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Cuprous oxide (Cu<sub>2</sub>O) is naturally p-type, which has prevented an efficient Cu<sub>2</sub>O solar cell. n-Type doping of Cu<sub>2</sub>O is demonstrated during electrochemical deposition by adding a chlorine (Cl) precursor to the aqueous solution. Current-voltage characterization reveals that the resistivity of undoped Cu<sub>2</sub>O by electrochemical deposition is  $\sim 40 \text{ M}\Omega$  cm, while that of electrochemically doped Cu<sub>2</sub>O with Cl is significantly reduced to as low as  $\sim 7 \Omega$  cm. X-ray diffraction confirms that the films are pure Cu<sub>2</sub>O. Photocurrent measurements verify that Cl-doped Cu<sub>2</sub>O is n-type. The solution-based doping method is particularly suitable for low-cost, large-area, and high-throughput fabrication of Cu<sub>2</sub>O solar cells. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3065976] All rights reserved.

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With its direct bandgap of 2.0 eV, abundant source materials, and nontoxicity, Cu<sub>2</sub>O has been regarded as one of the most promising materials for photovoltaic solar cells.<sup>1,2</sup> Cu<sub>2</sub>O films can be prepared from solution including electrochemical deposition<sup>3,4</sup> and sol-gel-like dip coating,<sup>5</sup> promising low-cost fabrication of Cu<sub>2</sub>O solar cells. Although the theoretical efficiency of Cu<sub>2</sub>O solar cells is ~19%, the best-reported efficiency is only ~2%.<sup>6</sup> The low efficiency was attributed to the natural p-type conduction in Cu<sub>2</sub>O,<sup>7</sup> which prevented a p-n junction in Cu<sub>2</sub>O, the basic device structure in most inorganic solar cells. There was a report on n-type Cu<sub>2</sub>O by electrochemical deposition with low solution pH,<sup>8</sup> and Wang et al. recently demonstrated a p-n junction in Cu<sub>2</sub>O by electrochemical deposition.<sup>9</sup> A more-detailed study of the Cu<sub>2</sub>O p-n junction revealed highly resistive n-type Cu<sub>2</sub>O by electrochemical deposition in the range of  $2.5 \times 10^7$  to  $8.0 \times 10^8 \Omega$  cm, leading to a low efficiency of  $\sim 0.1\%$  for a solar cell built on the Cu<sub>2</sub>O p-n junction.

In this article, we report an electrochemical method to dope Cu<sub>2</sub>O n-type and to reduce its resistivity from megaohm centimeters to below 10  $\Omega$  cm. This enables Cu<sub>2</sub>O p-n junction solar cells with a much-improved efficiency, potentially exceeding 10%. More importantly, the n-type doping method is applicable to many metal oxides and metal chalcogenides prepared from solution, allowing cost-effective improvement of efficiency in many current and future solar cells made on these materials. Furthermore, doping is accomplished by one of the following methods in the conventional semiconductor technology: (i) diffusion of a dopant into a semiconductor at high temperatures, (ii) implantation of a dopant into a semiconductor with energetic ions, and (iii) codeposition of a dopant during growth of a semiconductor. The last method is typically carried out by chemical vapor deposition,<sup>11</sup> molecular beam epitaxy, or related processes. All these methods require vacuum systems. Besides their inherently high cost, the vacuum systems also limit throughput and size of the substrate. Our doping method is solution-based, which is particularly suitable for low-cost, large-area, and high-throughput fabrication of solar cells.

Substitutional n-type doping in Cu<sub>2</sub>O can go into either Cu or O sites. Based on the valence of Cu, +1, and O, -2, in Cu<sub>2</sub>O, potential n-type dopants include group VII elements, i.e., halogens, for O sites and group II elements for Cu sites. Our work focuses on halogens as n-type dopants in Cu<sub>2</sub>O, because such a method is in principle universal for n-type doping in any metal oxide and metal chalcogenide. The valence of O or chalcogen in these materials is always -2. Out of all the halogens, F is best size-matched to O, but CuF is soluble in water. In this article, we report Cl as a successful n-type dopant in electrochemically deposited Cu<sub>2</sub>O. Although Cl doping of Cu<sub>2</sub>O has been attempted by introducing HCl into oxidation of Cu, it was

reported to be a p-type dopant.<sup>12</sup> To the best of our knowledge, solution-based doping in Cu<sub>2</sub>O has never been reported.

# Experimental

Electrochemical experiments were carried out using a Princeton Applied Research VERSTAT II potentiostat. Electrochemical deposition was performed in a three-electrode cell with a Pt counter electrode, a Ag/AgCl/saturated NaCl reference electrode, and a Cucoated glass substrate as the working electrode with a typical dimension of  $1 \times 4$  cm<sup>2</sup>. Electrochemical doping of n-type Cu<sub>2</sub>O with Cl has also been demonstrated on Au and Ti substrates. The thickness of the Cu coating was  $\sim$ 400 nm. Prior to electrochemical deposition, the Cu-coated glass substrates were rinsed with acetone and then sonicated in distilled water for  $\sim 15$  min. The deposition solution contained 0.3 M  $\rm CuSO_4$  and 4 M sodium lactate (60% w/w aqueous solution), with solution pH adjusted to 7.5 by adding 4 M NaOH.<sup>13</sup> CuSO<sub>4</sub> was first dissolved in deionized water to the desired concentration of 0.3 M. Lactic acid was then added to the solution to a concentration of 4 M. Lactic acid served as the complexing agent to prevent Cu precipitation when NaOH was added to the solution. NaOH (4 M) was added to the solution to adjust its pH. Therefore, the exact amount of NaOH added to the solution was determined by monitoring solution pH to a desired value. For deposition of n-type Cu<sub>2</sub>O, solution pH was adjusted to below 9.<sup>9</sup> CuCl<sub>2</sub> was used as the Cl precursor, with its concentration in the solution varying from 0.01 to 0.15 M to control the doping level in Cu<sub>2</sub>O. The deposition temperature was controlled by a Precision 280 water bath, and the deposition time was 1 h. All the chemicals used were reagent grade.

The thickness of the Cu<sub>2</sub>O films was measured with a KLA-Tencor Alpha-Step IQ profilometer. The structural properties of the Cu<sub>2</sub>O films were determined by a Simens D-500 X-ray diffractometer (XRD) using the Cu K $\alpha$  line. Photocurrent characterization was carried out in a three-electrode electrochemical cell with a broad-spectrum 90 W white lamp shining onto the working electrode. A Pt foil, a Ag/AgCl/saturated NaCl reference electrode, and a Cu<sub>2</sub>O/Cu/glass sample were used as the counter, reference, and working electrode, respectively. For photocurrent measurements, the solution contained 0.5 M Na<sub>2</sub>SO<sub>4</sub>. To measure the resistivity of Cldoped n-type Cu<sub>2</sub>O, circular dots of Cu were deposited as the top electrode by a thermal evaporator through a shadow mask on Cu<sub>2</sub>O films. The area of the electrodes was  $3.6 \times 10^{-4}$  cm<sup>2</sup>. Current– voltage (I-V) characterization was performed with an HP 4155C semiconductor parameter analyzer. The resistivity of the Cl-doped Cu<sub>2</sub>O films was calculated from the slope of the I-V relations and the thickness of the Cu<sub>2</sub>O films.

## **Results and Discussion**

Electrochemical deposition of Cu<sub>2</sub>O is achieved by applying a constant potential between a Cu-coated glass substrate (working electrode) and a Pt foil (counter electrode), but the quoted potential

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**Figure 1.** CV of a deposition solution containing 0.3 M CuSO<sub>4</sub>, 4 M lactic acid, and 0.1 M CuCl<sub>2</sub>. The solution temperature is 60°C, and the solution pH is 7.5. There are two reduction reactions for Cu<sup>2+</sup> ions, which lead to Cu<sup>+</sup> ions and metallic Cu. The reduction potential for Cu<sup>+</sup> ions is between -0.05 and -0.15 V.

in this paper is referred to the Ag/AgCl/saturated NaCl reference electrode. Before deposition, cyclic voltammetry (CV) is performed in a deposition solution containing 0.1 M CuCl<sub>2</sub> at 60°C. As shown in Fig. 1, CV reveals two reduction reactions for Cu<sup>2+</sup> ions; one leads to Cu<sup>+</sup> ions and the other to metallic Cu

$$\mathrm{Cu}^{2+} + \mathrm{e}^{-} \to \mathrm{Cu}^{+}$$
<sup>[1]</sup>

$$Cu^{2+} + 2e^- \rightarrow Cu$$
 [2]

The potential for Reaction 1 is between -0.05 and -0.15 V vs the Ag/AgCl/saturated NaCl reference electrode. This potential range is different from our previous report.<sup>9</sup> It is suggested that Cl<sup>-</sup> ions added to the solution change the reduction potential of Cu<sup>2+</sup> to Cu<sup>+</sup> ions. In this study, we choose -0.1 V as the deposition potential applied to the working electrode. The produced Cu<sup>+</sup> ions react with OH<sup>-</sup> ions in the solution to form Cu<sub>2</sub>O<sup>14</sup>

$$2Cu^{+} + 2OH^{-} \rightarrow Cu_{2}O \downarrow + H_{2}O$$
[3]

With the presence of  $Cl^-$  ions in the solution,  $Cu^+$  ions also react with  $Cl^-$  ions to form CuCl, which incorporates Cl into  $Cu_2O$  and thus dope the  $Cu_2O$  film

$$Cu^+ + Cl^- \rightarrow CuCl\downarrow$$
 [4]

The solubility product constant of CuCl, i.e., the product of  $[Cu^+]$  and  $[Cl^-]$ , is  $1.72 \times 10^{-7}$  at  $25^{\circ}C$ .<sup>15</sup> This means that even small amounts of Cu<sup>+</sup> and Cl<sup>-</sup> in the solution react with each other and form solid CuCl.

Several samples have been prepared with different CuCl<sub>2</sub> concentrations in the deposition solution at 60°C. All the samples appear polycrystalline with a gain size of ~100 nm. The thickness of the films is controlled to between 300 and 400 nm, measured with a profilometer. After deposition, photocurrent measurements are performed to determine the conduction type of the Cl-doped Cu<sub>2</sub>O samples. Photocurrent from a Cl-doped Cu<sub>2</sub>O sample deposited with 0.1 M CuCl<sub>2</sub> is shown in Fig. 2. The anodic current indicates an n-type semiconductor.<sup>8</sup> During the measurement, the applied potential is 0 V vs the reference electrode. The solution contains 0.5 M Na<sub>2</sub>SO<sub>4</sub>. A 90 W white lamp is used as the light source, with the light chopped on and off by a rotating disk. To further confirm the n-type conduction of the Cl-doped Cu<sub>2</sub>O samples, the photocurrentpotential characterization is performed between -0.6 and 0.1 V (data not shown). At about -0.3 V, there is a direction change in



Figure 2. Photocurrent measured from Cl-doped Cu<sub>2</sub>O. For the measurement, the applied potential is 0 V vs an Ag/AgCl/saturated NaCl reference electrode. The solution contains 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The sample is illuminated with a 90 W white-light source. The anodic current indicates an n-type semiconductor.

photocurrent from negative (cathodic) to positive (anodic). For p-type Cu<sub>2</sub>O between -0.6 and 0 V, the photocurrent should always be negative.<sup>16</sup>

To confirm that the films deposited under the conditions described above are pure Cu<sub>2</sub>O, several samples have been prepared under the same conditions on Au substrates for XRD analysis. Figure 3 shows the XRD pattern on such a sample deposited with 0.1 M CuCl<sub>2</sub>, with one difference. The thickness of this Cl-doped Cu<sub>2</sub>O film is  $\sim$ 700 nm, twice as thick as other samples reported in this paper. Although the (111) peak from Cu<sub>2</sub>O is still weak as compared to the Au(111) peak, it is clear from XRD that Cu<sub>2</sub>O is the only phase present in the film.

For *I-V* characterization, circular Cu dots of 200  $\mu$ m in diameter and 300 nm in thickness are deposited by thermal evaporation on Cl-doped Cu<sub>2</sub>O samples through a shadow mask. These dots, with an area of 3.6 × 10<sup>-4</sup> cm<sup>2</sup>, serve as the top electrodes, and the Cucoated glass substrate serves as the bottom electrode for *I-V* characterization. All the *I-V* relations from Cl-doped Cu<sub>2</sub>O samples show



**Figure 3.** XRD of Cl-doped Cu<sub>2</sub>O on Au substrate. The CuCl<sub>2</sub> concentration is 0.1 M, and the film thickness is 700 nm. Only the Cu<sub>2</sub>O(111) peak is observed, indicating that Cu<sub>2</sub>O is the only phase present in the film. The Au(111) and (200) peaks come from the substrate.



Figure 4. Resistivity of undoped and Cl-doped Cu<sub>2</sub>O as a function of CuCl<sub>2</sub> concentration in the solution. This is a logarithmic plot, and the inset is a linear plot. Without doping, the resistivity of Cu<sub>2</sub>O is  $\sim$ 40 M $\Omega$  cm, while that of Cl-doped Cu<sub>2</sub>O is reduced to between 157 and 48  $\Omega$  cm. The solution temperature is 60°C.

linear behavior. From the slope of the I-V relations and the thickness of the Cu<sub>2</sub>O films, the resistivity of the Cl-doped Cu<sub>2</sub>O samples is extracted.

The resistivity of undoped and Cl-doped Cu<sub>2</sub>O samples as a function of CuCl<sub>2</sub> concentration in the solution is shown in Fig. 4. Without doping, the resistivity of electrochemically deposited Cu<sub>2</sub>O is  $\sim 40 \text{ M}\Omega$  cm, which is too high to produce an efficient solar cell. However, with 0.1 M CuCl<sub>2</sub> in the solution, the resistivity of the  $Cu_2O$  sample is significantly reduced to ~75  $\Omega$  cm, a reduction in Cu<sub>2</sub>O resistivity of over 5 orders of magnitude.

The most important parameter to control the resistivity of Cldoped Cu<sub>2</sub>O is the concentration of CuCl<sub>2</sub> in the solution; the higher the concentration, the more Cl incorporated into Cu<sub>2</sub>O and the lower the resistivity of the sample. In other words, by adjusting the Cl concentration in the solution, the resistivity of the Cu<sub>2</sub>O film can be controlled. The inset in Fig. 4 shows the resistivity of Cl-doped Cu<sub>2</sub>O samples as a function of CuCl<sub>2</sub> concentration in the solution. As expected, a higher Cl concentration reduces the resistivity of Cu<sub>2</sub>O. Between 0.01 and 0.15 M of CuCl<sub>2</sub>, the resistivity of Cu<sub>2</sub>O is reduced from  $\sim 157$  to  $\sim 48 \Omega$  cm.

Solution temperature primarily affects the growth rate and grain size of the polycrystalline Cu<sub>2</sub>O film. As the temperature increases, the growth rate and grain size increase. Large grains can improve the electrical properties of the Cu<sub>2</sub>O film, such as carrier mobility and minority carrier lifetime. In an aqueous solution, evaporation occurs when the temperature is close to 100°C, which changes the solution concentration and pH. We have investigated the effect of solution temperature on Cu<sub>2</sub>O resistivity with a fixed CuCl<sub>2</sub> concentration of 0.1 M. Figure 5 shows the resistivity of Cl-doped Cu<sub>2</sub>O as a function of solution temperature. Between 50 and 80°C, the resistivity is reduced from  $\sim\!103$  to  $~\sim~7~\Omega$  cm. The latter is close to the optimum resistivity for an efficient solar cell,  $\sim 1 \ \Omega$  cm. Efforts are underway to bring down the resistivity of Cl-doped Cu<sub>2</sub>O to below  $1 \Omega$  cm.

The decrease in resistivity with temperature may be attributed to increased Cl incorporation into Cu<sub>2</sub>O at higher temperatures. It is speculated that Cl incorporation creates a concentration gradient for Cl<sup>-</sup> ions in the deposition solution. However, the diffusion coeffi-



Figure 5. Resistivity of Cl-doped Cu<sub>2</sub>O as a function of solution temperature. Between 50 and 80°C, the resistivity of Cl-doped Cu<sub>2</sub>O is reduced from 103 to 7  $\Omega$  cm. The CuCl<sub>2</sub> concentration is 0.1 M.

cient of typical ions in a solution increases by 2-3%/°C around 25°C,<sup>15</sup> which reduces the concentration gradient for Cl<sup>-</sup> ions and increases Cl incorporation into Cu2O.

## Conclusion

In summary, an electrochemical method is demonstrated to dope Cu<sub>2</sub>O n-type during electrochemical deposition from an aqueous solution. By adjusting the Cl concentration in the solution, the resistivity of the Cu<sub>2</sub>O film is reduced from  $\sim$ 157 to  $\sim$  48  $\Omega$  cm. By increasing deposition temperature from 50 to 80°C, the resistivity of the Cu<sub>2</sub>O film is further reduced from  $\sim 103$  to  $~\sim 7~\Omega$  cm. XRD confirms that the films are pure Cu<sub>2</sub>O. Photocurrent measurements demonstrate that the Cl-doped Cu<sub>2</sub>O samples are n-type semiconductors. The low-resistivity n-type Cu<sub>2</sub>O films are expected to significantly improve the efficiency of Cu<sub>2</sub>O solar cells. Compared to conventional vacuum-based doping methods, this solution-based doping method is particularly suitable for low-cost, large-area, and high-throughput fabrication of solar cells.

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