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IMPROVEMENTS IN ELECTRODEPOSITED Cu_2O AS THE WIDE BANDGAP CELL FOR A TANDEM SOLAR ARCHITECTURE

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ABSTRACT

Cuprous oxide is a well-known wide-bandgap material with E_{gap} commonly reported around 2.0 eV, but with some reports ranging from 1.7eV to 2.5eV. With a bandgap around 2.0 eV it is a great candidate for the top cell of a stack tandem architecture paired with a bottom silicon cell. However the actual reported efficiencies of single junction devices are usually much lower than would be expected, probably rooted in possible defects, nonstoichiometry or microstructural flaws. We report on electrodeposited thin films and their growth modes under different conditions. Microstructural improvements have been made using seeding layers before electrodeposition; these are mainly focused on growing columnar shaped grains. Cu_2O that has been electrodeposited has a flowering or dendritic microstructure. When the electrodeposition is seeded appropriately the dendrite arms from the flower no longer grow resulting in nicely faceted grains and a columnar shape. This well-crystallized columnar structure is meant to increase the hole collection length by avoiding recombination at grain boundary defects as a means of increasing the efficiency. Seeding the growth on the films has resulted in Cu_2O films that are more controllable in the electrodeposition process, with a more consistent grain orientation. SEM and XRD analysis were performed to show these results.

INTRODUCTION

Cuprous oxide is a material that has been investigated for years with regard to solar cells due to its high theoretical efficiency and low cost.[1-4] This theoretical efficiency is determined using the Shockley Queisser analysis summarized graphically in Figure 1. With its reported band gap of around 2 eV, Cu_2O would have a theoretical efficiency of about 20%,[3,5-7] which isn't optimized for a single junction device in the SQ analysis. However, when paired with silicon in a stacked-tandem architecture, the wider band gap Cu_2O could be ideal. In a four junction solar tandem structure the two devices are mechanically stacked which releases the current matching constraint that is imposed in the III-V multijunction solar cells that are epitaxially grown. Figure 2 shows a simple derivation of the expected total efficiency using a coupled SQ analysis of this stack; the maximum efficiency, over 45%, for this stacked design would require the top cell to have a band gap around 2eV with a bottom cell at 1.1eV. This stacked theoretical efficiency is based on achieving the individual theoretical efficiencies for each of the two cells, yet the experimental efficiencies for Cu_2O solar cells that have been reached to date have only been as high as 3.83%.[8] There is quite a bit of work to bring the experimental efficiency up to maximize the efficiency of the stacked tandem solar structure.

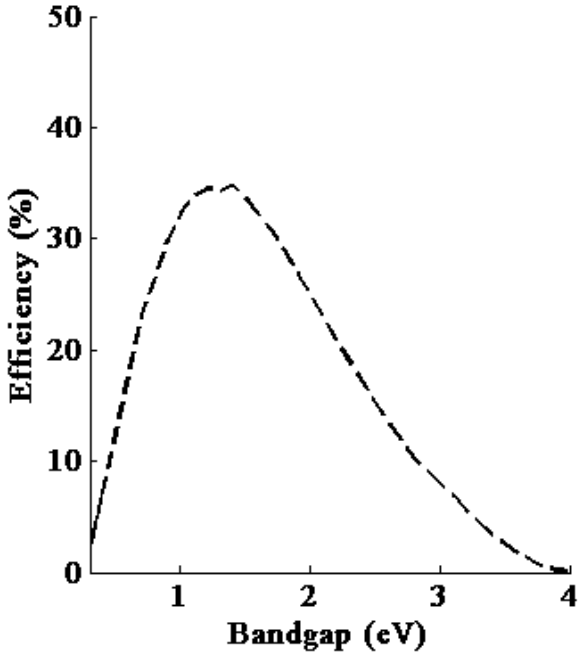

Figure 1 Intrinsic efficiency limit for single junction solar cell.[12]

The goal of this research, therefore, was to improve the microstructure of the Cu_2O layer by growing large columnar grains, and in turn decreasing the recombination that is occurring, which should increase the experimental efficiency.

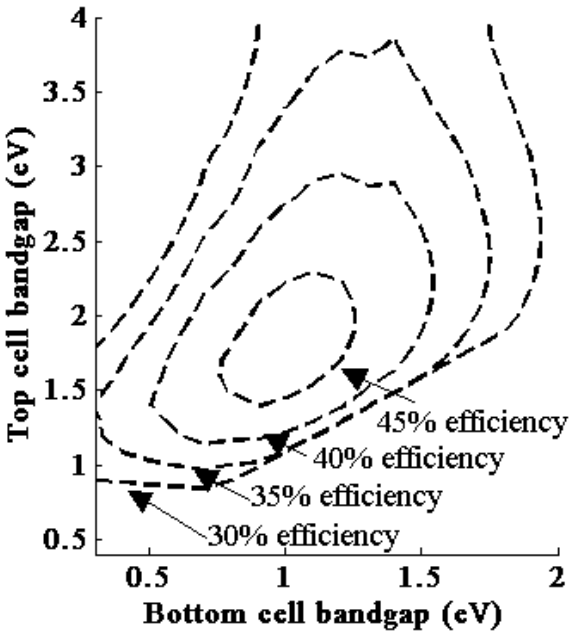

Figure 2 Intrinsic efficiency limit of 4-terminal mechanical stack tandem solar cell.[12]

EXPERIMENTAL

Electrodeposition was used to produce the cuprous oxide films, and two chemistries were investigated for the electrolyte solution. The deposition process employed a two electrode, single compartment electrolytic cell. The working electrode was a piece of FTO coated glass, and the counter electrode was a piece of platinum foil. The first electrolyte contained 0.02 M copper (II) sulfate, and 0.06 M sodium DL lactate, and to adjust the pH, 6 drops of sodium hydroxide were added to bring the solution to a slightly acidic 6.31 pH.[9] The second electrolyte was made up of 0.1 M sodium acetate and 0.1 M copper (II) acetate monohydrate.[10] The electrodeposition was performed at a potential of 1.5 volts, for various times ranging from 30 seconds up to one hour.

GOLD NANOISLANDS

The ideal grain shape for the electrodeposited Cu_2O would be columnar, which would allow conduction through the full device depth within individual columns and thus should prevent some recombination, specifically at the grain boundaries. The current structure found with electrodeposited Cu_2O is flower-like grains, which do not develop into columnar grains. In the presented work we explore the use of growth seeding to improve the microstructure. In earlier work, gold nanoislands have been used to seed the growth of Cu_2O nanowires[11] so this was tested for applicability to the electrodeposition process. To form these nanowires a bottom up technique is used, with either a solution methods or vapor based methods. For our purposes we are looking to use the gold nanoislands that naturally form when a thin layer of gold is deposited on a surface. Gold and cuprous oxide have similar cubic structures and lattice parameter sizes so epitaxial growth could occur during the electrodeposition. To obtain the gold nanoislands a 15nm layer of gold was sputtered onto the FTO side of the glass that is used as the working electrode in our standard electrodeposition process. In order to expedite the formation of distinct nanoislands the gold coated glass was baked for 6 hours at 600ºC. The resulting gold nanoparticles were an average of 200nm and were evenly distributed on the glass. This can be seen in Figure 3. The FTO and gold nanoisland coated glass is then used as the working electrode in the electrodeposition.

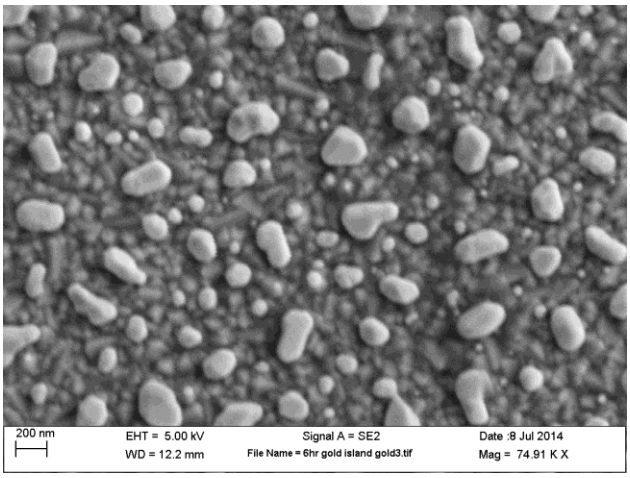

Figure 3 FESEM image of gold nanoislands on FTO coated glass, with an average size of 200nm

SEM IMAGING

To characterize these films SEM images were taken after five minutes and one hour for the two chemistries described above. The comparisons can be seen in Figure 4. Electrolyte 1 did not show the flowering microstructure that was expected, it was more of a cauliflower structure however electrolyte 2 did show the more dendritic grains. We believe that the cauliflower structure was produced because the voltage was higher than what is traditionally used causing overly rapid growth. Both electrolytes produced even coatings that were relatively flat.

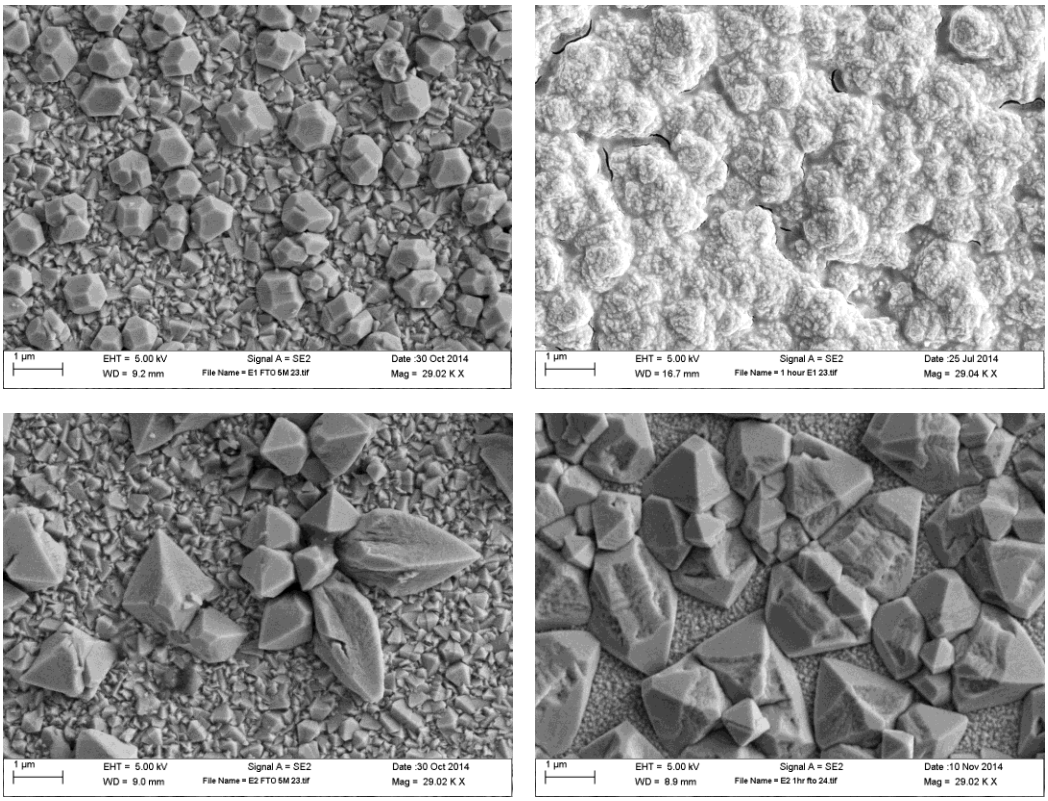

Figure 4 SEM images of Cu_2O deposition using electrolyte 1 (top row) and electrolyte 2 (bottom row) electrodeposited FTO coated glass for 5 minutes, and 1 hour respectively. All images are at the same size scale.

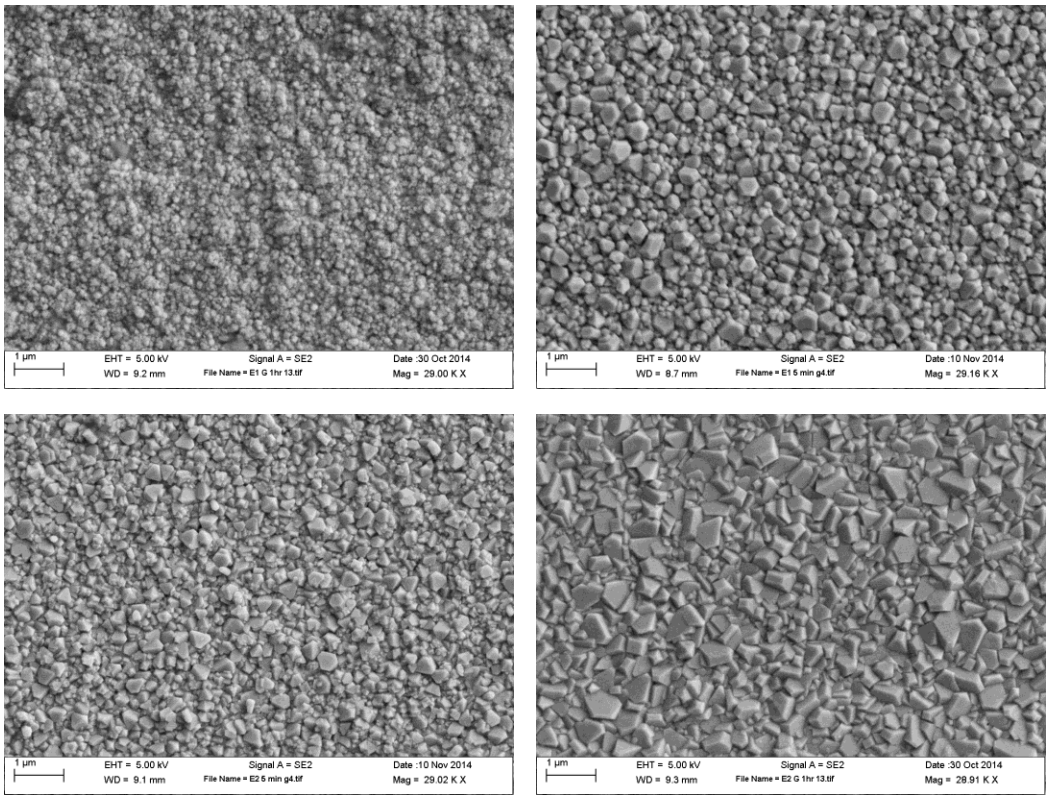

Figure 5 SEM images of Cu_2O deposition using electrolyte 1 (top row) and electrolyte 2 (bottom row) electrodeposited on gold coated, FTO coated glass for 5 minutes, and 1 hour respectively. All images are at the same size scale.

When deposited on the gold seeding layers both electrolyte 1 and electrolyte 2 showed differences in their microstructure but electrolyte 2 showed the greatest difference. Electrolyte 2 no longer grew flowering grains but instead faceted grains resulted, as shown in Figure 5. The grains grown using gold seeding layers were significantly smaller than those without, but the growth that did occur suggests that the growth is more controlled compared to the growth on just FTO

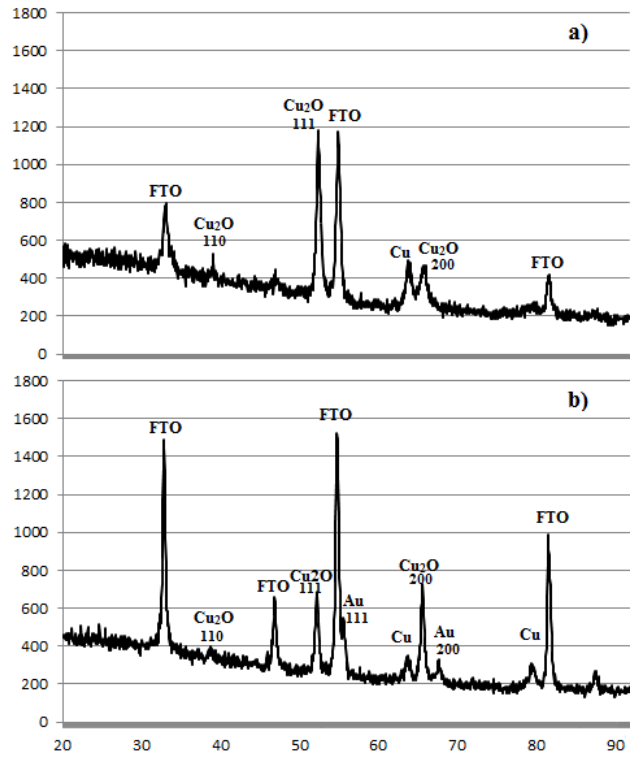

Figure 6 XRD patterns for electrolyte 1: a) electrodeposited for 1 hour on FTO coated glass (top), and b) electrodeposited for 1 hour on gold coated FTO coated glass (bottom).

XRD ANALYSIS

X-ray diffraction patterns were collected from coatings deposited from electrolytes 1 and 2 on FTO coated glass, both before and after the addition of gold seeding layers, for 1 hour of deposition. These patterns can be seen in Figures 6 and 7. All patterns clearly showed the formation of Cu_2O. Trace amounts of copper are also present in every XRD graph except for in Figure 7b, copper in this film has basically disappeared. In all cases the FTO substrate peaks are well represented (as noted on the graphs). It is also important to note that in the samples deposited on FTO/gold substrates, the primary peak of FTO remains strong, and has the added shoulder from the Au (111) peak reflection (at ~38° 2θ). This is consistent with the Au/FTO SEM image shown in Figure 3 where the Au is only providing a fraction of surface coverage.

When electrolyte 1 was used to deposit Cu_2O on bare FTO the XRD pattern showed distinct peaks for Cu_2O and FTO, additionally the pattern showed evidence of copper formation.

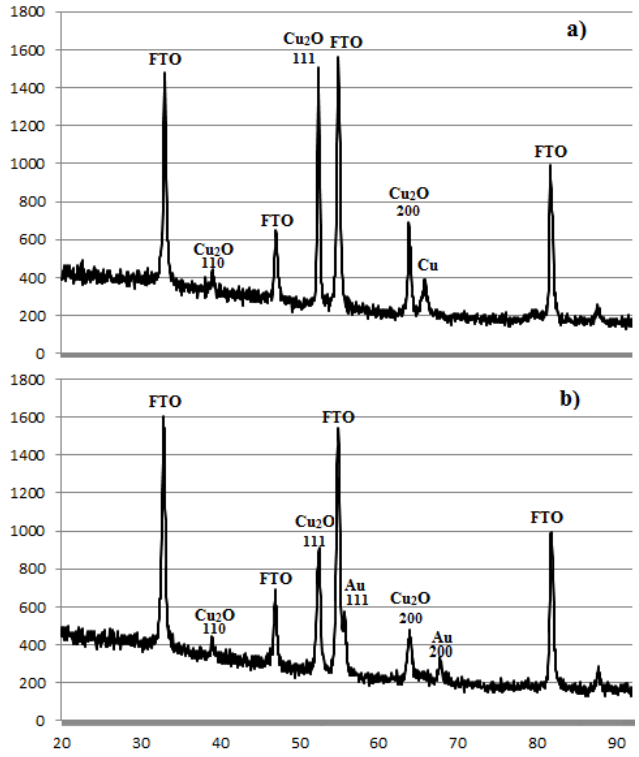

Figure 7 XRD patterns for electrolyte 2: a) electrodeposited for 1 hour on FTO coated glass (top), and b) electrodeposited for 1 hour on gold coated FTO coated glass (bottom).

When the same electrolyte was used with gold coated substrates, cuprous oxide peaks were less intense than those on FTO at each time interval, suggesting a lowering in the average Cu_2O growth rate. When the gold is add to the substrate of electrolyte 1 the Cu_2O peak in the (111) direction decreases, but the Cu_2O peak in the (200) direction increases showing that the (200) orientation is preferred under these growth conditions. When using electrolyte 2 on the gold both the peak heights for the (111) and (200) orientations changed slightly, but not as dramatically as was found for electrolyte 1.

CONCLUSION

Cuprous oxide is a promising semiconductor material with likely value for future tandem solar cells stacks. However, it has been held back in the past by low efficiency in spite of high theoretical expectations based on the bandgap alone. In order to improve this efficiency we are looking to grow cuprous oxide thin films that have columnar shaped grains, which in turn will decrease recombination at the grain boundaries. Gold nanoislands that are about 200nm in size have been formed on the surface of FTO coated glass. This glass was then used as the working electrode in electrodeposition.

Two different electrolytes were used and it was found that electrolyte 2 was the more desirable of the two. Without the gold this electrolyte grew predictable flower like grains that are common in electrodeposited Cu_2O; when the gold was added to

the FTO coated glass the grains were faceted and did not grow dendritically.

From the XRD patterns that were obtained from these samples it was established that Cu_2O was growing well on the FTO and Au/FTO substrates and that the presence of the Au nanoislands had encouraged the growth of (200)-textured Cu_2O in this process.

In the future we would like to focus more on the grain size and lowering the potential used in the deposition to increase the size of the grains, and gain further control over the deposition process.

REFERENCE

[1] L. C. Olsen, F. W. Addis, and W. Miller. *Solar Cells*, Experimental and Theorectical Studies of Cu_2O Solar Cells vol. 7, 247-279, 1982.

[2] C. M. McShane, and K. Choi. *Journal of the American Chemical Society*, Photocurrent Enhancement of n-Type Cu_2O Electrodes Achieved by Controlling Dendritic Branching Growth vol. 131, 2561-2569, 2009.

[3] K. Han, and M. Toa. *216th ECS Meeting*, Cu Diffusion Doping in Electrodeposition N-Type Cu_2O 2009.

[4] N. Gupta, S. Rajandra, F. Wu, J. Narayan, C. McMillen, K. F. Poole, G. F. Alapatt, D. Sulejmanovic, S. Hwu, M. Young, G. Teeter, and H. S. Ullal. *Journal of Materials Research*, Deposition and Characterization of Nanostructured Cu_2O Thin-Film for Potential Photovoltaic Applications vol. 28, (13), 1740-1746, 2013.

[5] T. Minami, H. Tanaka, T. Shimakawa, T. Miyata, and H. Sato. *Japanese Journal of Applied Physics*, High-Efficiency Oxide Heterojunction Solar Cell Using Cu_2O Sheets vol. 43, L917-L919, 2004.

[6] M. Li, W. Wu, K. Liu, G. Hu, and H. Xu. *Electrochimica Acta*, Three-dimensional assembly and electrical properties of Cu_2O/ZnO heterojunction via an electrochemical superfilling method vol. 71, (0), 100-105, 2012.

[7] L. Chen. *Materials Science in Semiconductor Processing*, Review of preparation and optoelectronic characteristics of Cu_2O-based solar cells with nanostructure vol. 16, (5), 1172-1185, 2013.

[8] T. Minami, Y. Nishi, T. Miyata, and J. Nomoto. *Applied Physics Express*, High-Efficiency Oxide Solar Cells with ZnO/Cu_2O Heterojunction Fabrication on Thermally Oxidized Cu2O Sheets. vol. 4, 2011.

[9] A. Osherov, C. Zhu, and M. J. Panzer. *Chemistry of Materials*, Role of Solution Chemistry in Determining the Morphology and Photoconductivity of Electrodeposited Cuprous Oxide Films vol. 25, 692-698, 2013.

[10] W. Zhoa, W. Fu, H. Yang, C. Tian, M. Li, L. Yixing, L. Zhang, Y. Sui, X. Zhou, H. Chen, and C. Zou. *Crystal Engineering Communications*, Electrodeposition of Cu_2O films and Their Photoelectrochemical Properties vol. 13, 2871-2877, 2011.

[11] M. E. Messing, K. Hillerich, J. Johansson, K. Deppert, and K. A. Dick. *Gold Bulletin*, The Use Of Gold For Fabrication Of Nanowire Structures vol. 42, (3), 172-188, 2009.

[12] V. Vijayakumar, and D. P. Birnie. *Solar Energy*, Optical and Electronic Simulation of Gallium Arsenide/Silicon Tandem Four Terminal Solar Cells vol. 97, 85-92, 2013.