FORMATION OF CADMIUM TELLURIDE THIN FILMS AND METAL THIN FILMS USING INNOVATIVE ELECTROCHEMICAL DEPOSITION METHOD FOR PHOTOVOLTAIC APPLICATIONS

by

XIAOYUE ZHANG

(Under the Direction of John L. Stickney)

ABSTRACT

This dissertation discusses the formation of cadmium telluride (CdTe) using potential pulse atomic layer deposition (PP-ALD) and metal thin films (copper and gold) using surface limited redox replacement (SLRR). Both materials play important roles in photovoltaic devices. PP-ALD is an electrodeposition methodology similar to co-deposition because it uses one solution containing all precursors. However, instead of maintaining one deposition potential as with codeposition, potentials are varied quickly between a cathodic and an anodic potential throughout deposition. Each short pulse aims to limit the amount deposited during cathodic potential and strip the excess in the following anodic potential so that thermodynamically stable compound remains without elemental excess buried beneath the later-grown film. To achieve high quality CdTe thin film, changes in deposition potential and solution flow effects were first monitored and optimized. Parametric variables for controlling the Cd/Te ratio and morphology are also established. X-ray diffraction (XRD), Scanning electron microscope (SEM), Electron probe microanalysis (EPMA), Energy dispersive X-Ray Analyzer (EDX) were used to characterize the resulting CdTe films. Results indicated that deposited CdTe was stoichiometric,

high crystalline with a smooth, continuous morphology using an optimized PP-ALD method. The optimized PP-ALD method was also applied on nanostructured Au electrodes. Initial results showed high quality deposits with reproducible stoichiometry, which could open pathways for semiconductor and nanostructure incorporation.

Cu and Au thin films were formed on metal and semiconductor substrates via surface limited redox replacement (SLRR). An atomic layer of cadmium was first deposited as a sacrificial layer, and then replaced with ions of more noble metals such as Cu²⁺ or Au³⁺ to form Cu or Au atomic layer. Uniform and reasonably flat metal thin films with controllable thickness were produced by multiple repetitions of SLRR cycles with great linear growth with respect to cycle numbers. The resulting metal thin films were characterized using coulometry, SEM, EDX and EPMA. They confirmed deposited metal thin films had a conformal, flat morphology with no roughness development, nor Cd incorporation in the deposition process.

INDEX WORDS: potential pulse deposition, co-deposition, cadmium telluride, solar, photovoltaics, electrochemistry, thin film, metal nanofilm, photoelectrochemistry, nanostructured Au, plasmonic structure, cyclic voltammetry, UPD, XRD, EPMA, SEM

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BE, Dalian University of Technology, China, 2012

A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial

Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2019

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DEDICATION

I would love to dedicate this dissertation to my family, my friends and anyone who has helped me. Without their love and support, I would not have been able to finish this part of journey. All those experiences and moments have made me who I am. Thank you all for help shape a better me.

ACKNOWLEDGEMENTS

I would like to thank John Stickney for being a great mentor, who has inspired me with his great passion to science, to life and let me know what a real scientist should look like. Even at the moments he is not in perfect physical health condition, he did not stop instructing us and discussing science with us. Thank you for your advice, your challenge, your support and your caring in all these years. I would also like to thank Syed Mubeen, who has given me a lot of brilliant ideas to move my research to an upper level. And thank all the past and present group members. It is you that make me realize I am not alone on this journey. And everyone I know in UGA, you are some of the best people I have ever met.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

It is well known that many environmental problems are direct results of increased fossil fuel consumption: increase in global average air and sea temperature, snow and ice melting, rising sea level, etc.¹ Despite of this, fossil fuels are still the main source in the globe energy system, due to the low cost. Thus, there is a large drive towards using a renewable energy source that has low cost and low carbon emission. Solar energy is considered to be a promising candidate as a sustainable energy supply. In 2011, to reduce the cost of solar energy and help it become competitive with conventionally generated electricity, U.S. Department of Energy set targets with \$0.10, \$0.08 and \$0.06 per kilowatt hour (kWh) for residential solar, commercial solar and utility-scale solar respectively by 2020.² In 2017, the price reduction target corresponds to utility-scale solar costing to \$0.06 per kWh had been achieved three years earlier than expected,³ dropping from about \$0.28 per kWh.⁴Another goal set by the Solar Energy Technologies Office was \$0.03 per kWh electricity from utility-scale solar by 2030.⁴

Photovoltaics (PV) technology is the main way to harvest the solar energy which converts sunlight to electricity directly.⁵⁻⁸Achieving these goals would make photovoltaics among the least expensive options for new power generation. And it would be below the cost of most fossil fuel-powered generators, making solar energy a possibility for more people.

The photovoltaic effect was discovered by Edmond Becquerel in 1839, and in 1954 the scientists found silicon can generate electric charge when exposed to light. Soon after that, silicon became prime semiconductor material. PV technologies are usually classified into three

generations. The first generation is based on crystalline silicon. In PV markets, 90% of the solar panel sold around the world are 1st generation silicon based solar cells.⁹ However, their cost is relatively high compared to other energy technologies, and technological barriers like efficiency limitation, life cycle emissions still need to be explored.¹⁰ Second and third generation solar cells with new solar cell architectures and materials have the potential to overcome some of the barriers faced by first generation. The second generation is mainly thin film PVs made from Si, CdTe¹¹ and copper indium gallium selenide (CIGS).¹² Couples of companies like BP and First Solar had commercialized thin film CdTe photovoltaic technology.¹³⁻¹⁴ The highest efficiency of laboratory CdTe solar cell was reported to be 22.1% ¹⁵ and the record for commercial CdTe PV module in market was 18.6% both by First Solar.¹⁶ The basic structure of a CdTe solar cell includes four layers: a transparent and conducting oxide layer (front contact), a buffer layer (or window layer), an absorb layer and metal back contact.

The third generation solar cells focus on incorporating nanotechnology.¹⁷⁻¹⁸ This new generation is based on variety of new materials including nanorods, silicon wires, dyes and conductive plastics. By taking advantages of nanomaterials, third generation solar cell can potentially reduce material use, cost and life emissions. An example of nanomaterial advantage is the four junction cell tandem. It has achieved 46% efficiency under concentrated light, the highest efficiency of any solar cell to date.¹⁹ The efficiency of third generation solar cell is beyond the Schockly-Quesser limit because it is not limited to one electron-hole pair per absorbed photon. By nanostructuring, the solar-cell surface can increase light trapping, so the photocurrent will be enhanced accordingly.²⁰ However, the third generation solar cells is still in laboratory stage not commercially available.

A PV or also called solar cell, is essential a p-n junction formed by a semiconductor with excess holes (p type) and a semiconductor with excess electrons (n type). When two types of semiconductors were brought together, holes will diffuse from p type side to the n type side, with electrons move in the other direction. As electrons and holes are moving, an electrical filed (depletion zone) is forming at the interface. When light strikes the solar cell, more electron-hole pairs will be generated. Under the effect of the build-in electrical field, photogenerated carrier (electrons and holes) will move to different electrodes, thus forming a current. As long as light is continuously absorbed by the semiconductor, the build-in voltage will drive a current through a circuit.

CdTe is one of the most promising absorber candidates for PV device applications because of its high absorption coefficient (>104 cm-1)²¹⁻²² and ideal band gap (Eg=1.37-1.54 eV)²³for efficient solar energy conversion. But one of the shortcomings of CdTe and other absorber candidates, is the short hole diffusion length, which will further affect the solar cell performance. Because when carriers are generated in the semiconductor, only those that can travel to the p-n junction can be collected and contribute to the light-generated current. If the hole diffusion length is too short, it will recombine with electrons. The closer the carrier is generated to the p-n junction, the larger chance for it to be caught. Hence, recently years a lot of effort has been put on the fabrication of ultra-thin CdTe solar cells²⁴⁻²⁵ and/or semiconductor materials in a variety of different morphologies including nanosheets, nanotubes, and nanorods.²⁶⁻³⁰

Another solution to overcome the short carrier diffusion length is to incorporating semiconductors with plasmonic nanostructures. Recently, plasmonic concentration and propagation have been recommended and confirmed as promising solutions for enhancing

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photovoltaic and photocatalytic performance in semiconductor/plasmonic metal hybrid nanostructures. Plasmonic nanostructures are usually patterned metal nanostructures made of gold, silver and copper which can active localized surface plasmon (LSP) resonances.

When a plasmonic metal such as gold or silver is appropriately interfaced with a semiconductor it can act as a means of collecting light from a region outside the semiconductor absorber whose energy is nevertheless converted to e-h pairs in the absorber.³¹⁻³² This would permit one to reduce the thickness of semiconductor material while collecting all the light falling on the device. Additionally, the nanostructure can redirect light that would have been reflected or scattered away from the absorber material, into the absorbing film. In this way carriers can be produced in numbers that, in the absence of the plasmonic concentrator, would have required a much thicker device to achieve, thereby reducing the quantity of semiconductor used. Alternatively, properly engineered plasmonic nanostructures could be used to concentrate light into regions of space close to the carrier collecting surfaces once again allowing less semiconductor material to be used and increasing the collection efficiency of carriers before recombination.

The physical properties of CdTe thin films depend markedly on the fabrication conditions and play an important role in its performance when incorporated into thin film-based devices. CdTe has been grown in numerous ways including close-spaced sublimation (CCS),³³⁻³⁴ thermal evaporation,³⁵ sputtering,³⁶⁻³⁷ spray pyrolysis³⁸. Almost all of these physical fabrication methods require high temperature, vacuum and sophisticated gas control. Thus the operations are usually expensive and energy consuming. Also, these high temperature and vacuum based technologies have difficult to coat small features conformally. One of the alternative technologies is electrodeposition, which is known as a low cost and scalable thin film synthesis method that can easily be used to form a deposit on various types of electrode materials and structures.³⁹⁻⁴⁰ Electrodeposition does not require high temperatures or vacuum, avoiding toxic vapor associated with some UHV based methods. The primary electrochemical process for the formation of compounds is codeposition, developed by Kroger and Panicker.³⁹ During codeposition, a solution containing both elements is held at one constant potential to obtain stoichiometric CdTe films.

Potential pulse atomic layer deposition (PP-ALD) is an electrodeposition methodology similar to codeposition because it also uses one solution containing all the precursors. However, instead of maintaining one deposition potential as with codeposition, potentials are varied quickly throughout deposition. Each short pulse aims to limit the amount deposited during cathodic potential and strip the excess in the following anodic potential so that there is no element excess buried beneath the later-grown film.⁴¹PP-ALD allows better control over the quality of semiconductor films in comparison to codeposition, and the use of potential pulse could open pathways for enabling formation of compounds that cannot formed under one fixed potential.⁴¹⁻⁴² Additionally, proper choice of pulse parameters can improve the quality of films significantly.⁴³

Electrochemical atomic layer deposition (E-ALD) is another electrodeposition methodology designed for high quality metal and semiconductor depositions.⁴⁴⁻⁴⁶ It was pioneered by Stickney group and is a condensed phase ALD.⁴⁷ It controls the film deposited in atomic layer scale by employing underpotential deposition (UPD). Underpotential deposition (UPD) ⁴⁸ is a phenomenon where one element can be deposited on a second element at potential prior to that needed to deposit on itself. Solutions of different precursors will be alternatively

introduced to the cell at respective UPD potentials. E-ALD can also deposit thin metal films by using redox replacement reaction.⁴⁹⁻⁵⁰UPD is first used to deposit a metal(M_1)in less than 1 monolayer, then a solution with ions of a more noble metal (M_2) will flow in at open circuit potential to replace M_1 . Metal M_2 formed accordingly is also less than 1 monolayer. The whole process was surface limited due to UPD deposition of the first kind, so it was referred as surface limited redox replacement (SLRR).⁵¹⁻⁵²Thin metal films with desired thickness can be produced by multiple repetition of the SLRR cycle. E-ALD will stand out as a critical fabrication method for 3rd generation PVs.

All the electrochemical studies and deposits throughout this dissertation were performed using an automated flow-cell system as shown in Figure 1.1 (Electrochemical ALD L.C., Athens, GA). Solutions of different precursors were stored in bottles that connected to distribution valves. An LabView program was used to control the valves. Under the effect of pump, one solution was flowed through the opened valve to the flow cell and ended up in a waste bottle. The flow cell was a three electrode cell using a 3M Ag/AgCl as reference electrode and an Au wire inlayed into the cell as the auxiliary electrode. All potentials were reported versus Ag/AgCl. Before each electrochemical study, the whole system was purged with N₂ for at least one hour to eliminate the oxygen effect in study. In this paper, coverage was frequently described as monolayer (ML), where a ML was always defined as one adsorbate atom for every Au (111) substrate surface atom. The atomic density of Au (111) surface was about 1.17*10¹⁵ atom/cm^{2.53}

Chapter 2 discusses the fabrication of cadmium telluride (CdTe) thin films using codeposition and potential pulse atomic layer deposition (PP-ALD). Changes in deposition potential and effect of solution flow were first monitored to optimize CdTe co-deposition. A significant crystallinity enhancement was achieved by introducing periodic potential control in accordance with solution flow. Based on the optimized solution control, small pulses with potential rapidly alternated between a cathodic and an anodic value were introduced to the deposition process. Both cathodic potential and anodic potential were systematically varied and optimized respectively to study their effect on Cd/Te ratio and morphology. To ascertain the feasibility of PP-ALD methodology, two sets of solution with different Cd, Te ion concentrations (10 mM CdSO₄, 0.2 mM TeO₂ and 1mM CdSO₄, 0.1 mM TeO₂) were used. Despite the difference in Cd, Te ion concentration ratio (50:1 and 10:1), stoichiometric CdTe films were formed using PP-ALD for both cases. X-ray diffraction (XRD), Scanning electron microscope (SEM), Electron probe microanalysis (EPMA), Energy dispersive X-Ray Analyzer (EDX) were used to characterize resulting CdTe films. The optimized potential pulse method was also used to deposit CdTe on nanostructured Au electrodes. At the end of chapter 2, a comparative study of CdTe deposit quality on Au-based substrates using co-deposition and PP-ALD technique was also performed. Potential pulse atomic layer deposition exhibited strong ability of covering dendritic nanostructured Au substrates with stoichiometric and conformal CdTe deposit. Samples deposited with PP-ALD showed great consistency when the structure of the substrates varied, while the quality of codepsotion CdTe on dendritic Au nanostructured were unstable.

Chapter 3 reports a plasmonic structure composed of Au nanorods (Au NR) array covered with CdTe thin film as part of the solar cell to enhance power conversion efficiency. CdTe was grown by electrodeposition outside the ordered Au nanorods. Nanorod length was varied between 250 nm to 600nm. An investigation into effect of length of CdTe-Au NR on photocurrent was performed with the highest photocurrent showed by 600nm CdTe/Au NR. The photoelectrochemical result was also compared between CdTe on Au nanorod substrate and on planar Au substrate. Due to the broad spectra absorbed by the plasmonic structure, the effective carrier generation and transportation, CdTe on Au nanorods showed greatly enhanced photovoltaic performance when compared to CdTe on planar Au. Heat treatment was also performed on CdTe/Au NR sample, which further improved the photocurrent. More works on fabricating high quality Au nanorods with stable reproducibility were on the way. And further optical, chemical characterizations were still conducting.

Chapter 4 of this dissertation explores Cu and Au films epitaxial deposition on metal substrate by surface limited redox replacement (SLRR). A detailed experimental approach for carrying out SLRR deposition cycle was described, including the study of UPD potentials of Cd sacrificial layer, the exchange time for the deposited layer and so on. After a well-studied Cd-Cu SLRR cycle was established, (A-B SLRR, indicted A as a sacrificial metal and is replaced by metal B), a uniform and reasonably flat Cu thin film was produced by multiple repetition of SLRR cycles. Quantitative analysis of Cu growth was conducted by electrochemically stripping Cu films in blank solution. A linear growth of Cu film with repetitive cycle numbers indicated a layer-by–layer Frank van der Merwe type growth. Characterization of the deposited Cu films was also performed using SEM and EDX, EPMA, which all showed a continuous, smooth morphology without Cd incorporation in the formation of the Cu films. And the same SLRR cycles was then employed to deposit Au layer by using AuCl₃ solution, a flat and homogenous Au film was also successfully fabricated using the proposed SLRR method.

Finally, related to the work done in chapter 4, chapter 5 implements the application of thin metal films fabricated using SLRR on CdTe semiconductor substrates. Electrochemical and SEM, EPMA characterizations of deposited Cu film on CdTe substrates show a conformal, flat morphology without roughness development for up to 30 cycles. For Au film deposition on CdTe, results indicated that CdTe substrates were oxidatively dissolved due to high oxidative ability of Au³⁺. Thus, couples of parameters in the established SLRR are readjusted accordingly to successfully deposit Au film with CdTe substrate unaffected. However, unlike Cu, Au films deposited using adjusted SLRR method showed a tendency to nucleate and grow in clusters. At the end, a method was proposed by using a smooth Cu layer as a template and Au³⁺ oxidized and replaced the whole Cu layer. With careful time/potential control, the nucleus of Au film is effectively avoided. The proposed approaches provide a feasible, cost-effective thin film deposition options for various metal- semiconductor systems.

References

Pachauri, R. K.; Allen, M. R.; Barros, V. R.; Broome, J.; Cramer, W.; Christ, R.; Church,
 J. A.; Clarke, L.; Dahe, Q.; Dasgupta, P., Climate change 2014: synthesis report. Contribution of
 Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on
 Climate Change. IPCC: 2014.

Office of Energy Efficincy & Reneable Energy Goals of the Solar Energy Technologies
 Office. https://www.energy.gov/eere/solar/goals-solar-energy-technologies-office (accessed
 Access).

3. The SunShot Initiative, S. E. T. O. Mission Outlined. https://www.energy.gov/eere/solar/sunshot-initiative (accessed Access).

4. Energy, O. o. E. E. R. New Solar Opportunities for a New Decade. https://www.energy.gov/eere/solar/sunshot-2030 (accessed Access).

5. Grätzel, M., Photoelectrochemical cells. Nature 2001, 414, 338.

6. Tyagi, V.; Rahim, N. A.; Rahim, N.; Jeyraj, A.; Selvaraj, L., Progress in solar PV technology: Research and achievement. Renewable and sustainable energy reviews 2013, 20, 443-461.

7. Shah, A.; Torres, P.; Tscharner, R.; Wyrsch, N.; Keppner, H., Photovoltaic technology: the case for thin-film solar cells. science 1999, 285 (5428), 692-698.

8. Pandey, A. K.; Rahim, N. A.; Hasanuzzaman, M.; Pant, P. C.; Tyagi, V. V., Solar Photovoltaics (PV): A Sustainable Solution to Solve Energy Crisis. In Green Technologies and Environmental Sustainability, Singh, R.; Kumar, S., Eds. Springer International Publishing: Cham, 2017; pp 157-178.

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9. Lee, T. D.; Ebong, A. U., A review of thin film solar cell technologies and challenges. Renewable and Sustainable Energy Reviews 2017, 70, 1286-1297.

10. Dang, H.; Singh, V. P.; Guduru, S.; Rajaputra, S.; Chen, Z. D., Nanotube photovoltaic configuration for enhancement of carrier generation and collection. Nano Research 2015, 8 (10), 3186-3196.

11. Wu, X., High-efficiency polycrystalline CdTe thin-film solar cells. Sol. Energy 2004, 77(6), 803-814.

Jackson, P.; Hariskos, D.; Lotter, E.; Paetel, S.; Wuerz, R.; Menner, R.; Wischmann, W.;
 Powalla, M., New world record efficiency for Cu (In, Ga) Se2 thin-film solar cells beyond 20%.
 Progress in Photovoltaics: Research and Applications 2011, 19 (7), 894-897.

13. Turner, A.; Woodcock, J.; Özsan, M.; Cunningham, D.; Johnson, D.; Marshall, R.; Mason, N.; Oktik, S.; Patterson, M.; Ransome, S., BP solar thin film CdTe photovoltaic technology. Solar energy materials and solar cells 1994, 35, 263-270.

14. Gloeckler, M.; Sankin, I.; Zhao, Z., CdTe Solar Cells at the Threshold to 20% Efficiency.IEEE Journal of Photovoltaics 2013, 3 (4), 1389-1393.

15. Energy, O. o. E. E. R. Cadmium Telluride. https://www.energy.gov/eere/solar/cadmium-telluride (accessed Access).

16. First Solar Achieves World Record 18.6 % Thin Film Module Conversion Efficiency http://investor.firstsolar.com/news-releases/news-release-details/first-solar-achieves-world-record-186-thin-film-module. 2015.

17. Green, M. A., Third generation photovoltaics: solar cells for 2020 and beyond. Physica E: Low-dimensional Systems and Nanostructures 2002, 14 (1-2), 65-70.

18. Green, M. A., Third generation photovoltaics: Ultra-high conversion efficiency at low cost. Progress in Photovoltaics: Research and Applications 2001, 9 (2), 123-135.

19. National Renewable Rnergy Laboratory (NREL) Best Research-Cell Efficiencies. https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf (accessed Access).

20. Polman, A.; Atwater, H. A., Photonic design principles for ultrahigh-efficiency photovoltaics. Nature materials 2012, 11 (3), 174.

21. Strauss, A., The physical properties of cadmium telluride. Revue de Physique Appliquée 1977, 12 (2), 167-184.

22. Rangel-Cárdenas, J.; Sobral, H., Optical Absorption Enhancement in CdTe Thin Films by Microstructuration of the Silicon Substrate. Materials 2017, 10 (6), 607.

23. Fonthal, G.; Tirado-Mejía, L.; Marín-Hurtado, J. I.; Ariza-Calderón, H.; Mendoza-Alvarez, J. G., Temperature dependence of the band gap energy of crystalline CdTe. Journal of Physics and Chemistry of Solids 2000, 61 (4), 579-583.

24. Gupta, A.; Parikh, V.; Compaan, A. D., High efficiency ultra-thin sputtered CdTe solar cells. Solar Energy Materials and Solar Cells 2006, 90 (15), 2263-2271.

25. Jones, E.; Barrioz, V.; Irvine, S.; Lamb, D., Towards ultra-thin CdTe solar cells using MOCVD. Thin Solid Films 2009, 517 (7), 2226-2230.

26. Liyanage, W. P. R.; Wilson, J. S.; Kinzel, E. C.; Durant, B. K.; Nath, M., Fabrication of CdTe nanorod arrays over large area through patterned electrodeposition for efficient solar energy conversion. Solar Energy Materials and Solar Cells 2015, 133, 260-267.

27. Mishra, S.; Nath, M., Growth of vertically aligned CdTe nanorod arrays through patterned electrodeposition. Nano Energy 2013, 2 (6), 1207-1213.

28. 6 - Nanostructured semiconductor composites for solar cells. In Nanostructured Semiconductor Oxides for the Next Generation of Electronics and Functional Devices, Zhuiykov, S., Ed. Woodhead Publishing: 2014; pp 267-320.

29. Goddeti, K. C.; Lee, C.; Lee, Y. K.; Park, J. Y., Three-dimensional hot electron photovoltaic device with vertically aligned TiO2 nanotubes. Scientific Reports 2018, 8 (1), 7330.

30. Cao, L.; White, J. S.; Park, J.-S.; Schuller, J. A.; Clemens, B. M.; Brongersma, M. L., Engineering light absorption in semiconductor nanowire devices. Nat Mater 2009, 8 (8), 643-647.

31. Fei Guo, C.; Sun, T.; Cao, F.; Liu, Q.; Ren, Z., Metallic nanostructures for light trapping in energy-harvesting devices. Light: Science &Amp; Applications 2014, 3, e161.

32. Lee, J.; Mubeen, S.; Ji, X.; Stucky, G. D.; Moskovits, M., Plasmonic photoanodes for solar water splitting with visible light. Nano letters 2012, 12 (9), 5014-5019.

33. Chu, T.; Chu, S. S.; Ferekides, C.; Wu, C.; Britt, J.; Wang, C., 13.4% efficient thin-film CdS/CdTe solar cells. Journal of applied physics 1991, 70 (12), 7608-7612.

34. Romeo, N.; Bosio, A.; Menossi, D.; Romeo, A.; Aramini, M., Last Progress in CdTe/CdS Thin Film Solar Cell Fabrication Process. Energy Procedia 2014, 57, 65-72.

35. Lalitha, S.; Karazhanov, S. Z.; Ravindran, P.; Senthilarasu, S.; Sathyamoorthy, R.; Janabergenov, J., Electronic structure, structural and optical properties of thermally evaporated CdTe thin films. Physica B: Condensed Matter 2007, 387 (1), 227-238.

36. Moutinho, H.; Hasoon, F.; Abulfotuh, F.; Kazmerski, L., Investigation of polycrystalline
CdTe thin films deposited by physical vapor deposition, close-spaced sublimation, and
sputtering. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 1995, 13
(6), 2877-2883.

37. Soliman, M. M.; Shabana, M. M.; Abulfotuh, F., CdS/CdTe solar cell using sputtering technique. Renewable Energy 1996, 8 (1), 386-389.

38. Boone, J. L.; Van Doren, T. P.; Berry, A. K., Deposition of CdTe by spray pyrolysis. Thin Solid Films 1982, 87 (3), 259-264.

39. Panicker, M. P. R.; Knaster, M.; Kroger, F. A., Cathodic Deposition of CdTe from Aqueous Electrolytes. J. Electrochem. Soc. 1978, 125 (4), 566-572.

40. Bhattacharya, R.; Rajeshwar, K., Electrodeposition of CdTe thin films. J. Electrochem. Soc. 1984, 131 (9), 2032-2037.

41. Czerniawski, J. M.; Stickney, J. L., Electrodeposition of In2Se3 Using Potential Pulse Atomic Layer Deposition. The Journal of Physical Chemistry C 2016, 120 (29), 16162-16167.

42. Czerniawski, J. M.; Perdue, B. R.; Stickney, J. L., Potential Pulse Atomic Layer Deposition of Cu2Se. Chemistry of Materials 2016, 28 (2), 583-591.

Banga, D.; Lensch-Falk, J. L.; Medlin, D. L.; Stavila, V.; Yang, N. Y. C.; Robinson, D.
B.; Sharma, P. A., Periodic Modulation of Sb Stoichiometry in Bi2Te3/Bi2–xSbxTe3
Multilayers Using Pulsed Electrodeposition. Crystal Growth & Design 2012, 12 (3), 1347-1353.

44. Banga, D.; Jarayaju, N.; Sheridan, L.; Kim, Y.-G.; Perdue, B.; Zhang, X.; Zhang, Q.; Stickney, J., Electrodeposition of CuInSe2 (CIS) via electrochemical atomic layer deposition (E-ALD). Langmuir 2012, 28 (5), 3024-3031.

45. Banga, D.; Perdue, B.; Stickney, J., Electrodeposition of a PbTe/CdTe superlattice by electrochemical atomic layer deposition (E-ALD). J Electroanal Chem 2014, 716, 129-135.

46. Liang, X.; Zhang, Q.; Lay, M. D.; Stickney, J. L., Growth of Ge nanofilms using electrochemical atomic layer deposition, with a "bait and switch" surface-limited reaction. Journal of the American Chemical Society 2011, 133 (21), 8199-8204.

47. Gregory, B. W.; Stickney, J. L., Electrochemical atomic layer epitaxy (ECALE). Journal of electroanalytical chemistry and interfacial electrochemistry 1991, 300 (1-2), 543-561.

48. Kolb, D. M. G., H., Tobias, C. W., Eds.; John Wiley, Advances in Electrochemistry and Electrochemical Engineering. 1978, 11, 125.

49. Brankovic, S.; Wang, J.; Adzic, R., New methods of controlled monolayer-to-multilayer deposition of Pt for designing electrocatalysts at an atomic level. Journal of the Serbian Chemical Society 2001, 66 (11-12), 887-898.

50. Brankovic, S. R.; Wang, J. X.; Adžić, R. R., Metal monolayer deposition by replacement of metal adlayers on electrode surfaces. Surface Science 2001, 474 (1), L173-L179.

51. Dimitrov, N., Recent Advances in the Growth of Metals, Alloys, and Multilayers by Surface Limited Redox Replacement (SLRR) Based Approaches. Electrochimica Acta 2016, 209, 599-622.

52. Kim, Y.-G.; Kim, J. Y.; Vairavapandian, D.; Stickney, J. L., Platinum Nanofilm Formation by EC-ALE via Redox Replacement of UPD Copper: Studies Using in-Situ Scanning Tunneling Microscopy. The Journal of Physical Chemistry B 2006, 110 (36), 17998-18006.

53. Thambidurai, C.; Kim, Y.-G.; Jayaraju, N.; Venkatasamy, V.; Stickney, J. L., Copper Nanofilm Formation by Electrochemical ALD. J. Electrochem. Soc. 2009, 156 (8), D261-D268.



Fig.1.1: Schematic of electrochemical flow system and flow cell.Solutions are stored in bottles and drawn by a pump through the distribution valve and a flow cell. The flow cell is a threeelectrode cell with an Au wire inlayed into the cell as the auxiliary electrode

CHAPTER 2

POTENTIAL PULSE ALD FOR ROOM TEMPERATURE FABRICATION OF STOICHIOMETRIC CDTE NANOFILMS¹

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Abstract

In this work, cadmium telluride (CdTe) thin films were electrodeposited onto flat Au substrates from an acidic aqueous solution of CdSO₄ and TeO₂ at room temperature. Changes in deposition potential and effect of solution flow were monitored to optimize potential pulse atomic layer deposition for CdTe. Potential pulse atomic layer deposition (PP-ALD) is a promising method for producing high quality films faster than in E-ALD¹⁻² as it does not require alternating different precursor solutions. And Compared with codeposition³, PP-ALD maintains better control of compound deposition. In this paper, parametric variables for controlling the Cd/Te ratio and morphology were established. X-ray diffraction (XRD), Scanning electron microscope (SEM), Electron probe microanalysis (EPMA), Energy dispersive X-Ray Analyzer (EDX) were used to characterize resulting CdTe films. XRD studies of the films show evolution of a much sharper peak corresponding to CdTe cubic (111) than is customarily observed for CdTe thin films grown at room temperature.3-4 The optimized PP-ALD method was also used to deposit CdTe on nanostructured Au electrodes. Initial results show high quality deposits with reproducible stoichiometry, which could open pathways for semiconductor and nanostructure incorporation.

Introduction

Research in semiconductor photovoltaic modules on thin metallic substrates has been increasing continuously for decades.⁵⁻⁸Recently, interest has grown in incorporating semiconductors with nanostructured materials for solar energy research.⁹⁻¹² The electronic and optical responses of semiconductors strongly correlate to size, possibly due to quantum and photon confinement at the nanoscale¹³. A variety of different morphologies of semiconductor materials have been studied including thin films, nanosheets, nanotubes, and nanorods.¹⁴⁻¹⁵By incorporating semiconductors with nanostructures, higher solar conversion efficiency can be achieved while using less semiconductor material. After depositing an ultra-thin film of semiconductor material on odd shaped nanostructures light absorption increases as the effective area increases, carrier pathways to the surface shorten, and the reflection of the incident light and scattering light among nanostructures is suppressed.¹⁶All of these factors combined can result in a great enhancement of the PEC properties.¹⁷

CdTe is one of the most promising absorber candidates for device applications because of its high absorption coefficient $(>10^4 \text{ cm}^{-1})^{18-19}$ and ideal band gap $(\text{Eg}=1.37-1.54 \text{ eV})^{20}$ for efficient solar energy conversion. Also, due to its high resistivity, high mean Z-number of,⁵⁰21 and carrier transport properties,²² it is widely used as a component of x-ray and gamma-ray detectors.²³⁻²⁵ CdTe is unique among II-VI semiconducting compounds as it exhibits both n-type and p-type conductivity by changing the stoichiometry of the material.^{3, 26}A Cd-rich CdTe results in n-type, while a Te-rich film results in p-type. P-type CdTe is a good photocathode for high efficiency CO₂ reduction.^{27,28} Type conversion can be achieved by doping, however the doping of CdTe is often hard to control and the mechanisms behind its chemistry have not been well understood.²⁹

The physical properties of CdTe thin films depend markedly on the fabrication conditions and play an important role in its performance when incorporated into thin film-based devices. CdTe has been grown in numerous ways including close-spaced sublimation (CCS),³⁰⁻³¹ thermal evaporation,³² sputtering,³³⁻³⁴spray pyrolysis³⁵ and electrodeposition.³⁻⁴Electrodeposition is known as a low cost and scalable thin film synthesis method that can easily be used to form a deposit on various types of electrode materials and structures. Electrodeposition does not require high temperatures or vacuum, avoiding toxic vapor associated with some UHV based methods. The primary electrochemical process for the formation of compounds is codeposition, developed by Kroger and Panicker.³ During codeposition, a solution containing both elements is held at one constant potential to obtain stoichiometric CdTe films. While many pioneering works have followed co-deposition approach to grow CdTe films, it has some inherent limitations. This includes the narrow potential range where stoichiometric CdTe can be formed,³⁶the strong dependence of the quality on mass transfer rate and discharge rates of elemental precursors.

PP-ALD is an electrodeposition methodology similar to codeposition because it also uses one solution containing all the precursors. However, instead of maintaining one deposition potential as with codeposition, potentials are varied quickly throughout deposition. Each short pulse aims to limit the amount deposited during cathodic potential and strip the excess in the following anodic potential so that there is no element excess buried beneath the later-grown film.³⁷ Potential pulses allow better control over the quality of semiconductor films in comparison to codeposition, and the use of potential pulse could open pathways for enabling formation of compounds that cannot formed under one fixed potential.³⁷⁻³⁸ Additionally, proper choice of pulse parameters can improve the quality of films significantly.³⁹

This work reports a comparative study of CdTe deposit quality on Au-based substrates using co-deposition and PP-ALD technique. Studies were first done to examine the effect of solution flow during deposition. A significant crystallinity enhancement was achieved by introducing periodic potential control in accordance with solution flow. Then a series of experiments were performed based on the optimized method and further introduced small pulses into the deposition program. To ascertain the feasibility of potential pulse deposition methodology, two sets of solution with different cadmium and tellurium ion concentration (10 mM CdSO₄, 0.2 mM TeO₂ and 1mM CdSO₄, 0.1 mM TeO₂) were used. Despite the difference in cadmium and tellurium ion concentration ratio (50:1 and 10:1), stoichiometric CdTe can be formed using PP-ALD for both cases. We also investigate the feasibility of the PP-ALD process for depositing conformal layers of CdTe on high aspect ratio nanostructures such as gold nanowire arrays. CdTe were deposited on nanostructured Au substrates using codeposition and PP-ALD method. Samples deposited with PP-ALD showed great consistency when the structure of the substrates varied. However, the codeposition sample resulted in much higher Cd content on dendritic substrate structures.

Experimental

The solution for electrodeposition of CdTe thin film contained 10 mM CdSO4 (Sigma-Aldrich), 0.2 mM TeO₂ (Alfa Aesar 99.999% pure), and 0.1 M NaClO₄ (GFS). A diluted version of the solution consisted of 1 mM CdSO₄ (Sigma-Aldrich), 0.1 mM TeO₂ (Alfa Aesar 99.999%

pure), and 0.1 M NaClO₄ (GFS) was used as well for the pulse deposition part. Due to the low solubility of TeO₂ in water, TeO₂ was first dissolved in concentrated H₂SO₄ before being mixed with CdSO₄ solution. The pH is adjusted to 2.0 with NaOH (Fisher). The solution is made with 18 MQ water supplied from a Milipore water filtration system. Prior to the electrochemical study, all solutions were purged with N₂ for 1h. Flat Au substrates for CdTe electrodeposition were 100 nm thick Au films on 5nm of Ti on glass, purchased from Evaporated Metal Films (Ithaca, NY), and were carefully degreased and rinsed with acetone and 18 MQ water followed by N₂-drying. They were then dipped in concentrated nitric acid for 30s, rinsed with 18 MQ water, and dried with N₂ again before being placed in an automated flow cell (Figure 2.1). Au nanorods were fabricated using nanoporous anodized aluminum oxide (AAO) template.⁴⁰

The flow cell is a three electrode cell using a 3M Ag/AgCl reference electrode and an Au wire inlayed into the cell as the auxiliary electrode. All potentials are reported versus Ag/AgCl. Before deposition, the cell was flushed with 0.1 M H₂SO₄, and potential was swept between -200 and +1400 mV to clean the Au surface. All deposits were carried out at room temperature.

X-ray diffraction was performed on a PANalytical X'PERT Pro with an open Eulerian cradle utilizing a1.54 Å Cu Kα1 source and a parallel plate collimator. Scanning electron microscopy and energy dispersive X-ray spectroscopy were performed on the FEI Teneo (FEI Co., Hillsboro, OR) equipped with EDAX. Spectroscopic ellipsometry was performed on a J.A. Woolam M-200 V instrument.

Results and Discussion

To investigate the mechanism of CdTe deposition, we performed cyclic voltammograms (CV) on gold electrodes in different electrolytes containing just Cd precursor (CdSO₄), Te precursor (TeO₂) and both Cd and Te precursor (CdSO₄+TeO₂). Figure 2.2(A) shows CV for a gold electrode in pH 2 10 mM CdSO₄ solution. As the potential is scanned cathodically from open circuit potential (OCP: +300mV), a under potential deposition (UPD) feature of Cd is observed at from 100 mV to -200 mV (Figure 2.2(A) left inset; all potentials are referenced to 3M Ag/AgCl reference electrode). The application of potential more cathodic than -600 mV resulted in increase in deposition currents due to formation of Cd/Au alloy and H₂ evolution. Beyond -700 mV the deposition currents increased dramatically due to formation of bulk Cd deposition (also coincident with H₂ evolution; Figure 2.2(A) right inset). During the reverse scan, the peak oxidation currents corresponding to stripping of bulk Cd, Cd/Au alloy and Cd UPD is observed at -800 mV, -700 mV and -20 mV respectively.

The CV for a gold electrode in 0.2 mM TeO₂, pH 2 solution is shown in Figure 2.2(B). The UPD features of Te can be seen at 300mV and -100mV respectively (Figure 2.2(B) inset) with its corresponding anodic stripping peak appearing as small shoulder at 600mV during the reverse scan. With increasing cathodic potential (beyond -200mV), the deposition currents increase due to bulk Te deposition. Anodic currents due to stripping of bulk Te appears at potential 400mV during the reverse scan. As the scan potential in the cathodic direction increases the resulting stripping currents at 400 mV increases. However, it is to be noted that at -700mV and beyond, the bulk Te can be further reduced to Te²⁻ ions - a water soluble species, resulting in

observed decrease in bulk stripping currents when potential is scanned cathodically beyond -600 mV (Figure 2.2(B), black trace).

Figure 2.2(C) displays CV for a gold electrode in electrolyte containing both CdSO₄ (10mM) and TeO₂ (0.2 mM) at pH 2. The CVs were scanned from OCP (400 mV) to -700 mV. The characteristic peaks for Te UPD and Cd UPD (Figure 2.2(C) inset) along with Te bulk deposition were observed, indicating that by appropriate selection of deposition potentials, it is possible to UPD both Cd and Te from the same electrolyte.

A series of CdTe films were deposited using codeposition at various potentials to establish a basis for comparison to potential pulse deposition. The solution used contained 10 mM CdSO₄, 0.2 mM TeO₂ and 0.1 M NaClO₄. Films were made by flowing solution for 15 minutes at the chosen potential. Figure 2.3 illustrates the variation in Cd and Te atomic percentages and the Cd/Te ratio versus deposition potential. As the potential becomes more negative, there is a gradual increase in Cd/Te ratio up to -700 mV. At -800 mV the ratio rapidly increases, corresponded to being near the equilibrium potential for bulk cadmium deposition.

Stoichiometric CdTe films were obtained at the potential slightly positive of the formal potential for bulk cadmium deposition,⁴¹⁻⁴² which was near -800mV based on cyclic voltammetric study.²⁶ Visual image of the film deposited at -700mV was shown in Figure 2.4 (A) with atomic percentage of Cd,Te and Cd/Te ratio acquired across the sample and shown in Figure 2.4 (B). The bottom of the deposit corresponded with the inlet of the flow cell. A macroscopic flow pattern can be observed on the sample, along with areas of higher thickness at the bottom. The flow patterns between the nine ingress and egress holes show parallel layers, indicative of a laminar flow. The thicker deposits at the ingress are an indication of excessive growth where the effect of convection is the highest. At the ingress, the fresh solution hits the

electrode at right angles like a wall jet electrode. These observations were supported by EPMA measurements over the deposit as the atomic percentages are higher in the bottom circles.(Figure 2.4(B))

Figure 2.5 (B)-I shows an SEM image of the -700mV codeposition CdTe film. The film displays dense, granular morphology with small grain size. Based on XRD pattern, the film showed strong CdTe (111) habit as shown in Figure 2.6, red line. With the exception of Au diffraction peaks, the peak at 2Θ = 23.8 ° corresponds to CdTe cubic zinc blend structure preferentially orientated along (111) phase.

To eliminate the effect of solution flow on the deposition pattern, potential was periodically utilized to ensure a quiescent environment during the deposition. A waveform of the potential is shown in Figure 2.5 (A)-II. Each cycle included two steps: potential control at -700 mV for 10s in the stationary codeposition solution followed by termination of the potential control for 7s so that the cell was left on open circuit potential (OCP) and solution is flowing. The OFF period corresponds to when it is at OCP and solution begins to be refreshed, while the ON period is when the potential deposition is occurring. The time selected for the OFF step was chosen based on flow rate of 3.5 ml/min and cell volume of 0.35 ml.

The previously described potential pulse deposition methodology is referred to as method (II). The author believes introducing a quiescent environment before applying a deposition potential helps atoms establish their respective equilibrium positions and avoid the flow pattern observed with method (I). The XRD result (Figure 2.6, blue line) proved that adding the flow step at OCP leads to the formation of a more ordered, crystalline arrangement with increased grain size. It is worth noting that previously reported CdTe films electrodeposited at room temperature were amorphous³⁻⁴ and post–annealing was used to provide crystallinity and better stoichiometry of CdTe.⁴³ No post-annealing was used in the present work.

To ensure solution is completely quiescent when a potential is applied, a 2 second pause was added before and after flowing the solution to further optimize film growth (Figure 2.5 (A)-III). One cycle in method III is as follows: flow solution for 7 seconds at OCP, stop flowing at OCP for 2 seconds, applies potential control for 10 seconds with no flow, and returning to OCP for 2 seconds before flowing solution again. Figure 2.5 (B)-III is an SEM image of the deposit using method (III). It shows that the morphology of CdTe films is compact, densely packed uniform granules. In Figure 2.5(B), the top image (I) showed obvious granular features packed together. From I to III in Figure 2.5(B), a trend of grains joining more tightly with each other and continuous linked together can be seen. The XRD data showed that the FWHM becomes smaller from method (I) to (III) (from 1.3° to 0.7° to 0.5°), indicating the grain size is getting bigger. Both the SEM images and XRD results prove the importance of potential interval control in accordance with solution flow.

In order to better control the quality of films at the atomic scale, smaller pulses were introduced based on method (III) which is the potential pulse atomic layer deposition. A potential time diagram for 2 cycles of PP-ALD is shown in Figure 2.7. One cycle consists of 2 sections: solution refreshment and pulse deposition. The refresh region is the same as in method (III), solution is refreshed for 7 seconds with a 2 second gap before applying potential. PP-ALD is composed of thirteen 0.3 second pulses at a cathodic potential, and 0.5 seconds at an anodic potential. The duration of cathodic and anodic potential control is in millisecond scale so that less than one monolayer is deposited and any traces of bulk deposition are stripped. Figure 2.7 is a potential-time profile of an example using -700 mV as the cathodic potential and -500 mV as
the anodic potential. Deposits formed with small pulses limit the deposition per pulse to submonolayer quantities with the desired elemental ratio. In the cathodic pulse, both elements are deposited while the anodic pulse will selectively strip the excess element deposited.

A series of CdTe pulse samples were deposited using a diluted solution containing 1mM $CdSO_4$ and 0.1 mM TeO₂. The cathodic potential was kept at -800mV. At this potential, a fraction of a monolayer of CdTe and bulk Cd were deposited. The potential was then pulsed to an anodic potential where excess Cd clusters can be removed. SEM and EDX were used to investigate the relationship between anodic potentials and elemental composition. Figure 2.8 displays the change in Cd/Te ratio for a set of deposits where the deposition cycle was repeated 90 times at anodic potentials varying between -700 mV and 0 mV. The cathodic potential was maintained at -800 mV, as previously investigated. It was observed that the ratio of Cd to Te decreased as the anodic potential increased from -700mV to 0mV. When the anodic potential is -700mV, bulk Cd is not stripped completely leaving a slight excess amount Cd. As the anodic potential increases, more Cd is removed and the preferred 1:1 stoichiometry can be attained. At the most positive anodic potential, the removal of most Cd including those bonded to Te in CdTe compound happens leaving mainly Te present. Figure 2.8(B) shows corresponding SEM images in same scaled from sample 1-6 in Figure 2.8 (A). Samples 1-3 in Figure 2.8 (B) exhibit a smooth morphology with negligible nucleation formation. In 4-6, nucleation clusters are increasingly evident, as well as some pitting. Those results are consistent with excessive of Cd during the anodic pulse, leaving an excess of Te on the surface.

SEM and EDX indicate control over stoichiometry and morphology for deposits 1-3 in Figure 2.8, using PP-ALD, over a wide potential range. That results in a greatly increased

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flexibilitycompared with co-deposition, where control of potential and mass transfer must be carefully controlled.

Additional studies were performed to investigate the rate of growth depending on number of repeated cycles. The deposition conditions chosen for the cathodic and anodic potentials were -800 mV and -300 mV, based on the previous results. Figure 2.9 shows the resulting atomic percentages of Cd and Te. A linear trend is observed for Cd and Te At%, indicating the composition remains stoichiometric regardless of thickness. The linear trend is an indication of layer-by-layer growth.

Furthermore, CdTe potential pulse depositions using solution with 10 mM CdSO₄ and 0.2 mM TeO₂ were completed. Two studies were performed to investigate the dependence of elemental composition on the chosen potentials, a cathodic potential study and an anodic potential study. In Figure 2.10, the red line represents the Cd/Te ratio of a set of 90 cycles' thick deposits, where the anodic potential was held constant at -500mV and the cathodic potential was varied. The blue line shows results from a set of CdTe films made by constant cathodic potential at -700 mV with various anodic potentials. From the observed stoichiometry (Cd/Te) variation in response to potential changes, two trends could be seen, first being that cathodic potential impacts total deposition of both elements. The further negative it is, the more Cd deposited. Secondly, when the anodic potential is kept constant (red line), using -800mV as cathodic potential will result in primarily Cd clusters as shown in the top SEM picture in the inset of Figure 2.10. The role of the anodic potential is stripping the excess element. As can be seen from the blue line, the anodic potential slowly changes the stoichiometry (Cd/Te) until 0 mV, where almost all Cd is removed leaving a film of elemental Te. (Bottom inset picture in Figure 2.10)

Based on results presented in Figure 2.10, the optimal potential pulse deposition conditions chosen are a cathodic potential at -700mV, anodic potential at -500mV using solution of 10 mM CdSO₄ and 0.2 mM TeO₂. This pulse condition was employed on Au nanorod substrates with differing morphologies. Figure 2.11 (A) and (B) are the SEM images of 100nm Au nanorods before and after deposition of CdTe. Figure 2.11 (C) is the top view of CdTe-coated Au nanorods under CBS (circular backscatter detector). In Figure 2.11 (B) CdTe is assumed to have successfully coated the Au nanorods based on comparison to the bare Au nanorods seen in Figure 2.11 (A). Figure 2.12 is the cross section SEM of side view on Au nanorods with CdTe covered uniformly. Figure 2.12 (a) is imaged under CBS (circular backscatter detector) mode. CBS mode can provide more elemental composition information as heavier elements which backscatter more efficiently appear brighter. In the image, the brighter center columns are Au nanorods. Figure 2.12 (B) is under ETD (Everhart-Thornley Detector) mode which is a secondary electron detector mode. ETD mode is more surface sensitive and has greater resolution. Both the top and side view indicated deposited CdTe covered the whole nanorods structure evenly. And from EDX data, the ratio of Cd/Te on Au nanorods is 0.94, which is stoichiometric.

In Figure 2.13, three variations of Au nanostructured substrates are shown. From (A) to (C), the nanorods were grown longer and form branched hierarchical structures with additional Au growth. Both the pulse deposition and codeposition method were used to deposit CdTe on these substrates. Cd/Te ratio of codeposited CdTE vs. pulse deposited CdTe was listed in Table 2.1. When comparing the elemental composition of CdTe deposits on Au nanorod samples with different morphology, little effect was seen in stoichiometry when using a pulse deposition method. However, CdTe-Au nanorods samples made using the codeposition method have

fluctuations in Cd/Te ratio. Codeposition methods have a slight excess of Cd in comparison to the pulse method for sample (A) and (B). While unexpected Cd excess occurs on sample (C) using codeposition. It is believed that the solution may have become stagnant below the branched hierarchical structures due to inhibited solution flow. Without efficient transportation of Te to the electrode, deposition conditions are not suitable for a stoichiometric deposit. This problem is not observed with the pulse deposition method due to its ability to strip excess Cd effectively. Pulse deposition proved successful even on odd shaped substrates, indicating it to be an effective method that can be applied to many types of nanostructured substrates.

Conclusion

CdTe films were formed both on flat Au and nanostructured Au substrates using electrodeposition. Quiescent environment and solution refreshment during deposition allowed elements to establish their respective equilibrium positions. Further improvement was achieved with potential pulse deposition by varying the potential rapidly between a cathodic and anodic value, helping the formation of a stoichiometric compound at the atomic scale. In this paper, potential pulse deposition showed great ability in reproducibly controlling composition and morphology of the deposit. It also showed promising results when applied on the nanostructured electrode. It's been proved the branched hierarchical structured cadmium chalcogenide can display a much higher photoconversion performance.⁴⁴⁻⁴⁶ Deposition of stoichiometric semiconductors on nanostructure plays a key role in incorporation of semiconductor materials with nanotechnology. Herein, potential pulse deposition provides a viable option for semiconductor deposition on nanostructured substrates.

Acknowledgements

Support from the National Science Foundation, DMR 1410109, is gratefully acknowledged. Thanks are extended to Chris Fleisher and the UGA Microprobe lab.

References

1. Banga, D.; Perdue, B.; Stickney, J., Electrodeposition of a PbTe/CdTe superlattice by electrochemical atomic layer deposition (E-ALD). J Electroanal Chem 2014, 716, 129-135.

2. Vaidyanathan, R.; Cox, S. M.; Happek, U.; Banga, D.; Mathe, M. K.; Stickney, J. L., Preliminary Studies in the Electrodeposition of PbSe/PbTe Superlattice Thin Films via Electrochemical Atomic Layer Deposition (ALD). Langmuir 2006, 22 (25), 10590-10595.

3. Panicker, M. P. R.; Knaster, M.; Kroger, F. A., Cathodic Deposition of CdTe from Aqueous Electrolytes. J. Electrochem. Soc. 1978, 125 (4), 566-572.

4. Bhattacharya, R.; Rajeshwar, K., Electrodeposition of CdTe thin films. J. Electrochem. Soc. 1984, 131 (9), 2032-2037.

Hamakawa, Y., Thin-film solar cells: next generation photovoltaics and its applications.
 Springer Science & Business Media: 2013; Vol. 13.

6. Ali, N.; Hussain, A.; Ahmed, R.; Wang, M. K.; Zhao, C.; Haq, B. U.; Fu, Y. Q., Advances in nanostructured thin film materials for solar cell applications. Renewable and Sustainable Energy Reviews 2016, 59 (Supplement C), 726-737.

Kranz, L.; Gretener, C.; Perrenoud, J.; Schmitt, R.; Pianezzi, F.; La Mattina, F.; Blösch,
 P.; Cheah, E.; Chirilă, A.; Fella, C. M.; Hagendorfer, H.; Jäger, T.; Nishiwaki, S.; Uhl, A. R.;
 Buecheler, S.; Tiwari, A. N., Doping of polycrystalline CdTe for high-efficiency solar cells on
 flexible metal foil. Nature communications 2013, 4, 2306.

8. Mathew, X.; Enriquez, J. P.; Romeo, A.; Tiwari, A. N., CdTe/CdS solar cells on flexible substrates. Sol. Energy 2004, 77 (6), 831-838.

9. Singh, V. P.; Singh, R. S.; Sampson, K. E., Chapter 6 - Thin-Film Solar Cells Based on Nanostructured CdS, CIS, CdTe and Cu2S. In Nanostructured Materials for Solar Energy Conversion, Soga, T., Ed. Elsevier: Amsterdam, 2006; pp 167-190.

10. 6 - Nanostructured semiconductor composites for solar cells. In Nanostructured Semiconductor Oxides for the Next Generation of Electronics and Functional Devices, Zhuiykov, S., Ed. Woodhead Publishing: 2014; pp 267-320.

11. Mubeen, S.; Lee, J.; Lee, W.-r.; Singh, N.; Stucky, G. D.; Moskovits, M., On the Plasmonic Photovoltaic. ACS Nano 2014, 8 (6), 6066-6073.

12. Goddeti, K. C.; Lee, C.; Lee, Y. K.; Park, J. Y., Three-dimensional hot electron photovoltaic device with vertically aligned TiO2 nanotubes. Scientific Reports 2018, 8 (1), 7330.

13. Cao, L.; White, J. S.; Park, J.-S.; Schuller, J. A.; Clemens, B. M.; Brongersma, M. L., Engineering light absorption in semiconductor nanowire devices. Nat Mater 2009, 8 (8), 643-647.

14. Liyanage, W. P. R.; Wilson, J. S.; Kinzel, E. C.; Durant, B. K.; Nath, M., Fabrication of CdTe nanorod arrays over large area through patterned electrodeposition for efficient solar energy conversion. Solar Energy Materials and Solar Cells 2015, 133, 260-267.

15. Mishra, S.; Nath, M., Growth of vertically aligned CdTe nanorod arrays through patterned electrodeposition. Nano Energy 2013, 2 (6), 1207-1213.

White, J. L.; Baruch, M. F.; Pander, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.;
 Liao, K.; Gu, J.; Yan, Y.; Shaw, T. W.; Abelev, E.; Bocarsly, A. B., Light-Driven Heterogeneous
 Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. Chemical Reviews 2015, 115
 (23), 12888-12935.

17. Wang, X.; Li, G.; Zhu, H.; Yu, J. C.; Xiao, X.; Li, Q., Vertically aligned CdTe nanotube arrays on indium tin oxide for visible-light-driven photoelectrocatalysis. Applied Catalysis B: Environmental 2014, 147, 17-21.

Strauss, A., The physical properties of cadmium telluride. Revue de Physique Appliquée
 1977, 12 (2), 167-184.

19. Rangel-Cárdenas, J.; Sobral, H., Optical Absorption Enhancement in CdTe Thin Films by Microstructuration of the Silicon Substrate. Materials 2017, 10 (6), 607.

20. Fonthal, G.; Tirado-Mejía, L.; Marín-Hurtado, J. I.; Ariza-Calderón, H.; Mendoza-Alvarez, J. G., Temperature dependence of the band gap energy of crystalline CdTe. Journal of Physics and Chemistry of Solids 2000, 61 (4), 579-583.

21. Vogt, A.; Schütt, S.; Frei, K.; Fiederle, M., CdTe layer structures for X-ray and gammaray detection directly grown on the Medipix readout-chip by MBE. Journal of Crystal Growth 2017, 477, 114-117.

 Aoki, T.; Gnatyuk, V. A.; Kosyachenko, L. A.; Maslyanchuk, O. L.; Grushko, E. V., Transport Properties of CdTe X/γ-Ray Detectors With p-n Junction IEEE Trans. Nucl. Sci. 2011, 58 (1), 354-358.

23. Niraula, M.; Yasuda, K.; Ishiguro, T.; Kawauchi, Y.; Morishita, H.; Agata, Y., Metalorganic vapor-phase epitaxy growth and characterization of thick (100) CdTe layers on (100) GaAs and (100) GaAs/Si substrates. Journal of Electronic Materials 2003, 32 (7), 728-732.

24. Lovergine, N.; Prete, P.; Tapfer, L.; Marzo, F.; Mancini, A. M., Hydrogen transport vapour growth and properties of thick CdTe epilayers for RT X-ray detector applications. Crystal Research and Technology 2005, 40 (10-11), 1018-1022.

34

25. Pennicard, D.; Pirard, B.; Tolbanov, O.; Iniewski, K., Semiconductor materials for x-ray detectors. MRS Bull. 2017, 42 (6), 445-450.

26. Duffy, N. W.; Peter, L. M.; Wang, R. L.; Lane, D. W.; Rogers, K. D., Electrodeposition and characterisation of CdTe films for solar cell applications. Electrochimica Acta 2000, 45 (20), 3355-3365.

27. Aurian-Blajeni, B.; Ahsan Habib, M.; Taniguchi, I.; Bockris, J. O. M., The study of adsorbed species during the photoassisted reduction of carbon dioxide at a p-CdTe electrode. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1983, 157 (2), 399-404.

28. Taniguchi, I.; Aurian-Blajeni, B.; Bockris, J. O. M., Photo-aided reduction of carbon dioxide to carbon monoxide. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1983, 157 (1), 179-182.

Burst, J. M.; Duenow, J. N.; Albin, D. S.; Colegrove, E.; Reese, M. O.; Aguiar, J. A.;
Jiang, C. S.; Patel, M. K.; Al-Jassim, M. M.; Kuciauskas, D.; Swain, S.; Ablekim, T.; Lynn, K.
G.; Metzger, W. K., CdTe solar cells with open-circuit voltage breaking the 1 V barrier. 2016, 1, 16015.

30. Chu, T.; Chu, S. S.; Ferekides, C.; Wu, C.; Britt, J.; Wang, C., 13.4% efficient thin-film CdS/CdTe solar cells. Journal of applied physics 1991, 70 (12), 7608-7612.

Romeo, N.; Bosio, A.; Menossi, D.; Romeo, A.; Aramini, M., Last Progress in CdTe/CdS
 Thin Film Solar Cell Fabrication Process. Energy Procedia 2014, 57, 65-72.

32. Lalitha, S.; Karazhanov, S. Z.; Ravindran, P.; Senthilarasu, S.; Sathyamoorthy, R.; Janabergenov, J., Electronic structure, structural and optical properties of thermally evaporated CdTe thin films. Physica B: Condensed Matter 2007, 387 (1), 227-238.

35

33. Moutinho, H.; Hasoon, F.; Abulfotuh, F.; Kazmerski, L., Investigation of polycrystalline
CdTe thin films deposited by physical vapor deposition, close-spaced sublimation, and
sputtering. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 1995, 13
(6), 2877-2883.

34. Soliman, M. M.; Shabana, M. M.; Abulfotuh, F., CdS/CdTe solar cell using sputtering technique. Renewable Energy 1996, 8 (1), 386-389.

35. Boone, J. L.; Van Doren, T. P.; Berry, A. K., Deposition of CdTe by spray pyrolysis. Thin Solid Films 1982, 87 (3), 259-264.

36. Osial, M.; Widera, J.; Jackowska, K., Influence of electrodeposition conditions on the properties of CdTe films. Journal of Solid State Electrochemistry 2013, 17 (9), 2477-2486.

37. Czerniawski, J. M.; Stickney, J. L., Electrodeposition of In2Se3 Using Potential Pulse Atomic Layer Deposition. The Journal of Physical Chemistry C 2016, 120 (29), 16162-16167.

38. Czerniawski, J. M.; Perdue, B. R.; Stickney, J. L., Potential Pulse Atomic Layer Deposition of Cu2Se. Chemistry of Materials 2016, 28 (2), 583-591.

Banga, D.; Lensch-Falk, J. L.; Medlin, D. L.; Stavila, V.; Yang, N. Y. C.; Robinson, D.
B.; Sharma, P. A., Periodic Modulation of Sb Stoichiometry in Bi2Te3/Bi2–xSbxTe3
Multilayers Using Pulsed Electrodeposition. Crystal Growth & Design 2012, 12 (3), 1347-1353.

40. Lee, J.; Mubeen, S.; Ji, X.; Stucky, G. D.; Moskovits, M., Plasmonic Photoanodes for Solar Water Splitting with Visible Light. Nano Letters 2012, 12 (9), 5014-5019.

41. Ohgai, T.; Gravier, L.; Hoffer, X.; Ansermet, J.-P., CdTe semiconductor nanowires and NiFe ferro-magnetic metal nanowires electrodeposited into cylindrical nano-pores on the surface of anodized aluminum. J. Appl. Electrochem. 2005, 35 (5), 479-485.

42. Hsiu, S. I.; Sun, I. W., Electrodeposition Behaviour of Cadmium Telluride from 1-ethyl-3-methylimidazolium Chloride Tetrafluoroborate Ionic Liquid. J. Appl. Electrochem. 2004, 34 (10), 1057-1063.

43. Luo, H.; Ma, L.; Xie, W.; Wei, Z.; Gao, K.; Zhang, F.; Wu, X., Synthesis of CdTe thin films on flexible metal foil by electrodeposition. Applied Physics A 2016, 4 (122), 1-7.

44. Huang, Y.; Xu, Y.; Zhang, J.; Yin, X.; Guo, Y.; Zhang, B., Hierarchical ultrathinbranched CdS nanowire arrays with enhanced photocatalytic performance. Journal of Materials Chemistry A 2015, 3 (38), 19507-19516.

45. Han, Z.; Wang, M.; Chen, X.; Shen, S., CdSe-sensitized branched CdS hierarchical nanostructures for efficient photoelectrochemical solar hydrogen generation. Physical Chemistry Chemical Physics 2016, 18 (16), 11460-11466.

46. Heo, K.; Lee, H.; Jian, J.; Lee, D.-J.; Park, Y.; Lee, C.; Lee, B. Y.; Hong, S., Bi-Assisted CdTe/CdS Hierarchical Nanostructure Growth for Photoconductive Applications. Nanoscale Res. Lett. 2015, 10 (1), 331.



Figure 2.1: Schematic of electrochemical flow system and flow cell.



Figure 2.2. Cyclic voltammogram of (A) Au in 10 mM CdSO4, $pH\neg 2$ (Inset is -800mV cycle in a larger scale), (B) Au in 0.2 mM TeO $\neg 2$, pH 2 and (C) Au in solution containing both 10 mM CdSO4 and 0.2 mM TeO $\neg 2$, pH 2. Potential was measured vs. Ag/AgCl (3M) reference electrode at a scan rate of 10mV/s. The electrode area was 1.8 cm2.



Figure 2.3: Cd/Te ratio and Cd, Te atomic percent vs. deposition potential.



(B)

(A)



Figure 2.4: (A) Visual image of -700 mV codeposition sample. (B) Atomic percentage of Cd, Te and Cd/Te ratio as a function of position marked in (A).



Figure 2.5: (A) Potential profile for 5 cycles (I) codeposition at -700 mV (II) 7s flow solution at OCP and then10s deposit at -700mV (III) 7s flow solution at OCP+2s gap+10s deposit at -700mV+2s. (B) SEM of deposits made by method (I), (II), (III) with the visual pictures of corresponding sample.



Figure 2.6: X-ray diffraction patterns of CdTe films deposited by method (I), (II), (III) as shown in Figure 2.4 (A).



Figure 2.7: Potential-time profile for 2 cycles of PP-ALD using -700 mV as cathode potential and -500 mV as anodic potential.



Figure 2.8: (A) Cd/Te ratio versus anodic potential under constant cathodic potential at -800 mV.(B) SEM of 90 cycles CdTe deposits using -800 mV as cathodic potential, and anodic potential were varied from (1) -700mv to (6) 0 mV. The acceleration voltage used was 10 kV.



Figure 2.9: Elemental Atomic percent vs. number of cycles. (cathodic pulse=-800mV, anodic pulse =-300mV)



Figure 2.10: Deposit stoichiometry, determined by EDX of 2 sets of CdTe films made under constant anodic (red) and constant cathodic potentials (blue). Each deposit was formed using 90 cycles. The total time for each sample includes 15min potential controlled state and 16.5min in OCP state.



Figure 2.11: SEM images of (A) top view of bare Au nanorods; (B) top view of CdTe deposited

on Au nanorods (C) top view of CdTe deposited on Au nanorods under CBS mode.



Figure 2.12: Cross section SEM images on coated Au nanorods on the same spot with (A) backscatter electron detector and (B) secondary electron detector.



Figure 2.13: Au nanorods substrates with different nanostructures. (A)straight forward Au nanorods (B) nanorods trends to touching on the top (C) hierarchical nanostructured Au nanorods.

Substrate	(A)	(B)	(C)
Cd/Te ratio of			
codeposition CdTe	1.04	1.15	1.9
Cd/Te ratio of			
pulse deposition CdTe	0.98	0.92	1.2

Table 2.1. Cd/Te ratio of codeposited samples vs. pulse deposited samples on different nanostructured Au substrates as shown in Figure 2.12. The data were from EDX.

CHAPTER 3

CONFORMAL DEPOSITION OF ULTRATHIN CDTE FILMS ON AU NANOWIRE ARRAYS FOR PLASMON ENHANCED SOLAR ENERGY CONVERSION²

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Abstract

The conversion efficiency of sunlight to electricity by solar cell is largely depends on how much light can be absorbed. Here an ultra-thin CdTe films covered plasmonic Au nanorod structure was introduced to achieve solar energy conversion efficiency. The Au nanorod (Au NR) structures have broad absorption spectra, and can collect light efficiently even from regions of space beyond the geometrical boundaries. With CdTe deposited on this Au nanorod structures, a great increase was noticed compared to CdTe deposition on planar Au. In this study, electrochemical characterization and structural characterization were performed before measure photoperformance. SEM and the high resolution TEM studies demonstrate the high-quality and mono-disperse nanocrystals. Moreover, photocurrent of the CdTe-Au NR was further improved after heat treatment.

Introduction

Scientists have spent decades developing materials and devices to replace fossil fuels with environmental-friendly renewable energy. Big portion of renewable energy technologies rely on harvesting and storing energy from sun. The energy received from the sun for an hour is much more than all the energy consumed by humans in an entire year. ¹ This huge energy can be utilized through PV devices, which convert sunlight to electricity,² or by storing the energy in chemical fuels with a photochemical cell (PEC) by splitting water.³⁻⁶ No matter through which method, finding materials with strong absorption of solar spectrum and good photoactivity is the key.

Recently, plasmonic concentration and propagation have been recommended and confirmed as promising solutions for enhancing photovoltaic and photocatalytic performance in semiconductor/plasmonic metal hybrid nanostructures. Plasmonic nanostructures can improve solar energy conversion efficiency via photonic enhancement.⁷⁻⁸ They are usually patterned metal nanostructures made of gold, silver and copper which can active localized surface plasmon (LSP) resonances.

LSP was a plasmon that oscillates locally around the nanofeatures with a specific frequency when light interacts with features much smaller than the wavelength.⁹ The specific frequency is called LSPR. At resonance, the collective charge oscillations can create an electromegatic field with strength up to ~10³ times the incident field.¹⁰ In semiconductor/plasmonic metal hybrid nanostructures, where plasmonic nanostructures were appropriately incorporated with semiconductor materials, the high energy contained in the oscillating electrons or in the strong electric field can be relieved through heat, or be transferred to the adjacent semiconductor via (a) direct electron transfer (DET) and (b) plasmon-induced resonant energy transfer (PIRET),¹⁰ thereby can contribute to the photocurrent.¹¹ Also, plasmonic nanostructures can enhance the charge separation in the semiconductor,¹² which can further contribute to electrical or chemical energy.¹³

Plasmoic structure also showed strong absorption ability in the visible spectrum.¹⁴ For instance, when a plasmonic metal such as gold or silver is appropriately interfaced with a semiconductor it can act as a means of collecting light from a region outside the semiconductor absorber whose energy is nevertheless converted to e⁻-h pairs in the absorber. This would permit one to reduce the thickness of a rare but efficient solar material while collecting all the light falling on the device or redirecting light that would have been reflected or scattered away from

the absorber, into the absorbing film. In this way carriers can be produced in numbers that, in the absence of the plasmonic concentrator, would have required a much thicker device to achieve, thereby reducing the quantity of a rare or costly material used or its cost. Alternatively, properly engineered plasmonic nanostructures could be used to concentrate light into regions of space close to the carrier collecting surfaces once again allowing less semiconductor to be used and increasing the collection efficiency of carriers before recombination (Fig.3.1).

While many materials systems show promise for efficient plasmon induced energy conversion at metal/semiconductor hybrid nanostructures, nano-wire array geometries are of particular interest for solar energy harvesting.^{11,15} This is because: 1) coupled arrays of plasmonic nanowires have broad absorption spectra; 2) they can collect light efficiently even from regions of space beyond the geometrical boundaries of the nanostructure; 3) an array of closely spaced plasmonic nanowire arrays will harvest incident photons and concentrate their energy uniformly in the space between the nanowire arrays and medium above.

However, formation of core-shell plasmon/semiconductor nanowire-array structures so far has been mostly limited to colloidal synthesis which is difficult to assemble for solid-state device applications and/or uses expensive vacuum deposition tools. Here, we show for the first time that electrodeposition can be used as a powerful tool to deposit conformal layers of ultrathin CdTe films on gold nanowire arrays and investigate its optical and photoelectrochemical properties.

Briefly, a dense array of aligned gold nanorods serve as light harvest concentrator, covered with CdTe forming a Schottky metal/ semiconductor interface, which can collect and conduct hot electrons.¹⁴ From fabrication of the materials to various characterizations will be presented in this chapter.

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Experimental

For growth of CdTe, a codeposition solution consisted of 10 mM CdSO₄ (Sigma-Aldrich), 0.2 mM TeO₂ (Alfa Aesar 99.999% pure) and 0.1 M NaClO₄ (GFS) was used. Due to the low solubility of TeO₂ in water, TeO₂ was first dissolved in concentrated H₂SO₄ before being mixed with CdSO₄ solution. The pH is adjusted to 2.0 with NaOH (Fisher). The solution is made with 18 MQ water supplied from a Milipore water filtration system. Prior to the electrochemical study, all solutions were purged with N₂ for at least 1h. The quality of CdTe depends on deposition potential, flow control, concentration of the precursors. Here the condition was optimized based on previous work with -700mV as deposition potential and carful flow control. Approximately 30nm thick CdTe on Au NR was fabricated with grown time in 30mins.

Planar Au substrates for CdTe electrodeposition were 100 nm thick Au films on 5nm of Ti on glass, purchased from Evaporated Metal Films (Ithaca, NY), and were carefully degreased and rinsed with acetone and 18 MQ water followed by N₂-drying. They were then dipped in concentrated nitric acid for 30s, rinsed with 18 MQ water, and dried with N₂ again before being placed in an automated flow cell. Au nanorods substrates were fabricated using nanoporous anodized aluminum oxide (AAO) template.¹⁴ They were provided by Dr. Mubeen at the University of Iowa.

The flow cell used for CdTe deposition is a three electrode cell using a 3M silver/silver chloride (Ag/AgCl) reference electrode and an Au wire inlayed into the cell as the auxiliary electrode. All potentials are reported versus Ag/AgCl. Before deposition, the cell was flushed with 0.1 M H2SO4, and potential was swept between -200 and +1400 m to clean the Au surface. All deposits were carried out at room temperature.

The morphologies of materials were observed using a scanning electron microscope, FEI Teneo (FEI Co., Hillsboro, OR) equipped with EDAX. The detailed microscopic structure and chemical composition of the coaxial nanorods were characterized using a transmission electron microscope and energy dispersive X-ray spectroscopy (EDAX). The photoelectrochemical measurements were carried out in a three-electrode system. The electrolyte used in photoelectrochemical measurement was 0.1 M methyl viologen (1,1'-dimethyl-4,4'-bipyridinium) dichloride (MVCl₂) and 0.1 M potassium chloride (KCl) because MV²⁺ has the strong electron accepting ability and its radical cation (MV⁻⁺), which is produced by one electron reduction enjoys high stability.¹⁶ Silver/silver chloride (1 M KCl) (Ag/AgCl) and platinum coil were used as reference and counter electrode, respectively. A 300 W xenon lamp source fitted with AM 1.5 and IR filter was used to simulate sunlight with an intensity of 100 mW cm⁻² measured using a thermopile sensor (Newport). All linear sweep voltammetry measurements were carried out at a scan rate of 20 mV s⁻¹.

Results and Discussion

The fabrication of gold nanorods was summarized schematically in Figure 3.2. Aluminum film was deposit through ebeam evaporation on a flat gold covered Si substrate. The aluminum was then anodized in oxalic acid to form membrane of highly ordered nanoporous aluminum oxide (AAO). In order to widen pores and remove the barrier layer at the bottom of the nanopores, etching of AAO was performed in phosphoric acid. In the widened AAO template, ordered and vertically oriented gold nanorods (Au NR) were electrodeposited. After that, AAO template was dissolved away using strong base (NaOH). Then the gold nanorod array was conformally coated with 30 nm thick CdTe films using codeposition in a solution containing 10 mM CdSO₄ and 0.2 mM TeO₂. Scanning electron microscopy (SEM) images in Figure 3.3 further illustrated the main fabrication steps.

Electrodeposition results for CdTe growth on gold nanowire arrays were first presented. 90 cycles codeposition CdTe was deposited on a set of Au nanorods in different height (250nm, 300nm and 600 nm). Figure 3.3 is a potential and current vs. time diagram of first three cycles for sample S1, which was CdTe deposited on an array of 600nm Au NR. Basically each cycle included two sections: deposition at potential of -700mV and solution refreshment at open circuit potential (OCP). There was a reductive current in the deposition region and current was about zero when potential was at OCP. The deposition process had been precisely discussed in chapter 1, so here the detailed explanation of deposition was omitted.

In order to quantitatively determine the amount of the deposited CdTe, the total reduction charge was integrated, which was approximately 43200μ C. The geometry area of deposition as shown in Figure 3.4 (B) is 0.283 cm². Considering six electron process during the deposition, the thickness of the whole deposit is around 116 ML, approximately 62nm.

The SEM images of S1 under different detection mode were provided in Figure 3.5. Figure 3.5 (A) was an image under ETD (Everhart-Thornley Detector) mode which was a secondary electron detector mode. The morphology of the deposit exhibited was smooth and uniform. Further in Figure 3.4 (B), which was imaged under CBS (circular backscatter detector) mode, it was more directly noticeable that CdTe cover the brighter Au nanorods conformally. As heavier elements can backscatter more efficiently, Au appears brighter than CdTe in the image.

From SEM image of Figure 3.5 (B), the thickness of outer loop was estimated with a mean value of 30nm, indicating 30nm CdTe deposition covering Au nanorod. The thickness

seemed contradictory with the calculation showed earlier using reduction charge. Au nanoods substrate, more like array of small cylinders made of gold, thus the deposit covered along the rod and the top. So it makes sense that the total thickness calculated from deposition charge is two times of the thickness shown visually in SEM considering the deposition occurred on the wall of the cylinder as well.

The SEM images of CdTe deposited on 250nm and 300nm Au nanorods were shown in Figure 3.6, together with image of S1 (CdTe on 600nm Au nanorod) in the same magnification. In Figure 3.6(A), some nanorods were touching on the top due to poor control over the fabrication step of Au nanorods. Our collaborators have improved their fabrication process and more Au nanorod substrates of high quality are on the way. Figure 7 is transmission electron micrographs of an newly produced CdTe covered Au NR in 350 nm height. We can notice, CdTe cover Au NR conformally. Studies will be done on more CdTe-Au NR with different height.

The photoelectrochemical properties of CdTe-Au NR samples were characterized using a three-electrode setup with CdTe-Au NR as working electrode, platinum coil as counter electrode and Ag/AgCl as reference electrode. Figure 8 showed a linear sweep voltammetry measurement on three CdTe-Au nanorod samples in different height (250 nm, 300 nm and 600nm). Samples were measured in a solution of 0.1 M methyl viologen dichloride (MVCl₂) and 0.1 M potassium chloride (KCl) under chopped AM 1.5white light illumination at 100 mW cm⁻². Both dark and light currents were monitored simultaneously.

In Figure 3.8, Sample (A) barely showed any photoresponse due to the poor structure formed as shown in Figure 3.6 (A), where some Au nanorods were bundling together with a big chunk of Au formed on top. When deposition CdTe, this dendritic structure severely affect solution among the nanorod, which result in non-stoichiometric CdTe. EDX data of sample (A)

showed an average Cd/Te ratio of 1.86, which indicated excess Cd bulk formation. Bulk Cd might have reacted with MV^{2+} in the electrolyte, that's why there was a big background current even without illumination. On the other hand, sample (B) and (C) had almost zero background current. Their EDX results proved nearly 1:1 ratio of Cd to Te, and their SEM images in Figure 6 exhibited ordered, vertically stand nanorods structures. Sample (C) was 30 nm CdTe deposited on 600 nm Au nanorod, which so far exhibited the best photoperfomance with the highest photocurrent under illumination. Together with SEM images in Figure 3.6, we believed the increased photocurrent of sample (C) can be attributed to its high density, order structure and the increased length of Au nanorods.

A comparison between planar and nanorod structured Au substrates with same CdTe deposition condition was performed. Their photocurrent as a function of potential under chopped AM 1.5 white light illumination was plotted in Figure 3.9. The black line presented the photocurrent from CdTe film on planar Au substrate. The increase of photocurrent for CdTe on Au NR was due to the effective and broad light collection ability from Au plasmonic structure beneath the CdTe, which can absorb photons and transfer the hot electrons to CdTe, and contribute to photocurrent accordlingly. Light reflection was greatly suppressed on the array of nanorods, compared to a flat surface. Additionally, scattering between the nanorods will increase the optical path through CdTe film, thus enhance the optical absorption as well.¹⁷ Relatively small photocurrent from the planar sample can be attributed to a low electron transfer probability from bulk CdTe to surface.

To study the effect of post deposition heat treatment on the photoelectrochemical properties of CdTe-Au NR, sample (c) was annealed at 300 °C for 1 hour in a furnace. During the heat treatment, CdTe film will undergo some structure changes including improvement of

crystallinity,¹⁸ grain size,¹⁹ decrease in grain boundary defects and so on.²⁰⁻²¹ These structure change can reduce carrier recombination, thus the optical and electrical of the whole structure will be influenced accordingly. PEC results of non-annealed sample vs. annealed sample were shown in Figure 3.10.

From Figure 10, the photocurrent was greatly increased when sample S1 (CdTe-Au NR in 600 nm) was annealed at 300 °C. The annealing also affected the on-set potential, which got significant anodic potential shift of 0.166 V. It was in accordance with the literature that annealing has a promoted effect on the photoelctrochemical light conversion efficiency of nanorod stucutres.²²⁻²⁴

The reason of an enhanced PEC result after annealing can be attributed to a recrystallization of CdTe.²⁵⁻²⁶ During the high heat treatment, grains might be coalesced with number of grain boundaries decreased. Thus, decrease the carriers recombination probability, which improve the photoperformance.²⁷⁻²⁸ More investigations on effect of annealing temperature on photocurrent was on the way.

To evaluate donor concentration, a Mott-Schottky measurement of Cd-Au NR sample of 600 nm collected at a frequency of 1 kHz was presented in Fig.3.11, with (A) before annealing and (B) after annealing. The negative slope of M-S plot confirms p-type conductivity of CdTe deposited. Further, the flat-band potential (V vs, Ag/AgCl) was found to be 0.22 before annealing, and 0.25 after annealing, indicating an anodic shift after the annealing. Moreover, p type donor density was calculated from the Mott-Schottky equation as following:

 $1/C_{sc}^{2}=2/(\xi\xi_{0}eN_{A})(V_{fb}-V-K_{b}T/e)$

In the equation, e represents electron charge, \mathcal{E} the dielectric constant of CdTe, \mathcal{E}_0 the permittivity of free space, N_Ahole acceptor density and V is applied bias at the electrode, V_{fb}is the flatband potential, K_bis the Boltzmannconstant and T is the absolute temperature. The hole acceptor density of CdTe-Au NR sample was calculated to be $3.79*10^{19}$ cm⁻³ and $1.75*10^{18}$ cm⁻³ before and after annealing.

Conclusion

In this study, we show that by incorporating an array of gold nanorods, which function as a plasmonic structure with CdTe semiconductor, photoperformance of CdTe was greatly increased. The morphological, structure and composition studies were conducted to ascertain stoichiometric CdTe with smooth surface was conformally deposited and covered the Au nanorods completely. The photoelectrochemical results of three CdTe-Au NR samples with different NR height indicated that photocurrent sensitively depended on the length or/and morphology of the Au nanorod substrate. CdTe-Au NR in 600 nm height exhibited the highest photocurrent and same time with the lowest dark current. Further, post deposition annealing was performed on this 600 nm CdTe-Au NR sample. The higher photocurrent with a positively shifted on-set potential after annealing indicated the profound effect of post heat treatment on the photoperformance of the structure. Thus, enhanced power conversion efficiency can be expected for a PV device based on this nanorod structures.

Acknowledgements

Support from the National Science Foundation, DMR 1410109, is gratefully acknowledged. Thanks are extended to Chris Fleisher and the UGA Microprobe lab.
References

1. Lewis, N. S.; Nocera, D. G., Powering the planet: Chemical challenges in solar energy utilization. Proceedings of the National Academy of Sciences 2006, 103 (43), 15729.

2. Grätzel, M., Photoelectrochemical cells. Nature 2001, 414, 338.

3. Fujishima, A.; Honda, K., Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 1972, 238, 37.

4. Heller, A., Conversion of sunlight into electrical power and photoassisted electrolysis of water in photoelectrochemical cells. Accounts of Chemical Research 1981, 14 (5), 154-162.

5. Khaselev, O.; Turner, J. A., A monolithic photovoltaic-photoelectrochemical device for hydrogen production via water splitting. Science 1998, 280 (5362), 425-427.

6. Khan, S. U.; Al-Shahry, M.; Ingler, W. B., Efficient photochemical water splitting by a chemically modified n-TiO2. science 2002, 297 (5590), 2243-2245.

7. Park, J.-E.; Kim, J.; Nam, J.-M., Emerging plasmonic nanostructures for controlling and enhancing photoluminescence. Chemical science 2017, 8 (7), 4696-4704.

8. Tamirat, A. G.; Rick, J.; Dubale, A. A.; Su, W.-N.; Hwang, B.-J., Using hematite for photoelectrochemical water splitting: a review of current progress and challenges. Nanoscale Horizons 2016, 1 (4), 243-267.

9. Willets, K. A.; Van Duyne, R. P., Localized surface plasmon resonance spectroscopy and sensing. Annu. Rev. Phys. Chem. 2007, 58, 267-297.

10. Cushing, S. K.; Wu, N., Plasmon-enhanced solar energy harvesting. The Electrochemical Society Interface 2013, 22 (2), 63-67.

11. Mubeen, S.; Lee, J.; Lee, W.-r.; Singh, N.; Stucky, G. D.; Moskovits, M., On the plasmonic photovoltaic. ACS nano 2014, 8 (6), 6066-6073.

12. Wu, X.; Thrall, E. S.; Liu, H.; Steigerwald, M.; Brus, L., Plasmon induced photovoltage and charge separation in citrate-stabilized gold nanoparticles. The Journal of Physical Chemistry C 2010, 114 (30), 12896-12899.

13. Tatsuma, T.; Nishi, H.; Ishida, T., Plasmon-induced charge separation: chemistry and wide applications. Chemical science 2017, 8 (5), 3325-3337.

14. Lee, J.; Mubeen, S.; Ji, X.; Stucky, G. D.; Moskovits, M., Plasmonic photoanodes for solar water splitting with visible light. Nano letters 2012, 12 (9), 5014-5019.

15. Mubeen, S.; Lee, J.; Singh, N.; Krämer, S.; Stucky, G. D.; Moskovits, M., An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. Nature nanotechnology 2013, 8 (4), 247.

16. Peon, J.; Tan, X.; Hoerner, J. D.; Xia, C.; Luk, Y. F.; Kohler, B., Excited state dynamics of methyl viologen. Ultrafast photoreduction in methanol and fluorescence in acetonitrile. The Journal of Physical Chemistry A 2001, 105 (24), 5768-5777.

17. Belaidi, A.; Konenkamp, R., Solar Cell with Extreme Thin Absorber on Highly Structured Subtrate". Semiconductor Science Technology 2003, 18, 475-479.

18. Rahman, K.; Haque, F.; Khan, N.; Islam, M.; Alam, M.; AlOthman, Z.; Sopian, K.; Amin, N. In Influence of thermal annealing on CdTe thin film deposited by thermal evaporation technique, Developments in Renewable Energy Technology (ICDRET), 2014 3rd International Conference on the, IEEE: 2014; pp 1-4. 19. Luschitz, J.; Siepchen, B.; Schaffner, J.; Lakus-Wollny, K.; Haindl, G.; Klein, A.; Jaegermann, W., CdTe thin film solar cells: Interrelation of nucleation, structure, and performance. Thin Solid Films 2009, 517 (7), 2125-2131.

20. Enríquez, J. P.; Mathew, X., The effect of annealing on the structure of CdTe films electro-deposited on metallic substrates. Journal of crystal growth 2003, 259 (3), 215-222.

21. Major, J. D., Grain boundaries in CdTe thin film solar cells: a review. Semiconductor Science and Technology 2016, 31 (9), 093001.

22. Schierhorn, M.; Boettcher, S. W.; Kraemer, S.; Stucky, G. D.; Moskovits, M., Photoelectrochemical performance of CdSe nanorod arrays grown on a transparent conducting substrate. Nano letters 2009, 9 (9), 3262-3267.

23. Amano, F.; Mukohara, H.; Shintani, A., Rutile Titania Particulate Photoelectrodes
Fabricated by Two-Step Annealing of Titania Nanotube Arrays. J. Electrochem. Soc. 2018, 165
(4), H3164-H3169.

24. Dondapati, H.; Ha, D.; Pradhan, A., Enhanced photocurrent in solution processed electronically coupled CdSe nanocrystals thin films. Applied Physics Letters 2013, 103 (12), 121114.

25. Romeo, A.; Bätzner, D.; Zogg, H.; Tiwari, A., Recrystallization in CdTe/CdS. Thin Solid Films 2000, 361, 420-425.

26. Qi, B.; Kim, D.; Williamson, D.; Trefny, J. U., Effects of Postdeposition Heat-Treatment on Morphology and Microstructure of CdTe Grown by Electrodeposition. J. Electrochem. Soc. 1996, 143 (2), 517-523.

27. Card, H. C.; Yang, E. S., Electronic processes at grain boundaries in polycrystalline semiconductors under optical illumination. IEEE Trans. Electron Devices 1977, 24 (4), 397-402.

28. Romeo, A.; Artegiani, E.; Menossi, D., Low substrate temperature CdTe solar cells: A review. Sol. Energy 2018.



Figure 3.1: Schematic of properly engineered plasmonic nanostructures used to concentrate light into near region.



Figure 3.2: Schematic of gold nanorod fabricated using porous anodic aluminum oxide (AAO) template. (1)Aluminum was deposited on Au covered Si substrate. (2) Anodization of aluminum in oxalic acid to AAO. (3)Subsequent etching to widen pores and remove the barrier layer at the bottom (4) Electrodeposition of Au. (5) Remove AAO template in NaOH.



Figure 3.3: SEM images of one CdTe-Au NR sample in different fabrication steps. (A) AAO template used to fabricate Au nanorod array (B) Bare Au nanorod array after AAO had been dissolved away (C) Au nanorods with CdTe conformally covered.



(A)

Figure 3.4: (A) Potential and current vs. time diagram for sample S1 with ~20nm CdTe deposited on '600 nm' Au NR. Only first three cycles were shown here. (B) Visual image of S1.



Figure 3.5: SEM of sample S1, CdTe on 600nm'Au NR. (A) under secondary electron detector,

(B) under backscatter electron detector



Figure 3.6: SEM image of CdTe deposition on Au nanorod in different height: (A) 250 nm(B)300 nm (C) 600 nm.



Figure 3.7: High resolution transmission electron micrographs of a newly produced CdTe covered Au NR with a 350 nm height.



Figure 3.8: Current density vs. potential (J-V) curves obtained under chopped AM 1.5white light illumination at 100 mW cm-2 from three CdTe-Au NR samples with different height: (A) 250 nm (B)300 nm (C) 600 nm. AM 1.5 simulated sunlight at 100mWcm-2 was used. CdTe was deposited using the same method.



Figure 3.9: Comparison of CdTe on Au slide and on '600 nm' Au nanorods, S1: co-deposition CdTe on '600 nm' Au nanorods, SR4: co-deposition CdTe on planar Au slide.



Figure 3.10: PEC results of sample S1 before and after annealing. S1 is CdTe-Au NR in 600 nm height.



Figure 3.11: Mott-Schottky measurement collected from CdTe-Au NR (A) before and (B) after annealing. Measurement was performed at a frequency of 1 kHz.

CHAPTER 4

CU AND AU FILMS EPITAXIAL DEPOSITION BY SURFACE LIMITED REDOX REPLACEMENT (SLRR) ON METAL SUBSTRATE³

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Abstract

Epitaxial Cu and Au films were deposited on metal substrates by surface limited redox replacement (SLRR) using cadmium as sacrificial element. A Cu²⁺ electrolyte was used to replace the UPD Cd at an open circuit potential (OCP). A detailed experimental approach for carrying out SLRR deposition cycle was described, including the study of UPD potentials of the sacrificial layer, the exchange time for the deposited layer and so on. After a well-studied Cd-Cu SLRR cycle was established, (A-B SLRR, indicted A as a sacrificial metal and is replaced by metal B), a uniform and reasonably flat metal thin film of Cu was produced by multiple repetition of SLRR cycles. Characterization of deposited Cu films was performed by electrochemically stripping Cu films in blank solution. A linear growth of Cu stripping charge with repetitive cycle numbers indicated a layer-by–layer growth behavior of Cu layer. And the same SLRR cycles was then employed to deposit Au layer by using AuCl₃ solution.

Introduction

The growth of uniform, smooth and continuous metal and alloy layers can be of paramount importance in a lot of practical fields, such as corrosion protection application,¹⁻² fuel cell electrocatalysts,³ electrocatalytic activity towards CO oxidation⁴ and methanol oxidation⁵, ultra large scale integrated circuits (IC) metallization⁶⁻⁸ and so on. For ultra-large-scale integrated circuit (IC) metallization, aluminum⁹⁻¹⁰ and copper¹¹ were the main metal for interconnections. While Al interconnection is prone to voids formation because of electromigration, Cu has been an attractive interconnector material due to its high electrical

conductivity (40% lower resistance than Al) and excellent electromigration.^{6,12-13} Therefore, there is a significant need for fine control of Cu layer deposition.

In industry, a damascene process is used for Cu interconnection on ultra large scale integrated circuits (IC). A seed layer of Cu is required to start with. And after the formation of a seed layer, a bulk Cu layer is deposited using a wet electrochemical method. For smoother layers to further deposit on, the seed layer should be uniform, smooth, and conformally cover the trenches used to hold the Cu interconnects. Because high temperature can increase the mobility of the atoms and helps to form a uniform, smooth deposited layer that follow the morphology of the substrate beneath, the seed layer usually deposited at high temperature vacuum based method, such as sputter deposition,¹⁴ physical vapor deposition (PVD),¹⁵ and chemical vapor deposition.¹⁶ However, one of the shortcomings of high temperature is decreasing the resistivity of the Cu film. Alternative approaches to produce the ultra-thin seed Cu layer need to be explored.

Another concern about high temperature vacuum base technology is it is difficulty to coat small sized features conformally. According to Moore's law,¹⁷ the dimensions of the integrated circuits continue to scaled down every year. Vacuum based sputter process become problematic as it cannot deposit thin layers uniformly when feature sizes reduced to nanometer scale. Alternative technologies like molecular beam epitaxy, chemical vapor deposition using organometallic precursors (MOCVD),¹⁸ plasma-enhanced chemical vapor deposition are thus developed to overcome this problem. However, the growth of so usually leads to 3D cluster formation and non-uniform coverage even under ultra-high vacuum.¹⁹

Electrochemical atomic layer deposition is an alternative technology designed for high quality metal deposition. It controls the film deposited layer by layer in atomic layer scale by employing underpotential deposition (UPD) and redox replacement reaction.²⁰⁻²¹ Underpotential deposition (UPD) 22 is a phenomenon where one element (M₁) can be deposited on a second element (M₂) at potential prior to that needed to deposit on itself. In simple word, one element is more likely to bond to a different kind element than bonding to the same kind, due to the free energy of compound formation. It is a surface limited reaction because once the surface of M₂ is fully covered by an atomic layer of M₁, there is no space for M₁ to deposit except on predeposited M₁ so the reaction terminates accordingly. Not all the metal can be deposited at a under potential because of the sluggish electrodeposition kinetics like Au and Pt.²³

Redox replacement (galvanic displacement) is a well-known process where ions of a more noble element can oxide a less noble element. No external power supply or reducing agent is required for this process. The mechanism of reduction replacement is the differences in electrochemical redox potentials of two elements. When UPD is used first to form a metal layer less than 1 monolayer, the nobler element formed accordingly is also less than 1 monolayer. In a word, the interaction between the two kinds element was in atomic scale. The whole process was surface limited due to UPD deposition of the first kind, so it was referred as surface limited redox replacement (SLRR). Thin films with desired thickness can be produced by multiple repetition of the SLRR cycle.

This atomic level controlled SLRR deposition method can be applied on a wide range of metals. In this chapter we focused on using SLRR to deposit Cu and Au films. There are extensive studies for Au SLRR deposition, Pb is usually used as sacrificial metal.²⁴⁻²⁵While the growth of Au film usually results in dendritic structure²⁶ or 3D layer²⁴ due to Au nucleation and

growth. Successful formation of smooth, continuous thin films of Cu and Au can benefit integrated circuits (IC) metallization and many other practical fields where deposition of ultrathin metal films is needed.

Experimental

Cu and Au films were prepared on Au substrates using SLRR method. The electrolyte for electrodeposition of Cd contained 10 mM CdSO₄ (Sigma-Aldrich), 0.1 M NaClO₄ (GFS) and 0.45 M H2SO₄ (Fisher). The Cu electrolyte was consisted of 0.1mM CuSO₄-5H₂O (Sigma-Aldrich,99.99%) and 0.45M H₂SO₄. The electrolyte for Au included 0.1mM AuCl₃ (Aldrich,99.99%) and 0.1 M NaClO₄ (GFS). All solutions were made with 18 MQ water supplied from a Milipore water filtration system and were adjusted to pH 2 with NaOH (Fisher). Prior to the electrochemical study, solutions were purged with N₂ for at least 1h. Au substrates were 100 nm thick Au films on 5nm of Titanium on glass, purchased from Evaporated Metal Films (Ithaca, NY). Before use, Au substrates were carefully degreased and rinsed with acetone and 18 MQ water followed by N₂-drying. They were then dipped in concentrated nitric acid for 30s, rinsed with 18 MQ water, and dried with N₂ again.

An automated flow-cell system was employed to finish all the electrochemisty study and deposit metal films. It is a three electrode cell using a 3M Ag/AgCl reference electrode and an Au wire inlayed into the cell as the auxiliary electrode. All potentials were reported versus Ag/AgCl. Before deposition, the cell was flushed with 0.1 M H₂SO₄, and potential was swept between -200 and +1400 m at scan rate of 10mV/s for three to five cycles to clean the Au surface. All deposits were carried out at room temperature.

Results and Discussion

In Cd-Cu SLRR, Cd was used as the sacrificial metal and it was deposited at under potential to form a Cd layer less than on monolayer. Then metal ion solution (Cu^{2+} or Au^{3+}) then flowed in at open circuit potential and reduced by the Cd⁰ on the substrate. Because Cu²⁺ (or Au³⁺) has a lower oxidation potential than Cd²⁺, the Cd will be oxidized to Cd²⁺ and left in the solution with Cu²⁺(Au³⁺) reduced on the surface.

The relative potential range for Cd UPD deposition was first determined by the cyclic voltammetry measured in 10 mM CdSO₄ solution (Figure 4.1). A small reduction peak first showed up at -50mV (a) which was the UPD of Cd. As potential was scanned more negatively, a bulk deposition peak was observed starting at -600mV. The sharp peak showed up after-650mV was due to hydrogen evolution. During the subsequent scan in positive direction, a corresponding bulk oxidation peak and the alloy stripping shoulder were indicated on the figure as peak b'. And the oxidation of UPD Cd was always noticeable at -50mV on the positive scan.

To form a UPD-Cd adlayer, the potential used should be smaller (more positive) than the equilibrium potential of Cd^{2+}/Cd to prevent bulk Cd deposition and also Cd-Au alloy should be minimized. Therefore taking into account that the equilibrium potential of the Cd^{2+}/Cd was around -800 mV and knowing that at -700mV incorporation of Cd into Au substrate occurred as witnessed in the CV curves in Figure 4.1, the UPD of Cd was first studied and quantified at a potential range of -300mV to -650 mV.

Figure 4.2 is a potential, current vs. time diagram of UPD Cd deposition and stripping which was used to quantify the deposited Cd. The UPD Cd was deposited at -300mV for 15s and then stripped off by scanning potential positively to 750mV in a blank solution. The positive

potential limit was chosen to be anodic to the most positive stripping peak of the Cd metal.²⁴ Following the black dash line marked on Figure 4.2, a peak showed up at potential of -100mV. This oxidative peak was assigned as UPD Cd oxidation but a 50mV peak shift was noticed by comparing the oxidative peak showed up at -50mV in the cyclic voltammetry (Figure 4.1). The explanation is that the cyclic voltammetry was performed in a Cd²⁺ solution while in Figure 4.2, Cd was stripped in a blank solution, meaning no Cd²⁺ near the surface. According to Le Châtelier's Principle, the equilibrium will shift right (product side) due to decrease in product concentration. So the stripping of Cd in a zero Cd²⁺ environment will be easier than in a Cd²⁺ solution, thus the stripping (oxidation) peak showed up earlier (at a more negative potential).

By analyzing the subsequent anodic stripping curves in Figure 4.2, the oxidation charge was integrated to be 193 μ C, equivalent to 0.22 monolayer (ML). Here on ML is defined as one deposited atom for one Au (111) substrate atom. The atomic density of Au (111) surface was about 1.17*10¹⁵ atom/cm².²⁷ To investigate the dependence of Cd deposition amount on the UPD potential, a series of deposits were obtained using different potentials for 15s then stripped in a blank solution. Their stripping peaks were compared in Figure 4.3 and the corresponding charge and coverage in ML were shown in Figure 4.4.

In Figure 4.3, a broad peak of alloy/ bulk stripping was seen for the deposits performed at -600 mV and -650mV (blue and purple line), indicating too much deposition were formed at these potentials. So -500mV was chosen as the UPD potential to deposit Cd in a Cd-Cu SLRR cycle since it resulted in the highest UPD stripping peak of 334 μ C at -200mV without the bulk stripping peak indicating the complete of Cd UPD. Base on the integrated charge of 334 μ C, approximately 0.38 ML of Cd were formed on Au substrate.

To illustrate the Cd-Cu SLRR process, Figure4.5 is a schematic of the SLRR cycle used to form Cu thin film in the present study. One Cd-Cu SLRR cycle was composed of a sequence steps: an initial UPD-Cd was grown on Au slide for 15s at -500mV followed by rinsing with blank to flushing out the Cd^{2+} electrolyte. After this, Cu^{2+} was flushed into the cell for 10s at open circuit simultaneously an exchange of the Cd atoms for Cu occurred (Step (b) and (c)). And then blank solution flowed in for another 5s to remove excess ions in the cell leaving a monolayer of Cu on the surface. The potential and current vs. time diagram for 1 Cd-Cu SLRR cycle was shown as the first 35s in Figure 4.6 (A).

In order to quantitatively determine the amount of the deposited Cu, stripping of accordingly grown layers was carried out by positive potential scans in blank solution which was shown in Figure 4.6 (A), after 35s. In Figure 4.6 (A), only one peak showed up at 200mV which is in accordance with the Cu UPD oxidation peak showed in Figure 4.7. And No Cd peak was observed to ascertain no trace of Cd incorporation into the deposited Cu.

As first try, the time of Cu replacement in Figure 4.6(A) was 10s. A study to optimize the exchange time was done by performing a series of experiments using different Cu exchange time. The corresponding UPD-Cu stripping charge was listed in Table 4.1. In a Cd-Cu SLRR process using -500mV as deposition potential for UPD Cd, the reduction charge from deposited Cd was 334μ C. From the data in Table 4.1, Cu stripping charge reached 328μ C when given 20s for exchange, indicating the completion of the replacement. (Here the Cu oxidation charge was 98% of Cd deposition charge, considering there may be trace amount of oxygen in the solution which might be reduced and contribute to the reduction charge, 98.2% was big enough to believe all Cd had been exchanged.)

Time needed for Cu^{2+} replacement can also be estimated by observing the open circuit potential. For example, starting from 15s in Figure 4.6 (A), the open circuit potential began to shift from -500mV where Cd was deposited, up to -200mV due to Cu^{2+} flow in. While the equilibrium potential for Cu^{2+}/Cu was near 0 mV, so the cutoff of potential of -200mV is a mix potential which is an indication of non-completion of exchange for Cu. In the case where 20s was given for Cu exchange (Figure 4.6(B)), open circuit potential stabilized near 0mV upon a complete exchange. Therefore, the optimized exchange time for Cu^{2+} was set to be 20s.

With optimized Cd UPD potential and Cu^{2+} exchange time, one cycle of Cd-Cu SLRR was established as follows: (i)deposit UPD Cd at -500mV in CdSO4 solution for 15s, (ii) flow in blank solution for 5s at OCP to rinse away excess Cd^{2+} , (iii) Cu solution flowing in at OCP for 20s, (iv) rinse with blank solution for 5s at OCP.

After one cycle of Cd-Cu SLRR was established, Cu films were formed by multiple repetition of one cycle. To prove the layer-by-layer growth behavior of Cu, films formed by different number of cycles were stripped in a blank solution, and the amount of Cu was estimated according to the striping charge. In Figure 4.8, the Cu stripping charge vs. cycle number was plotted. And the Cu strip charge was directly proportional to the number of cycles performed. A linear date with R^2 = 0.99 was obtained using the established Cd-Cu SLRR cycle.

The proposed layer-by-layer growth method offers a feasible atomic deposition capability for fabrication of Cu films. Based on successful establishment of the linear growth by repeating SLRR cycle, a thin film of Cu was produced by using 50 cycles of SLRR mentioned before. Figure 4.9 showed the current and potential vs. time diagram for 50 cycles Cd-Cu SLRR deposition. For each cycle, the open circuit potential shifted to near 0 mV and stabilized indicating the replacement is completed. Every five cycles, Cd reduction charge was analyzed and coverage in ML was calculated. The data was listed in the Table in Figure 4.9. An average reduction charge corresponding to 0.58ML/cycle was achieved during the whole deposition process. The steady Cd deposition charge with the number of deposition cycles (1-50) is an indication of unchanged surface texture and roughness as Cu film growth on the substrate. This conclusion could be further confirmed by the homogeneity and morphology study performed by SEM.

In Figure 4.10, the SEM images of bare Au substrate and Cu films formed was shown. The morphology of Cu film was equivalent with that of the bare Au substrate without Cu nucleation formation.

To establish a comparison with conventional electrodeposition method, a Cu thin film with relatively same thickness was produced using electrodeposition. The deposition condition was -100mV in 0.1 mM CuSO₄ solution for 15min.

The SEM image of electrodeposited Cu film was shown in Figure 4.11, with the EDX date acquired along the line. A rough morphology was observed with Cu nucleus distributed across the surface. The elemental composition of the Cu films deposited by two different methods was investigated using EPMA with data shown in Table 4.2. Line 1-5 was acquired from top to the bottom on the samples. Table 4.2 (A) was from Cu film produced by 50 Cd-Cu SLRR cycles and (B) was from Cu film by electrodeposition. Cu Atomic percent was very close for these two samples, indicating the relatively similar thickness of the two Cu films.

To compare the morphology of two Cu films, the SEM image was provided in Figure 4.10 (B) and Figure 4.11 (A) respectively. Clearly the Cu films formed by SLRR method proved to be more uniform, smoother with no nucleus development, thus proved the success of SLRR method to form a conformal, continuous metal layer.

After Cd-Cu SLRR has been confirmed as a promising method for forming good quality Cu thin films, Au films were produced by repeating the same SLRR cycle. In each cycle, parameters were kept the same with the only difference being AuCl3 solution was flown in after UPD Cd deposition and perform an exchange between UPD Cd and Au instead of using Cu. A potential and current vs. time diagram of an example of 30 cycles Cd-Au SLRR was provided in Figure 4.12.

It could be clearly seen that in each cycle, during the exchange potential increased readily to equilibrium potential of Au³⁺/Au at 1000mV, indicating a completion of Cd-Au exchange. SEM of the corresponding Au film produced by 30 cycles of Cd-Au SLRR was shown in Figure 4.13, together with an image of bare Au substrate. We noticed that the deposited Au film followed the structure and morphology of the underlying Au substrate, and the image was in a better resolution. The author believed that was due to the lower resistivity of the deposited Au films compared to the Au substrate purchased.

It was worth to note that the surface diffusivity of Au was lower than Cu, with surface diffusion coefficient (Ds) of Au in the order of 10⁻¹⁴cm²s⁻¹²⁸ and for Cu was in the order of 10⁻⁶ cm²s⁻¹.²⁹ While here both Au and Cu films exhibited similar flat morphology when using the same SLRR method, meaning there was no diffusion limitation during the Cd-metal (Cu or Au) replacement event. It was believed a good control over the UPD Cd deposition played an important role in this diffusion limitation-free exchange process. According to literature, metals with slow kinetics such as Au can exhibit a film with 3D clusters formation even the system was thermodynamically expected to grow in 2D mode.¹⁹

At last, EDX was measured on several spots of the Au film, and there was no Cd signal in any of the measurement, which further concluded that no trace Cd was left or incorporated in the grown Au film.

Conclusion

This chapter introduced a new deposition technique using UPD-Cd as a sacrificial layer and surface limited redox replacement (SLRR) as a method to deposit Cu ultra-thin films. To optimize the SLRR cycle, several parameters were studied from Cd UPD potential to Cu solution exchange time. Based on the optimized cycle information, Cu films with controllable thickness were produced by multiple repetitions of SLRR cycles with great linear growth with respect to cycle numbers.

To establish a comparison, conventional electrodeposition was used to produce a Cu film with comparable thickness with the one made using SLRR method. Like many other metal depositions methods,³⁰⁻³¹conventional electrodeposition of Cu illustrated a tendency to nucleation and growth in Cu clusters.³² In contrast to conventional electrodeposition, no Cu nanoclusters were observed on the Cu film formed by SLRR method. And both EPMA and EDX results confirmed there was no Cd incorporation in the formation of the Cu films when Cd was used as sacrificial metal in the deposition process. The same SLRR method was also proved to be success when using AuCl₃ to deposit smooth, flat and homogenous Au film.

Within a conclusion, SLRR method established here showed strong ability to produce continuous uniform metal films covering the entire substrate. The present SLRR technique will be useful for many applications where conformal metal coating is required. Besides, using Cd as sacrificial metal also broaden the application of SLRR method for growth of many other metals such as Ni, Co whereby most used sacrificial metals Pb, Cu cannot work.

Acknowledgements

Support from the National Science Foundation, DMR 1410109, is gratefully acknowledged. Thanks are extended to Dr. Mubeen Group at University of Iowa; Chris Fleisher at UGA and the UGA Microprobe lab.

References

1. Van Phuong, N.; Park, M.-S.; Yim, C. D.; You, B. S.; Moon, S., Corrosion protection utilizing Ag layer on Cu coated AZ31 Mg alloy. Corrosion Science 2018, 136, 201-209.

 Chen, X. B.; Yang, H. Y.; Abbott, T. B.; Easton, M. A.; Birbilis, N., Corrosion-Resistant Electrochemical Platings on Magnesium Alloys: A State-of-the-Art Review. Corrosion 2012, 68 (6), 518-535.

Adzic, R. R.; Zhang, J.; Sasaki, K.; Vukmirovic, M. B.; Shao, M.; Wang, J. X.; Nilekar,
 A. U.; Mavrikakis, M.; Valerio, J. A.; Uribe, F., Platinum Monolayer Fuel Cell Electrocatalysts.
 Top. Catal. 2007, 46 (3), 249-262.

4. Strbac, S.; Petrovic, S.; Vasilic, R.; Kovac, J.; Zalar, A.; Rakocevic, Z., Carbon monoxide oxidation on Au(111) surface decorated by spontaneously deposited Pt. Electrochimica Acta 2007, 53 (2), 998-1005.

5. Du, B.; Tong, A Coverage-Dependent Study of Pt Spontaneously Deposited onto Au and Ru Surfaces: Direct Experimental Evidence of the Ensemble Effect for Methanol Electro-Oxidation on Pt. The Journal of Physical Chemistry B 2005, 109 (38), 17775-17780.

 Arita, Y.; Awaya, N.; Ohno, K.; Sato, M. In CVD copper metallurgy for ULSI interconnections, International Technical Digest on Electron Devices, 9-12 Dec. 1990; 1990; pp 39-42.

7. Andricacos, P. C., Copper on-chip interconnections. The Electrochemical Society Interface 1999, 8 (1), 6.

Adams, D.; Alford, T. L., Encapsulated silver for integrated circuit metallization.
 Materials Science and Engineering: R: Reports 2003, 40 (6), 207-250.

9. Ghate, P. B., Aluminum alloy metallization for integrated circuits. Thin Solid Films 1981, 83 (2), 195-205.

10. Fuller, C. R.; Ghate, P. B., Magnetron-sputtered aluminum films for integrated circuit interconnections. Thin Solid Films 1979, 64 (1), 25-37.

11. Hu, C. K.; Luther, B.; Kaufman, F. B.; Hummel, J.; Uzoh, C.; Pearson, D. J., Copper interconnection integration and reliability. Thin Solid Films 1995, 262 (1), 84-92.

Awaya, N.; Arita, Y., Double-level copper interconnections using selective copper CVD.
 Journal of Electronic Materials 1992, 21 (10), 959-964.

Gardner, D.; Bai, G.; Wittenbrock, S.; Ochoa, V.; Villasol, R.; Chiang, C.; Marieb, T.;
 Mu, C.; Fraser, D.; Bohr, M., Effectiveness and Reliability of Metal Diffusion Barriers for
 Copper Interconnects. 1995; Vol. 403.

14. Chin, B.; Ding, P. J.; Sun, B. X.; Chiang, T.; Angelo, D.; Hashim, I.; Xu, Z.; Edelstein,
S.; Chen, F. S., Barrier and seed layers for damascene copper metallization. 1998; Vol. 41, p
141-147.

15. Reid, J.; Mayer, S.; Broadbetrt, E.; Klawuhn, E.; Ashtiani, K., Factors influencing damascene feature fill using copper PVD and electroplating. 2000; Vol. 43, p 86-103.

 Proust, M.; Judong, F.; Gilet, J. M.; Liauzu, L.; Madar, R., CVD and PVD copper integration for dual damascene metallization in a 0.18 μm process. Microelectronic Engineering 2001, 55 (1), 269-275.

Schaller, R. R., Moore's law: past, present and future. IEEE Spectrum 1997, 34 (6), 52-

18. Röber, J.; Kaufmann, C.; Gessner, T., Structure and electrical properties of thin copper films deposited by MOCVD. Applied Surface Science 1995, 91 (1), 134-138.

 Dimitrov, N., Recent Advances in the Growth of Metals, Alloys, and Multilayers by Surface Limited Redox Replacement (SLRR) Based Approaches. Electrochimica Acta 2016, 209, 599-622.

20. Brankovic, S. R.; Wang, J. X.; Adžić, R. R., Metal monolayer deposition by replacement of metal adlayers on electrode surfaces. Surface Science 2001, 474 (1), L173-L179.

21. Brankovic, S.; Wang, J.; Adzic, R., New methods of controlled monolayer-to-multilayer deposition of Pt for designing electrocatalysts at an atomic level. Journal of the Serbian Chemical Society 2001, 66 (11-12), 887-898.

22. Kolb, D. M. G., H., Tobias, C. W., Eds.; John Wiley, Advances in Electrochemistry and Electrochemical Engineering. 1978, 11, 125.

Xim, Y.-G.; Kim, J. Y.; Vairavapandian, D.; Stickney, J. L., Platinum Nanofilm
Formation by EC-ALE via Redox Replacement of UPD Copper: Studies Using in-Situ Scanning
Tunneling Microscopy. The Journal of Physical Chemistry B 2006, 110 (36), 17998-18006.

24. Mitchell, C.; Fayette, M.; Dimitrov, N., Homo- and hetero-epitaxial deposition of Au by surface limited redox replacement of Pb underpotentially deposited layer in one-cell configuration. Electrochimica Acta 2012, 85, 450-458.

25. Fayette, M.; Liu, Y.; Bertrand, D.; Nutariya, J.; Vasiljevic, N.; Dimitrov, N., From Au to Pt via Surface Limited Redox Replacement of Pb UPD in One-Cell Configuration. Langmuir 2011, 27 (9), 5650-5658.

26. Hazzazi, O. A.; Attard, G. A.; Wells, P. B.; Vidal-Iglesias, F. J.; Casadesus, M., Electrochemical characterisation of gold on Pt{hkl} for ethanol electrocatalysis. J Electroanal Chem 2009, 625 (2), 123-130.

27. Thambidurai, C.; Kim, Y.-G.; Jayaraju, N.; Venkatasamy, V.; Stickney, J. L., Copper Nanofilm Formation by Electrochemical ALD. J. Electrochem. Soc. 2009, 156 (8), D261-D268.

28. Alonso, C.; Salvarezza, R. C.; Vara, J. M.; Arvia, A. J., The surface diffusion of gold atoms on gold electrodes in acid solution and its dependence on the presence of foreign adsorbates. Electrochimica Acta 1990, 35 (9), 1331-1336.

29. Hinatsu, J. T.; Foulkes, F. R., Diffusion Coefficients for Copper (II) in Aqueous Cupric Sulfate-Sulfuric Acid Solutions. J. Electrochem. Soc. 1989, 136 (1), 125-132.

Al Amri, Z.; Mercer, M. P.; Vasiljevic, N., Surface Limited Redox Replacement
 Deposition of Platinum Ultrathin Films on Gold: Thickness and Structure Dependent Activity
 towards the Carbon Monoxide and Formic Acid Oxidation reactions. Electrochimica Acta 2016,
 210, 520-529.

31. Nagahara, Y.; Hara, M.; Yoshimoto, S.; Inukai, J.; Yau, S.-L.; Itaya, K., In Situ Scanning Tunneling Microscopy Examination of Molecular Adlayers of Haloplatinate Complexes and Electrochemically Produced Platinum Nanoparticles on Au(111). The Journal of Physical Chemistry B 2004, 108 (10), 3224-3230.

32. Ambrozik, S.; Rawlings, B.; Vasiljevic, N.; Dimitrov, N., Metal deposition via electroless surface limited redox replacement. Electrochemistry Communications 2014, 44, 19-22.



Figure 4.1: Cyclic voltammetry of Au in a CdSO₄ solution consisted of 10 mM CdSO₄and 0.1 M NaClO₄in pH 2.



Figure 4.2: The Cd was deposited at -300mV for 15s, and then striped in a blank solution. Red line is current, blue line is potential. The black dash line was used to define potential where the peak showed up.



Figure 4.3: C-V of stripping of deposited Cd at different potential.



Figure 4.4: Integrated charge and ML of Cd deposited at different potentials.


Figure 4.5: Schematic, illustrating one cycle of Cd-Cu SLRR and by repeating the cycle a thicker Cu film formed.



Figure 4.6: Current and potential vs. time diagram for Cd-Cu SLRR process (A) Cu flushing in time is 10s, (B) Cu flushing in time is 20s.



Figure 4.7: Cyclic voltammetry of Au in a Cu solution of 0.1 mM CuSO4, pH 2.



Figure 4.8: Linear study of different cycles of Cd-Cu SLRR.



Figure 4.9: 50 Cd-Cu SLRR on Au substrate. (A) current and potential vs. time profile (B) Cd reduction charge for different cycles.



Figure 4.10: SEM images of (A) bare Au substrate and (B) Cu film formed by 50 cycles Cd-Cu SLRR using Cd deposition potential at -500mV and Cu exchange time of 20s.



Figure 4.11: SEM images of (A) conventional electrodeposition Cu film on Au substrate (B) EDX line scan of bright Cu particles, showing high signals of Cu compared to the background.



Figure 4.12: 30 cycles Cd-Au SLRR on Au slide. (A) Current and potential vs. time profile (B) Cd reduction charge for different cycles.



Figure 4.13: SEM images of (A) bare Au substrate and (B) Au film formed by 30 cycles Cd-Au SLRR using Cd deposition potential at -500mV and Au exchange time of 20s.

Cu ²⁺ flushing time (s)	10	15	20	30
UPD-Cu stripping charge	250 μC	327 μC	328 μC	203 µC

Table 4.1: Oxidative charge of SLRR deposited Cu when Cu flushing time varied from 10s to30s.

(A) LINE	Au AT%	Cu	I	(B) LINE	Au AT%	Cu
		AT%				AT%
1	93.20	7.09		1	92.99	7.17
2	93.14	7.03		2	91.34	8.77
3	92.85	6.99		3	91.90	7.16
4	90.96	9.12		4	90.07	10.40
5	89.00	11.09		5	82.85	17.40

Table 4.2: EPMA data for two Cu films made by different methods. (A) Cu film produced by 50 Cd-Cu SLRR cycles and (B) Cu film by electrodeposition.

CHAPTER 5

METAL THIN FILM EPITAXIAL DEPOSITION BY SLRR ON SEMICONDUCTOR

 $SUBSTRATE^4$

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Abstract

A recent result for surface limited redox replacement (SLRR) deposition of copper, gold thin films onto CdTe substrate was present in this chapter. Cd-Cu SLRR cycle established in chapter 4 was used to form Cu films on CdTe in different thickness. Electrochemical and SEM, EPMA characterizations of deposited Cu film show a conformal, flat morphology without roughness development for up to 30 cycles of Cd-Cu SLRR on CdTe. Due to strong oxidizing ability of Au³⁺, couples of parameters were adjusted to successfully form Au thin layer on CdTe. However, SLRR-produced Au films showed a tendency to nucleate and grow in clusters. This problem was then solved by using a smooth Cu layer as a template and Au³⁺ oxidized and replaced the whole Cu layer with careful time control.

Introduction

Couples of companies like BP and First Solar had commercialized thin film CdTe photovoltaic technology.¹⁻² The highest efficiency of laboratory CdTe solar cell was reported to be 22.1% ³ and the record for commercial CdTe PV module in market was 18.6% both by First Solar.⁴ The basic structure of a CdTe solar cell includes four layers: a transparent and conducting oxide layer (front contact), a buffer layer (or window layer), an absorb layer and metal back contact. The whole structure could be fabricated in substrate or superstrate configuration depending on the fabrication direction. The highest efficiency of CdTe solar cell was achieved by superstrate configuration start with a front contact.

CdTe is one of the most promising candidates for absorber layer due to its high absorption coefficient and ideal band gap (1.44-1.5 eV) for efficient solar energy conversion. But one of the shortcomings of CdTe absorb layer is the low carrier density. To enhance CdTe carrier concentration, Cu is one of the most used doping materials used and it can be incorporated in the CdTe or applying a Cu/metal layer at the back junction.⁵ But due to the high mobility of Cu, it can easily diffuse into bulk CdTe or into the interface between CdTe and CdS ⁶⁻⁷ which will severely affect the stability of the cell. Also, excessive Cu doping can result in device degradation due to the defect sites for the carriers to recombination and carrier lifetime was shorten to affect the cell performance. Furthermore, Cu might diffuse in to the CdS window layer ⁸ thus has deleterious effects on the property of CdS and whole cell. ⁷

High temperature are usually used for CdTe fabrication as it can provide enough energy for CdTe crystallization.⁹ The main high temperature process includes closed space sublimation,¹⁰⁻¹¹ sputtering,¹² and physical vapor deposition.^{11, 13} While, when physical vapor deposition or sputtering technology were used to fabricate the device, the high temperature makes it even harder to control Cu diffusion among the layer structured cell.¹⁴ One solution researchers used to solve the high temperature diffusion problem is to separate the deposition and heating stages.⁶ For example, to deposit a doped layer at room temperature and then followed by rapid thermal processing (RTP).¹⁵ Other concerns about high temperature vacuum based technology is the high cost, high energy consumption and sophisticated flow control. Therefore, it is of paramount importance to develop a cheap, versatile low temperature method to deposit thin Cu layers on semiconductors and have a good control over Cu diffusion issues.

Another application of ultra-thin metal layers on semiconductors is the tunneling layer for multijunction photovoltaics. Multijunction solar cell enjoys the highest solar conversion efficiency of 46%.¹⁶Usually multijunction solar cells are made of two or more p-n junctions with different bandgap materials and each junction (subcell) absorbs a part of the solar spectrum thus adding together, ideally can increase the range of the solar spectrum absorbed. However, there is a lot of issue need to solve like the lattice match between different junctions.¹⁷

Schottky multijunction solar cell is one form of multijuntion solar cell is. Instead of forming a junction between p-n semiconductor materials, in Schottky junction solar cell the junction was formed between a metal and semiconductor.¹⁸ When metal and semiconductor were brought together, there are two kinds of contact, Schottky contacts and Ohmic contacts. Schottky junction will be formed when there is a big difference in work functions between semiconductor and metal.

Electrodeposition is a quick, inexpensive and versatile method for metal film formation as it is readily controllable by potential or current. The metal deposition rate, its uniformity and other film properties depend on the electrolyte composition and the applied current and voltage. For electrodeposition study, metals are usually used as substrates as they have a well-defined surface topography such as Au (111) slides and high conductivity. Semiconductor substrates is seldom studied due to their complicated surface structure and low conductivity compared to metal substrates. In addition, the bonding between semiconductors and metals is usually very weak which can easily result in a 3D island growth on semiconductors.¹⁹

But as mentioned before, metal deposition on semiconductor plays an important role in many practical fields such as adding Cu/metal layer in PV device, forming metal-semiconductor contacts for Schottky junctions in solar industry, the integrated circuit metallization in electronics industry and so on. There are some studies on metal deposition on semiconductors including metal doping on semiconductors, ²⁰ metal films on Si²¹ and Ge substrates,²² but only a

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few concentrated on metal growth on compound semiconductor substrates. Herein, we introduce an electrochemical method (SLRR) that can introduce ultra-thin Cu films on the surface of CdTe at room temperature. As the whole process finished at room temperature, Cu diffusion issues can be avoided. To the best of our knowledge, there are no reports of utilizing SLRR method to deposit metal tunneling layer on CdTe substrate. The goal is to form homogenous thin metal layer (Cu or Au) on CdTe semiconductor surface.

In a Cd-Cu SLRR cycle, Cd sacrificial layer was first deposited at an under potential to form less than 1 ML coverage. Then Cu²⁺ solution was introduced at open circuit potential to replace UPD-deposited Cd. The reduction replacement is the result of the differences in redox potentials of two metals. The first step ensured the deposition in less than one monolayer of Cd, so the second step of Cu replacement is also less than on monolayer. And by repeating the cycle, a thin Cu film is formed through layer-by-layer growth. It is a versatile process which is suitable to yield a metallic coating on a variety of substrates.²³

Furthermore, a high-quality Au layer without roughness development was successfully formed by replacing a thin layer of Cu metal after carefully control the time and monitoring the potential change during the exchange. This approach accomplished even better result than obtained by multiple repetition of SLRR.

Experimental

An automated flow cell system (Figure 5.1) was used in metal deposition and electrochemical characterization experiments. The flow cell is a three electrodes cell with 3M Ag/AgCl serving as reference electrode and an Au wire inlayed into the cell as the auxiliary electrode. All potentials were presented with respect to Ag/AgCl. Before deposition, solutions were purged with N_2 for at least one hour.

The solution used was prepared as following: Cd containing electrolyte was a mixture of 10 mM CdSO4 (Sigma-Aldrich), 0.1 M NaClO₄ (GFS) and 0.45 M H2SO₄ (Fisher). The Cu electrolyte was consisted of 0.1mM CuSO₄-5H₂O and 0.45M H₂SO₄. The electrolyte for Au included 0.1mM AuCl3 (Aldrich,99.99%) and 0.1 M NaClO4 (GFS). All solutions were made with 18 MQ water supplied from a Milipore water filtration system and were adjusted to pH 2 with NaOH (Fisher). CdTe substrates used were deposited by optimized pulse deposition method described in Chapter 2. The deposition condition for CdTe was using -700 mV as cathodic potential and -500 mV as anodic potential. The pulse duration was same as in Chapter 2 with 300 milliseconds at cathodic and 500 milliseconds at anodic potential. Two sets of CdTe with different thickness were investigated as substrates with 30 pulse cycles and 90 pulse cycles thick respectively. All depositions were carried out at room temperature.

Cu and Au films were deposited on CdTe substrates respectively by multiple SLRR cycles. In SLRR cycles, to avoid contamination, Cd was chosen as a sacrificial metal because it is one of the composition elements in CdTe. And Cd²⁺/Cd formal potential is lower than Cu or Au so it can provide enough impetus for the redox replacement. Briefly, each cycle consisted of a UPD Cd formation at an under potential followed by a blank solution flushing in for 5s at open

circuit potential (OCP) to remove the excess Cd^{2+} ions. Then Cu^{2+} or Au^{3+} solution was introduced to the cell for certain time until the exchange was completed. The OCP changes were monitored during the exchange.

Results and Discussion

Following the optimized Cd-Cu SLRR cycle described in chapter 4, Cu films produced by 30 Cd-Cu SLRR cycles were deposited on different thickness of CdTe substrate. Here the thickness of CdTe was referred as pulse cycle numbers and there were two sets of thicknesses: 30 cycles and 90 cycles. The potential and time profile for 30 cycles Cd-Cu SLRR on 30 cycles of CdTe was shown in Figure 5.2. There were two sections: the first section within 700s was the pulse deposition of CdTe and the second section was 30 cycles Cd-Cu SLRR afterwards. Since pulse deposition of CdTe had been descripted in Chapter 2, here we only focus on the second section which was Cu deposition on CdTe. The positive limit of OCP during the exchange reached -200mV for the first 15 cycles of Cd-Cu SLRR and inthe following cycles stabilized at 0 mV, where was the equilibrium potential for Cu²⁺/Cu in the cycles afterwards. The positive limit of the OCP was used to determine the process of the Cu deposition on CdTe. The potential increases to 0 mV is an indication of masking off the CdTe substrate by the growing Cu layer.

It was worth noting that according to Pauling et al.²⁴ for the layer-by-layer deposition of metal films on metal substrate, two monolayers of metal deposition are sufficient for screening off the underlying substrate.²⁵However, for the results showed here when Cu film deposited on CdTe semiconductor compound substrate, it was not the case. The covering was no completed until 15 cycles. The author believed that due to the complicated surface structure of CdTe

substrate, the Cd atoms deposited must have penetrated CdTe matrix and some might fit into the Cd vacancy in CdTe. This explanation could also be supported by comparing the current and potential–time profile for Cd-Cu SLRR on 30 cycles CdTe and on 90 cycles CdTe in Figure 5.2 and 5.3. In Figure 5.3 where 90 cycles of CdTe was used as a substrate, the positive limit of OCP did not reach 0mV during the whole process. That was because some of the deposited Cd atom penetrated downwards and since there were more Cd vacancy sites available in thicker CdTe substrate, more cycles of Cd deposition were required to fill up and cover the underlying CdTe substrate.

The Cd reduction charge/cycle could also be used to further support the explanation. In the tables in Figure 5.2 and 5.3, Cd reduction charge and corresponding coverage (in ML) per cycle were list every 5 cycles. As we compare the two tables, Cd reduction charge on 90 cycles CdTe (Figure 5.2 (B)) was bigger than on 30 cycles CdTe (Figure 5.1(B)). Again, more Cd deposition / cycle were due to more Cd vacancy sites available in thicker CdTe substrate. The comparison was further shown in Figure 5.4.

Another interesting phenomenon was Cd reduction charge was decreasing with the cycle number during the whole process no matter CdTe of which thickness was used as substrate (Figure 5.4), suggesting that the surface area was decreasing. The decreasing area was believed due to a smoother surface forming as Cu films were covering the CdTe surface. In Figure 5.5, SEM of CdTe substrate and Cu film grown by 30 Cd-Cu SLRR cycles on top of the substrate were shown. From the SEM, it was noticeable that the deposited Cu layer followed the morphology of the underlying CdTe layer and was smoother and more continuous. A flattening of the surface during Cu film formation was also consisted to the literature.²⁶ The morphology of

Cu film produced on CdTe substrates in different thickness were also studied using SEM as shown in Figure 5.6.

When Cu films were deposited on CdTe substrate using Cd-Cu SLRR method, we notice the Cd deposition amount (Figure 5.3 (B)) is larger than that on Au substrate (Figure 4.9 (B)) in Chapter 4). Especially at the beginning of the SLRR growth presented in the tables in Figure 5.2 and 5.3, the reduction charge for Cd/cycle is more than 1 ML. To study the behavior of Cd²⁺ on CdTe electrode, a cyclic voltammetry (CV) of CdTe in CdSO₄ solution was performed in Figure 5.7. As a comparison, CV result of Au in CdSO₄ solution with same concentration was displayed in Figure 5.8.

Even the composition of electrolyte, potential scanning range, scan rate (10mV/s) were all the same in Figure 5.7 and 5.8, a great difference was noticeable. At same potential range, the oxidation peak(s) of Cd on CdTe substrate was much bigger than on Au substrate. In Figure 5.7, the oxidation peak (A) was first showed up at-100mV. As the potential limit pushed more negative, the oxidation peak of Cd shifted positively and after-400mV a second oxidation peak appeared and eventually the two peaks merged into a big one (B) at 150mV during the subsequent scan in positive direction.

On Au substrate, there is only one UPD feature showed up at -50 mV on the anodic scan. There could be several reasons for the excess deposition of Cd on CdTe, such as the area increased due to surface roughness, Cd vacancies in the CdTe substrate. More study and research need to be done to fully understand the behavior of Cd^{2+} on CdTe surface.

For Au thin film deposition on CdTe, the same Cd-Cu SLRR cycle parameters was first employed in AuCl₃ solution on 30 and 90 cycles of CdTe. Current and potential vs. time diagrams were shown in Figure 5.9 and 5.10. What need to keep in mind is the formal potential of Au^{3+}/Au (~1100 mV) was much positive than the oxidation potential of CdTe (~400mV). So the OCP change during the exchange process should not exceed the oxidation potential of CdTe thus could not be used to estimate the completion of exchange as did on Au substrate in Chapter 4.

However, the Cd reduction charge was still informative. Cd reduction charge /cycle were increasing during the whole deposition process as shown in Figure 5.9 (B) and 5.10 (B). (The first cycle in Figure 5.10 (B)is an exception which might due to the charging current.) This increasing trend was on the contrary with Cu film deposition using Cd-Cu SLRR as mentioned in the first part of this chapter. The reason was the morphology of the deposited Au layer was very different from the Cu layer deposited. Even though the deposition methods used were the same, the characters were varied from metal to metal. This was confirmed by the SEM image of Au layer deposited on CdTe shown in Figure 5.11. In contrast with a smooth morphology of Cu film (Figure 5.6 (B)), Au film was consisted of nuclei covering the substrate. As the number of cycles increase, more nuclei form on the surface, the Au surface area greatly increases, and the charge for Cd increase with cycle number. The OCP shown is a mix potential with a Cd partially covered CdTe as a surface and Au3+, Cd2+flowing in the solution. More Cd deposited per cycles meaning more cd will be oxidized to Cd²⁺ by Au³⁺, according to Nernst equation more Cd²⁺ near the electrode surface, the potential will move more negatively.

Another explanation is as Cd deposition was increasing per cycle, at certain stage diffusion of Au^{3+} might become the limiting factor during and Cd- Au^{3+} exchange, which in turn affected the OCP. This could be the reason why the positive limit of OCP was decreasing with more cycles SLRR growth. Similar result had been shown on the Pb-Pt SLRR on FTO. ²⁷

The average EDX data of the Au film formed by 30 cycles of Cd-Au SLRR on CdTe (90 cycles thick) was 9.57 atomic percent for Cd and 10.87 atomic percent for tellurium with Cd/Te ratio being 0.88 indicating the CdTe beneath was still near stoichiometric.

However, after analyzing the data in tables in Figure 5.9 and 5.10, one concern about this Cd-Au SLRR cycle was using -500mV as deposition potential result in too much excess Cd that more than one monolayer per cycle. That could also be the reason of Au nucleation formation. To achieve layer by layer growth within monolayer scale per cycle, a more positive potential should be used. So Cd deposition potential was changed to-300 mV on CdTe substrate with other parameters unchanged. Au film produced with 30 cycles of Cd-Au SLRR with -300 mV as Cd adlayer deposition potential was grown on 90 cycles CdTe. The according potential-time diagram was provided in Figure 5.12 (A). Different from potential-time diagram in Figure 5.10, OCP reached and stabilized at approximately 400mV in each cycle during the whole process. Although Cd reduction charge /cycle was controlled to be less than one monolayer (Table inset in Figure 5.12), from the visual image of the sample except brow color from Au, any other color from CdTe was barely seen. With the concern of oxidation of CdTe substrate during the SLRR process, a sample with 50 Cd-Au SLRR cycles were performed on CdTe substrate, the corresponding potential-time diagram a and visual picture of the sample were shown in Figure 5.13. After 40 cycles Cd-Au SLRR deposition, OCP eventually reached 1100mV which was Au^{3+}/Au formal potential. As mentioned before, CdTe will be oxidized at 400mV so a stop potential of 1100mV was an indication of completely strip off of CdTe substrate. This was further confirmed by the fact that no CdTe oxidation peak appeared in anodic potential scan in blank solution. (Figure 5.14)

The oxidation/ stripping of CdTe substrate was due to Au³⁺, which is a strong oxidizing agent. In Cd-Au³⁺ exchange process, Au³⁺ not only oxidized the Cd adlayer but also the CdTe beneath. Thus, an adjusted deposition process that can preserve the quality of the underlying CdTe substrate was required. To solve this problem, a shorter exchange time of 10s was used for Cd-Au SLRR cycle. An established Cd-Au SLRR was then change to deposit Cd adlayer at - 300mV for 15s followed by 5s blank solution flowing at open circuit potential to rinse away excess Cd²⁺ ion. Then AuCl₃ was introduced in the cell for 10s at open circuit potential. The last step was flowing blank solution for 5s to terminate the cycle.

Au film produced with 30 cycles adjusted Cd-Au SLRR was grown on CdTe substrate (90 cycle thickness). Accordingly, the potential-time diagram was shown in Figure 5.15. It was worth to note that OCP still went up to approximately 400mV after the parameters had been adjusted, however, it did not stay long due to the short time set for the exchange. When the OCP reach the ~400mV, blank solution immediately flow in and OCP dropped accordingly. Also the positive limit of OCP was constantly at 400mV for each cycle. That was an indication of effectively avoiding diffusion limitation of Au³⁺ during the process. And the author believed that was due to the good control of Cd adlayer deposition. To further prove it, the amount of Cd deposited per cycle was quantitatively determined. Cd reduction charge was integrated and converted to monolayer (ML) every 5 cycles, as shown in Figure 5.15 (B). Herein, less than 1 ML of Cd was deposited on the substrate as desired, which solve the excess Cd deposition problem mentioned before. A gradual increase of Cd deposition ML with cycle number was also observed, this was because deposition of Au film resulted in a rougher surface, accordingly the surface area is increasing. So the Cd deposition charge increased with cycle number increasing.

SEM of the Au film proved the fact that surface roughness was developing and will be discussed in more detail.

To investigate the morphology and study the Au film growth process, serials of Au films produced with different cycles of SLRR were prepared on CdTe substrates. They were made with 10, 30, 50 and 80 cycles of Cd-Au SLRR. The SEM images were provided at the same magnification in Figure 5.16. From (A) to (D), the deposition process of Au films started with Au nucleus distributed dispersively on substrate and gradually grew into small islands. During further growth, these individual islands were grouped together producing a homogeneous distribution of Au islands spread across the whole surface. For sample (D), which was consisted of 80 cycles of Cd-Au SLRR on CdTe, its Cd reduction charge/cycle was analyzed and presented in Figure 5.17. An increase of Cd ML/cycle was shown which due to the surface increase from Au nuclear formation. It was worth noting that Cd deposition amount was always within one ML even for 80 cycles SLRR process. Both EDX data and visual observation proofed CdTe beneath the Au layer was intact even after 80 cycles of SLRR.

The adjusted Cd-Au SLRR cycle was a success considering formation of Au layers on an unaffected CdTe substrate. However, in terms of the surface morphology, according to the SEM images presented in Fig.5.16, Au deposition on CdTe was more like a distribution of Au nuclear islands than a conformal, continuous film. In contrast with Au film, Cu film deposited using SLRR method exhibited a more continuous, smoother morphology (Figure 5.6 (B)). Inspired by the high quality of Cu film, an innovative method was proposed and performed using the entire Cu thin film as a template to be redox replaced in Au³⁺ solution.

Several samples were produced using the deposition protocol as following: CdTe substrates were first made by 90 cycles pulse deposition method. Then Cu films was grown on

CdTe substrates using 30 cycles Cd-Cu SLRR method. Briefly speaking, in each SLRR cycle, Cd was deposited at -500mV for 15s then replaced in a CuSO₄ for 20s. Detailed SLRR protocol and solution composition could be found in the first part of this chapter. Basically, samples with the same composition and morphology as in Figure 5.6 (B) were reproduced. After Cu film formed on CdTe, Au³⁺ flowed into the cell and the potential was monitored to estimate the process as shown in Figure 5.18. At the moment sample was in contact with AuCl₃ solution, potential quickly moved to 220mV and stabilized there for approximately 75s. Then it continued to increase until 460mV, where it reached the plateau and stabilized again.

Three samples were produced based on different stages where to terminate the exchange as marked A, B and C in Figure 5.18. The corresponding SEM images of these three samples were present in Figure 5.19. To study the film composition, EDX and EPMA was performed on the three samples. For sample A, EDX date showed an average 10 for Cd Atomic percent (AT %), 12.2 for Te AT% and 5 for Cu AT%, indicating the Au-Cu exchange just started with certain amount of Cu film left on the substrate. However, there was 0 Cu AT% in EDX data for sample B and C. And there was more Au AT% in sample C than in sample B. The elemental composition data together with potential change profile helped illustrated the whole Cu-Au³⁺ exchange process. At point A in Figure 5.18, it was the initial stage of exchange, Cu film was partially oxidized by Au³⁺, and 220mV was a mix potential with Cu as substrate and Cu²⁺, Au³⁺ in solution. After approximately 75s, when potential began to climb up, Cu film was completely oxidized away leaving an Au film on the substrate together with Au³⁺ ions flowing in the solution. As mentioned before, due to the strong oxidizing ability of Au³⁺, Au³⁺ began to penetrate the CdTe substrate and oxidize CdTe. Hence the potential was stabilized at 460mV, where was near CdTe oxidation potential.

In Figure 5.20, a picture of sample B was shown, whose exchange process was terminated at ~350mV. There were two circles on the picture, the inner circle was the area where in contact with Au³⁺ solution, the outer loop was the Cu film to start with and was covered by a tape when Au³⁺ was flowed in the cell. Both EPMA and EDX were measured in the inner circle and on the outer loop. And both measurements showed no Cu content in the inner area, further confirmed Cu thin film was completely exchanged to Au film through redox replacement with Au³⁺. From EDX and EPMA, the average Cd/Te ratio of sample B was determined to be 0.89 indicating the CdTe was not affected by Au³⁺ due to a timely termination of the exchange. And surprisingly to note that according to SEM image of Figure 5.19 (B), the morphology of Au layer in sample B was continuous, conformal and smooth with negligible nucleation forming.

The possible explanation for this could be the Cu layer formed earlier set the template for Au^{3+} ion. Through the direct adatom-ion interaction, Au^{3+} ions were reduced in the place where Cu atoms were, so Au film followed the morphology of Cu film replaced accordingly.

Conclusion

The development of Cd-M SLRR (M presents a metal) on compound semiconductors was demonstrated by the deposition of Cu and Au layers on CdTe. Electrochemical and SEM, EPMA characterizations of deposited Cu film show a conformal, flat morphology without roughness development for up to 30 cycles of Cd-Cu SLRR on CdTe. To successfully deposit Au thin film on CdTe substrates, couples of parameters in the established SLRR were adjusted accordingly, including Cd adlayer deposition potential and Cd-Au³⁺ exchange time. Unlike Cu, Au films deposited using SLRR method showed a tendency to nucleate and grow in clusters. However, the

nucleus of Au film could be effectively avoided by using a smooth Cu layer as a template and Au^{3+} oxidizing and replacing the whole Cu layer with careful time control. The proposed approaches provide a feasible, cost-effective thin film deposition options for various metal-semiconductor systems.

Acknowledgements

Support from the National Science Foundation, DMR 1410109, is gratefully acknowledged. Thanks are extended to Chris Fleisher and the UGA Microprobe lab.

References

1. Turner, A.; Woodcock, J.; Özsan, M.; Cunningham, D.; Johnson, D.; Marshall, R.; Mason, N.; Oktik, S.; Patterson, M.; Ransome, S., BP solar thin film CdTe photovoltaic technology. Solar energy materials and solar cells 1994, 35, 263-270.

Gloeckler, M.; Sankin, I.; Zhao, Z., CdTe Solar Cells at the Threshold to 20% Efficiency.
 IEEE Journal of Photovoltaics 2013, 3 (4), 1389-1393.

3. Energy, O. o. E. E. R. Cadmium Telluride. https://www.energy.gov/eere/solar/cadmium-telluride (accessed Access).

4. First Solar Achieves World Record 18.6 % Thin Film Module Conversion Efficiency http://investor.firstsolar.com/news-releases/news-release-details/first-solar-achieves-world-record-186-thin-film-module. 2015.

5. Ferekides, C. S.; Viswanathan, V.; Morel, D. L. In RF sputtered back contacts for CdTe/CdS thin film solar cells, Conference Record of the Twenty Sixth IEEE Photovoltaic Specialists Conference - 1997, 29 Sept.-3 Oct. 1997; 1997; pp 423-426.

6. Uličná, S.; Isherwood, P. J. M.; Kaminski, P. M.; Walls, J. M.; Li, J.; Wolden, C. A., Development of ZnTe as a back contact material for thin film cadmium telluride solar cells. Vacuum 2017, 139, 159-163.

7. Deng, Y.; Yang, J.; Yang, R.; Shen, K.; Wang, D.; Wang, D., Cu-doped CdS and its application in CdTe thin film solar cell. AIP Advances 2016, 6 (1), 015203.

8. Gessert, T. A.; Metzger, W. K.; Dippo, P.; Asher, S. E.; Dhere, R. G.; Young, M. R., Dependence of carrier lifetime on Cu-contacting temperature and ZnTe:Cu thickness in CdS/CdTe thin film solar cells. Thin Solid Films 2009, 517 (7), 2370-2373.

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9. Romeo, A.; Artegiani, E.; Menossi, D., Low substrate temperature CdTe solar cells: A review. Sol. Energy 2018.

 Sites, J.; Pan, J., Strategies to increase CdTe solar-cell voltage. Thin Solid Films 2007, 515 (15), 6099-6102.

Moutinho, H.; Hasoon, F.; Abulfotuh, F.; Kazmerski, L., Investigation of polycrystalline
 CdTe thin films deposited by physical vapor deposition, close-spaced sublimation, and
 sputtering. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 1995, 13
 (6), 2877-2883.

12. Soliman, M. M.; Shabana, M. M.; Abulfotuh, F., CdS/CdTe solar cell using sputtering technique. Renewable energy 1996, 8 (1-4), 386-389.

13. Lalitha, S.; Karazhanov, S. Z.; Ravindran, P.; Senthilarasu, S.; Sathyamoorthy, R.; Janabergenov, J., Electronic structure, structural and optical properties of thermally evaporated CdTe thin films. Physica B: Condensed Matter 2007, 387 (1-2), 227-238.

Li, J. V.; Duenow, J. N.; Kuciauskas, D.; Kanevce, A.; Dhere, R. G.; Young, M. R.; Levi,
D. H., Electrical Characterization of Cu Composition Effects in CdS/CdTe Thin-Film Solar Cells
With a ZnTe:Cu Back Contact. IEEE Journal of Photovoltaics 2013, 3 (3), 1095-1099.

15. Li, J.; Diercks, D. R.; Ohno, T. R.; Warren, C. W.; Lonergan, M. C.; Beach, J. D.; Wolden, C. A., Controlled activation of ZnTe:Cu contacted CdTe solar cells using rapid thermal processing. Solar Energy Materials and Solar Cells 2015, 133, 208-215.

16. https://www.nrel.gov/pv/assets/pdfs/pv-efficiencies-07-17-2018.pdf.

17. Amin, A.; Tabinna Salim, S.; Salam, K. M. A.; Galib, M., Cadmium Selenide and Cadmium Telluride Based High Efficiency Multijunction Photovoltaics for Solar Energy Harvesting. 2013; Vol. 1, p 1-5.

18. Byrnes, S., Schottky junction solar cells. 2008.

19. Oskam, G.; Long, J. G.; Natarajan, A.; Searson, P. C., Electrochemical deposition of metals onto silicon. Journal of Physics D: Applied Physics 1998, 31 (16), 1927.

20. Sakthivel, S.; Shankar, M. V.; Palanichamy, M.; Arabindoo, B.; Bahnemann, D. W.; Murugesan, V., Enhancement of photocatalytic activity by metal deposition: characterisation and photonic efficiency of Pt, Au and Pd deposited on TiO2 catalyst. Water Research 2004, 38 (13), 3001-3008.

21. Magagnin, L.; Maboudian, R.; Carraro, C., Selective Deposition of Thin Copper Films onto Silicon with Improved Adhesion. Electrochemical and Solid-State Letters 2001, 4 (1), C5-C7.

22. Magagnin, L.; Maboudian, R.; Carraro, C., Gold Deposition by Galvanic Displacement on Semiconductor Surfaces: Effect of Substrate on Adhesion. The Journal of Physical Chemistry B 2002, 106 (2), 401-407.

23. Carraro, C.; Maboudian, R.; Magagnin, L., Metallization and nanostructuring of semiconductor surfaces by galvanic displacement processes. Surface Science Reports 2007, 62 (12), 499-525.

24. Pauling, H. J.; Staikov, G.; Jüttner, K., Layer-by-layer formation of heterostructured ultra-thin films by UPD and OPD of metals. J Electroanal Chem 1994, 376 (1), 179-184.

25. Mitchell, C.; Fayette, M.; Dimitrov, N., Homo- and hetero-epitaxial deposition of Au by surface limited redox replacement of Pb underpotentially deposited layer in one-cell configuration. Electrochimica Acta 2012, 85, 450-458.

26. Thambidurai, C.; Kim, Y.-G.; Jayaraju, N.; Venkatasamy, V.; Stickney, J. L., Copper Nanofilm Formation by Electrochemical ALD. J. Electrochem. Soc. 2009, 156 (8), D261-D268.

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27. Yliniemi, K.; Wragg, D.; Wilson, B. P.; McMurray, H. N.; Worsley, D. A.; Schmuki, P.; Kontturi, K., Formation of Pt/Pb nanoparticles by electrodeposition and redox replacement cycles on fluorine doped tin oxide glass. Electrochimica Acta 2013, 88, 278-286.



Figure 5.1: Schematic of electrochemical flow system. Solution is stored in bottles and drawn by a pump through the distribution valve and flow cell. The flow cell is a three electrode cell with an Au wire inlayed into the cell as the auxiliary electrode.



Figure 5.2:(A) Potential vs. time diagram for 30 cycles pulsed CdTe deposition followed by 30 cycles Cd-Cu SLRR. (B) Cd reduction charge and coverage analysis per cycle.

(A)



(B)

1.61

0.95

0.80

0.64

0.57

0.53

0.51

Figure 5.3:(A) Potential vs. time diagram for 90 cycles pulsed CdTe deposition followed by 30 cycles Cd-Cu SLRR.(B) Cd reduction charge and coverage analysis per cycle.



Figure 5.4: SLRR produced Cu films deposited on CdTe substrates. Deposited Cd ML/cycle vs. cycle number.



Figure 5.5: SEM of 30 cycles CdTe substrate (A) before and (B) after coving with Cu film produced by30 cycles Cd-Cu SLRR.


Figure 5.6: SEM images of 30 cycles Cd-Cu SLRR on (A) 30 cycles CdTe and (B) 90 cycles CdTe. In Cd-Cu SLRR, -500mV was used to deposit Cd UPD and 20s were giving for the Cu replacement.



Figure 5.7: CdSO₄ window opening on 30 cycles CdTe substrate. The concentration of CdSO₄was 10 mM at pH 2.



Figure 5.8: CdSO₄ window opening on Au substrate.The concentration of CdSO4 was 10 mM at pH 2.



Figure 5.9: (A) Potential and current vs. time diagram of 30 cycles Cd-Au SLRR on CdTe substrate (30 cycles thick). (B) Cd reduction charge and coverage analysis per cycle.



Figure 5.10: (A) Potential and current vs. time diagram of 30

cycles Cd-Au SLRR on CdTe substrate (90 cycles thick). (B) Cd reduction charge and coverage analysis per cycle. Cd deposition potential was -500mV in SLRR.



Figure 5.11: SEM image of Au film produced by 30 cycles Cd-Au SLRR on CdTe substrate (90 cycles thick). Cd deposition potential was -500mV in SLRR.



Figure 5.12:(A) Potential vs. time diagram of 30 cycles Cd-Au SLRR on CdTe substrate (90 cycles thick) using -300 mV for Cd deposition. (B) Cd reduction charge and coverage analysis per cycle.



Figure 5.13: Potential vs. time diagram of 50 cycles Cd-Au SLRR on CdTe substrate (90 cycles thick) using -300 mV for Cd deposition. (B) Visual image of the corresponding sample.



Figure 5.14: Cyclic voltammetry (CV) profiles of stripping of 50 cycles Cd-Au SLRR on CdTe substrate in 0.5 M HClO₄ blank solution.



Figure 5.15: (A) Potential-time diagram of 30 cycles Cd-Au SLRR with Cd deposition potential at -300mV and AuCl₃ solution exchange time 10s. The substrate was a 90 cycles thick CdTe. (B) Cd reduction charge analysis with SLRR cycle numbers. The charge was converted to monolayer (ML).



Figure 5.16: SEM images of Au particles deposited on the surface of CdTe substrate for different number of Cd-Au SLRR: (A) 10 cycles; (B) 30 cycles; (C) 50 cycles and (D) 80 cycles.



Figure 5.17: Cd reduction charge in ML for 80 cycles SLRR Au film on CdTe substrate(90 cycles thick). This analysis was corresponding to sample (D) in Figure 5.15.



Figure 5.18: Potential-time diagram of Cu film in AuCl₃ solution.



Figure 5.19: SEM images of three samples immersed in AuCl₃ solution for different time. (A), (B) and (C) were corresponding to the experiment termination time marked as A, B and C in Figure 5.17.



Figure 5.20: Visual image of sample B in Figure 5.18, whose exchange process was terminated at ~350mV.

CHAPTER 6

CONCLUSION AND FUTURE STUDIES

This dissertation focuses on the fabrication of metal and compound semiconductors for photovoltaic applications using electrodeposition method. Chapter 2 investigated the deposition of CdTe films using co-deposition and potential pulse atomic layer deposition (PP-ALD) methods. Cyclic voltammetry study of Au substrates in CdSO₄ and TeO2solution was first performed to understand the electrochemical behavior of cadmium and tellurium precursors. Then serials of CdTe samples were deposited at different constant potentials over a large range from -100 to -800mV. The best quality of CdTe with unity Cd/Te ratio, and smooth, continuous morphology was formed at -700mV. Based on this value, potential was periodically applied in accordance with solution flow to ensure a quiescent environment during deposition. A significant crystallinity enhancement was achieved by employing this method.

Further, a series of experiments were performed to introduce small potential pulses by varying the potential rapidly between a cathodic and an anodic value in a wide potential range. The dependence of the film morphology and composition as a function of cathodic and anodic potentials was investigated using two sets of solution with different cadmium and tellurium ion concentrations. In both cases (10 mM CdSO₄ with 0.2 mM TeO₂ and 1mM CdSO₄ with 0.1 mM TeO₂), stoichiometric CdTe with smooth surface were formed using optimized potential pulse atomic layer deposition. At the end of chapter 2, we also investigated the feasibility of the PP-ALD process for depositing conformal layers of CdTe on high aspect ratio nanostructures such as gold nanowire arrays. As a result, we found that PP-ALD showed great ability in reproducibly

controlling composition and morphology of the deposit on the nanostructured electrode. It's been proved the branched hierarchical structured cadmium chalcogenide can display a much higher photoconversion performance.^{1,2} Thus, the described potential pulse atomic layer deposition provided a viable option for incorporation of semiconductor materials with nanotechnology.

Continued with Chapter 2, Chapter 3 was focused on deposition of ultrathin CdTe films on plasmonic Au nanostructures for enhanced photoperformance. A set of Au nanorod (Au NR) samples in different height was prepared using AAO as template. CdTe was deposited on Au nanorod substrate using electrodeposition method.

Photoelectrochemical measurement of as deposited CdTe-Au NR samples was performed in a methyl viologen dichloride solution under chopped simulated sunlight, the results showed that the photoresponse for CdTe-Au NR of 600 nm was the highest. To make a comparison, photoactivity of as deposited CdTe on planar Au sample was also tested. A great increase of photocurrent was noticed for CdTe-Au NR sample, which supported the plasmonic effect of the Au nanostructure. At last, CdTe-Au NR was annealed at 300 °C to study the effect of post deposition heat treatment on the photoelectrochemical properties of CdTe-Au NR, both photocurrent and the on-set potential were affected in a way that proved annealing had promoted photoelctrochemical light conversion efficiency.

Started from Chapter 4, the focus shifted to fabricate metal layers using a new deposition technique called surface limited redox replacement (SLRR), where a solution of a more noble metal ion was brought in contact with UPD layer of a less noble metal (sacrificial layer) and to replace it. In chapter 4, copper and gold ultra-thin films were deposited on Au substrates using cadmium as sacrificial element. To optimize the SLRR cycle, several parameters were studied including Cd UPD potential and Cu solution exchange time. Based on the optimized cycle

information, Cu films with controllable thickness were produced by multiple repetitions of SLRR cycles with great linear growth with respect to cycle numbers. And both EPMA and EDX results confirmed there was no Cd incorporation in the formation of the Cu films when Cd was used as sacrificial metal in the deposition process. Additionally, SLRR produced Cu layer showed a much smoother and conformal morphology than electrodeposited Cu, which exhibited high densed Cu cluster on the surface. The same SLRR method was also proved to be successful when using AuCl₃ to deposit smooth, flat and homogenous Au films.

Finally, Chapter 5 discussed the development of Cd-M SLRR (M presents a metal, Cu or Au) on compound semiconductor was demonstrated by the deposition of Cu and Au layers on CdTe. Electrochemical and SEM, EPMA characterizations of deposited Cu film show a conformal, flat morphology without roughness development for up to 30 cycles of Cd-Cu SLRR on CdTe. While when using the same Cd-M SLRR method to deposit Au thin layers on CdTe, deposited Cd sacrificial layer resulted in much more than 1 monolayer (ML) per cycle, which was in contradiction of atomic layer control. Thus, a more positive deposition potential was used to deposit Cd sacrificial layer, which resulted in less than 1 ML deposition per cycle. Due to the strong oxidative ability of Au³⁺, the Cd-Au³⁺ exchange time was adjusted accordingly in order to protect CdTe from being oxidized. Unlike Cu, Au films formed using adjusted SLRR method still showed a tendency to nucleate and grow in Au clusters.

Surprisingly, we found that by using a smooth Cu layer as a template and controlling Au³⁺to oxidize and replace the whole Cu layer by monitoring the potential change, the nucleus of Au film was effectively avoided. The proposed approaches provide a feasible, cost-effective thin film deposition options for various metal- semiconductor systems.

Future work will aim at three aspects: (1) designing CdTe-Au based nanostructures with higher energy conversion efficiency, (2) optimizing SLRR method to fabricate smooth Au thin films and (3) increasing metal deposition rate in SLRR. The first one is the extension of chapter 2 and 3, to form CdTe covered plasmonic nanostructures that can further improve solar energy conversions. The absorption spectra of a plasmonic nanostructure can be controlled, which depends on the geometry and metal species.³ Thus, the lengths, filling ratios and the diameter of Au nanorod structure could all be tunneled to broaden and/or optimize its absorption spectra. After tunneling the geometry of Au nanorod substrates, CdTe will be deposited on and characterized. When a plasmonic metal structure is appropriately interfaced with CdTe, it will act as a means of collecting light from a region outside the CdTe absorber whose energy is nevertheless converted to e⁻-h pairs in the absorber. Therefore an improvement can be expected for photoperformance of CdTe on optimized Au nanostructure. The dependence of photocurrent enhancement on the thickness of CdTe can be investigated as well. Such studies will permit one to produce properly engineered plasmonic nanostructures which can exhibit the highest solar energy conversion efficiency using the least semiconductor material.

The second aspect of the future work is optimization of Cd-Au SLRR method to fabricate conformal, smooth Au layers on CdTe surface. In chapter 5, Au films produced by Cd-Au SLRR method showed a nucleation and growth behavior with Au nucleus distributed on the surface. Although at the end of chapter 5, a novel method effectively solved the nucleation problem, by using a flat SLRR produced Cu layer as a template. However, in this method in order to generate a flat Au layer, both copper and cadmium were sacrificed, which is a waste and will prevent this method from being broadly applied. Thus, efforts need to be made on investigating Metal-Au SLRR method to fabricate smooth Au film with minimum sacrificial metal used. Au nucleation

formation might due to the limited surface diffusion of Au atom. Halides are known to facilitate surface diffusion in electrolyte solutions,⁴ so further step will be increasing CI^- or I^- ions concentration of the electrolyte, and studying the effect of halides on the morphology of Au films.

Another reason of Au nucleation formation could be the long potential transients during the replacement.Researches have shown that longer potential transients and the higher achieved OCP value during the replacement can result in more Au clusters. Increasing the reactant ion concentration (Au^{3+}) can effectively shorten the time for a complete exchange in SLRR, so studies on Au^{3+} concentration will be performed, with the expectations that higher Au^{3+} concentration will shorten the potential transient time, and suppress Au nucleation formation.

The last focus of the future work is to increase the deposition rate of SLRR produced metal. In chapter 4, the optimum deposition conditions to deposit Cu was concluded to be 15s Cd UPD deposition at -500mV followed by 20s Cu²⁺- Cd exchange, the process can be repeated to achieve the desired thickness. More concentrated solution could result in more rapid exchange,⁵ thus rapid metal deposition. In the present study, the concentration of the reactants (CuSO₄) was kept at 0.1mM. Further studies will be performed by increasing CuSO₄ concentration to improve Cu deposition rate. Deposition rate can also be altered by changing materials as sacrificial layer. Because the amount of the deposited metal is limited to the coverage of the sacrificial layer, also limited to how much electrons per Cd adatom, if aluminum or indium serve as sacrificial elements, three electrons will be provided and result in more Cu deposition per cycle, so the deposition rate may increase accordingly.

References

1. Huang, Y.; Xu, Y.; Zhang, J.; Yin, X.; Guo, Y.; Zhang, B., Hierarchical ultrathinbranched CdS nanowire arrays with enhanced photocatalytic performance. Journal of Materials Chemistry A 2015, 3 (38), 19507-19516.

2. Heo, K.; Lee, H.; Jian, J.; Lee, D.-J.; Park, Y.; Lee, C.; Lee, B. Y.; Hong, S., Bi-Assisted CdTe/CdS Hierarchical Nanostructure Growth for Photoconductive Applications. Nanoscale Res. Lett. 2015, 10 (1), 331.

3. Robatjazi, H.; Bahauddin, S. M.; Macfarlan, L. H.; Fu, S.; Thomann, I., Ultrathin AAO membrane as a generic template for sub-100 nm nanostructure fabrication. Chemistry of Materials 2016, 28 (13), 4546-4553.

 Villegas, I.; Ehlers, C. B.; Stickney, J. L., Ordering of Copper Single-Crystal Surfaces in Solution: Confirmation by Low Energy Electron Diffraction. J. Electrochem. Soc. 1990, 137 (10), 3143-3148.

5. Thambidurai, C.; Kim, Y.-G.; Jayaraju, N.; Venkatasamy, V.; Stickney, J., Copper nanofilm formation by electrochemical ALD. J. Electrochem. Soc. 2009, 156 (8), D261-D268.