Project Final Report

Doping Cu₂O in Electrolyte Solution:
Dopant Incorporation, Atomic Structures and Electrical Properties

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1. Accomplishments:

We have pursued a number of research activities between April 2010 and April 2011:

- A detailed study on n-type doping in Cu_2O by Br;
- An analysis of natural resource limitations to terawatt-scale solar cells;
- Attempt to achieve a 1.4-eV direct band gap in Ni sulfides (NiS_x);
- First-principles studies of doping in Cu_2O and electronic structures of NiS_x .

The following is a more detailed description of these activities.

1.1 N-Type Doping of Cu_2O by Br

We performed a detailed study on an alternative n-type dopant for Cu_2O , Br, by electrodeposition. The most interesting result from this study is the extremely large grain size in Br-doped Cu_2O , up to $10,000 \mu\text{m}^2$ in area, while the film is only 1–5 μm thick. Large grains are desirable in photovoltaic and photochemical cells, as they reduce carrier recombination or carrier scattering by grain boundaries. The large grain size is enabled by branched growth of Cu_2O crystals. The effect of deposition conditions on grain size, including deposition potential, solution pH, Br concentration, Cu concentration and deposition temperature, have been revealed.

Electrodeposition of Br-doped Cu_2O was carried out in a 3-electrode cell with a Pt counter electrode, an Ag/AgCl reference electrode, and an ITO-coated glass substrate as the working electrode. The aqueous deposition solution typically contained 20 mM Cu(II) acetate ($\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$) as the Cu precursor and 100 mM Na acetate ($\text{NaOOCCH}_3 \cdot 3\text{H}_2\text{O}$) as the complexing agent. NaBr was added to the solution as the Br precursor. The solution pH varied from 5.2 and 6.4 by adding acetic acid (HOOCCH_3). The deposition potential varied from 0 and –75 mV vs. the reference electrode. The typical deposition temperature was 60°C.

The effect of deposition conditions on grain size can be understood through the effect of over-potential on nucleation density. The grain size of the deposited film is related to the nucleation density if the nuclei are produced only at the beginning of the deposition process and grow continuously in subsequent deposition. The nucleation density in electrodeposition can be controlled by the over-potential, η , which is related to the applied potential (E_A) and the reduction potential (E_R):

$$\eta = |E_A - E_R| \quad (1)$$

The reduction potential of Cu^{2+} to Cu^+ is:

$$E_R = 0.159 - 0.05916 \log \frac{[\text{Cu}^+]}{[\text{Cu}^{2+}]} \quad (2)$$

The solubility of Cu^+ ions in an aqueous solution follows:

FIG. 1 Grain size in Br-doped Cu_2O as a function of solution pH. The films were deposited at (a) 0; (b) –25; (c) –50; and (d) –75 mV vs. the reference electrode.

FIG. 2 Grain size in Br-doped Cu_2O as a function of NaBr concentration in the solution. The films were deposited at (a) 0 and (b) –25 mV vs. the reference electrode.

FIG. 3 SEM images of Br-doped Cu_2O deposited at 0 V and with various NaBr concentrations: (a) 0; (b) 1; (c) 2; and (d) 3 mM.

deposition solution contained 5 mM NaBr. The nucleation density of Br-doped Cu_2O increases with solution pH. Here a larger grain size is correlated to a lower nucleation density. From equation (4), an increase in solution pH produces a more positive reduction potential. Therefore, a larger over-potential is established at higher solution pH, leading to a higher nucleation density and a smaller grain size. This hypothesis is supported by the fact that a more negative applied potential from 0 to -0.075 V increases the over-potential at fixed pH, resulting in a higher nucleation density and a smaller grain size as seen in Fig. 1.

Fig. 2 shows the grain size of Br-doped Cu_2O as a function of NaBr concentration in the solution. The grain size increases with NaBr concentration. It has been demonstrated that the $\text{Cu}^{2+}/\text{Cu}^+$ redox reaction is significantly catalyzed by a small amount of Cl^- ions due to enhanced electron transfer by a Cl-bridged reaction.¹ A similar effect by Br^- ions is expected in Br-doped Cu_2O , i.e. a higher Br^- concentration increases the reduction reaction of Cu^{2+} ions, and grain growth rather than nucleation dominates the deposition process of Br-doped Cu_2O .

SEM images of Br-doped Cu_2O deposited at 0 V and with different NaBr concentrations are shown in Fig. 3. The nucleation density decreases as the NaBr concentration increases, leading to larger gains of Br-doped Cu_2O . In addition, Br^- ions promote branched growth of Cu_2O , resulting in extremely large grains. At 0 mM NaBr, there is little branched growth (Fig. 3(a)). With 1 mM NaBr, branched growth is noticeable (Fig. 3(b)). With 3 mM NaBr, there is not only branched growth, but also sub-branched growth, i.e. branched growth on the primary branches (Fig. 3(d)). It is conceivable that nucleation is significantly suppressed with a high Br^- concentration, and growth has to proceed along existing crystals.

$$\log[\text{Cu}^+] = 0.84 - \text{pH} \quad (3)$$

The reduction potential is thus:

$$E_R = 0.1093 + 0.05916 \log[\text{Cu}^{2+}] + 0.05916 \text{pH} \quad (4)$$

Therefore, the over-potential increases when a more negative potential is applied.

Fig. 1 shows the average grain size of Br-doped Cu_2O in μm^2 as a function of deposition potential and solution pH. Since the grains are irregular in shape, the area of the grains, instead of their linear dimension, is used as an indication of their size. The

FIG. 4 Grain size in Br-doped Cu_2O as a function of Cu^{2+} concentration in the solution. The films were deposited with NaBr concentration of: (a) 4 and (b) 2 mM.

¹ Z. Nagy, J. P. Blaudeau, N. C. Hung, L. A. Curtiss and D. J. Zurawski, J. Electrochem. Soc. **142**, L87 (1995).

The reduction potential of Cu^{2+} to Cu^+ is also controlled by the concentration of Cu^{2+} ions in the solution, according to equation (4), i.e. an increase in Cu^{2+} concentration leads to a higher nucleation density. The grain size of Br-doped Cu_2O as a function of Cu^{2+} concentration is shown in Fig. 4. The average grain size at 5 mM Cu^{2+} is ~ 40 times bigger than at 25 mM Cu^{2+} .

The effect of deposition temperature on grain size is shown in Fig. 5. It was reported that the reduction potential for Cu^{2+} to Cu^+ in an acetic bath shifted slightly positive with solution temperature.² This indicates that a larger over-potential is produced at a higher solution temperature, at a fixed applied potential. Therefore, a smaller grain size of Br-doped Cu_2O is expected at a higher deposition temperature, which contradicts the common wisdom that higher temperatures produce larger crystals. A grain size of $\sim 10,000 \mu\text{m}^2$ was obtained at deposition temperature of 50°C vs. $\sim 225 \mu\text{m}^2$ at 80°C .

Fig. 6 shows that the film thickness increases with NaBr concentration in the solution at a fixed deposition time. When the NaBr concentration is < 1.5 mM, the film thickness is stable at $\sim 1 \mu\text{m}$. However, the film thickness increases with NaBr concentration above 2 mM. It is interesting that the film thickness at 4 mM NaBr is only $\sim 4 \mu\text{m}$, while the grain size at this condition is $\sim 400 \mu\text{m}^2$.

1.2 Natural Resource Limitations to Terawatt-Scale Solar Cells

This is the most significant accomplishment this year. The paper was submitted to the European MRS Spring Meeting in May 2011 as a regular paper, and the organizing committee upgraded it to an invited talk. The manuscript is about to be submitted to Energy and Environmental Science, which will publish selected papers on photovoltaics from the Meeting.

The predicted energy demands will reach 28 terawatts (TW) by 2050 and 46 TW by 2100.³ The deployment of solar cells will have to expand to a scale of tens of peak terawatts (TWp) in order to become a noticeable source of energy in our future. Of the current commercial and developmental cell technologies, the majority suffer from natural resource limitations that prevent them from reaching a terawatt scale. These limitations include high energy input for crystalline-Si cells, limited material production for GaAs cells, and material scarcity for CdTe, CIGS, dye-sensitized, crystalline-Si and amorphous

FIG. 5 Grain size and deposition time of Br-doped Cu_2O as a function of deposition temperature. The deposition solution contained 10 mM $\text{Cu}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ and 2 mM NaBr. The deposition potential was 0 V and solution pH 5.25.

FIG. 6 Thickness and roughness of Br-doped Cu_2O as a function of NaBr concentration in the solution. The deposition potential was -0.05 V, solution pH 5.25 and deposition time 90 min.

² Y. Tang, Z. Chen, Z. Jia, L. Zhang and J. Li, Mater. Lett. **59**, 434 (2005).

³ M. I. Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter, M. E. Schlesinger, S. H. Schneider, R. G. Watts, T. M. L. Wigley and D. J. Wuebbles, Nature, **395**, 881 (1998).

Si cells. Our work provides a comprehensive, quantitative and up-to-date analysis on these resource limitations under the best scenarios, i.e. the maximum possible power from each of these cell technologies. The analysis provides strategic directions for photovoltaic research. Some of the important conclusions include:

- If monocrystalline-Si cells were deployed at 1 TWp per year, they would consume ~20% of the current global electricity production. With the cell lifetime at ~25 years, annual deployment of 1 TWp would result in 25 TWp total installation. Can the Earth squeeze out 20% of its electricity consumption for solar cells? The answer is not easy, since the question is not a purely technical one.
- The scarcest material for each cell technology is: Ag for crystalline-Si, Te for CdTe, In for CIGS, Ru for dye-sensitized and Ag/In for amorphous Si cells. The maximum possible power from each of these technologies, based on the known reserve of the limiting material, is listed in Table 1. Amorphous Si is not listed, since it competes with CIGS and crystalline-Si for In and Ag. These technologies combined would provide <4% of our energy in 2100 under best scenarios; practically maybe just 1–2%.

Table 1. The estimated, best-scenario maximum wattages for various solar cell technologies based on reserve base of the limiting material.

Cell Technology	Efficiency Used	Limiting Material	Reserve Base (tonne)	Maximum Wattage	Averaged Output (GW)	% of 2100 Demand
CdTe	10.6%	Te	48,000	816 GWp	120–160	0.4%
CIGS	11.5%	In	16,000	1.3 TWp	100–130	0.6%
Dye-sensitized	7%	Ru	5,000	890 GWp	135–180	0.4%
Crystalline-Si	15%	Ag	400,000	5.7 TWp	860–1150	2.5%

- The material production rates limit the deployment rates of various cell technologies. Table 2 lists the current production rates of the limiting materials for several cell technologies, and thus the maximum possible annual production for these technologies. Unless the material production is significantly increased, these technologies combined would allow <350 GWp annual production under best scenarios; practically maybe 100–200 GWp/yr.

Table 2. The estimated, best-scenario maximum annual production of various solar cell technologies based on the annual production of the limiting material.

Cell Technology	Efficiency Used	Limiting Material	Annual Production (tonne)	Annual Peak Wattage (GWp)	Years to Depletion
CdTe	10.6%	Te	135	2.3	355
CIGS	11.5%	Ga	167	26	25
Dye-sensitized	7%	Ru	12	2.2	405
Crystalline-Si	15%	Ag	21,400	305	19
GaAs	19.3%	Ga	167	7.3	N/A

- Several research directions are strategically important for solar cells to become a noticeable source of energy in our future. They include 1) energy-efficient production of Si feedstock; 2) substitution of Ag electrode with an abundant metal; 3) substitution of In-based transparent conducting oxide with an abundant material; and 4) development of a new terawatt-scale low-cost solar cell material with a direct bandgap of ~1.4 eV.

1.3 Ni Oxysulfide as Terawatt-Scale Solar Cell Material

Last year we started our pursuit of metal oxysulfide as our approach to a post-Si terawatt-scale solar cell material. We focused on Cu oxysulfide ($\text{Cu}_2\text{S}_x\text{O}_{1-x}$) last year and demonstrated an indirect bandgap of 1.5 eV in $\text{Cu}_2\text{S}_x\text{O}_{1-x}$. This year we focused to Ni oxysulfide ($\text{NiS}_x\text{O}_{1-x}$), in our attempt to find a solar cell material with a direct bandgap of ~ 1.4 eV. $\text{NiS}_x\text{O}_{1-x}$ meets most of the requirements for terawatt-scale solar cells: abundance, low-cost, non-toxicity. The bandgap of NiO is ~ 3 eV direct and that of NiS ~ 0.3 eV indirect. By mixing NiO and NiS in the right ratio, a direct bandgap of ~ 1.4 eV maybe be achievable.

Our effort so far has been on electrodeposition of NiS_x . The aqueous deposition solution contained NiSO_4 and NaS_2O_3 . Our plan is to synthesize $\text{NiS}_x\text{O}_{1-x}$ in two steps:

- Deposit a NiS_x film onto a substrate such as TCO-coated glass; and
- Anneal the NiS_x film in an O-containing ambient to form $\text{NiS}_x\text{O}_{1-x}$.

Important results from this study so far include:

- Electrodeposition of Ni_3S_2 : We have investigated many deposition conditions for NiS_x and have found the right recipe to reproducibly deposit Ni_3S_2 . Since Ni_3S_2 behaves metallic, our next goal is to deposit NiS, which should be a semiconductor;
- Prevention of S precipitation: S atoms formed during electrodeposition of NiS_x tend to agglomerate and then precipitate, making the deposition hard to control. We have successfully applied gelatin as an additive to prevent S precipitation.

The results from this study are still being analyzed and a more detailed description will be available in a few weeks.

1.4 First-Principles Studies of Doping in Cu_2O and Electronic Structures in NiS_x

N-type doping in Cu_2O by F, Cl and Br was studied last year. This year n-type doping by Mg, Ca and Zn in Cu_2O has been investigated by first-principles calculations. Each dopant is introduced in a 48-atom cubic supercell of Cu_2O . The high symmetry sites, which are usually stable, have been considered. They include two interstitial sites (tetrahedral and octahedral) and the substitution of a Cu

atom. The formation energies of the dopant at these sites as a function of Fermi level, which varies from the valence band maximum (VBM) to the conduction band minimum (CBM) have been calculated at pH=3. The energetically lowest interstitial site is compared with the

FIG. 7 Formation energies as a function of Fermi level within the bandgap of Cu_2O for Mg, Ca and Zn doping. Interstitial (I_X) and substitutional (X_{Cu}) doping with positive, neutral and negative charges are calculated. The lowest values indicate n-type doping.

substitutional site for each dopant. The likely charge states for each site are also calculated. The results are shown in Fig. 7. Both interstitial and substitutional sites for all three dopants have very low or even negative formation energies, indicating that doping is energetically favored. Unlike n-type doping by halogens where the formation energy for substitution of an oxygen atom by a halogen atom is always several eV lower than that of the lowest interstitial site, the formation energies of interstitial sites compete with those of substitutional sites. For Ca and Zn, the formation energies of the lowest interstitial site are ~ 0.6 eV lower than that of the substitutional site. For Mg doping, the formation energies of the two sites are almost identical.

We have also started a theoretical study on p-type doping in Cu_2O by N, P and As. Our preliminary results show that in a very acidic solution, substitution of a Cu atom by these three dopants has very low formation energies and the negatively charged state is lower than the neutral state when the Fermi level moves slightly above VBM, a typical p-type property. The transition states of neutral and charged ones suggest that they are likely shallow level acceptors. For example, the calculated transition state of N on an O site is only 0.1 eV above VBM.

We have also started a study on NiS, NiS_2 and NiO as potential solar cell material. Just like CuO, these materials are challenging for the methods such as local density approximation (LDA) or general gradient approximation (GGA) usually adopted by DFT. Although experiments showed NiS and NiS_2 as semiconductors with a small gap (< 0.3 eV), while NiO has a large gap (~ 3.8 eV), previous first-principles calculations with LDA or GGA always obtained metallic structures. To get a firm hold on these materials, we firstly focused on their electronic structures using GGA, GGA+U, and hybrid functional methods. More time-consuming spin-polarized calculations have been used since those materials were reported with anti-ferromagnetic or ferromagnetic phases. For NiS, a type-I anti-ferromagnetic arrangement with the hybrid method is the most promising, resulting in a small bandgap (0.175 eV) while GGA result is metallic, as shown in Fig. 8. For NiO, the prime cell of a NaCl structure gives metallic results for all methods. A type-II anti-ferromagnetic arrangement combined with the GGA+U method gave a 3.3 eV bandgap, in excellent agreement with experimental results. For NiS_2 , GGA and GGA+U gave conclusive yet unsatisfactory results, as compared to experiments, and the hybrid calculation has not been finished.

FIG. 8 Calculated density of states for NiS using GGA (top) and hybrid functional (bottom). The GGA result is a metal at Fermi level ($E=0$). The hybrid method with 25% Hartree-Fock exchange has a 0.175 eV bandgap.

2. Publications (BES is the sole sponsors of all these papers):

1. X. Han, K. Han, and M. Tao, Characterization of Cl-Doped N-Type Cu_2O Prepared by Electrodeposition, *Thin Solid Films*, 518, **5363** (2010).
2. W. Wang, D. Wu, Q. Zhang, L. Wang, and M. Tao, pH-dependence of Conduction Type in Cuprous Oxide Synthesized from Solution, *Journal of Applied Physics*, **107**, 123717 (2010).
3. C. S. Tao, J. Jiang, and M. Tao, Natural Resource Limitations to Terawatt-Scale Solar Cells, *Solar Energy Materials and Solar Cells*, submitted (Note: the manuscript was submitted in

August 2010, and an inquiry was made in February 2011, but we have not received any response. One of our colleagues had a similar experience with this journal).

4. K. Han, F. Kang, X. Han, and M. Tao, Enhanced Crystal Grain Size by Bromine Doping in Electrodeposited Cu₂O, *J. Cryst. Growth*, submitted
5. C. S. Tao, J. Jiang, and M. Tao, Natural Resource Limitations to Terawatt Solar Cell Deployment, ECS Transactions, **33**(17), 3 (2010) (This is a conference proceeding).
6. M. Tao and X. Han, Yttrium-Doped Zinc Oxide as a Terawatt-Scale Transparent Conducting Oxide, ECS Transactions, **33**(17), 13 (2010) (This is a conference proceeding).
7. Q. Zhang, W. Wang, D. Wu, Q. Bai, and M. Tao, Amphoteric Conductivity of Cu₂O: First-Principles Studies, 3rd Annual Meeting of DOE Computational Materials and Chemical Science Network on Predictive Modeling of Growth and Properties of Energy-Relevant Thin Film and Nanostructures (Dallas, 2011) (This is an invited talk).
8. C. S. Tao, J. Jiang, and M. Tao, Resource Limitations to Terawatt Solar Cells, European Materials Research Society Symposium on Advanced Inorganic Materials and Concepts for Photovoltaics (Nice, France, 2011) (This is an invited talk).

3. Participants:

1. Xiaofei Han, PhD student, 100%
2. Qiong Bai, PhD student, 100%
3. Munteha Pac, MS student (PhD intended), 100% (started in June 2010)