum deposition potential for Pb. An automated flow cell deposition system was employed to grow metal nano films. No Pb was present in the thin film was evident with electron probe microanalysis (EPMA). It was also shown that the Pb % in a deposit increased, as more negative Pb deposition potential were used. Deposits were characterized using X-ray diffraction (XRD), EPMA, scanning electron micrscopy (SEM), Atomic force microscopy and scanning tunneling microscopy (STM).

INDEX WORDS: Copper, Ruthenium, RuSe, STM, EPMA, XRD, EQCM, Atomic Layer Deposition (ALD), Under Potential Deposition (UPD), Surface Limited Redox Replacement Reaction (SLRRR).

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DEDICATION

I dedicate this dissertation to my wonderful parents, Thambidurai and Usha Thambidurai. Without their support, I would not have made it this far. I think this achievement in my life is as meaningful to them as it is to me.

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CHAPTER 1

INTRODUCTION

Many applications require formation of a nanofilm. Control in their growth can be facilitated by atomic layer deposition (ALD), a methodology for forming deposits one atomic layer at a time via surface limited reactions (*1-3*). Surface limited reactions come in a number of forms, with the classic example involving careful control of the substrate temperature. Higher temperatures promote reaction between the substrate and the depositing element, while at the same time, the temperature must be kept low enough that the depositing element does not react with itself, and form a bulk deposit. In this way, only one atomic layer is formed. To grow thicker films, the process is repeated, in an cycle, with the number of cycles performed determining the thickness of the deposit.

The electrochemical form of ALD has previously been referred to as EC-ALE, or electrochemical atomic layer epitaxy, for the last 15 years (4-20). EC-ALE is now being referred to as ALD, in line with the ubiquitous use of the term ALD in the literature. Most electrochemical surface limited reactions are referred to as underpotential deposition (UPD), known for 50 years (21-26). UPD involves the formation of an atomic layer of one element on a second at a potential prior to that needed to deposit the element on itself. UPD is a thermodynamic process, where an atomic layer is formed as the result of the free energy of formation of a surface compound or alloy. UPD has been used for ALD, in a cycle, to form nanofilms of a wide variety of compounds, such as: II-VI (4, 6-7, 10, 15, 17, 27-46) and III-V

(47-51) compounds like CdTe and InAs. It has also been used for form IV-VI (4, 52-54), V-VII compounds (18, 55-58) and compounds such as PbSe and In_2Se_3 (33). Such compounds can be formed using electrochemical ALD due to the fact that Cd UPD occurs on Te and Te UPD occurs on Cd, creating a workable ALD cycle.

Formation of elemental deposits was originally thought, by the authors, to be impossible, as UPD is the formation of one atomic layer on a different element, after which deposition stops (22-23, 25-26). However, more recent studies by Brankovic and Adzic showed that another route to the formation of a surface limited atomic layer is possible (59-60). They used what is referred to here as a surface limited redox replacement (SLRR) to form nanoclusters of Pt, and Ag on Au electrodes. They were motivated by the fact that it is essentially impossible to form an atomic layer of Pt by UPD deposits, and they wished to control the amount of Pt for the purposes of making unique catalyst surfaces. They showed that you could first form an atomic layer of Cu via UPD, on either Au or Pt, and then exchange it in a Pt^{+4} solution, forming an atomic layer of Pt, and Cu^{2+} ions. They simply performed Cu UPD, and then exchanged it at open circuit (OCP) for the more noble element Pt. The amount of Pt deposited was dependent on the number of electrons available from the Cu UPD. Extension of this SLRR process to the formation of nanofilms by ALD was attempted by the late Michael Weaver, where he repeated the replacement of Cu UPD by Pt ions, a cycle, eight times, forming a Pt coated Au surface (61). He did not refer to his work as ALD, though it is clear that he intended to form Pt nanofilms an atomic layer at a time.

More recently, work by the author's group (62-65), as well as Dimitrov *et. al.* (66-69) have attempted to expand this method and determine the limitations etc. Most of this authors work has involved the alternation of solutions of the sacrificial element (the less noble element

formed by UPD) with the element to be deposited. However, Dimitrov has developed a very simple and clever one solution method, that takes advantage of pulse deposition (*66*). At present, the author is familiar with work on the growth of Cu, Pt, and Ag deposits using SLRR for nanofilm formation by electrochemical ALD. The present paper describes deposition of Ru on a Au surface. Due to the importance of Ru for fuel cell catalysts, there have been a number of atomic level studies of Ru deposition (*70*) (*71*). In general, these studies have shown the formation of clusters, and step decoration on Au electrodes. The basis of such studies has been the spontaneous deposition of Pt-Ru on carbon-supported Pd nanoparticles, using the galvanic displacement method, for the enhancement of oxygen reduction reaction kinetics in the fuel cells (*74*). Galvanic displacement is referred to here as SLRR.

This dissertation mainly focuses on electrochemical ALD of metal and bimetallic thin film using an automated flow cell deposition system. In chapter2 and 3, a method to grow Ru and Cu metal thin films on Au substrate, upto 200 cycles, was investigated using Electrochemical-ALD. In chapter 4, electrodeposition of RuSe thin films was presented for direct methanol fuel cell application. Chapter 5, explains the ALD cycle for Cu deposition on Ru/Ta wafer using UHV and flow cell deposition system. In chapter 6, the conclusions are drawn are presented.

References

- 1. G. Beyer *et al.*, *Microelectron*. Eng. **64**, 233 (2002).
- 2. M. Y. Ho et al., Applied Physics Letters 81, 4218 (2002).
- 3. J. M. Jensen *et al.*, *Chemistry of Materials* **14**, 2276 (May, 2002).
- 4. B. W. Gregory, D. W. Suggs, J. L. Stickney, J. Electrochem. Soc. 138, 1279 (1991).
- 5. J. L. S. I. Villegas, J. Vac. Sci. Technol. A 10, 3032 (1992).
- 6. U. Demir, C. Shannon, *Langmuir* **12**, 6091 (1996).
- 7. B. E. Hayden, I. S. Nandhakumar, *Journal of Physical Chemistry B* **101**, 7751 (1997).
- 8. T. E. Lister, L. P. Colletti, J. L. Stickney, *Israel Journal of Chemistry* **37**, 287 (1997).
- 9. L. P. Colletti, J. L. Stickney, J. Electrochem. Soc. 145, 3594 (1998).
- 10. M. L. Foresti et al., Journal of Physical Chemistry B 102, 7413 (1998).
- 11. I. Villegas, *JACS*, **55** (1998).
- 12. A. Gichuhi, B. E. Boone, C. Shannon, *Langmuir* **15**, 763 (1999).
- M. Innocenti, G. Pezzatini, F. Forni, M. L. Foresti, *Proceedings Electrochemical Society* 99-9, 294 (1999).
- H. Yoneyama, A. Obayashi, S. Nagakubo, T. Torimoto, *Abstracts of the Electrochemical Society Meeting* 99-2, 2138 (1999).
- K. Varazo, M. D. Lay, T. A. Sorenson, J. L. Stickney, *J. Electroanal. Chem.* **522**, 104 (2002).
- R. Vaidyanathan, J. L. Stickney, S. M. Cox, S. P. Compton, U. Happek, *J. Electroanal. Chem.* 559, 55 (2003).
- M. K. Mathe, S. M. Cox, V. Venkatasamy, U. Happek, J. L. Stickney, J. Electrochem. Soc. 152, C751 (2005).

- 18. W. Zhu et al., J. Electroanal. Chem. 585, 83 (2005).
- 19. M. Muthuvel, L. Stickney John, *Langmuir FIELD Full Journal Title:Langmuir : the ACS journal of surfaces and colloids* **22**, 5504 (2006).
- 20. V. Venkatasamy, J. L. Stickney, *ECS Transactions* **3**, (2006).
- L. B. Rogers, D. P. Krause, J. C. Griess, Jr., D. B. Ehrlinger, *J. Electrochem. Soc.* 95, 33 (1949).
- 22. E. Herrero, L. J. Buller, H. D. Abruna, *Chemical Reviews* **101**, 1897 (2001).
- 23. A. A. Gewirth, B. K. Niece, *Chem. Rev.* 97, 1129 (1997).
- 24. A. Aldaz, J. Clavilier, J. M. Feliu, Journal de Physique IV: Proceedings 4, 75 (1994).
- R. R. Adzic, in *Advances in Electrochemistry and Electrochemical Engineering*, H.
 Gerishcher, C. W. Tobias, Eds. (Wiley-Interscience, New York, 1984), vol. 13, pp. 159.
- D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, H.
 Gerischer, C. W. Tobias, Eds. (John Wiley, New York, 1978), vol. 11, pp. 125.
- 27. I. V. D. W. Suggs, B.W. Gregory, J.L. Stickney, J. Vac. Sci. Technol. A 10, 886 (1992).
- 28. D. W. Suggs, J. L. Stickney, Surf. Sci. 290, 375 (1993).
- 29. U. Demir, C. Shannon, *Langmuir* **10**, 2794 (1994).
- E. S. Streltsov, I. I. Labarevich, D. V. Talapin, *Doklady Akademii Nauk Belarusi* 38, 64 (1994).
- L. B. Goetting, B. M. Huang, T. E. Lister, J. L. Stickney, *Electrochimica Acta* 40, 143 (1995).
- 32. B. E. Boone, C. Shannon, J. Phys. Chem. 100, 9480 (1996).

- R. D. I. Herrick, J. L. Stickney, in *New Directions in Electroanalytical Chemistry*, J. Leddy, M. Wightman, Eds. (The Electrochemical Society, Pennington, NJ, 1996), vol. 96-9, pp. 186.
- 34. G. D. Aloisi et al., Journal of Physical Chemistry B 101, 4774 (1997).
- 35. L. P. Colletti, B. H. Flowers, J. L. Stickney, JECS, (1997).
- 36. A. Gichuhi, B. E. Boone, C. Shannon, *Langmuir* submitted, (1998).
- 37. T. Torimoto, S. Nagakubo, M. Nishizawa, H. Yoneyama, *Langmuir* 14, 7077 (1998).
- G. Pezzatini, S. Caporali, M. Innocenti, M. L. Foresti, J. Electroanal. Chem. 475, 164 (Oct 14, 1999).
- 39. S. Z. Zou, M. J. Weaver, *Journal of Physical Chemistry B* **103**, 2323 (1999).
- T. Torimoto, A. Obayashi, S. Kuwabata, H. Yoneyama, *Electrochem. Commun.* 2, 359 (2000).
- 41. M. Innocenti, G. Pezzatini, F. Forni, M. L. Foresti, *J. Electrochem. Soc.* **148**, C357 (2001).
- 42. J. Flowers, Billy H. et al., J. Electroanal. Chem. 524-525, 273 (2002).
- 43. M. D. Lay, J. L. Stickney, J. Electrochem. Soc. 151, C431 (2004).
- 44. F. Loglio, M. Innocenti, G. Pezzatini, M. L. Foresti, J. Electroanal. Chem. 562, 117 (2004).
- 45. F. Loglio et al., J. Electroanal. Chem. 575, 161 (2005).
- V. Venkatasamy, N. Jayaraju, S. M. Cox, J. L. Stickney, J. Electrochem. Soc. 154, H720 (2007).
- I. Villegas, J. L. Stickney, Journal of Vacuum Science & Technology, A: Vacuum, Surfaces, and Films 10, 3032 (1992).

- 48. I. Villegas, J. L. Stickney, J. Electrochem. Soc. 139, 686 (1992).
- T. L. Wade, T. Sorenson, A., J. L. Stickney, in *Interfacial Electrochemistry*, A. Wieckowski, Ed. (Marcel Dekker, New York, 1999), pp. 757-768.
- 50. T. L. Wade, L. C. Ward, C. B. Maddox, U. Happek, J. L. Stickney, *Electrochemical and Solid-State Letters* **2**, 616 (1999).
- 51. T. L. Wade, R. Vaidyanathan, U. Happek, J. L. Stickney, *JEC* **500**, 322 (2001).
- 52. T. Torimoto, S. Takabayashi, H. Mori, S. Kuwabata, *JEC* submitted, (2000).
- 53. T. Oeznuelueer, I. Erdogan, I. Sisman, U. Demir, *Chemistry of Materials* 17, 935 (2005).
- 54. V. Vaidyanathan et al., langmuir : ACS journal of surfaces and colloids In press (2006).
- 55. J. Yang, W. Zhu, X. Gao, S. Bao, X. Fan, J. Electroanal. Chem. 577, 117 (2005).
- 56. W. Zhu *et al.*, *Electrochimica Acta* **50**, 4041 (2005).
- 57. W. Zhu *et al.*, *Electrochimica Acta* **50**, 5465 (2005).
- 58. W. Zhu et al., Transactions of Nonferrous Metals Society of China 15, 404 (2005).
- 59. S. R. Brankovic, J. X. Wang, R. R. Adzic, SS 474, L173 (2001).
- 60. S. R. Brankovic, J. X. Wang, R. R. Adzic, *Journal of the Serbian Chemical Society* 66, 887 (2001).
- 61. M. F. Mrozek, Y. Xie, M. J. Weaver, *Analytical Chemistry* **73**, 5953 (2001).
- 62. Y.-G. Kim, Y. Kim Jay, C. Thambidurai, L. Stickney John, *Langmuir* 23, 2539 (2007).
- 63. J. Y. Kim, Y.-G. Kim, J. L. Stickney, J. Electrochem. Soc. 154, D260 (2007).
- 64. Y.-G. Kim, Y. Kim Jay, D. Vairavapandian, L. Stickney John, J Phys Chem B Condens Matter Mater Surf Interfaces Biophys FIELD Full Journal Title: The journal of physical chemistry. B, Condensed matter, materials, surfaces, interfaces & biophysical 110, 17998 (2006).

- 65. J. Y. Kim, Y.-G. Kim, J. L. Stickney, *ECS Transactions* 1, 41 (2006).
- L. T. Viyannalage, R. Vasilic, N. Dimitrov, *Journal of Physical Chemistry C* 111, 4036 (2007).
- 67. R. Vasilic, L. T. Viyannalage, N. Dimitrov, J. Electrochem. Soc. 153, C648 (2006).
- 68. R. Vasilic, N. Dimitrov, *ECS Transactions* 1, 33 (2006).
- 69. R. Vasilic, N. Dimitrov, *Electrochemical and Solid-State Letters* 8, C173 (2005).
- S. Strbac, F. Maroun, O. M. Magnussen, R. J. Behm, *J. Electroanal. Chem.* 500, 479 (Mar, 2001).
- 71. S. Strbac, R. J. Behm, A. Crown, A. Wieckowski, Surf. Sci. 517, 207 (2002).
- 72. W. Chrzanowski, A. Wieckowski, *Langmuir* **13**, 5974 (1997).
- 73. S. Strbac, C. M. Johnston, G. Q. Lu, A. Crown, A. Wieckowski, Surf. Sci. 573, 80 (2004).
- 74. M. B. Vukmirovic *et al.*, *Electrochimica Acta* **52**, 2257 (2007).
- 75. S. Gottesfeld, T. A. Zawodzinski, *Advances in Electrochemical Science and Engineering*5, 195 (1997).
- 76. R. Chan et al., Electrochemical and Solid-State Letters 7, G154 (2004).
- 77. O. Chyan et al., Proceedings Electrochemical Society 2003-10, 174 (2003).
- D. Josell, D. Wheeler, C. Witt, T. P. Moffat, *Electrochem. Solid State Lett.* 6, C143 (Oct, 2003).
- 79. T. P. Moffat *et al.*, *J. Electrochem. Soc.* **153**, C37 (2006).
- 80. B. C. Schardt *et al.*, *Langmuir* **3**, 239 (1987).
- 81. J. L. Stickney et al., J. Electroanal. Chem. 213, 293 (1986/11/25, 1986).
- 82. B. C. Schardt et al., Surf. Sci. 175, 520 (1986/10/1, 1986).
- 83. R. Vasilic, N. Vasiljevic, N. Dimitrov, J. Electroanal. Chem. 580, 203 (2005).

- N. Dimitrov, W. Obretenov, A. Popov, Godishnik na Sofiiskiya Universitet \"Sv. Kliment Okhridski\", Khimicheski Fakultet 92-94, 175 (2001).
- 85. R. R. Adzic, D. N. Simic, A. R. Despic, D. M. Drazic, JEC 65, 587 (1975).
- A. Hamelin, J. Lipkowski, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 171, 317 (1984).
- 87. M. Hepel, S. Bruckenstein, *Electrochimica Acta* **34**, 1499 (1989).
- B. E. Conway, J. S. Chacha, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 287, 13 (1990).
- S. Yoshihara, M. Okamoto, K. Endo, E. Sato, *Interfinish 92, Int. Congr. Surf. Finish.* 3, 1434 (1992).
- G. M. Brisard, E. Zenati, H. A. Gasteiger, N. M. Markovic, P. N. Ross, *Langmuir* 13, 2390 (Apr 16, 1997).
- N. M. Markovic, B. N. Grgur, C. A. Lucas, P. N. Ross, *J. Electroanal. Chem.* 448, 183 (May 20, 1998).
- 92. T. P. Moffat, Journal of Physical Chemistry B 102, 10020 (1998).
- 93. X. Zeng, S. Bruckenstein, J. Electrochem. Soc. 146, 2549 (1999).
- 94. E. A. Streltsov, S. K. Poznyak, N. P. Osipovich, *JEC* **518**, 103 (2002).
- 95. N. Dimitrov, N. Vasiljevic, R. Vasilic, *Abstracts, 32nd Northeast Regional Meeting of the American Chemical Society, Rochester, NY, United States, October 31-November 3,* GEN (2004).
- 96. M. Seo, M. Yamazaki, J. Electrochem. Soc. 151, E276 (2004).
- 97. S. Hwang, J. Lee, J. Kwak, J. Electroanal. Chem. 579, 143 (2005).
- 98. Y. B. Zhang et al., Electrochem. Solid State Lett. 7, C107 (2004).

- 99. I. Oh, A. A. Gewirth, J. Kwak, Journal of Catalysis 213, 17 (2003).
- 100. S. J. Hsieh, A. A. Gewirth, Surf. Sci. 498, 147 (Feb 1, 2002).
- J. Lee, W. B. Wang, M. S. Zei, G. Ertl, *Physical Chemistry Chemical Physics* 4, 1393 (2002).
- 102. M. B. Vukmirovic, R. L. Sabatini, R. R. Adzic, Surf. Sci. 572, 269 (2004).
- S. Hadzijordanov, H. Angersteinkozlowska, M. Vukovic, B. E. Conway, J. Electrochem. Soc. 125, 1471 (1978).
- 104. M. A. Quiroz, Y. Meas, E. Lamypitara, J. Barbier, *J. Electroanal. Chem.* 157, 165 (1983).
- 105. C. N. Vanhuong, M. J. Gonzaleztejera, J. Electroanal. Chem. 244, 249 (Apr, 1988).
- P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, H. Deligianni, *IBM Journal of Research and Development* 42, 567 (1998).
- 107. S. P. Murarka, S. W. Hymes, *Critical Reviews in Solid State and Materials Sciences* 20, 87 (1995).
- T. F. Kuech, P. D. Dapkus, Y. Aoyagi, *Atomic Layer Growth and Processing*. (Materials Research Society, Pittsburgh, 1991), vol. 222, pp. 360.
- 109. S. Bedair, Atomic Layer Epitaxy. (Elsevier, Amsterdam, 1993), pp. 304.
- 110. C. H. L. Goodman, M. V. Pessa, JAP 60, R65 (1986).
- 111. M. Leskela, M. Ritala, *Thin Solid Films* **409**, 138 (2002/4/22, 2002).
- 112. E. B. Yousfi, B. Weinberger, F. Donsanti, P. Cowache, D. Lincot, *Thin Solid Films* 387, 29 (2001/5/29, 2001).
- 113. V. Sammelselg et al., Applied Surface Science 134, 78 (1998).
- 114. M. Ylilammi, *Thin Solid Films* **279**, 124 (1996).

- 115. L. T. Viyannalage, R. Vasilic, N. Dimitrov, *Journal of Physical Chemistry C* 111, 4036 (2007).
- 116. Y.-G. Kim, J. Kim, D. Vairavapandian, J. L. Stickney, *Journal of Physical Chemistry B* 110, 17998 (2006).
- 117. Y.-G. Kim, J. Kim, C. Thambidurai, J. L. Stickney, *Langmuir* 23, 2539 (2007).
- 118. J. Kim, Y.-G. Kim, J. L. Stickney, *Electrochemical Society Transaction* 1, 41 (2006).
- 119. R. Vasilic, N. Dimitrov, *Electrochemical and Solid State Letters* 8, C173 (2005).
- 120. D. M. Kolb, M. Przasnyski, H. Gerisher, JEC 54, 25 (1974).
- 121. K. Juttner, W. J. Lorenz, Z. Phys. Chem. N. F. 122, 163 (1980).
- A. T. Hubbard *et al.*, in *New Dimensions in Chemical Analysis*, B. L. Shapiro, Ed. (Texas A & M University Press, College Station, Texas, 1985), pp. 135.
- J. L. Stickney, in *Advances in Electrochemical Science and Engineering*, R. C. Alkire, D. M. Kolb, Eds. (Wiley-VCH, Weinheim, 2002), vol. 7, pp. 1-105.
- 124. B. W. Gregory, J. L. Stickney, Journal of Electroanalytical Chemistry 300, 543 (1991).
- 125. J. Kim, Y.-G. Kim, J. L. Stickney, *Journal of The Electrochemical Society* 154, D260 (2007).
- 126. J. L. Stickney, *Electroanalytical Chemistry* **21**, 75 (1999).
- 127. M. Hegner, *Surface Science* **291**, 39 (1993).
- 128. in *Metal Based Thin Films for Electronics*, K. Wetzig, C. M. Schneider, Eds. (Wiley-VCH, Weinheim, 2003).
- 129. R. Dillon, S. Srinivasan, A. S. Aricò, V. Antonucci, *Journal of Power Sources* 127, 112 (2004).
- 130. S. Litster, G. McLean, Journal of Power Sources 130, 61 (2004).

- 131. V. Mehta, J. S. Cooper, Journal of Power Sources 114, 32 (2003).
- 132. T. A. Zawodzinski Jr, T. E. Springer, F. Uribe, S. Gottesfeld, *Solid State Ionics* 60, 199 (1993).
- 133. S. Wasmus, A. Küver, Journal of Electroanalytical Chemistry 461, 14 (1999).
- 134. A. Heinzel, V. M. Barragán, Journal of Power Sources 84, 70 (1999).
- 135. A. K. Shukla, R. K. Raman, Annual Review of Materials Research 33, 155 (2003).
- 136. X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, *Journal of Power Sources* 86, 111 (2000).
- 137. J. Fournier et al., J. Electrochem. Soc. 144, 145 (Jan, 1997).
- M. Lefevre, J. P. Dodelet, P. Bertrand, *The Journal of Physical Chemistry B* 106, 8705 (2002).
- S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J. M. Léger, *Journal of Electroanalytical Chemistry* 577, 223 (2005).
- 140. A. J. Wagner, G. M. Wolfe, D. H. Fairbrother, Applied Surface Science 219, 317 (2003).
- 141. P. H. Matter, L. Zhang, U. S. Ozkan, Journal of Catalysis 239, 83 (2006).
- 142. A. A. Serov et al., Journal of Power Sources 175, 175 (2008).
- 143. N. A. Vante, W. Jaegermann, H. Tributsch, W. Hoenle, K. Yvon, *Journal of the American Chemical Society* 109, 3251 (2002).
- 144. M. Bron et al., Journal of Electroanalytical Chemistry 500, 510 (2001).
- 145. N. Alonso-Vante, H. Tributsch, O. Solorza-Feria, *Electrochimica Acta* 40, 567 (1995).
- 146. T. E. Lister, J. L. Stickney, JPC,(1997).
- 147. M. Muthuvel, J. L. Stickney, J. Electrochem. Soc. 153, C67 (2006).

- J. L. Stickney, T. L. Wade, B. H. Flowers, R. Vaidyanathan, U. Happek, *Encyclopedia of Electrochemistry* 1, 513 (2003).
- R. R. Adzic, in *Advances in Electrochemistry and Electrochemical Engineering*, H.Gerishcher, C. W. Tobias, Eds. (Wiley-Interscience, New York, 1984), vol. 13, pp. 159.
- C. Thambidurai, Y. G. Kim, N. Jayaraju, V. Venkatasamy, J. L. Stickney, J. *Electrochem. Soc.* 156, D261 (2009).
- 151. C. Thambidurai, Y. G. Kim, J. L. Stickney. (Pergamon-Elsevier Science Ltd), vol. 53, pp. 6157-6164.

CHAPTER 2

ELECTRODEPOSITION OF RU BY ATOMIC LAYER DEPOSITION $\left(\text{ALD}\right)^1$

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Abstract

Studies are presented describing attempts to form a cycle for the growth of Ru nanofilms using the electrochemical form of atomic layer deposition (ALD). Au substrates have been used to form Ru nanofilms, based on layer by layer growth of deposits, using surface limited reactions. These deposits were formed using surface limited redox replacement (SLRR), where an atomic layer of a sacrificial element is first deposited by underpotential deposition (UPD), and is then exchanged for the element of interest. The use of the UPD atomic layer limits subsequent growth by limiting the number of electrons available for deposition. In the present study, Pb atomic layers were used, and exposed to solutions of Ru³⁺ ions at open circuit. This process can then be repeated to grow films of the desired thickness. It was shown that less than an atomic % of Pb was evident in the deposits, using electron probe microanalysis (EPMA), and even that could be removed if a stripping step was added to the ALD cycle. The deposits displayed the expected Ru voltammetry, as well as the Ru hcp XRD pattern. There were some differences in the first 20 cycle, compared with subsequent, suggesting some nucleation process that must be investigated. However, after 20 cycles, the deposit showed the linear growth with the number of cycles expected for an ALD process. The morphology of Ru films, deposited on template stripped Au was studied using ex-situ scanning tunneling microscopy (STM), and showed no evidence of 3D growth.

Introduction

Ru is a well known constituent of fuel cell electrodes, where it is found to help prevent CO poisoning of the anode(75). It is also being studied as a possible barrier layer for the deposition of Cu in the formation of ultra large scale integration (ULSI) (76-79).

Many applications require formation of a nanofilm. Control in their growth can be facilitated by atomic layer deposition (ALD), a methodology for forming deposits one atomic layer at a time via surface limited reactions (*1-3*). Surface limited reactions come in a number of forms, with the classic example involving careful control of the substrate temperature. Higher temperatures promote reaction between the substrate and the depositing element, while at the same time, the temperature must be kept low enough that the depositing element does not react with itself, and form a bulk deposit. In this way, only one atomic layer is formed. To grow thicker films, the process is repeated, in an cycle, with the number of cycles performed determining the thickness of the deposit.

The electrochemical form of ALD has previously been referred to as EC-ALE, or electrochemical atomic layer epitaxy, for the last 15 years (4-20). EC-ALE is now being referred to as ALD, in line with the ubiquitous use of the term ALD in the literature. Most electrochemical surface limited reactions are referred to as underpotential deposition (UPD), known for 50 years (21-26). UPD involves the formation of an atomic layer of one element on a second at a potential prior to that needed to deposit the element on itself. UPD is a thermodynamic process, where an atomic layer is formed as the result of the free energy of formation of a surface compound or alloy. UPD has been used for ALD, in a cycle, to form nanofilms of a wide variety of compounds, such as: II-VI (4, 6-7, 10, 15, 17, 27-46) and III-V

(47-51) compounds like CdTe and InAs. It has also been used for form IV-VI (4, 52-54), V-VII compounds (18, 55-58) and compounds such as PbSe and In_2Se_3 (33). Such compounds can be formed using electrochemical ALD due to the fact that Cd UPD occurs on Te and Te UPD occurs on Cd, creating a workable ALD cycle.

Formation of elemental deposits was originally thought, by the authors, to be impossible, as UPD is the formation of one atomic layer on a different element, after which deposition stops (22-23, 25-26). However, more recent studies by Brankovic and Adzic showed that another route to the formation of a surface limited atomic layer is possible (59-60). They used what is referred to here as a surface limited redox replacement (SLRR) to form nanoclusters of Pt, and Ag on Au electrodes. They were motivated by the fact that it is essentially impossible to form an atomic layer of Pt by UPD deposits, and they wished to control the amount of Pt for the purposes of making unique catalyst surfaces. They showed that you could first form an atomic layer of Cu via UPD, on either Au or Pt, and then exchange it in a Pt^{+4} solution, forming an atomic layer of Pt, and Cu^{2+} ions. They simply performed Cu UPD, and then exchanged it at open circuit (OCP) for the more noble element Pt. The amount of Pt deposited was dependent on the number of electrons available from the Cu UPD. Extension of this SLRR process to the formation of nanofilms by ALD was attempted by the late Michael Weaver, where he repeated the replacement of Cu UPD by Pt ions, a cycle, eight times, forming a Pt coated Au surface (61). He did not refer to his work as ALD, though it is clear that he intended to form Pt nanofilms an atomic layer at a time.

More recently, work by the author's group (62-65), as well as Dimitrov *et. al.* (66-69) have attempted to expand this method and determine the limitations etc. Most of this authors work has involved the alternation of solutions of the sacrificial element (the less noble element

formed by UPD) with the element to be deposited. However, Dimitrov has developed a very simple and clever one solution method, that takes advantage of pulse deposition (66). At present, the author is familiar with work on the growth of Cu, Pt, and Ag deposits using SLRR for nanofilm formation by electrochemical ALD. The present paper describes deposition of Ru on a Au surface. Due to the importance of Ru for fuel cell catalysts, there have been a number of atomic level studies of Ru deposition (70) (71). In general, these studies have shown the formation of clusters, and step decoration on Au electrodes. The basis of such studies has been the spontaneous deposition of Pt-Ru on carbon-supported Pd nanoparticles, using the galvanic displacement method, for the enhancement of oxygen reduction reaction kinetics in the fuel cells (74). Galvanic displacement is referred to here as SLRR. The present article reports initial developments in the formation of an electrochemical ALD cycle for Ru deposition.

Experimental

Depositions were performed using a thin layer flow electrodeposition system consisting of pumps, valves, a flow cell and a potentiostat. All components were computer controlled using a LABVIEW program. The flow cell has been described previously, with minor design changes to the reference compartment and the auxiliary electrode (*17*). The auxiliary electrode was a gold wire, and the reference electrode was Ag/AgCl (3M NaCl) (Bioanalytical systems, Inc.). Ru thin film cyclic voltammetry (CV) was performed in an H-cell using 1M H₂SO₄ solution.

Substrates were glass slides with a 3nm Ti adhesion layer and 300 nm of Au. Substrates were formed by first etching the glass in 15 % HF for 2 minutes, then rinsed in ultrapure water, and inserted into the vapor deposition chamber. Au substrates were vapor deposited at 280° C

and annealed at 400° C for 12 hours, resulting in a prominent (111) growth habit. These gold electrodes were cleaned in concentrated nitric acid by immersion for 2 minutes and then by electrochemical cycling, after insertion into the flow cell.

Solutions used were 1mM Pb(ClO₄)₂, 1mM CuSO₄, and 0.1 mM RuCl₃ 3 H₂O. To study the pH effect, the Pb solution was made with 50 mM HClO₄ (pH 1.3), as well as with 0.1 M NaClO₄ and 50 mM CH₃COONa (pH 5). The Cu solution was made with 50 mM H₂SO₄ (pH 1.5). The Ru solution was made with 50 mM HCl (pH 1.5). The blank solution was 0.1 M NaClO₄ and 50 mM CH₃COONa (pH 5). The water used for the solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better.

The basic cycle used to deposit Ru films was as follows: the Pb solution was flushed into the cell for 2 sec at a controlled potential, then the solution was held static for 8 s. The blank solution was then flushed through the cell for 2 sec to rinse out the Pb at the same controlled potential. Next, the Ru solution was flushed into the cell at OCP for 3 sec and held static for 60 seconds, to provide time for the redox replacement and finally the blank was rinsed through the cell at OCP for 2 sec. This cycle was repeated 200 times to form thicker Ru deposits.

The deposits were initially inspected with a Jenavert metallo-graphic microscope. A Scintag PAD-V diffractometer with CuK α radiation (λ = 1.5418 Å), was used to obtain glancing angle X-ray diffraction patterns. Electron probe microanalysis (EPMA) was run on a Joel 8600 wavelength dispersive scanning electron microprobe for elemental analysis. STM experiments were performed using a Nanoscope III (Digital instruments, Santa Barbara, CA) equipped with W tips, electrochemically etched (15 V ac in 1 M KOH) from 0.25 mm wires.

Results and Discussion

The work presented below was intended to develop an electrochemical ALD cycle based on surface limited redox replacement (SLRR) for the formation of Ru nanofilms. The cycle began with deposition of a sacrificial atomic layer via UPD, at controlled potential. The resulting deposit was then exposed to a solution containing ions of the desired element, and redox replacement occurs until the sacrificial element was removed. Figure 2.1 is cartoon of the scheme used to form Ru atomic layers.

Studies of ALD by this group have usually involved deposit formation on Au substrates. Au is well known as a stable electrode material in electrochemical environments. The Au on glass substrates, described in the last section, have been used for the present studies. These Au films are relatively reproducible and inexpensive, so that once a deposit was formed, it could be retained for subsequent characterization. Initially, Cu was investigated as the sacrificial element. That is, an atomic layer of Cu was formed by UPD on the deposit surface, and then exposed it to a solution of Ru^{3+} ions. In principle, Ru should displace the Cu, to form a Ru layer with 2/3 the coverage of the original Cu atomic layer, as $Ru^{3+} + 3e^- = Ru$ is a three electron process, while Cu = $Cu^{2+} + 2e^-$ is a two electron process, and Ru deposition should be limited by the electrons available from the Cu atomic layer.

The initial cycle mechanics involved Cu UPD at 0.05 V vs. Ag/AgCl, from the Cu solution described in the experimental section. That solution was then flushed from the flow cell, with the blank solution, followed by introduction of the Ru³⁺ solution at open circuit. Figure 2.2 shows a potential vs. time trace, as well as current vs. time, for two ALD cycles. The horizontal linear portions of the potential time trace (solid line) correspond to Cu deposition at 0.05 V, and reduction peaks for Cu UPD are visible in the dashed current time trace. Upon introduction of

the Ru^{3+} , the cell was allowed to go open circuit, and the potential rapidly drifted positive, coming to rest at about 0.6 V. In theory, if the Cu was replaced by Ru in the Ru^{3+} solution, the potential should shift to the Ru^{3+}/Ru formal potential, for a Ru electrode in a Ru^{3+} ion solution, or about 0.15 V. This is clearly not the case. Instead, the potential drifted significantly positive of the expected potential. As the Ru^{+3} solution concentration was correct, it appears the surface was not coated with Ru. Two hundred cycles were performed using Cu as the sacrificial element, and no Ru was detected with EPMA. Apparently, Ru did not replace the Cu and deposit on the substrate. This is consistent with the potential drifting to potentials associated with an Au substrate, not a Ru surface.

This raises the question of where the Cu went? At 0.6 V, no Cu should be present on the deposit surface. If the Cu UPD dissolved, where did the electrons go? If they were collected by Ru³⁺ ions, Ru should be present on the surface. One possibility is reduction of oxygen, present in the solution, essentially corrosion. That the Cu did not result in reduction of Ru³⁺ ions to form a Ru film, is probably a by product of the limited difference in formal potentials between Cu and Ru, about 0.1 V. The underpotential for Cu on Au is more than 0.1 V, for the most part, suggesting that Ru⁺³ should not be able to replace Cu UPD.

To drive the SLRR, Pb UPD was then chosen for sacrificial atomic layers, as its formal potential is more negative, and should provide a sufficient decrease in free energy for redox replacement. Figure 2.3 shows two current time traces, each for two cycles of Pb UPD and replacement by Ru: two ALD cycles. The dashed line was for Pb UPD from a pH 1.5 solution, while the solid line was for a pH 5 solution. The dashed line displays extensive reduction current, enough to deposit several MLs of Pb, though charge for a single atomic layer was expected. The definition of a monolayer in this work follows the surface science convention, where one

adsorbate for every substrate surface atom would correspond to one monolayer (ML). When a deposit is referred to as an atomic layer, it simply means that the deposit should be no more than one atom thick, but does not specify the coverage. Thus atomic layers can have a coverage anywhere between 0 and about 1 ML. Previous studies by the author have shown Pb UPD to generally result in the formation of about 1 ML, not the multiple MLs indicated by the dashed line. A number of different substrates have been studied by various investigators: including Au, Pt, Ag, and Cu (62-63, 66-67, 80-84). In the present case, after UPD from the pH 1.5 solution, subsequent oxidative stripping of the UPD resulted only in the expected atomic layer, not the multiple MLs. By comparison of Pb UPD from the pH 1.5 solution and the pH 5 solutions, it appears that the hydrogen evolution reaction (HER) was responsible for the excess current during UPD in the pH 1.5 solution (Figure 2.3). The solid line for Pb UPD from the pH 5 solution resulted only in current for deposition of an atomic layer. Pb has a high hydrogen overpotential, so the HER should not be significant on Pb, even on Pb UPD. However, in the studies presented here, the deposit surface was Ru initially, until covered by Pb UPD. As Pb UPD reaches completion, current for both UPD and the HER ceases. Ru has a very low hydrogen over potential, and thus the HER is prominent in a low pH solution, until the Pb coats the Ru surface. For this reason, the pH 5 solution was chosen for subsequent studies, allowing coulometric characterization of Pb UPD each cycle.

A basic cycle for Ru ALD (Figure 2.4), using the SLRR and the pH 5 Pb²⁺ solution, was created, and work begun to optimize it. Variables studied included: exchange time, Pb deposition potential, and use of a Pb removal (stripping) step. Those studies were performed by running 200 cycles of deposition on gold on glass substrates. Studies of exchange time for Pb by Ru involved formation of deposits where 10, 30, 60 and 90 seconds were used for the exchange step in the

cycle. Figure 2.5 displayed both the current time trace and potential time trace for three cycles of Ru deposition. It appears that the potential drifts positively to about -0.1 V as the Pb is replaced by Ru. Figure 2.6 is a graph of the Ru atomic % from EPMA for the surface as a function of exchange time. Note, EPMA stimulates X-ray emission from more than a micron deep into the sample, so Au signal from the substrate always contributes the predominate % in these studies. However, the Ru atomic %, measured for these deposits can be used as a relative measure of the Ru coverage. In addition to Ru and Au signals, some signal from Pb was detected, though less than 1 %. What is evident from the graph is that the coverage of Ru plateaus at times above 30 seconds, suggesting that at least 60 seconds should be used for the exchange, under the present set of conditions.

UPD of Pb has been studied by a number of workers on various metal substrates (66-67, 69, 82-83, 85-97), and recently by this group on Cu (62-63). It has also been studied on Ru (98). Figure 2.7 shows a graph of the average Pb coverage per cycle for 200 cycles of deposition, as a function of the potential used for UPD. These charges are higher than expected, however, for the initial cycles, some oxygen appears to be reduced during Pb deposit, while as the surface becomes Ru, the HER probably contributes to the measured charges. The most important point is to avoid bulk deposition of Pb, and to keep the amount of Pb deposit to an atomic layer. Thus a potential of -0.44 V was chosen for subsequent experiments, as -0.48 V corresponds to the beginning of bulk Pb deposition, and there are indications that the coverage increase was accelerating more negative potentials (Figure 2.7).

Ideally, every three Pb UPD atoms should be exchanged for two Ru atom, given the oxidation states of the respective ions. In many electrochemical ALD cycles there are indications that the exchange efficiency is less than 100%. For instance, using the acidic Pb^{2+} solution to

form the atomic layers resulted in significant charge from the HER during formation of Pb atomic layers. Even though the pH was changed to 5, some hydrogen evolution can still occur, decreasing the apparent exchange efficiency. In addition, some oxygen reduction probably occurred at those potentials, as Pb is known to catalyze oxygen reduction (*99-100*).

Another problem has been that, even using 60 sec for exchange and keeping the coverage of Pb low, some Pb remained on the surface, as observed with EPMA, after 200 cycles. All Pb deposited must be removed, or the deposit will become an alloy. For many of the deposits formed in this study, 1 atomic %, or less, of Pb was measured using EPMA for deposits. To help remove these last traces of Pb, a stripping step was added to the cycle. The idea was to replace as much of the Pb as possible via the direct exchange reaction for Ru, within the first 60 seconds, and then to make sure the last traces of Pb.

Figure 2.8 displays a current time trace where a stripping step to 0.25 V was used to remove the last traces of Pb. Significant oxidation current is evident, upon shifting to the stripping potential, resulting from a combination of charging current, Pb oxidation, and possibly some oxidation of the Ru surface, given the high potential. Any Ru surface oxide formed during this step would be reduced during the subsequent Pb UPD step. Table 2.1 list the atomic % of Ru and Pb as measured with EPMA for deposits formed with various stripping conditions. Stripping potentials of 0.05, 0.15, 0.25, and 0.35 V were all used to form deposits, and for each potential, two deposits were formed, one using a 2 second stripping step, and a second using a 10 second stripping step. The EPMA results for these deposits suggested that the amounts of Pb in the deposits were all 1% or less, but that the higher the potential and the longer the time, the less

Pb was evident. Most importantly, no detectable Pb was observed for the 200 cycle deposits if 0.25 V was applied for 10 sec.

Deposits formed with 200 cycles, such as those discussed above, with no evidence of Pb by EPMA, displayed the expected gray metallic surface. A window opening sequence of cyclic voltammetry is shown in Figure 2.9. This sample had been on the shelf for a week before the CV was performed, long enough for a surface oxide to form in air. It was thus understandable that the initial OCP was near 0.6 V upon immersion, consistent with the presence of significance oxide. The scan was then started negatively from 0.6 V and displayed a large reduction feature peak at 0.05 V. Subsequent scans were performed to increasingly positive potentials, resulting in increasing amounts of oxidation. These associated negative going scans displayed broad features, attributed to oxide reduction. The more positive the scan, the more negative and larger the reduction feature. However the charge for the first reduction feature, after the sample was first immersed (for the air oxidized surface), was nearly equivalent to that obtained by scanning to 1.2 V, but the reduction feature was shifted positive by 75 mV. This suggested that the oxide formed upon exposure to air, may have been different in some way, reduced more easily than the oxide formed electrochemically. Various Ru(0001) single crystal (101-102) and polycrystalline Ru (70, 103-105) CV studies have been reported in the literature. The voltammetry displayed in Fig. 9, shows the expected behavior for a polycrystalline Ru electrode. There was little evidence for the hydrogen adsorption feature (101, 103) felt to be indicative of well ordered Ru(0001) planes. As the Au on glass substrates used were predominately composed of (111) terraces, the hexagonal plane for FCC, it was anticipated that the hexagonal Ru planes, the (0001), might show some evidence of epitaxy. Apparently this is not the case. The voltammetry clearly shows
the strong irreversibility expected for Ru oxidation and reduction, as well as the strong reversibility for hydrogen evolution and oxidation.

XRD patterns for the deposits showed the (002) peak for Ru, consistent with its hexagonal crystal structure (Figure 2.10). Evidence for other diffraction peaks for Ru were absent, although, two of the major peaks, the (100) and the (101), were obscured by overlap with the Au(111) and Au(200) substrate peaks, respectively. That the Ru(002) peak was prominent is consistent with growth on a Au film with a strong (111) habit, the hexagonal plane, as in the Ru hexagonal crystal structure, the (002) is the hexagonal plane. Evidence of epitaxy was not available from this data, but was also not expected, give the lattice mismatch of 8%. Although the data does suggest that the c axis was perpendicular to the deposit surface.

Figure 2.11 shows the atomic % of Ru for deposits as a function of the number of cycles performed. A linear graph would be expected for an ALD process, as is observed in the present case. However, if the graph of the last three points is extrapolated to zero coverage, it hits at about 25 cycles. This suggests either the exchange efficiency is less then 100% for the first 20 cycles, or that the growth of the layers is not layer by layer initially, though becomes layer by layer after about 2 nm. This may suggest some nucleation and growth process limits the deposition under the time frame of the cycles. Figure 2.12 shows the potential time traces for the first 30 cycles. What is evident, is that the OCP during exchange starts out near 0.3 V, but quickly drops to 0.0 V after 25 cycles. This is an indication that the surface has substantial Au character, which only slowly goes away. When the OCP drops low enough, suggesting a Ru surface, the deposit becomes layer by layer, and typical ALD behavior is obtained for the rest of the deposit.

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Charges for Ru oxidation and reduction were an order of magnitude greater than expected, assuming they should be proportional to the deposit surface area, and so should Pb UPD. The reasons for this are not yet clear. However, initial ex-situ STM studies of deposits formed on template stripped Au (Figure 2.13) indicate a fine grain structure, possibly related to the excessive oxidation charge. The template stripped Au substrates are quite flat, consisting of 200-500 nm terraces. The resulting 200 cycle ALD deposits formed showed features only a few nm in height, attesting to the layer by layer nature of ALD growth. More work is required to understand the nanostructure development for as deposited films vs. oxidized films.

Conclusion

Development of an electrochemical ALD cycle for the formation of Ru nano-films has been initiated. Pure Ru films were formed which showed the expected XRD pattern and voltammetry. There are some questions concerning why the OCP for the first 20 cycles was as positive as it was. This suggests that complete coverage of the Au substrate was not achieved during the first few cycles as expected. Atomic level in-situ EC-STM studies could help answer such questions. Initial ex-situ STM studies, however, evidenced very flat films, with feature heights of only a couple of nm, after 200 ALD cycles. There was no evidence of 3D growth. However, an apparent grain structure to the deposits suggests that some roughening has occurred. The charges for Pb UPD suggested only a small increase in deposit surface area, while integration of the charges for Ru oxidation and reduction after 200 cycles were an order of magnitude greater than expected. This is a topic of current study by this group. The use of a stripping step during the Ru ALD cycle has been shown to remove the last traces of Pb, although less than an atomic % of Pb was present when no stripping step was used.

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References

- S. Gottesfeld, T. A. Zawodzinski, *Advances in Electrochemical Science and Engineering* 5, 195 (1997).
- 2. R. Chan et al., Electrochemical and Solid-State Letters 7, G154 (2004).
- 3. O. Chyan *et al.*, *Proceedings Electrochemical Society* **2003-10**, 174 (2003).
- D. Josell, D. Wheeler, C. Witt, T. P. Moffat, *Electrochem. Solid State Lett.* 6, C143 (Oct, 2003).
- 5. T. P. Moffat *et al.*, *J. Electrochem. Soc.* **153**, C37 (2006).
- 6. G. Beyer *et al.*, *Microelectron*. *Eng.* **64**, 233 (2002).
- 7. M. Y. Ho et al., Appl. Phys. Lett. 81, 4218 (2002).
- 8. J. M. Jensen *et al.*, *Chemistry of Materials* **14**, 2276 (May, 2002).
- 9. B. W. Gregory, D. W. Suggs, J. L. Stickney, J. Electrochem. Soc. 138, 1279 (1991).
- 10. J. L. Stickney . I. Villegas, J. Vac. Sci. Technol. A 10, 3032 (1992).
- 11. U. Demir, C. Shannon, *Langmuir* **12**, 6091 (1996).
- 12. B. E. Hayden, I. S. Nandhakumar, *Journal of Physical Chemistry B* **101**, 7751 (1997).
- 13. T. E. Lister, L. P. Colletti, J. L. Stickney, *Israel Journal of Chemistry* 37, 287 (1997).
- 14. L. P. Colletti, J. L. Stickney, J. Electrochem. Soc. 145, 3594 (1998).
- 15. M. L. Foresti et al., Journal of Physical Chemistry B 102, 7413 (1998).

- 16. I. Villegas, *JACS*, **55**, (1998).
- 17. A. Gichuhi, B. E. Boone, C. Shannon, *Langmuir* **15**, 763 (1999).
- M. Innocenti, G. Pezzatini, F. Forni, M. L. Foresti, *Proceedings Electrochemical Society* 99-9, 294 (1999).
- H. Yoneyama, A. Obayashi, S. Nagakubo, T. Torimoto, *Abstracts of the Electrochemical Society Meeting* 99-2, 2138 (1999).
- K. Varazo, M. D. Lay, T. A. Sorenson, J. L. Stickney, *J. Electroanal. Chem.* 522, 104 (Mar 22, 2002).
- R. Vaidyanathan, J. L. Stickney, S. M. Cox, S. P. Compton, U. Happek, *J. Electroanal. Chem.* 559, 55 (2003/11/15, 2003).
- 22. M. K. Mathe, S. M. Cox, V. Venkatasamy, U. Happek, J. L. Stickney, *J. Electrochem. Soc.* **152**, C751 (2005).
- 23. W. Zhu et al., J. Electroanal. Chem. 585, 83 (2005).
- 24. M. Muthuvel, L. Stickney John, *Langmuir FIELD Full Journal Title:Langmuir : the ACS journal of surfaces and colloids* **22**, 5504 (2006).
- 25. V. Venkatasamy, J. L. Stickney, ECS Transactions 3, (2006).
- L. B. Rogers, D. P. Krause, J. C. Griess, Jr., D. B. Ehrlinger, J. Electrochem. Soc. 95, 33 (1949).
- 27. E. Herrero, L. J. Buller, H. D. Abruna, *Chemical Reviews* 101, 1897 (2001).

- 28. A. A. Gewirth, B. K. Niece, Chem. Rev. 97, 1129 (1997).
- 29. A. Aldaz, J. Clavilier, J. M. Feliu, Journal de Physique IV: Proceedings 4, 75 (1994).
- R. R. Adzic, in *Advances in Electrochemistry and Electrochemical Engineering*, H.
 Gerishcher, C. W. Tobias, Eds. (Wiley-Interscience, New York, 1984), vol. 13, pp. 159.
- D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, H.
 Gerischer, C. W. Tobias, Eds. (John Wiley, New York, 1978), vol. 11, pp. 125.
- 32. I. V. D. W. Suggs, B.W. Gregory, J.L. Stickney, J. Vac. Sci. Technol. A 10, 886 (1992).
- 33. D. W. Suggs, J. L. Stickney, Surf. Sci. 290, 375 (1993).
- 34. U. Demir, C. Shannon, *Langmuir* **10**, 2794 (1994).
- 35. E. S. Streltsov, I. I. Labarevich, D. V. Talapin, *Doklady Akademii Nauk Belarusi* **38**, 64 (1994).
- L. B. Goetting, B. M. Huang, T. E. Lister, J. L. Stickney, *Electrochimica Acta* 40, 143 (1995).
- 37. B. E. Boone, C. Shannon, J. Phys. Chem. 100, 9480 (1996).
- R. D. I. Herrick, J. L. Stickney, in *New Directions in Electroanalytical Chemistry*, J. Leddy, M. Wightman, Eds. (The Electrochemical Society, Pennington, NJ, 1996), vol. 96-9, pp. 186.
- 39. G. D. Aloisi et al., Journal of Physical Chemistry B 101, 4774 (1997).
- 40. L. P. Colletti, B. H. Flowers, J. L. Stickney, JECS, (1997).

- 41. A. Gichuhi, B. E. Boone, C. Shannon, *Langmuir*, (1998).
- 42. T. Torimoto, S. Nagakubo, M. Nishizawa, H. Yoneyama, *Langmuir* 14, 7077 (1998).
- 43. G. Pezzatini, S. Caporali, M. Innocenti, M. L. Foresti, *J. Electroanal. Chem.* **475**, 164 (1999).
- 44. S. Z. Zou, M. J. Weaver, *Journal of Physical Chemistry B* **103**, 2323 (1999).
- T. Torimoto, A. Obayashi, S. Kuwabata, H. Yoneyama, *Electrochem. Commun.* 2, 359 (2000).
- M. Innocenti, G. Pezzatini, F. Forni, M. L. Foresti, J. Electrochem. Soc. 148, C357 (2001).
- 47. J. Flowers, Billy H. et al., J. Electroanal. Chem. **524-525**, 273 (2002).
- 48. M. D. Lay, J. L. Stickney, J. Electrochem. Soc. 151, C431 (2004).
- F. Loglio, M. Innocenti, G. Pezzatini, M. L. Foresti, J. Electroanal. Chem. 562, 117 (2004).
- 50. F. Loglio et al., J. Electroanal. Chem. 575, 161 (2005).
- V. Venkatasamy, N. Jayaraju, S. M. Cox, J. L. Stickney, J. Electrochem. Soc. 154, H720 (2007).
- 52. I. Villegas, J. L. Stickney, *Journal of Vacuum Science & Technology, A: Vacuum, Surfaces, and Films* **10**, 3032 (1992).
- 53. I. Villegas, J. L. Stickney, J. Electrochem. Soc. 139, 686 (1992).

- T. L. Wade, T. Sorenson, A., J. L. Stickney, in *Interfacial Electrochemistry*, A. Wieckowski, Ed. (Marcel Dekker, New York, 1999), pp. 757-768.
- 55. T. L. Wade, L. C. Ward, C. B. Maddox, U. Happek, J. L. Stickney, *Electrochemical and Solid-State Letters* **2**, 616 (1999).
- 56. T. L. Wade, R. Vaidyanathan, U. Happek, J. L. Stickney, JEC 500, 322 (2001).
- 57. T. Torimoto, S. Takabayashi, H. Mori, S. Kuwabata, JEC, (2000).
- 58. T. Oeznuelueer, I. Erdogan, I. Sisman, U. Demir, *Chemistry of Materials* 17, 935 (2005).
- 59. V. Vaidyanathan et al., langmuir : ACS journal of surfaces and colloids (2006).
- 60. J. Yang, W. Zhu, X. Gao, S. Bao, X. Fan, J. Electroanal. Chem. 577, 117 (2005).
- 61. W. Zhu et al., Electrochimica Acta 50, 4041 (2005).
- 62. W. Zhu et al., Electrochimica Acta 50, 5465 (2005).
- 63. W. Zhu et al., Transactions of Nonferrous Metals Society of China 15, 404 (2005).
- 64. S. R. Brankovic, J. X. Wang, R. R. Adzic, SS 474, L173 (2001).
- S. R. Brankovic, J. X. Wang, R. R. Adzic, *Journal of the Serbian Chemical Society* 66, 887 (2001).
- 66. M. F. Mrozek, Y. Xie, M. J. Weaver, Analytical Chemistry 73, 5953 (Dec 15, 2001).
- 67. Y.-G. Kim, Y. Kim Jay, C. Thambidurai, L. Stickney John, *Langmuir* 23, 2539 (2007).
- 68. J. Y. Kim, Y.-G. Kim, J. L. Stickney, J. Electrochem. Soc. 154, D260 (2007).

- Y.-G. Kim, Y. Kim Jay, D. Vairavapandian, J. L. Stickney, *J Phys Chem B* 110, 17998 (2006).
- 70. J. Y. Kim, Y.-G. Kim, J. L. Stickney, *ECS Transactions* 1, 41 (2006).
- L. T. Viyannalage, R. Vasilic, N. Dimitrov, *Journal of Physical Chemistry C* 111, 4036 (2007).
- 72. R. Vasilic, L. T. Viyannalage, N. Dimitrov, J. Electrochem. Soc. 153, C648 (2006).
- 73. R. Vasilic, N. Dimitrov, ECS Transactions 1, 33 (2006).
- 74. R. Vasilic, N. Dimitrov, *Electrochemical and Solid-State Letters* 8, C173 (2005).
- S. Strbac, F. Maroun, O. M. Magnussen, R. J. Behm, *J. Electroanal. Chem.* 500, 479 (2001).
- 76. S. Strbac, R. J. Behm, A. Crown, A. Wieckowski, Surf. Sci. 517, 207 (2002).
- 77. W. Chrzanowski, A. Wieckowski, *Langmuir* **13**, 5974 (1997).
- 78. S. Strbac, C. M. Johnston, G. Q. Lu, A. Crown, A. Wieckowski, Surf. Sci. 573, 80 (2004).
- 79. M. B. Vukmirovic *et al.*, *Electrochimica Acta* **52**, 2257 (2007).
- 80. B. C. Schardt *et al.*, *Langmuir* **3**, 239 (1987).
- 81. J. L. Stickney et al., J. Electroanal. Chem. 213, 293 (1986).
- 82. B. C. Schardt et al., Surf. Sci. 175, 520 (1986).
- 83. R. Vasilic, N. Vasiljevic, N. Dimitrov, J. Electroanal. Chem. 580, 203 (2005).

- N. Dimitrov, W. Obretenov, A. Popov, Godishnik na Sofiiskiya Universitet \"Sv. Kliment Okhridski\", Khimicheski Fakultet 92-94, 175 (2001).
- 85. R. R. Adzic, D. N. Simic, A. R. Despic, D. M. Drazic, JEC 65, 587 (1975).
- A. Hamelin, J. Lipkowski, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 171, 317 (1984).
- 87. M. Hepel, S. Bruckenstein, *Electrochimica Acta* **34**, 1499 (1989).
- B. E. Conway, J. S. Chacha, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 287, 13 (1990).
- S. Yoshihara, M. Okamoto, K. Endo, E. Sato, *Interfinish 92, Int. Congr. Surf. Finish.* 3, 1434 (1992).
- G. M. Brisard, E. Zenati, H. A. Gasteiger, N. M. Markovic, P. N. Ross, *Langmuir* 13, 2390 (1997).
- N. M. Markovic, B. N. Grgur, C. A. Lucas, P. N. Ross, *J. Electroanal. Chem.* 448, 183 (1998).
- 92. T. P. Moffat, Journal of Physical Chemistry B 102, 10020 (1998).
- 93. X. Zeng, S. Bruckenstein, J. Electrochem. Soc. 146, 2549 (1999).
- 94. E. A. Streltsov, S. K. Poznyak, N. P. Osipovich, JEC 518, 103 (2002).

- 95. N. Dimitrov, N. Vasiljevic, R. Vasilic, *Abstracts, 32nd Northeast Regional Meeting of the American Chemical Society, Rochester, NY, United States, October 31-November 3,* GEN (2004).
- 96. M. Seo, M. Yamazaki, J. Electrochem. Soc. 151, E276 (2004).
- 97. S. Hwang, J. Lee, J. Kwak, J. Electroanal. Chem. 579, 143 (2005).
- 98. Y. B. Zhang et al., Electrochem. Solid State Lett. 7, C107 (2004).
- 99. I. Oh, A. A. Gewirth, J. Kwak, *Journal of Catalysis* **213**, 17 (2003).
- 100. S. J. Hsieh, A. A. Gewirth, Surf. Sci. 498, 147 (Feb 1, 2002).
- J. Lee, W. B. Wang, M. S. Zei, G. Ertl, *Physical Chemistry Chemical Physics* 4, 1393 (2002).
- 102. M. B. Vukmirovic, R. L. Sabatini, R. R. Adzic, Surf. Sci. 572, 269 (2004).
- S. Hadzijordanov, H. Angersteinkozlowska, M. Vukovic, B. E. Conway, J. Electrochem. Soc. 125, 1471 (1978).
- 104. M. A. Quiroz, Y. Meas, E. Lamypitara, J. Barbier, J. Electroanal. Chem. 157, 165 (1983).
- 105. C. N. Vanhuong, M. J. Gonzaleztejera, J. Electroanal. Chem. 244, 249 (Apr, 1988).



Cartoon A

Ru³ Pb² (Pb² Ru³ Ru Ru Pb Ru Ru Ru Ru Ru Ru Ru Au Au Au Au Au Au Au Au Au Au

Cartoon B

Cartoon C

Deposition of adlayer Pb UPD (cartoon A) @ -0.44V

Redox replacement reaction of Pb by Ru @ OCP (cartoon B+C)

Figure 2.1. Cartoon of scheme for the formation of an atomic layer of Ru using surface limited redox replacement.



Figure 2.2. This figure shows the potential vs. time graph for several cycles of replacement of Cu UPD with Ru.



Figure 2.3. A) Dark curve shows extensive reduction current for Pb UPD, well in excess of the ML expected. pH 1.5; B) Same process using a Pb solution with a pH of 5.



Figure 2.4. Schematic of one SLRR of Ru for Pb UPD. Initially the potential was controlled at -0.44 V, and reductive current was observed. The current then dropped, after the Pb UPD layer was formed. The next step was to let the potential go open circuit, and pump in the Ru³⁺, pH 1.5, solution, and the potential drifted positive to -0.2 V, completing one cycle.



Figure 2.5. Four ALD cycles for the deposition of Ru.



Figure 2.6. This graph displays the atomic % of Ru as a function of exchange time. Note, EPMA samples a micron deep into the sample, so even though 200 cycle were deposited, signal from the Au substrate was still present and predominant.



Figure 2.7. Graph of the average charge for Pb UPD, over 200 cycles, as a function of the deposition potential.



Figure 2.8. This graph shows the current time trace for three cycles for Ru ALD where a stripping step at 0.25 V was used.



E/mV vs Ag/AgCl

Figure 2.9. This figure displays a window opening experiment to higher and higher potentials for a Ru film formed with 200 cycles. The first scan started with a Ru film exposed to air, and resulted in the large reduction peak at 0.5 V. Subsequent scans to more positive potentials, subsequently resulted in reduction features, which increased in peak current, and shifted negatively in potential, the more positive the deposit was scanned. These scans were run in 1.0 M H₂SO₄; scan rate: 5mV/s.



Figure 2.10. X-ray diffraction pattern for a 200 cycle deposit of Ru, formed on a (111) textured Au on glass substrate.



Figure 2.11 Graph of Ru deposit coverage as a function of the number of ALD cycles performed.



Figure 2.12. This graph shows the potential vs. time graph for 30 ALD cycles for the deposition of Ru.



Figure 2.13. STM images of the 200 cycle Ru film, deposited on template stripped Au; bias voltage, 500 mV; tunneling current, 10 nA.

Stripping Potential (mV)	Stripping time: 2 sec		Stripping time: 10 sec	
	Ru atomic %	Pb atomic %	Ru atomic %	Pb atomic %
50	22	0.5	15	0.4
150	18	0.3		
250	20	0.6	18	0
350	23	0	16	0

Table 2.1 list the atomic % of Ru and Pb as measured with EPMA for deposits formed with various stripping conditions.

CHAPTER 3

COPPER NANO-FILM FORMATION BY ELECTROCHEMICAL \mbox{ALD}^1

¹ C. Thambidurai, Y.-G. Kim, N. Jayaraju, V. Venkatasamy, and J. L. Stickney, *Journal of the Electrochemical Society*, **156**, D26 (2009). Reprinted here with permission of publisher.

Abstract

This paper describes the formation of Cu nano-films using atomic layer deposition (ALD) via surface limited redox replacement (SLRR), also referred to as monolayer restricted galvanic displacement. An automated flow cell electrodeposition system was employed to make Cu nanofilms using 100, 200 and 500 ALD cycles. The cycle was composed of a sequence of steps: Pb UPD, rinsing with blank, introduction of Cu^{2+} at open circuit and exchange of the Pb atoms for Cu, rinsing with blank. The open circuit potential (OCP) was used to follow the replacement, exchange, of Pb for Cu, which shifted from that used to deposit Pb UPD (-0.44 V) up to the equilibrium potential for Cu^{2+}/Cu or -0.013 V, upon complete exchange. The resulting Cu films appeared homogeneous from inspection, optical microscopy, as well as by scanning electron microscopy (SEM). Electron probe microanalysis (EPMA) showed no Pb in deposits formed using -0.44 V for Pb UPD. However, for deposits formed with Pb deposition at potentials more negative than -0.44 V, Pb was evident in the deposit. A prominent Cu (111) peak was displayed in the X-ray diffraction (XRD) pattern for the Cu nano-films. Morphology studies of the Cu films were performed using ex-situ scanning tunneling microscopy (STM), and attested to the layer by layer growth of the Cu film. The 250 nm flat terraces suggested a surface which may have become smoother during growth, rather than roughening as normally experienced during electrodeposition or growth of thin films in general. A decrease in coulometry for Pb UPD during the first 30 cycles could also be interpreted as a decrease in surface roughness, or surface repair during ALD.

Introduction

Cu electrodeposition is the method of choice for the formation of interconnects in the back end of ultra-large scale integration (ULSI) because of its high conductivity and high electro-migration resistance.(*1*) Electrodeposition is used for a number of reasons, such as the low cost of tooling, a low tendency to form particles, and the ability to achieve bottom up filling in the trenches used to hold the Cu interconnects. This Cu deposition process is referred to as the Damascene process.(*2*)

Prior to Cu deposition via the Damascene process, a liner must be constructed, consisting of a very thin layer of Ta/TaN, deposited by physical vapor deposition, to act as a diffusion barrier. Even traces of Cu can change the electronic properties of Si, and Ta/TaN is the diffusion barrier of choice. The second part of the liner is a Cu "seed" layer, also deposited by physical vapor deposition. The seed layer is needed, as Cu Damascene electrodeposition is difficult to perform directly on Ta/TaN. Ideally the Cu seed layer should be uniform, conformal inside trenches, smooth, and able to be made thinner and thinner, in accordance with the ideas of scaling: Moore's law predicts that each year more and smaller transistors make up an IC, and scaling means use of last year's technology scaled it to tomorrows dimensions. Liners less than 10 nm thick are presently under investigation.

These linear thicknesses, formed in trenches, are presently difficult to obtain by physical vapor deposition (PVD), and a number of studies seeking an alternative route to trench filling using Damascene have been performed. Cu has been deposited by various vapor phase techniques such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), plasma enhanced chemical vapor deposition (PECVD) and catalyst enhanced chemical vapor deposition (CECVD). There have also been reports of Cu formation using pulsed

laser deposition (PLD), magnetron sputtering and electroless plating. Although Cu films have been prepared by most of the above techniques, they have not been adopted by the industry for various reasons. In general, as dimensions continue to decrease while the number of problems continue to increase.

Atomic layer deposition (ALD) is a method gaining acceptance for applications in the electronics industry, as it promotes layer by layer growth and conformal deposition. Electrochemical ALD is the electrochemical analog of atomic layer epitaxy (ALE)(3-5) and atomic layer deposition (ALD),(6-9) where deposits are formed using surface limited reactions, an atomic layer at a time. Electrochemical ALD is being investigated as a possible low cost methodology for the production of high quality metal nano-films.(10-14) The majority of surface limited reactions in electrodeposition are referred to as underpotential deposition (UPD).(15-19) UPD is a phenomenon where an atomic layer of one element deposits at a potential under, prior to, that needed to deposit the element on itself (form a bulk deposit). UPD is the result of the free energy of formation of a surface compound or alloy. By combining UPD with ALD, electrochemical ALD was invented.(20-22)

The layer by layer electrodeposition of pure metals in a 2D growth mode, by ALD, has only recently been possible with development of monolayer restricted galvanic displacement, an outgrowth of work by Adzic, Weaver, Dimitrov, and Stickney, also referred to as surface limited redox replacement (SLRR). Galvanic displacement referrers to a well known process where the ions of a more noble species oxidize a less noble species, and replace it. It becomes a surface limited reaction when UPD is used to form a single sacrificial atomic layer of the less noble species. That is, UPD is used to form a limited amount of a relatively reactive element, which is than replaced using a solution of ions of a more noble element. The more noble element removes the electrons from the sacrificial layer, dissolving it, with itself becoming reduced and plating out on the surface. The amount of the more noble element deposited is thus limited by the amount of the sacrificial element initially present. As UPD of the sacrificial metal results in an atomic layer, the amount of the more noble element formed should also be an atomic layer, depending on the relative oxidation states of two ions. To deposit thicker films, multiple replacement (ALD) cycles can be performed. Recently, a creative new processes has been used to form Cu film of up to 100 monolayers on Ag(111) and Au(111) substrates using SLRR and ALD, in what has been referred to as a one pot deposition, reported by Dimitrov *et al.* The atomic interaction between the growing metal and sacrificial metal, during the deposition of Cu and Pt on Au(111) were studied by Stickney *et al.*(*11,23*) and more recently, the electrodeposition of Ru metal nano-films have been deposited using SLRR to form up to 200 ALD cycles in a flow cell deposition system, by the Author's group.

In the present paper, optimization studies of Cu deposition using electrochemical ALD in an automated flow deposition system, where Pb was used as the sacrificial metal, are reported. The effect of the Pb deposition potential on Cu film formation and Cu film homogeneity are described. Deposit morphology was investigated using scanning electron microscopy (SEM), optical microscopy and scanning tunneling microscopy (STM). The elemental composition of the Cu thin films was determined using electron probe micro analysis (EPMA), while deposit structure was investigated using low angle X-ray diffraction. An electrochemical flow cell containing an electrochemical quartz crystal microbalance (EQCM) as the substrate was used to better understand the Cu deposition process. Cu films were formed using 100, 200 and 500 SLRR cycles, via the automated flow electrodeposition system. In principle a Cu ALD cycle could be used to form seed layers for Damascene, but issues concerning chemistry between Cu and a Ta/TaN surface have not yet been addressed. At present, it appears that there is no UPD of Cu on a Ta/TaN surface, so making a conformal Cu atomic layer to start the ALD process may be difficult.

Experimental

Deposits were formed using an electrochemical flow electrodeposition system(49, 123, 126) consisting of pumps, valves, an electrochemical flow cell and a potentiostat (Electrochemical ALD L.C.). All components were computer controlled using a LABVIEW program (National Instruments). The auxiliary electrode was a gold wire embedded in the cell wall opposite the deposit, and the reference electrode was a Ag/AgCl (3M NaCl) (Bioanalytical Systems, Inc.). Substrates consisted of 300 nm thick gold films on a 3 nm Ti adhesion layer, on glass. Au was vapor deposited onto substrates held at 280° C, and then the deposits were annealed at 400° C for 12 hours, resulting in a prominent (111) growth habit. The gold electrodes were cleaned in concentrated nitric, acid by immersion for 2 minutes, and then by electrochemical cycling upon insertion into the flow cell. The solution flow rate was 18 mL/min.

The solutions used were 1mM Pb(ClO₄)₂, pH 2 and 1mM CuSO₄, pH 2. The Pb solution was made with 50 mM HClO₄, while the Cu solution was made with 50 mM H₂SO₄, as a supporting electrolyte. The blank solution was 50 mM HClO₄, pH 2. The formal potentials for Pb²⁺/Pb and Cu²⁺/Cu, in the present solutions, were -0.462 V and -0.013 V respectively, *vs*. Ag/AgCl. A KI solution, 0.1 mM in 50 mM HClO₄, was used to initially modify the substrate. The Au substrate was first exposed to the KI solution for 3 minutes, to promote electrochemical annealing.²⁵ Solutions were prepared using water from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better.

A Scintag PAD-V diffractometer, with Cu K α radiation (λ =1.5418 Å), was used to obtain glancing angle X-ray diffraction patterns. EPMA was run on a Joel 8600 wavelength dispersive scanning electron microprobe. STM experiments were performed using a Nanoscope III (Digital instruments, Santa Barbara, CA) equipped with W tips, electrochemically etched (15 V ac in 1 M KOH) from 0.25 mm wires. SEM images were obtained using a LEO 982 Field emission microscope.

Optimal deposition conditions were studied using a flow cell electrochemically quartz crystal micro balance (EQCM). Ag electrodeposition coulometry was used to calibrate the EQCM. A 9 MHZ AT-cut quartz crystal was used, where both sides were coated with circular Au electrodes (ca. 0.2 cm², 5 mm in diameter). The electrodes were formed with 50 nm of Ti, followed by 300 nm of sputtered Au. The quartz crystal was cleaned with concentrated nitric acid in an ultrasonic bath (Cole-Parmer, Vernon Hills, IL) for two minutes, and then rinsed thoroughly with de-ionized water and carefully blown dry with N2.

Results and Discussion

Figure 3.1 is a cartoon of the ALD cycle used to form Cu nano-films in the present study: Pb UPD, replacement by Cu from a Cu²⁺ solution for the Pb atomic layer at open circuit (no potential control). Note, an "atomic layer" simply denotes a deposit one atom thick, but does not specify a particular coverage. Thicker films were formed by repeating this cycle. The principle of ALD is that deposit thickness is proportional to the number of cycles performed. The initial ALD cycle was as follows (Figure 3.2): The Pb solution was pumped into the cell for 2 s at -0.44 V. The solution was then held in the cell for 3 s, resulting in 0.8 monolayer (ML) of Pb, by UPD. Note that one ML is defined here as one deposited atom for each substrate surface atom, in this case the substrate has been approximated as a Au(111) surface with an atomic density of 1.17×10^{15} atoms/cm². Blank solution was then pumped through the cell, at the same controlled potential, to remove excess Pb²⁺ ions. The next step was to pump the Cu²⁺ solution in to the cell for 3.5 s at open circuit, allowing Cu²⁺ atoms to oxidize the Pb and form a Cu atomic layer, with a coverage of 0.58 ML. The cycle was completed by pumping blank solution through the cell to remove the resulting Pb²⁺ ions as well as the excess Cu²⁺ ions. This cycle was then repeated as many as 500 times, with 200 cycles used to form most of the deposits in this study.

In principle, the amount of Cu deposition was controlled by Faraday's Law, or the number of electrons available from the deposited Pb atomic layer. To optimize the dependence of the Cu ALD cycle on the Pb UPD potential, a series of 200 cycle deposits were performed using different Pb potentials, between -0.3 V and -0.48 V. The average Pb charges (described as ML vs. Au (111)) were determined for each deposit, and are displayed in Figure 3.3 A relative plateau is evident between -0.35 and -0.45 V, equivalent to about 0.3-0.6 ML per cycle. For potentials below -0.44 V, the average coverage per cycle increased sharply, while above -0.35 V the coverage dropped off to zero. At the more negative potentials, much thicker deposits were formed, for instance at -0.48 V, 4.6 ML/cycle was deposited, and evidenced strong 3D growth. Given those results, it was decided to use -0.44 V as it clearly resulted in a surface limited Pb coverage, no evidence of 3D growth, and more than ¹/₂ a ML/cycle. From the description of ALD, it might be construed that one monolayer should be deposited each cycle. However, most work in the area of ALD results in considerably less than one monolayer per cycle, with many cycles producing only 0.1 ML or less. In electrochemical ALD, higher coverages/cycle were frequently observed, between 0.2 and 0.8 ML/cycle. From experience with such cycles, the most important point is to keep the coverages/cycle below 1. Coverages above 1 ML/cycle generally result in some 3D growth with each cycle, and gradual roughening of the deposit.

The open circuit potential (OCP) can be used to follow the exchange process, as it reflects the activities of species both on the surface and in solution. After deposition of Pb UPD at -0.44 V (Figure 3.2), excess Pb^{2+} ions were flushed from the cell and the control program disconnected the auxiliary electrode, allowing the deposit to go open circuit while Cu²⁺ ions were flushed into the cell. The OCP potential was monitored during the resulting exchange, as shown in Figure 3.2. Initially the OCP moved positively for a number of reasons, including the fact that hydrogen is stable at these potentials, so that some proton reduction may have taken place. In addition, the Cu²⁺ ions entered the cell and oxidized Pb from the surface, creating a mixed potential, as the result of having some Pb on the Cu surface, and varying concentrations of both Pb²⁺ and Cu²⁺ in solution. Ideally, the potential would shift positive towards the equilibrium potential for Cu^{2+}/Cu , -0.013 V (Figure 3.2), as the majority of the Pb UPD oxidized, and the electrode surface was Cu again. In Figure 3.2., the deposit was formed using a Pb UPD potential of -0.44 V, and the exchange was given about 3.5 s, as evidenced from the potential time plot. Attainment of a potential near 0.0 V took less then two seconds, and indicated complete removal of the Pb atoms in the present system.

In studies by the authors of the electrochemical ALD of Pt and Ru nano-films, optimal replacement times of 60 s or higher were used, while less than 2 s was required for replacement of Pb UPD by Cu in the present study. Such relative replacement times are consistent with the electrodeposition kinetics for Cu *vs*. Pt or Ru. Cu electrodeposition is generally a reversible (fast) process, compared with the electrodeposition of Pt or Ru, which generally show relatively slow or irreversible kinetics. For the Cu film deposited using a Pb potential of -0.48 V, the OCP stabilized close to -0.47 V, near the formal Pb²⁺/Pb potential. This indicated the presence of significant amounts of Pb in the Cu film, again creating a mixed potential, suggesting that not all

the Pb was removed each cycle. This result is consistent with the data in Figures 3.3 and 3.4. It appears that some Pb atoms were buried under depositing Cu atoms during the exchange, when more than a ML of Pb (some bulk) was initially deposited. This buried Pb built up each cycle, resulting in the observed high Pb coverages seen for potentials lower than -0.46 V (Figures 3.3 and 3.4).

The elemental compositions of the set of 200 cycle Cu films, formed by varying the potential for Pb, were investigated using EPMA and the relative Pb and Cu coverages are displayed in Figure 3.4. Note that the coverages are listed as atomic %, from EPMA, and the sum of Pb% and Cu% do not equal 1. The rest of the signal was from the Au substrate, as the deposits were thin relative to the sampling depth of the electron beam used for EPMA. There is a short plateau in coverage, just before Pb starts to make up part of the films, between -0.40 and -0.45 V. Use of Pb potentials below -0.46 V resulted in a build up of Pb in the deposit (Figure 3.4), more than a ML/cycle. Apparently, when more than a monolayer of Pb was deposited on the surface each cycle, the exchange process was hindered, and some Pb was trapped below the depositing Cu. This is clear from the increasing atomic Pb % and decreasing Cu atomic %, observed at the most negative potentials.

The homogeneity and morphology of the 200 cycle Cu deposits were studied using both optical and scanning electron microscopy (SEM). SEM images of the substrate and Cu films formed using Pb deposition at -0.44 V and -0.48 V are shown in Figure 3.5. The Cu film formed using -0.44 V for Pb was uniform (Figure 3.5b), with a morphology equivalent to that of the initial Au substrate (Figure 3.5a). However, for the Cu deposit formed using -0.48 V for Pb deposition (Fig. 5c), a rough morphology was observed, with 3D growth consisting of clusters and lead pyramids. Clearly, Pb deposition at -0.48 V did not just result in UPD, or single Pb

atomic layers, but more than a ML each cycle, which built up, producing the observed crystals (Figure 3.5c).

Ideally, SLRR is a one atom to one ion reaction. That is, one Pb atom is oxidized by one Cu^{2+} ion, and the depositing Cu atom takes the place of the Pb atom. However, EPMA results from across the film suggest that more deposition occurs near the entrance to the flow cell, relative to the rest of the deposit. It has been pointed out that the exchange process is fast, about 3.5 s, or a little longer than the time it takes to flush the Cu solution into the cell. Flowing the Cu^{2+} solution through the cell will result in both a dead layer (where solution dose not initially exchange) near the electrode surface. In addition, as the solution of Cu^{2+} ions enter the cell, they will exchange for the Pb UPD, creating a layer of solution near the electrode where the concentration of Cu^{2+} ions will have been somewhat depleted. The highest Cu^{2+} ion flux will occur at the electrode surface where the solution enters the cell, in a sense a wall jet electrode configuration, as the solution stream hits the substrate at 30° from the plane. Ink tests clearly showed that the solution impinged the substrate surface in a spot at the center of the entrance and flowed down the cell most rapidly in the center.

This same pattern was also observed in the deposit distribution across the substrate. If the process was truly based on UPD of each atomic layer, and a one atom for one ion exchange, the flow patterns in the cell would be a moot point. The fact that the thickness was higher at the inlet, for these deposits, suggests that electron transfer was not from atom to ion, as much as from electrode to ion. That the deposit was thicker at the inlet suggests oxidation of Pb atoms anywhere across the deposit resulted donation of electrons to the electrode, which could then reduce Cu^{2+} ions anywhere across the deposit (electrode to ion), with the highest probability for
deposition at the entrance, where the Cu^{2+} ion flux was highest. This is similar to some forms of corrosion, where oxidation occurs at one place on a metal, and reduction at another.

In the present studies, there was generally twice as much Cu at the inlet, relative to the middle and outlet side of the deposit. This process should have been a function of the deposition kinetics and flow rate, but they have not yet been evaluated. An increase in flow rate increases convection, while a decrease would require more time for the solution to fill the cell, and a prolongation of any concentration gradients. A lower concentration of reactants might slow the exchange process until the concentration in the cell can become homogeneous, producing a more homogeneous deposit. Cell designs which allow a more laminar flow, and homogeneous concentration distribution across the deposit while exchanging solutions, are being investigated.

In the present investigation, the dependence of the deposit homogeneity and the exchange process were investigated by forming deposits using Cu^{2+} ion solution of 0.01 mM, 0.1 mM, 1 mM and 10 mM. Initially, ALD cycles were performed by pumping the Cu^{2+} solution at OCP for 3.5 s, followed by 2 s of pumping blank, for all four Cu^{2+} solutions. Figure 3.6 displays the potential changes during the exchange as a function of time for two cycles, for each solution. For the highest concentration solution (10 mM), the OCP shifted to -0.013 V (the formal potential for Cu^{2+}/Cu) in 1.5 s, while it took 2 s for the potential to reach -0.013 V for the 1.0 mM solution. For the more dilute solutions, 0.1 mM and 0.01 mM, the OCP did not get close to -0.013 V, within the 3.5 s for the Cu exchange. Instead, the potential shifted only to -0.20 V and -0.28 V, respectively, far negative of the expected formal potential for the Cu couple. This suggests the exchange was not completed using the more dilute Cu^{2+} ion solutions over the 3.5 s, and some Pb UPD was left on the surface.

Table 3.1 displays data for all four solutions, as a function of replacement time and concentration. Also listed are the average Pb coverages/cycle, the average Cu coverage/cycle actually formed, the relative efficiency of exchange, and the OCP achieved during the exchange. From Table 3.1 it is clear that the Pb deposition charge was lower than expected for the 0.01 mM and 0.1 mM solution, indicating that some Pb was left on the surface after the exchange time (Table 1), that the replacement at the low exchange time was incomplete.

Figure 3.7 shows the relative coverages as a function of the Cu^{2+} solutions used for the exchange. Clearly the 0.1 mM and 0.01 mM solutions were too dilute to be used with the 3.5 s exchange time, as essentially no deposits were formed. What is most striking about Figure 3.7 is the excess deposition observed with the 10 mM solution, which indicates nearly twice as much Cu deposited as the 1.0 mM solution. It appears that this was a result of inadequate rinsing after Cu exchange. That is, some Cu^{2+} ions were still in the cell when the Pb UPD was deposited. In this way, besides Pb UPD, some bulk Cu was also deposited at -0.44 V during this step in the cycle, accounting for the excess Pb charge.

The results in Table 3.1 indicate that a longer exchange time is needed for the lower the solution concentrations. A couple of deposits were formed, with the more dilute solutions, using 30 s and 60 s for the exchange, though the solution was pumped for only the first 3 s. As expected, the Cu % increased with exchange time (Table 3.1), but remained lower than that achieved using the 1.0 mM solution. In addition, the potential shifted further positive, as expected, nearly reaching the equilibrium Cu potential for the 0.1 mM solution, but only to -0.28 V for the 0.01 mM Cu²⁺ solution. Overall, reasonable deposits were formed using the 0.1 mM solution may result from the limited volume of the flow cell. The total Cu²⁺ ions in the cell for the 0.01 mM

solution were a few nano-moles, about what it would take to make a Cu monolayer. Using up the Cu^{2+} ions would result in some Pb left on the surface and a dramatic drop in the Cu^{2+} concentration, both of which would contribute to the low OCP value achieved with the 0.01 mM solution, even after 60 s.

Replacement efficiencies of Cu for Pb were calculated from the total charge for stripping the resulting Cu films, normalized by the number of cycles performed. The resulting Cu coverage/cycle was then normalized by the average Pb coverage/cycle, from Pb UPD, to determine the replacement efficiencies. Table 3.1 lists the replacement efficiencies for various deposits, which improved the higher the concentration and the longer the deposition times.

Reasons for less than 100% efficiency are felt, by these authors, to be associated with side reactions both during Pb deposition and during the exchange, such as the reduction of small amounts of oxygen or protons. Extra charge for Pb deposition can result from oxygen reduction, as Pb is known as a catalyst for this reaction. In addition, at -0.44 V some hydrogen reduction could take place, depending on the kinetics or the hydrogen over-potential. Small amounts of such side reactions would add to the charges recorded for Pb UPD, and account for lower efficiencies. As noted, the 10 mM solution appears to have resulted in some Cu depositing with the Pb, due to inadequate rinsing, which should have improved the efficiency. Figure 8 shows the stripping of a Cu film formed using the 1.0 mM Cu²⁺ ion solution, performed in 0.5 M sulfuric acid, corresponding to 0.57 ML/cycle, or an efficiency of 58% (Table 3.1), and represents the best conditions used in this study. It is evident that the longer it took to exchange Cu for Pb, the lower the efficiency. This suggests that there is a competition for the electrons in the Pb uPD, the more

time side reactions have to compete, such as the reduction of small amounts of oxygen or protons.

To further investigate the deposition process, a flow cell electrochemical quartz crystal microbalance was used. The EQCM electrode was first cleaned according to the procedures described in the experimental section. The deposition process started with blank pumped through the cell for 300 s, to stabilize the quartz crystal. The Au substrate was then modified with I atoms by flowing a 1 mM KI solution through the cell for 180 s, at open circuit, followed again by blank at open circuit for 15 s. The Pb solution was then rinsed through the cell for 33 s at -0.44 V, followed by blank for 8 s, also at -0.44 V, to remove extra Pb²⁺ ions. Finally, the Cu²⁺ solution was rinsed through the cell for 8 s at open circuit, followed by another blank rinse at open circuit for 11 s (Figure 9). Flow rates in the EQCM flow cell were 6 mL/minute. After 10 replacement cycles of Cu for Pb UPD, the charges for Pb deposition and the mass changes (Δf) for Cu deposition were determined (Figure 3.9). Figure 3.9 shows a decrease in frequency, or mass increase, during Pb deposition, as expected. During exchange of Cu for Pb, the mass was observed to decrease, again, as expected, since Cu weighs about a third of Pb.

The average charge for Pb deposition/cycle was around 0.91 ML, the average mass/cycle for Cu deposition was 0.54 ML, calculated from the frequency change between identical points in adjacent cycles (Figure 3.9). At the end of 10 cycles, the Cu film was oxidized in blank solution at 0.7 V, and the charge was used to calculate the average Cu coverage/cycle: 0.50 ML/cycle. The iodide solution was pumped for 2 minutes at open circuit before and after oxidation of the Cu film, in blank, in order to have identical surfaces and solutions, from which to calculate the Cu coverage from the total mass change due to oxidation. The result was 0.51 ML/cycle, in close agreement to the coulometry. Again, oxygen reduction was suspected as the

main reason for the high charge for Pb UPD, 0.91 ML/cycle, relative to the Cu coverages, Pb being known as an oxygen reduction catalyst. Quantitative measurements of frequency, or mass, changes within a cycle were not felt to be reliable, given the changes in the surface and solution composition, and any resulting changes in the double layer composition that may occur during the cycle, as the solutions exchange. However, direct comparisons from cycle to cycle, to points where the surface and solution should have equivalent composition, should be very accurate, as is evident from these results.

One of the advantages of an ALD method is that it should minimize surface roughening during deposition. This raises the question, can ALD decrease surface roughness? This is a very hard characteristic to quantify. In the present study, deposit morphology was investigated using scanning tunneling microscopy (STM) for a 200 cycle deposit, formed using a Pb UPD potential of -0.44 V. Figure 3.10 displays the charge in ML/cycle for such a 200 cycle deposit. The first cycle resulted in a Pb deposition charge equivalent to about 0.8 ML ²⁷ which then dropped to a steady state of around 0.55 ML/cycle over the first 25 cycles. Reasons for these changes are still being considered. One possibility is that the surface area decreased as the deposit was formed. If the initial substrate had some degree of roughness, it is possible that as the ALD deposit formed, smaller grains were covered, creating larger grains and flat terraces, resulting in a lower total surface area and lower deposited amounts of Pb. That the amount of Pb UPD on the Au substrate is different than on Cu is understandable, but should not be a factor for more than the first few cycles. On the other hand, it may very well take 25 cycles to decrease surface roughness to the point where the surface area does not continue to decrease. There do appear to be conditions where nucleation kinetics are responsible for variations in the growth rate during the initial

cycles. Such behavior has been observed in gas phase ALD, and is probably observed under certain conditions in electrochemical ALD, though none has yet been described.

To investigate the possibility of surface repairing in the present instance, a deposit was formed from 200 cycles on a sample of template stripped gold (TSG),(127) and imaged (Figure 3. 11) with scanning tunneling microscopy (STM). The TSG was formed by taking a Au film deposited on mica, and covering it with epoxy. The mica was then defoliated, leaving the Au film on the epoxy, and with the surface previously in contact with the ultra flat mica surface exposed. Figure 3.11 shows a STM image of both the clean template stripped Au surface, and the 200 cycle Cu film. The primary differences between the two sets of images are the slight rounding of the smooth domains on the TSG substrate, relative to the essentially atomically flat terraced domains for the Cu deposits. The Cu surface is composed of terraces with widths of 250-300 nm, as well as bunched steps, attesting to the layer by layer nature of the ALD growth. The TSG was used because of its tendency to have very flat domains, and the ability to get films large enough for the flow cell. From these images, the surface area of the deposit may have decreased during growth, possibly accounting from some of the decrease in Pb charge in Figure 3.10. Glancing angle X-ray diffraction was used to study the Cu film structure. Figure 3.12 displays the diffraction patterns for 100, 200 and 500 cycle Cu films, formed by electrochemical ALD. In order to maximize sensitivity for the thin Cu films, an incident angle of 1° from the surface plane was employed. The peak at 43.35° corresponded to reflections from Cu(111) planes, while a peak corresponding to Cu(200)(128) planes was also observed. The peak intensities for Cu clearly increased as the number of cycles increased, while those for Au decreased, as expected. The (111)/(200) peak intensity ratios were essentially the same for the Au substrate and Cu deposits, suggesting conformal deposition. The (111)/(200) ratio from

powder patterns is 2 for both Au and Cu (both fcc metals), while in the present study the ratio was closer to 5, indicating a strong (111) habit for both the Au substrate and the Cu deposit. The (111) habit is consistent with the roughly hexagonal facets observed with STM (Fig. 3.11). There was no evidence of Pb peaks, nor any Pb EPMA signal.

Conclusions

Initial studies of the formation of Cu films by Electrochemical ALD have been reported. The surface limited reactions are referred to here as surface limited redox replacement (SLRR). EPMA results confirmed the formation of Cu films using ALD, with no evidence of Pb. Monitoring the OCP during exchange allows monitoring of the reaction progress. Pb replacement by Cu was not completed until the OCP reached -0.013 V. There are indications that the deposition was not as homogeneous as desired, with some extra deposition occurring at the cell entrance. Studies of the deposit dependence on exchange time and the Cu²⁺ solution concentration have shown, as expected, that longer times give more complete exchange and more concentrated solutions result in a more rapid exchange. The XRD patterns showed the deposits to have a strong (111) habit, consistent with the substrate. STM showed wide, roughly hexagonal terraces, and an apparent decrease in surface roughness. A flow cell EQCM was used to follow the deposition process, and provided reliable data from cycle to cycle. However, within a cycle new questions were raised, mostly related to the double layer and surface compositions.

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References

- 1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, H. Deligianni, *IBM Journal of Research and Development* **42**, 567 (1998).
- S. P. Murarka, S. W. Hymes, *Critical Reviews in Solid State and Materials Sciences* 20, 87 (1995).
- T. F. Kuech, P. D. Dapkus, Y. Aoyagi, *Atomic Layer Growth and Processing*. (Materials Research Society, Pittsburgh, 1991), vol. 222, pp. 360.
- 4. S. Bedair, Atomic Layer Epitaxy. (Elsevier, Amsterdam, 1993), pp. 304.
- 5. C. H. L. Goodman, M. V. Pessa, *JAP* **60**, R65 (1986).
- 6. M. Leskela, M. Ritala, *Thin Solid Films* **409**, 138 (2002).
- E. B. Yousfi, B. Weinberger, F. Donsanti, P. Cowache, D. Lincot, *Thin Solid Films* 387, 29 (2001).
- 8. V. Sammelselg *et al.*, *Applied Surface Science* **134**, 78 (1998).
- 9. M. Ylilammi, *Thin Solid Films* **279**, 124 (1996).
- L. T. Viyannalage, R. Vasilic, N. Dimitrov, *Journal of Physical Chemistry C* 111, 4036 (2007).
- Y.-G. Kim, J. Kim, D. Vairavapandian, J. L. Stickney, *Journal of Physical Chemistry B* 110, 17998 (2006).
- 12. Y.-G. Kim, J. Kim, C. Thambidurai, J. L. Stickney, *Langmuir* 23, 2539 (2007).

- 13. J. Kim, Y.-G. Kim, J. L. Stickney, *Electrochemical Society Transaction* 1, 41 (2006).
- 14. R. Vasilic, N. Dimitrov, *Electrochemical and Solid State Letters* 8, C173 (2005).
- 15. D. M. Kolb, M. Przasnyski, H. Gerisher, *JEC* 54, 25 (1974).
- D. M. Kolb, in Advances in Electrochemistry and Electrochemical Engineering, H. Gerischer, C. W. Tobias, Eds. (John Wiley, New York, 1978), vol. 11, pp. 125.
- 17. K. Juttner, W. J. Lorenz, Z. Phys. Chem. N. F. 122, 163 (1980).
- A. T. Hubbard *et al.*, in *New Dimensions in Chemical Analysis*, B. L. Shapiro, Ed. (Texas A & M University Press, College Station, Texas, 1985), pp. 135.
- 19. A. A. Gewirth, B. K. Niece, *Chem. Rev.* 97, 1129 (1997).
- J. L. Stickney, in *Advances in Electrochemical Science and Engineering*, R. C. Alkire, D. M. Kolb, Eds. (Wiley-VCH, Weinheim, 2002), vol. 7, pp. 1-105.
- 21. B. W. Gregory, J. L. Stickney, *Journal of Electroanalytical Chemistry* **300**, 543 (1991).
- B. W. Gregory, D. W. Suggs, J. L. Stickney, *Journal of the Electrochemical Society* 138, 1279 (1991).
- J. Kim, Y.-G. Kim, J. L. Stickney, *Journal of The Electrochemical Society* 154, D260 (2007).
- 24. J. L. Stickney, *Electroanalytical Chemistry* **21**, 75 (1999).
- T. L. Wade, T. Sorenson, A., J. L. Stickney, in *Interfacial Electrochemistry*, A. Wieckowski, Ed. (Marcel Dekker, New York, 1999), pp. 757-768.

- 26. M. Hegner, *Surface Science* **291**, 39 (1993).
- 27. K. Wetzig, C. M. Schneider, Eds. *Thin Films for Electronics*, (Wiley-VCH, Weinheim, 2003).



Figure 3.1. Schematic diagram of ALD cycle for Cu deposition. The cycle starts with one monolayer of Pb using Pb UPD at -0.44 V, *vs.* Ag/AgCl. Cu solution enters the cell at OCP and then Pb atoms are replaced by Cu^{2+} ions, resulting in leaving Pb ions in the solution and formation of an atomic layer of Cu. Desired thickness is achieved by repeating the steps (b), (c) and (d).



Figure 3.2. Time-Potential-Current graph illustrating one cycle of surface limited redox replacement of 200 cycle Cu film at a Pb deposition potential of -0.44V. The exchange time for the replacement: 3.5 s. The formal potential for Pb^{2+}/Pb is - 0.462 V vs. Ag/AgCl.



Figure 3.3. This graph displays the average Pb charge as a function of Pb deposition potential for 200 cycle Cu film with an exchange time 3.5 s. The formal potential for Pb^{2+}/Pb is -0.462 V vs.

Ag/AgCl.



Figure 3.4. This graph displays the atomic % for Cu and Pb, over 200 cycle Cu film, as a function of Pb deposition potential.



Au substrate (A)



Cu Film @ Pb -0.44V (B)



Cu film @ Pb -0.48V (C)

Figure 3.5. SEM images of bare Au substrate (Image A), 200 cycle Cu film formed by SLRR using Pb deposition potential at -0.44V (Image B) and -0.48 V (Image C).



Figure 3.6. This graph displays OCP change *vs*. time, over 200 cycle Cu film, with different Cu concentrations and an exchange time of 3.5 s.



Figure 3.7. This figure displays the Cu atomic % as a function of Cu concentration, over 200 cycle Cu film with an exchange time 3.5 s



Figure 3.8. This figure displays the stripping of 200 cycle Cu film in 0.5 M sulfuric acid and Cu charge per cycle was calculated as 0.57 ML/cycle. Scan rate = 5 mV/s.



Figure 3.9. Time-Current-Frequency change graph illustrating 10 cycles of Cu ALD using Pb UPD, deposited at -0.44 V as the sacrificial layers. Two ALD cycle are displayed in the expansion. EQCM flow rate: 6mL/min.



Figure 3.10. This figure displays the Pb deposition charge as a function of number of cycles of 200 cycle Cu film at a Pb deposition potential of -0.44 V and with an exchange time of 3.5 s using 1mM Cu solution. The average Pb deposition charge was calculated as 0.58 ML.



Figure 3.11. STM images of surface morphology of (A) template stripped gold (TSG) and (B) 200 cycle Cu film on TSG using Pb deposition potential of -0.44 V; bias voltage, 500 mV; tunneling current, 10 nA; 500x500 nm², image size.



Figure 3.12. XRD diffraction of 100, 200 and 500 cycle Cu film deposited using Pb deposition potential -0.44 V and with an exchange time of 3.5 s.

Cu Concentration (mM)	Replacement time (s)	Cu atomic %	Pb deposition Charge (ML)	Cu charge / cycle (ML)	Efficiency (%)	OCP, 200 th cycle
0.01	3.5	1.4	0.22	0	0	- 0.33 V
	30	5.4	0.50	0.024	4.8	- 0.28 V
	60	7.3	0.63	0.018	2.85	- 0.28 V
0.1	3.5	5.7	0.5	0.01	2	- 0.32 V
	30	32	0.88	0.30	34	- 0.05 V
	60	28	0.71	0.31	44	- 0.04 V
1	3.5	41	0.98	0.57	58	- 0.01 V
10	3.5	75	2.32	1.86	80	-0.01 V

Table 3.1. 200 cycle Cu film, at -0.44 V Pb potential, was studied as a function of Cu solution concentration.

CHAPTER 4

FORMATION OF RUSE THIN FILM USING ELECTROCHEMICAL – \mbox{ALD}^1

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Abstract

Studies are presented describing attempts to form a cycle for the growth of RuSe nanofilms using the electrochemical form of atomic layer deposition (ALD). Au substrates have been used to form RuSe nanofilms, based on layer by layer growth of deposits, using surface limited reactions. Ru atomic layers were formed using surface limited redox replacement (SLRR), where an atomic layer of a sacrificial element is first deposited by underpotential deposition (UPD), and is then exchanged for the element of interest. In the present study, Pb atomic layers were used, and exposed to solutions of Ru³⁺ ions at open circuit to form Ru atomic layer. Se was electrodeposited on Ru, using potentials 100 mV, -150 mV and -450 mV. Then, the process was repeated to grow films of the desired thickness. It was evident from electron probe micro analysis (EPMA) that PbSe was being formed, not the RuSe desired. CVs of 100 cycle RuSe electrode in methanol solution, displayed its methanol resistant behavior, but its oxygen reduction catalyst behavior is still under investigation.

Introduction

Fuel cells are expected to become a main resource of clean energy. The six generic fuel cells in various stages of development are (*i*) polymer electrolyte membrane (PEM) fuel cells, (*ii*) direct methanol fuel cells, (*iii*) phosphoric acid fuel cells, (*iv*) molten carbonate fuel cells, (*v*) solid oxide fuel cells and (*vi*) alkaline fuel cells. Among these, PEM fuel cells and direct methanol fuel cells are the most promising systems for portable and residential power applications(*1*). Although, PEM fuel cells show steady improvement and high power efficiency, storage of hydrogen leads to an engineering complexity which is also added to the cost of the fuel cell (2-4). In direct methanol fuel cells, methanol can be easily transported and stored as a liquid and also there is no requirement for reforming, making them the simplest among all types of fuel cells (5-6).

In direct methanol fuel cells, methanol crossover from the anode to the cathode compartment leads to mixed potentials and also significant performance loss during the oxygen reduction reaction (ORR) at Pt based catalyst electrodes (6-8). This problem can be approached by using high platinum loading(9) or seeking alternative methanol resistant ORR catalyst electrode. Obviously, the first method leads to increase in the production cost. So the properties and types of non platinic ORR catalyst electrode have been studied extensively in the literature. Non-platinic ORR catalysts can be divided into two classes, i.e. derivatives of transition-metal macrocyclic compounds(*10-13*) and Ru-based catalysts(*7,14-17*). Among these, Ruthenium chalcogenides draws great attention because of their complete tolerance towards methanol poisoning.

In this paper, RuSe nanofilms are proposed as promising material for ORR catalyst electrode. Many applications require formation of nanofilms. Control in their growth can be facilitated by atomic layer deposition (ALD), a methodology for forming deposits one atomic layer at a time via surface limited reactions(*18-19*). The electrochemical form of ALD, previously referred to as EC-ALE or electrochemical atomic layer epitaxy, has been around since the early 90s (*20-24*). EC-ALE is now referred to as E-ALD, in line with the common usage of ALD in the literature. Most electrochemical surface limited reactions are referred to as underpotential deposition (UPD), known for 50 years(*25-29*). UPD involves the formation of an atomic layer of one element on a second at a potential prior to (under) that needed to deposit the element on itself. UPD is a thermodynamic process, where an atomic layer is formed as the result of the free energy of formation of a surface compound or alloy. In the authors group, UPD has been used in an ALD cycle, to form nanofilms of a wide variety of compounds and metal thin films.

Formation of elemental deposits like Cu, Ru and Pt using surface limited redox replacement reaction (SLRR), also known as monolayer restricted galvanic displacement, has been described in the author's previous work (*30-32*). In developing a process for the deposition of RuSe, Ru was deposited using Pb as a sacrificial metal. Pb UPD was deposited at -440 mV for 8 sec to form an atomic layer of lead atoms. The solution was then exchanged for a blank, followed by a Ru ion solution, at open circuit potential (OCP). The Ru ions oxidize the less noble Pb atoms and become reduced to Ru atoms. This redox replacement reaction of the Pb atomic layer for one of Ru takes around 60 seconds. The second cycle step was Se deposition, for which a number of potentials were investigated: 100 mV, -150 mV and -450 mV.

reductive stripping step was used as well, at -630 mV in the blank solution, to remove extra Se atoms from the surface.

Experimental:

Depositions were performed using a thin layer flow electrodeposition system consisting of pumps, valves, a flow cell and a potentiostat. All components were computer controlled using a LABVIEW program. The flow cell has been described previously, with minor design changes to the reference compartment and the auxiliary electrode. The auxiliary electrode was a gold wire, and the reference electrode was Ag/AgCl (3M NaCl) (Bioanalytical systems, Inc.).

Substrates were glass slides with a 3nm Ti adhesion layer and 300 nm of Au. Substrates were formed by first etching the glass in 15 % HF for 2 minutes, then rinsed in ultrapure water, and inserted into the vapor deposition chamber. Au substrates were vapor deposited at 280° C and annealed at 400° C for 12 hours, resulting in a prominent (111) growth habit. These gold electrodes were cleaned in concentrated nitric acid by immersion for 2 minutes and then by electrochemical cycling, after insertion into the flow cell.

Solutions used were 1mM Pb(ClO₄)₂, 1mM SeO₂, and 0.1 mM RuCl₃ 3 H₂O. The Pb and Se solutions were made with 0.1 M NaClO₄ and 50 mM CH₃COONa (pH 5). The Ru solution was made with 50 mM HCl (pH 1.5). The blank solution was 0.1 M NaClO₄ and 50 mM CH₃COONa (pH 5). The water used for the solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better.

The basic cycle used to deposit Ru films was as follows: the Pb solution was flushed into the cell for 2 sec at a controlled potential, then the solution was held static for 8 sec. The blank solution was then flushed through the cell for 2 sec to rinse out the Pb at the same controlled potential. Next, the Ru solution was flushed into the cell at OCP for 3 sec and held static for 60 seconds, to provide time for the redox replacement and then the blank was rinsed through the cell at OCP for 2 sec. This step was followed by Se deposition, where Se was electrodeposited at 100 mV, -150 mV or -450 mV. Finally, extra Se was stripped in the blank solution. This cycle was repeated 100 times to form thicker RuSe deposits. Electron probe microanalysis (EPMA) was run on a Joel 8600 wavelength dispersive scanning electron microprobe for elemental analysis.

Results and Discussion

The work presented below was intended to develop an electrochemical ALD cycle for RuSe nanofilms formation, using an automated flow cell deposition system. CVs were performed to determine initial deposition potentials for Ru and Se during the ALD cycle. Optimal potentials should, ideally, result in less than monolayer (ML). The definition of a monolayer in this work follows the surface science convention, where one adsorbate for every substrate surface atom would correspond to one monolayer (ML). Referred to an atomic layer indicates that the deposit is no more than one atom thick. No indication of a specific coverage is intended. Thus an atomic layer can correspond to a coverage anywhere between 0 and about 1 ML. Figure 4.1 represents the Au CV in a Se solution and the open circuit potential for the Au electrode was 350 mV vs Ag/AgCl. The CV was scanned in a negative direction first and continued using the window opening method to study the UPD features, as well as bulk. There is no underpotential deposition, though there does appear to be surface limited reactions, though due to the slow kinetics, those deposits are formed at an overpotential, at 200 mV and stripped at 800 mV. The respective charges were 0.33 and 0.39 ML. The chalcogenides, Se and Te, show significant

irreversibility from the CV (Figure 4.1). Deposition at potentials below 200 mV is expected to result in formation of bulk Se, though the kinetics are still slow.

Figure 4.2 is a CV for a Au electrode in the Ru solution. The open circuit potential for the Au electrode was around 900 mV. The CV scan was initiated in the negative direction, and a UPD feature for Ru appears at a potential of -100 mV. But the calculated charge for UPD is less than 0.2 ML, clearly indicating that the Ru UPD formation on Au electrode is thermodynamically unfavorable, meaning that, Ru could not be electrodeposited directly for RuSe formation. A 100 cycle deposit of RuSe was attempted using -100 mV for Ru deposition, and -150 mV for Se deposition. No film was formed. It is suspected that Ru UPD on Se is not a favorable process, at least not under those conditions.

Then, the above cycle was modified so that instead of reductive UPD, surface limited redox replacement (SLRR) was performed to deposit the Ru atomic layers, using Pb UPD as a sacrificial atomic layer. Figure 4.3 shows the current-time for one RuSe ALD cycle. The basic cycle used to deposit the Ru films was as follows: the Pb²⁺ solution was flushed into the cell for 2 sec at a controlled potential of -440 mV. The solution was then held static in the cell for 8 sec (no flow). The blank solution was then flushed through the cell for 2 sec to rinse out the Pb²⁺ ion solution, at the same potential. Next, the Ru solution was flushed into the cell at OCP for 3 sec and held static for 60 sec, providing time for the redox replacement to take place, and finally the blank was rinsed through the cell at OCP for 2 sec. The replacement reaction took about 60 seconds, which is consistent with the observed slow kinetics for Ru electrodeposition. This step was followed by the direct electro deposition of Se. A number of different potentials were used for Se deposition: 100, -150 and -450 mV. The potential was held for 10 seconds, followed by a blank rinse. When -450 mV was used, clearly come bulk Se was also formed. Thus, a reductive

stripping step was also used, where the deposit was held -630 mV in blank solution, allowing removal of any excess selenium atoms. Using -450 mV, the deposition charge was calculated to be a 1.65 ML, while the stripping charge was 0.58 ML, at -630 mV in blank solution. The net result was deposition of about 1.07 ML of Se each cycle. This cycle was repeated 100 times to achieve the desired thickness.

Table 4.1. shows the elemental atomic percentage of Ru, Se and Pb for 100 cycle RuSe deposits, using the conditions give ab ve. As we expected, a low Se atomic % was observed when 100mV was used for Se deposition, as the potential was positive of the surface limited reactions observed in Figure 4.1. The Se atomic % was very high, 39% and 34%, when -150mV and -450mV were used for Se deposition. Those films were also high in Pb, essentially the same % as Se. Almost no Ru was observed. This result is consistent with the high affinity of Pb for Se, and the formation of PbSe. This is a very stable compound, and has been understudy in our group for a number of years. Evidently, the Ru³⁺ was not able to oxidize the Pb from the PbSe, and thus to exchange. This has been proved with the OCP measurements where OCP was shifted to -200 mV at the end of 60 s replacement reaction, clearly indicates that there were Pb atoms left on the surface without being completely replaced by the Ru.

In order to overcome this problem, a stripping step was added to the cycle. The idea was to replace as much of the Pb as possible via the direct exchange reaction for Ru, within the first 60 seconds, and then to make sure the traces of Pb were removed by using a relatively positive potential to strip the last traces of Pb. Figure 4.4. shows an ALD cycle for RuSe thin film, where Pb was deposited at -440 mV and extra Pb atoms were stripped away from the surface at 400mV for 10 seconds at the end of each replacement cycle. The Pb stripping charges were calculated to be around 0.33 ML. By adding this step, OCP shifted to 350 mV which clearly indicates that all

the Pb atoms were removed even before Se electrodeposition on Ru. Then the Se was deposited at -450 mV, followed by stripping step to remove extra Se at a potential -630 mV using blank solution. Then the cycle was repeated for 100 cycles to get thick deposits. Then EPMA was done on this sample, confirmed the formation of $RuSe_2$ with 0 % Pb on the film. The actual Ru and Se atomic % on 100 cycle RuSe thin film were 3.5 and 7 % respectively.

After optimization studies of RuSe₂ cycle, experiments were performed to test the RuSe₂ electrodes. There are indications in the literature that such electrodes should be methanol resistant oxygen reduction catalysts, and could be used for a direct methanol fuel cell applications. Figure 4.5. shows the CV of RuSe₂ thin film in 1M methanol and 0.5 M H₂SO₄ solutions. In the CV, hydrogen evolution and oxidation of RuSe₂ were observed at -200 mV and 850 mV respectively. There are no signs of methanol oxidation, as seen in the literature, clearly indicates that the RuSe₂ electrode, formed using E-ALD, is inert to methanol oxidation.

In order to compare the methanol resistant property of RuSe₂ electrode with conventional Pt electrodes, the same experiments were repeated using Pt electrode, deposited using 25 ALD cycle. Figure 4.6. shows Pt electrode CV in the above mentioned solution. The OCP for Pt electrode in the blank solution was around 200 mV and the peak at -200 mV indicates hydrogen adsorption and corresponding desorption features of conventional Pt electrode. At a potential around 300 mV, methanol starts to oxidize on Pt and then the electrode is poisoned by CO formation at 900 mV. On the reversed bias, poisoned CO was started to oxidize at 800 mV and CO2 was produced as a byproduct on Pt electrode. The same feature was seen in the literature, which clearly indicate that Pt electrode is not methanol resistant electrode for fuel cells.

Conclusion

Initial studies of the formation of RuSe thin film by electrochemical ALD were reported. No film was deposited, when UPD potential for Ru was used. EPMA confirmed the formation of PbSe instead of RuSe, where Pb was used as a sacrificial metal to deposit Ru. Then the formation of RuSe thin film was made possible by including a stripping step at 400 mV to remove all extra Pb atoms available after the exchange process in blank solution. The actual atomic % of Ru and Se on 100 cycle film was found to be 3.5 and 7 % respectively. The CV experiments were done to show that RuSe is a promising candidate for methanol resistant oxygen catalyst electrode for direct methanol fuel cell. Detailed experiments need to be conducted using rotating disc electrode to study RuSe electrode's catalytic properties like oxygen reduction reaction for fuel cell application.

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References:

- R. Dillon, S. Srinivasan, A. S. Aricò, V. Antonucci, *Journal of Power Sources* 127, 112 (2004).
- 2. S. Litster, G. McLean, *Journal of Power Sources* **130**, 61 (2004).
- 3. V. Mehta, J. S. Cooper, *Journal of Power Sources* **114**, 32 (2003).
- T. A. Zawodzinski Jr, T. E. Springer, F. Uribe, S. Gottesfeld, *Solid State Ionics* 60, 199 (1993).
- 5. S. Wasmus, A. Küver, *Journal of Electroanalytical Chemistry* **461**, 14 (1999).
- 6. A. Heinzel, V. M. Barragán, Journal of Power Sources 84, 70 (1999).
- 7. A. K. Shukla, R. K. Raman, Annual Review of Materials Research 33, 155 (2003).
- X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, *Journal of Power Sources* 86, 111 (2000).
- 9. J. Fournier et al., J. Electrochem. Soc. 144, 145 (1997).
- M. Lefevre, J. P. Dodelet, P. Bertrand, *The Journal of Physical Chemistry B* 106, 8705 (2002).
- S. Baranton, C. Coutanceau, C. Roux, F. Hahn, J. M. Léger, *Journal of Electroanalytical Chemistry* 577, 223 (2005).
- 12. A. J. Wagner, G. M. Wolfe, D. H. Fairbrother, *Applied Surface Science* 219, 317 (2003).
- 13. P. H. Matter, L. Zhang, U. S. Ozkan, Journal of Catalysis 239, 83 (2006).

- 14. A. A. Serov et al., Journal of Power Sources 175, 175 (2008).
- 15. N. A. Vante, W. Jaegermann, H. Tributsch, W. Hoenle, K. Yvon, *Journal of the American Chemical Society* **109**, 3251 (2002).
- 16. M. Bron et al., Journal of Electroanalytical Chemistry 500, 510 (2001).
- 17. N. Alonso-Vante, H. Tributsch, O. Solorza-Feria, *Electrochimica Acta* 40, 567 (1995).
- 18. G. Beyer *et al.*, *Microelectronic Engineering* **64**, 233 (2002).
- 19. M. Y. Ho et al., Applied Physics Letters 81, 4218 (2002).
- 20. B. W. Gregory, D. W. Suggs, J. L. Stickney, J. Electrochem. Soc. 138, 1279 (1991).
- 21. T. E. Lister, J. L. Stickney, JPC, (1997).
- 22. M. Muthuvel, J. L. Stickney, J. Electrochem. Soc. 153, C67 (2006).
- J. L. Stickney, T. L. Wade, B. H. Flowers, R. Vaidyanathan, U. Happek, *Encyclopedia of Electrochemistry* 1, 513 (2003).
- V. Venkatasamy, N. Jayaraju, S. M. Cox, J. L. Stickney, J. Electrochem. Soc. 154, H720 (2007).
- L. B. Rogers, D. P. Krause, J. C. Griess, Jr., D. B. Ehrlinger, J. Electrochem. Soc. 95, 33 (1949).
- 26. A. A. Gewirth, B. K. Niece, Chem. Rev. 97, 1129 (1997).
- 27. A. Aldaz, J. Clavilier, J. M. Feliu, Journal de Physique IV: Proceedings 4, 75 (1994).

- 28. R. R. Adzic, in *Advances in Electrochemistry and Electrochemical Engineering*, H. Gerishcher, C. W. Tobias, Eds. (Wiley-Interscience, New York, 1984), vol. 13, pp. 159.
- 29. D. M. Kolb, in *Advances in Electrochemistry and Electrochemical Engineering*, H. Gerischer, C. W. Tobias, Eds. (John Wiley, New York, 1978), vol. 11, pp. 125.
- 30. C. Thambidurai, Y. G. Kim, N. Jayaraju, V. Venkatasamy, J. L. Stickney, J. *Electrochem. Soc.* **156**, D261 (2009).
- 31. C. Thambidurai, Y. G. Kim, J. L. Stickney. J. Electrochimica Acta 53, 6157 (2008).
- Y.-G. Kim, Y. Kim Jay, D. Vairavapandian, L. Stickney John, *J Phys Chem B* 110, 17998 (2006).


Au CV in 1mM SeO2

Figure 4.1 CVs of Au electrode in 1mM Se solution. The scan rate = 5mV/s and the open circuit potential of Au Electrode in Se solution is 450 mV vs Ag/AgCl



Figure 4.2 CVs of Au in Ru solution, where the Ru UPD was observed at -110 mV with a charge less than 0.2 ML. Scan rate = 5 mV/s. The open circuit potential is -890 mV.

One ALD cycle for RuSe deposition



Fiure 4.3.This plot represents one ALD cycle for RuSe deposition. The Pb was deposited at its UPD, - 440mV and its average charge per cycle is 0.8 ML. Se deposition and its stripping potentials were -450 mV and -630 mV respectively. Se stripping step was done in blank solution.

One ALD cycle for RuSe deposition



Figure 4.4 This fig represents the one ALD cycle of RuSe. The Pb deposition and its stripping potentials were -440 mV and 400 mV respectively. The Se was deposited and stripped at the potentials -450 mV and -630 mV, respectively.



RuSe CV in 1M methanol + 0.5M $H_2SO_4 + O_2$ free solution

Figure 4.5. CVs of 100 cycle RuSe electrode in methanol and sulfuric acid solution. Scan rate = 5mV/s. The OCP of RuSe electrode is -470 mV vs Ag/AgCl.



Pt CV in 1M methanol + 0.5M $H_2SO_4 + O_2$ free solution

Figure 4.6 CVs of 100 cycle Pt electrode in methanol solution. Scan rate = 5mV/s. The OCP of Pt electrode is 100 mV vs Ag/AgCl.

Table 4.1. This table gives the elemental % of Se, Ru and Pb on 100 cycle RuSe thin film. The 1:1 atomic % of Se and Pb confirms the formation of PbSe during RuSe ALD cycle.

	Avg Se at %	Avg Ru <i>at</i> %	Avg Pb <i>at</i> %
Se@ 100 mV	1.8	0.32	0.64
Se@ -150 mV	39	1.3	36
Se@ -450 mV, Strip @ -630 mV	34	2.8	22

CHAPTER 5

ELECTRODEPOSITION OF CU THIN FILMS ON RU/TA WAFER USING ELCTROCHEMICAL – ATOMIC LAYER DEPOSITION (EC-ALD) 1

¹ C. Thambidurai, D. K. Gebregzibiher, Q. Zhang and J. L. Stickney, To be submitted to *J. Crystal Growth* (2009).

Abstract

This paper describes the formation of Cu nano-films on a Ru/Ta coated wafer using electrochemical-atomic layer deposition (E-ALD). An UHV surface analysis instrument was employed to study the cleaning steps and oxide removal for the Ru/Ta coated wafer. In addition, a basic E-ALD cycle was developed to grow Cu on the Ru/Ta coated wafer, using surface limited redox replacement (SLRR). SLRR involves the formation of an atomic layer of a reactive element, in this case Pb, and then redox exchanging it for an atomic layer of a more noble, less reactive, desired element. Auger spectroscopy was used to investigate the relative amounts of oxygen and Ru on the as received sample, as well as the electrochemically treated and ion bombarded RuTa coated wafers. An automated flow cell electrodeposition system was employed to make Cu nano-films, up to 200 cycles. The homogeneity of the Cu films, across the substrate, was studied as a function concentration of a citrate complexing agent. The open circuit potential (OCP) was used to follow the replacement, exchange, of Pb for Cu. The OCP shifted from that used to deposit Pb UPD (440 mV) up to the formal potential for Cu²⁺/Cu, upon complete exchange. Electron probe microanalysis (EPMA) was employed to study the homogeneity of the Cu film, deposited using different [Cit³⁻] baths and it was found that high quality, homogenous Cu films could be deposited with 2 and 4 mM [Cit³⁻] baths. AFM images on Cu films deposited using 2 and 4 mM [Cit³⁻] baths, showed that the morphology at the inlet was same as the outlet of the deposits from the 4 mM citrate solution. A prominent Cu (111) peak was displayed in the Xray diffraction (XRD) pattern for the Cu nano-films on the RuTa coated wafer.

Introduction

Copper metal has been used widely as an interconnect in ultra large scale integration (ULSI) due to its low electrical resistivity (1.67 μ Ohm cm) and good electromigration resistivity(*1*). In order to avoid Cu diffusion through dielectrics interlayers into silicon, a barrier layer is used. The important issues in the formation of barrier layers are good adhesion to both Cu and the interlayer dielectric, and low electrical resistivity(*2*). In addition to this, the international technology road map for semiconductors demands a thin barrier layer (< 5nm), and for it, and IC device in general, to allow continued scaling(*3-4*). Currently, Ta/TaN films are used as barrier layers, though they tend to be more resistive then desired for direct Cu electroplating, especially in high aspect features. For these reasons, a Cu seed layer must deposited on Ta/TaN to ensure a good Cu electrofilling[3]

Recently, Ru has been studied intensively in the literature as a potential barrier layer material for an advanced technology node, to avoid the need for a Cu seed layer during the dual damascene process(5-7). Ru has lower resistivity, 1.67 \Box Ohm cm, when compared to Ta 13.5 \Box Ohm cm. More importantly Ru, like Ta, shows negligible solid solubility with Cu even at high temperatures based on the binary phase diagram(8).

Copper deposition on Ru using techniques like sputtering(9), electrodeposition(2, 8), molecular beam epitaxy(10), physical vapor deposition(3) and MOCVD(11-12) have been studied for the past 10 years. In this article, electrodeposition of Cu on Ru/Ta coated wafers, using electrochemical ALD with SLRR, is reported. E-ALD is the electrochemical analog of ALD, deposition of one atomic layer at a time using surface limited reaction called underpotential deposition (UPD). By definition, UPD is the deposition of one element on another

element at a potential before (under) that needed to deposit the element on itself: prior to bulk deposition(*13-16*).

Advantages to the use of E-ALD could include low cost, conformal growth and atomic layer control over deposit thickness. The layer by layer electrodeposition of pure metals in a 2D growth mode, by ALD, has only recently been possible with development of monolayer restricted galvanic displacement (MRGD), an outgrowth of work by Adzic(17), Weaver(18), Dimitrov(19-21), and Stickney(22-23), also referred to as surface limited redox replacement (SLRR). In SLRR, ions of the metal of interest are introduced over an atomic layer of a less noble metal, a sacrificial layer, at open circuit potential (OCP). The more noble element then takes electrons from the sacrificial layer, dissolving it, and plating an atomic layer in its place. Deposition cycles have been developed for a number of metals, such as: Cu(22, 24-26), Pt (27-30), Ag(31-34) and Ru(23), using MRGD have been reported in the literature.

In the present article, a UHV system has been employed to study the cleaning procedure for a Ru/Ta coated wafer, using electrochemical cycles and ion bombardment. In addition, an ALD program was developed to deposit Cu nano-films on a Ru/Ta coated wafer, using an automated flow cell deposition system, and UHV-EC chemistry(*35-39*). UHV-EC is a name for where electrochemical experiments are connected directly to a surface analysis instrument. This allow transfer of substrates from the electrochemical cell directly to the UHV analysis changer, without exposure to ambient. The deposition morphology was studied using atomic force microscopy (AFM), while the elemental compositions of the deposits were determined using electron probe microanalysis (EPMA). Deposit structure was characterized using low angle Xray diffraction (XRD).

Experimental

Substrates were 7 nm films of 90% Ru and 10%Ta, on 50nm SiO₂ wafer, formed by physical vapor deposition. The substrates were obtained from LETI (Grenoble, France). The as received substrates were cleaned using cyclic voltammetry in degassed 10mM HCIO₄ (Aldrich, doubly distilled), to remove the oxide layer formed in transit. The UHV-EC system(40-42) is a surface analysis chamber attached to an electrochemical SS ante-chamber, where experiments can be performed without taking the sample from the instrument. The ante-chamber was back filled with high purity Ar-gas (99.999%), to atmospheric pressure, while electrochemical experiments were performed. Subsequently, the electrochemical cell was removed from the ante-chamber through a 4.5" gate valve, and the ante-chamber was pumped down so the sample could be transferred to the main analysis chamber for characterization, without it being exposure to air. After characterization, the substrate was further cleaned by Ar⁺ ion bombardment, to remove any remaining contaminants. The analysis chamber was also equipped with optics for low energy electron diffraction (LEED) (Princeton Research Instruments, Inc.) and a cylindrical mirror analyzer for Auger Electron Spectroscopy (AES) (Perkin-Elmer).

Cu thin film deposits were formed using an electrochemical flow electrodeposition system consisting of pumps, valves, an electrochemical flow cell and a potentiostat (Electrochemical ALD L.C.)(43-44). All components were computer controlled using a LABVIEW program (National Instruments). The auxiliary electrode was a gold wire embedded in the cell wall opposite the deposit, and the reference electrode was a Ag/AgCl (3M NaCl) (Bioanalytical Systems, Inc.), inserted into the egress.

The solutions used in the UHV-EC system were 0.1mM Cu(ClO₄)₂ (Aldrich, 98%) in 10 mM HCl (Sigma Aldrich) and 0.1 mM Pb(ClO₄)₂ (Aldrich, 99.995%) in 10 mM NaClO₄. The

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same solutions were used in the flow cell system, but the Pb and Cu solution concentrations were increased by a factor of 10, and 50 mM NaClO₄ was added as a supporting electrolyte. The blank solution used in the flow cell system was 50 mM NaClO₄. The electrochemical reactions in the UHV-EC system were performed in a Pyrex cell with an Au-wire counter electrode and an Ag/AgCl (3M KCl) reference electrode (Bio Analytical Systems). A μ Autolab Type III Potentiostat/Galvanostat was used for potential control. All potentials were reported vs Ag/AgCl (3M KCl).

The solutions were degassed with high purity Ar-gas or Nitrogen gas in the UHV-EC system and flow cell deposition system, respectively, for one hour prior to electrochemical studies. In the UHV-EC system, Cu UPD was performed @ -30 mV for 1 min, to form the first Cu atomic layer. It was followed by the deposition of Pb UPD @ - 475 mV for 1 min, to form the sacrificial atomic layer. Pb UPD on Cu UPD was then exposed to the Cu²⁺ solution, at its open circuit potential (OCP) for the redox exchange, completing one ALD cycle. This basic cycle was used to Cu atomic layers, and is similar to that previously published (22). After confirmation that the cycle worked, using the UHV-EC instrument, subsequent experiments were performed in the flow cell deposition system to grow thicker Cu films.

A Scintag PAD-V diffractometer, with Cu K α radiation (λ =1.5418 Å), was used to obtain glancing angle X-ray diffraction patterns. EPMA was run on a Joel 8600 wavelength dispersive scanning electron microprobe. The morphology of the surface was characterized by intermittent contact mode atomic force microscopy (AFM, Molecular Imaging, PicoPlus). AFM image resolution was 512X512 and the image was processed and analyzed with WSxM software.

Results and Discussion

Figure 5.1 shows Auger spectra for a Ru/Ta coated wafer (a) as received (b) after cycling in blank solution (c) after cold ion bombardment, (d) with Cu upd at – 30 mV. The ratio of oxygen to Ru peak heights was calculated to be 0.41, for the as received wafer (Figure 5.1a). The high ratio is the result of surface oxide formation on the Ru/Ta after exposure to air. In an attempt to remove the oxide layer, the electrode was immersed in 10 mM HClO₄ and scanned negative from 55 mV, its OCP (Figure 5.2). During the first scan of the experiment, there was significant reduction current at a potential between -100 and -350 mV, which was absent in the subsequent scan. After those cycles in the blank solution, the O to Ru ratio had decreased to 0.27 (Figure 5.1b), but the ratio was still significant.

Similar studies with TaN surfaces, as yet unpublished, showed that there was always oxygen on the surface, from Auger, even when extreme electrochemical reductions were performed. This raised the question, was the oxide reduced from TaN in solution, but then re-oxidized upon sample transfer? Or was it never reduced under the electrochemical conditions used? That TaN work suggests that either way, the presences of Ta on the surface should be accompanied by oxygen (Figure 5.1b), while it is known that Ru surface oxide can be reduced (23, 45-47).

In an attempt to remove more of the oxide, or carbon that might be present, a cold ion bombardment was performed using Ar^+ ions. It can be seen from Figure 5.1c, that the oxygen signal went down significantly, to a ratio of 0.08. In addition, the ratio of the 231eV to the 273eV Ru signals indicate that there was no carbon present on the Ru surface.

Figure 5.1d shows an AES spectrum for the Ru/Ta surface after Cu UPD at -30 mV in the 0.1mM Cu(ClO₄)₂ solution. The charge calculated from coulometry for the Cu suggested a

coverage of 0.90 ML. Auger also indicated a ratio of Cu to Ru peak to peak heights of 0.09, and a small peak for chloride at 178ev. Cl is known to adsorb on Cu, and limit Cu oxidation (24, 42, 48). There is still oxygen evident in Figure 1d, which can be ascribed to any Ta at the surface, as well as any Cu which did not become covered with Cl. After characterization of the Cu UPD layer, the sample was transferred back to the electrochemistry ante-chamber, where the Cu UPD was stripped in the blank solution (Figure 5.3) at 150 mV. The charge calculated from the stripping step was 0.89 ML, which is essentially equivalent to that for the Cu UPD.

The initial ALD cycle chemistry for depositing atomic layers of Cu on the Ru/Ta surface by MRGD, also known as surface limited redox replacement (SLRR), was developed for deposition on Au (22, 49). The initial ALD cycle was designed as follow: Cu was deposited at an underpotential of -30 mV for 1 min on the Ru/Ta substrate, followed by Pb UPD at -475 mV for 1 min, on the Cu UPD. The Pb coated deposit was then exposed to the Cu²⁺ solution again, at OCP, which resulted in redox exchange of the Pb atomic layer for one of Cu, on that first Cu UPD. The replacement reaction of Pb for Cu was followed by monitoring the OCP. The exchange was completed when the OCP reached the formal potential for Cu²⁺/Cu. That procedure was repeated for 1 and 2 ALD cycles, and the resulting Cu deposit oxidatively stripped in blank in order to calculate the exchange efficiency during the replacement reaction, of Pb for Cu.

Figure 5.4 shows the ratio of Cu to Ru peak to peak heights, from Auger, as well as the Cu coverages, determined by oxidative stripping, after the replacement reactions. The Cu to Ru Auger ratio for Cu UPD on the Ru/Ta wafer, and its stripping charge, were calculated as 0.09 and 0.90 ML respectively. After one and two SLRR cycles on top of Cu UPD, the ratios and Cu

striping charges were slightly increased, but they do not appear to be linear with respect to the number of cycles.

A possible issue would be that not as much Pb UPD was formed on the Cu surface, than on the Ru/Ta surface. That is, the charges looked right for UPD on the Cu surface, but there may have been side reactions such as hydrogen evolution, or oxygen reduction (*50*) which suggested that there was more Pb on the surface than there actually was. The cycle using the UHV-EC instrument were performed in a simple Pyrex cell, where to change the solution, the solution must first be drained, and then refilled with the next solution. That is, once the Pb was deposited, solution was drained, and the deposit was allowed to go open circuit. It is probable that at that stage, some of the Pb UPD was oxidized, greatly reducing the amount of Pb left to transfer its electrons to Cu^{2+} . This could easily account for the minimal amounts of Cu deposited in the two cycles. In order to overcome such problem and also to grow thicker Cu films, an automated flow cell deposition system was used to grow Cu films up to 200 cycles. In the flow deposition system, potential control was not lost between solutions, so no Pb was oxidized prior to introduction of the Cu^{2+} solution.

Figure 5.5 displays the current time curves for 3 ALD cycle of Cu deposition on Ru/Ta wafer, using the flow cell deposition system. Nearly the same potentials and times were used for the cycles in Figure 5, as were used with the UHV-EC system, though potential control was not lost during rinsing. A rate of 10 ml per minute was used for solution flow. Other systems in the group have faster pumps, 40 mL/min, but the 7nm Ru/Ta films proved too fragile for faster pumps, and pealed. The basic E-ALD program was composed of the following Cu SLRR cycles: Pb solution was pumped into the cell for 8s at -450 mV. The solution was then held in the cell for 8 s, resulting in 0.8 monolayers (ML) of Pb, by UPD. Note that one ML is defined here as

one deposited atom for each substrate surface atom, in this case the substrate has been approximated as a Au(111) surface, with an atomic density of 1.17×10^{15} atoms/cm². Blank solution was then pumped through the cell, at the same controlled potential, to remove excess Pb²⁺ ions. The next step was to pump the Cu²⁺ solution in to the cell for 10 s at open circuit, allowing Cu²⁺ ions to oxidize the Pb and form a Cu atomic layer. The cycle was completed by pumping blank solution through the cell to remove the resulting Pb²⁺ ions as well as the excess Cu²⁺ ions.

The above cycle was repeated 2, 4 and 8 times. Afterwards, the resulting Cu films were stripped in a blank solution, at 400 mV, in order to determine the amount of Cu deposited during the SLRR. To determine the background charge from Ru/Ta wafer during the stripping steps, the same process was performed in a blank solution, using the same potential, 400 mV. The background charge was found to be 0.04 ML. Figure 5.6 shows the Cu coverage as a function of 2, 4 and 8 cycles. The Cu coverages for 2, 4 and 8 cycles were calculated as 0.83, 1.95 and 3.89 ML respectively: linear growth vs. cycle #. The average Cu coverage calculated from this graph was 0.49 ML per ALD cycle. Based on the average Pb deposition charge, 0.80 ML, the replacement efficiency was calculated to be 61 %. The reasons for less than 100% efficiency are associated with side reactions both during Pb deposition and during the exchange, such as the reduction of small amounts of oxygen or protons. Extra charge is likely measured for Pb deposition, as Pb is known as a catalyst for oxygen reduction, and it is very hard to remove all the O₂ from solution by purging with N₂.

The same ALD program for Cu deposition was used to grow thicker films, including 25, 100 and 200 cycle deposits, to better characterize morphology, crystal structure and deposit distribution. The average Cu atomic % of 200 cycle Cu film was calculated as around 33 % from

EPMA data(Figure 5.7a.) This graph gives the relative elemental percent of Cu across a Ru/Ta substrate from ingress to egress. The distribution is strikingly skewed to the ingress. This turns out to be an extreme case, but a similar pattern is observed with many of the E-ALD deposits formed using SLRR, with the flow cell hardware used by this group(22). Thick deposition at the inlet with thinner deposits in the middle and outlet of deposits are observed in EPMA data across the deposit, and with optical microscopy, for the metal nanofilms like Cu, Ru and Pt.

The cartoon of an SLRR involves an ion taking the electrons from one atom on a surface, thus dissolving that atom and reducing the ion onto the surface to take its place. That is, one Pb atom is oxidized by one Cu^{2+} ion, and the depositing Cu atom takes the place of the Pb atom. However, the fact that the deposit thickness is highest at the inlet suggests that the mechanism is different, that instead electrons transferring from one atom to one of the ions in solution, and they changing places, the electrons probably transfer through the substrate. That is, the substrates used to make the deposits are usually relatively conductive, so there is little reason for the electrons to transfer directly to an ion in solution and exchange places. Instead, the deposition will depend on the activity gradient in solution. That is, the reduction of ions will occur where the activity is greatest, and in a flow cell that would be at the ingress. The gradient in activity is transient, a function of the time it takes to fill the cell. If the cell can be filled homogeneously on a time scale which is short compared with the exchange, the deposit should be homogeneous. The solution is thus to speed up the introduction of the solution, or slow down the exchange process. As noted, the solution was pumped at 10 mL/min, instead of the 40 mL/min used in some cases, as the 7 nm Ru/Ta film would strip from the surface. In other words, with the present hardware and substrate, the solution can't be delivered faster. Figure 8 shows the OCP as a function of time for exchange of a Pb atomic layer using 1 mM Cu solutions.

The left most curve shows that the exchange time is about 5 seconds, that is, it takes about 5 seconds for the potential to shift from that used to deposit the Pb to that characteristic of the Cu surface. That is about as much time as it takes to pump solution into the cell. There is significant variability for the exchange process, some elements take considerably longer to exchange. Cu is fast compared to other metals (22).

The next alternative was to slow down the exchange of Pb for Cu. The most direct method would be to drop the concentration, assuming the rate of exchange was proportional. One problem is that the Cu^{2+} concentration was already 1 mM. Given the thickness of the cell, about 1 mm, and the low $[Cu^{2+}]$, there were only an order of magnitude or two of Cu^{2+} present in the cell at any time. So to dropping the concentration by a couple of orders of magnitude would result in less than a ML being present in the cell. It was thus decided to try using a complexing agent. In this way, the amount of Cu in the cell can remain at the 1 mM level, but would be present as the complex, with only a small amount present as Cu^{2+} ions. In the present studies, citrate was added to the Cu solution. The complex stoichiometry was 1:1, one Cu^{2+} to one citrate Cit³⁻ (51). One mM Cu solutions made with [Cit³⁻] to [Cu²⁺] ratios of 2 and 4, as well as a Cu^{2+} solution with no citrate, were used to exchange for the Pb atomic layer (Figure 5.8). In Figure 5.8, the shift in OCP during exchange is evident for each of those Cu^{2+} solutions. With no citrate present, as noted above, the exchange took about 5 seconds to level off. On the other hand, the exchange time was more like 15 seconds and 30 seconds for the 2 mM and 4 mM [Cit³⁻] solutions, respectively. Note that the potentials at which the deposits plateau shifts negative, as expected from the decreases in Cu^{2+} activity with the increases in citrate concentration.

Figure 5.7 b, shows the EPMA data for a 200 cycle Cu film, formed with plating baths containing 2, and 4 mM [Cit³⁻]. The relative atomic % of Cu was measured with respect to the

ingress to the egress. For the solution without [Cit³⁻] present, the deposit was observed to be much thicker at the inlet, then the rest of the deposit, nearly 10 times thicker (Figure 5.7a). This was also evident using optical microscopy, where significant roughening was evident near the ingress from the light scattering, not a morphology that would be expected for layer by layer growth. On the other hand, at the egress, the deposit reflected light specularly. By adding 2 and 4 mM citrate, the deposits became homogenous. The atomic % was essentially the same from very ingress to egress. The use of citrate in the Cu bath resulted in a homogeneous deposit, evidently by slowing down the exchange process, so that the Cu solution filled the cell before a significant fraction of the Pb had reacted.

To further investigate the deposits formed using the citrate baths, the homogeneity and morphology of the Cu films was studied using AFM. Figure 5.9 displays AFM images of 200 cycle Cu films, deposited with Cu solutions with 0, 2, and 4 mM [Cit³⁻]. As expected, the Cu film deposited with 0 mM [Cit³⁻] was very rough at the ingress, indicating that too much Cu was formed there each cycle. At the egress, however, for all three [Cit³⁻] baths, the deposits did not show extensive roughness. Evidently, the use of the complexing agent worked well at producing as smooth homogeneous deposit. It should be noted, in previous studies of Cu on Au substrates, under these imaging conditions. It is probable that the difference may have to do with the nature of the Ru/Ta substrates used here.

Glancing angle X-ray diffraction was used to characterize the Cu film structure. Figure 5.10, displays XRD pattern for a 200 cycle Cu film deposited using a Cu solution with 4mM [Cit³⁻]. The peak at 43.35° corresponded to a reflection from Cu(111) planes along with the

Ru(101) reflection. The peak corresponding to Cu(200) planes was also observed, without interference. There was no evidence of Pb peaks in the XRD pattern, or from EPMA.

Conclusion

Ru/Ta wafers were investigated for use as substrates for E-ALD of Cu. Using UHV-EC methodologies, initial surface treatments were examined to determine a cleaning procedure. It was determined that a part of a surface oxide layer on the Ru/Ta wafers was removed using electrochemical reduction, though some was not. From unpublished results from this group, it is suspected that the oxide present was associated with the Ta component of the substrates. Using an automated electrochemical flow cell deposition system, was showed that deposits tended to be thicker near the ingress than over the rest of the deposits. This appears to result from the mechanism for SLRR of Cu not being from electron transfer directly from atom to ion, and place exchange, but a mechanism where the electrons are transferred through the substrate. Thus, deposits were formed most readily near the ingress, where initially the activity for Cu^{2+} was higher. By using citrate as a complexing agent, the exchange of Pb for Cu was slowed, allowing the solution to enter the cell before the majority of the exchange had taken place. This resulted in homogeneous 200 cycle deposits, as evidenced using EPMA and AFM.

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Reference:

- 1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, H. Deligianni, *IBM Journal of Research and Development* **42**, 567 (1998).
- 2. T. P. Moffat *et al.*, *J. Electrochem. Soc.* **153**, C37 (2006).
- 3. M. Damayanti et al., J. Electrochem. Soc. 153, J41 (2006).
- 4. R. Chan et al., Electrochemical and Solid-State Letters 7, G154 (2004).
- T. N. Arunagiri, Y. B. Zhang, O. Chyan, M. J. Kim, T. Q. Hurd, J. Electrochem. Soc. 152, G808 (2005).
- 6. T. N. Arunagiri et al., Applied Physics Letters 86, (2005).
- D. Josell, D. Wheeler, C. Witt, T. P. Moffat, *Electrochemical and Solid State Letters* 6, C143 (2003).
- 8. O. Chyan, T. N. Arunagiri, T. Ponnuswamy, J. Electrochem. Soc. 150, C347 (2003).
- 9. J. Oh, J. Lee, C. Lee, *Materials Chemistry and Physics* **73**, 227 (2002).
- 10. R. Naik et al., Journal of Magnetism and Magnetic Materials 121, 60 (1993).
- 11. K. Weiss *et al.*, *Microelectronic Engineering* **50**, 433 (2000).
- 12. K. K. Choi, S. W. Rhee, *Thin Solid Films* **397**, 70 (2001).
- 13. D. M. Kolb, Przasnys.M, Gerische.H, Journal of Electroanalytical Chemistry 54, 25 (1974).
- 14. D. M. Kolb, in Advances in Electrochemistry and Electrochemical Engineering, Vol. 13,,
- H. Gerischer, C. W. Tobias, Eds. (Wiley-Interscience, New York, 1978), vol. 13, pp. 159.
- 15. K. Juttner, W. J. Lorenz, Z. Phys. Chem. N. F. 122, 163 (1980).
- 16. A. A. Gewirth, B. K. Niece, Chem. Rev. 97, 1129 (1997).
- 17. R. Adzic, *Encyclopedia of Electrochemistry* **1**, 561 (2003).

- 18. M. F. Mrozek, Y. Xie, M. J. Weaver, Analytical Chemistry 73, 5953 (15, 2001).
- 19. R. Vasilic, N. Dimitrov, *Electrochemical and Solid-State Letters* 8, C173 (2005).
- 20. R. Vasilic, L. T. Viyannalage, N. Dimitrov, J. Electrochem. Soc. 153, C648 (2006).
- 21. L. T. Viyannalage, R. Vasilic, N. Dimitrov, J. Phys. Chem. C 111, 4036 (2007).
- 22. C. Thambidurai, Y. G. Kim, N. Jayaraju, V. Venkatasamy, J. L. Stickney, J. *Electrochem. Soc.* **156**, D261 (2009).
- C. Thambidurai, Y. G. Kim, J. L. Stickney. (Pergamon-Elsevier Science Ltd), vol. 53, pp. 6157-6164.
- 24. J. Kim, Y.-G. Kim, J. L. Stickney, J. Electrochem. Soc. 154, D260 (2007).
- 25. L. T. Viyannalage, R. Vasilic, N. Dimitrov, Journal of Physical Chemistry, ACS (2005)
- 26. C. P. daRosa, R. Maboudian, E. Iglesia, J. Electrochem. Soc. 155, E70 (2008).
- 27. Y.-G. Kim, J. Kim, D. Vairavapandian, J. L. Stickney, *Journal of Physical Chemistry B* 110, 17998 (2006).
- 28. F. H. B. Lima et al., J. Solid State Electrochem. 12, 399 (Apr, 2008).
- 29. R. E. Rettew, J. W. Guthrie, F. M. Alamgir, J. Electrochem. Soc. 156, D513 (2009).
- 30. J. F. Huang, *Electroanalysis* **20**, 2229 (Oct, 2008).
- 31. S. Y. Sayed, B. Daly, J. M. Buriak, J. Phys. Chem. C 112, 12291 (Aug, 2008).
- 32. L. A. Porter, H. C. Choi, A. E. Ribbe, J. M. Buriak, *Nano Lett.* 2, 1067 (2002).
- 33. A. Gutes, I. Laboriante, C. Carraro, R. Maboudian, J. Phys. Chem. C 113, 16939 (2009).
- 34. R. Vasilic, N. Dimitrov, *ECS Transactions* **1**, 33 (2006).
- 35. A. T. Hubbard, J. L. Stickney, S. D. Rosasco, M. P. Soriaga, D. Song, *Journal of Electroanalytical Chemistry* **150**, 165 (1983).

- M. D. Lay, K. Varazo, N. Srisook, J. L. Stickney, *Journal of Electroanalytical Chemistry* 554, 221 (2003).
- 37. T. E. Lister, L. P. Colletti, J. L. Stickney, *Israel Journal of Chemistry* **37**, 287 (1997).
- 38. M. Muthuvel, J. L. Stickney, J. Electrochem. Soc. 153, C67 (2006).
- 39. M. Muthuvel, L. Stickney John, *Langmuir FIELD Full Journal Title:Langmuir : the ACS journal of surfaces and colloids* **22**, 5504 (2006).
- 40. D. W. Suggs, J. L. Stickney, *Surface Science* **290**, 362 (1993).
- 41. J. Y. Kim, Y.-G. Kim, J. L. Stickney, *ECS Transactions* **1**, 41 (2006).
- 42. Y.-G. Kim, Y. Kim Jay, C. Thambidurai, L. Stickney John, *Langmuir* 23, 2539 (2007).
- J. L. Stickney, in *Advances in Electrochemical Science and Engineering*, R. C. Alkire, D.
 M. Kolb, Eds. (Wiley-VCH, Weinheim, 2002), vol. 7, pp. 1-105.
- 44. T. L. Wade, T. Sorenson, A., J. L. Stickney, in *Interfacial Electrochemistry*, A. Wieckowski, Ed. (Marcel Dekker, New York, 1999), pp. 757-768.
- 45. M. B. Vukmirovic, R. L. Sabatini, R. R. Adzic, Surface Science 572, 269 (2004).
- 46. J. Lee, W. B. Wang, M. S. Zei, G. Ertl, Phys. Chem. Chem. Phys. 4, 1393 (2002).
- 47. E. M. Stuve et al., Chem. Phys. Lett. 149, 557 (Sep, 1988).
- 48. J. Y. Kim, Y.-G. Kim, J. L. Stickney, ECS Transactions, (2006).
- 49. C. Thambidurai, Y. G. Kim, J. L. Stickney, J. Electrochimica Acta, 6157, (2008)
- R. Vasilic, N. Vasiljevic, N. Dimitrov, *Journal of Electroanalytical Chemistry* 580, 203 (2005).
- 51. S. Kim, D. J. Duquette, J. Electrochem. Soc. 153, C417 (2006).



Figure 5.1. AES spectra of: a) as received Ru/Ta substrate, b) after CV in 10mM HClO4 at 5mV/s, c) after cold IBB and d) after Cu UPD.



Figure 5.2. shows the CV of Ru/Ta wafer in 10mM HClO₄ at a scan rate of 5mV/s. The open circuit potential for Ru/Ta wafer in blank solution was 55 mV.



Figure 5.3. I-t trace of Cu UPD stripping @ 0.15V in10mM HClO₄[·] The Cu UPD was deposited using -30 mV and UPD charge was calculated as 0.90 ML.



Figure 5.4. AES ratios of Cu to Ru and Cu coverage charges vs the # of cycles.



time, s

Figure 5.5. shows three ALD cycle for Cu deposition on Ru/Ta wafer. The Pb was deposited at - 450 mV and the average deposition charge was calculated as 0.80 ML. The Cu replacement reaction was done in OCP for 10 s.



Figure 5.6. represents the Cu stripping charge as a function of ALD cycle.



Figure 5.7. shows Cu atomic % as a function of deposit position. The EPMA was done on 200 Cu film deposited using 0, 2 and 4 mM [Cit³⁻] baths.



Figure 5.8. shows the OCP measurement as a function of [Cit³⁻] added to the Cu plating bath.



Figure 5.9. AFM images of 200 cycle Cu film deposited using different [Cit³⁻] baths. Image resolution was 512X512 and the image was processed and analyzed with WSxM software.



Figure 5.10. shows XRD pattern for the Cu film deposited using 4mM [Cit³⁻] bath.

CHAPTER 6

CONCLUSION

Electrochemical ALD of metal thin films is the main topic of this dissertation. In Chapter 2, development of an electrochemical ALD cycle for the formation of Ru nano-films has been initiated. Pure Ru films were formed which showed the expected XRD pattern and voltammetry. There are some questions concerning why the OCP for the first 20 cycles was as positive as it was. This suggests that complete coverage of the Au substrate was not achieved during the first few cycles as expected. Atomic level in-situ EC-STM studies could help answer such questions. Initial ex-situ STM studies, however, evidenced very flat films, with feature heights of only a couple of nm, after 200 ALD cycles. There was no evidence of 3D growth. However, an apparent grain structure to the deposits suggests that some roughening has occurred. The charges for Pb UPD suggested only a small increase in deposit surface area, while integration of the charges for Ru oxidation and reduction after 200 cycles were an order of magnitude greater than expected. The use of a stripping step during the Ru ALD cycle has been shown to remove the last traces of Pb, although less than an atomic % of Pb was present when no stripping step was used. In Chapter 3, Initial studies of the formation of Cu films by Electrochemical ALD have been reported. EPMA results confirmed the formation of Cu films using ALD, with no evidence of Pb. Monitoring the OCP during exchange allows monitoring of the reaction progress. Pb replacement by Cu was not completed until the OCP reached -0.013 V. There are indications that the deposition was not as homogeneous as desired, with some extra deposition occurring at the

cell entrance. Studies of the deposit dependence on exchange time and the Cu²⁺ solution concentration have shown, as expected, that longer times give more complete exchange and more concentrated solutions result in a more rapid exchange. The XRD patterns showed the deposits to have a strong (111) habit, consistent with the substrate. STM showed wide, roughly hexagonal terraces, and an apparent decrease in surface roughness. A flow cell EQCM was used to follow the deposition process, and provided reliable data from cycle to cycle. However, within a cycle new questions were raised, mostly related to the double layer and surface compositions. For instance, how does the EQCM frequency change when the solution composition changes, in the absence of electrodeposition? In Chapter 4, Initial studies of the formation of RuSe thin film by electrochemical ALD were reported. No film was deposited, when UPD potential for Ru was used. EPMA confirmed the formation of PbSe instead of RuSe, where Pb was used as a sacrificial metal to deposit Ru. Then the formation of RuSe thin film was made possible by including a stripping step at 400 mV to remove all extra Pb atoms available after the exchange process in blank solution. The actual atomic % of Ru and Se on 100 cycle film was found to be 3.5 and 7 % respectively. The CV experiments were done to show that RuSe is a promising candidate for methanol resistant oxygen catalyst electrode for direct methanol fuel cell. Detailed experiments need to be conducted using rotating disc electrode to study RuSe electrode's catalytic properties like oxygen reduction reaction for fuel cell application. In chapter 5, Ru/Ta wafers were investigated for use as substrates for E-ALD of Cu. Using UHV-EC methodologies, initial surface treatments were examined to determine a cleaning procedure. It was determined that a part of a surface oxide layer on the Ru/Ta wafers was removed using electrochemical reduction, though some was not. From unpublished results from this group, it is suspected that the oxide present was associated with the Ta component of the substrates. Using an automated
electrochemical flow cell deposition system, was showed that deposits tended to be thicker near the ingress than over the rest of the deposits. This appears to result from the mechanism for SLRR of Cu not being from electron transfer directly from atom to ion, and place exchange, but a mechanism where the electrons are transferred through the substrate. Thus, deposits were formed most readily near the ingress, where initially the activity for Cu^{2+} was higher. By using citrate as a complexing agent, the exchange of Pb for Cu was slowed, allowing the solution to enter the cell before the majority of the exchange had taken place. This resulted in homogeneous 200 cycle deposits, as evidenced using EPMA and AFM.