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# Annealing effects of the untreated and sulfur-treated electrodeposited n-type and p-type cuprous oxide thin films

K. M. D. C. Jayathilaka<sup>1,2</sup>, L. S. R. Kumara<sup>3</sup>, C. H. Song<sup>3</sup>, S. Kohara<sup>4,5</sup>, O. Sakata<sup>3,4</sup>, V. Kapaklis<sup>6</sup>, W. Siripala<sup>2</sup>, and J. K. D. S. Jayanetti<sup>\*1</sup>

<sup>1</sup> Department of Physics, University of Colombo, Colombo 3, Sri Lanka

<sup>2</sup> Department of Physics, University of Kelaniya, Kelaniya, Sri Lanka

<sup>3</sup> Synchrotron X-ray Station at SPring-8, National Institute for Materials Science (NIMS), 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

<sup>4</sup> Synchrotron X-ray Group, Quantum Beam Unit, NIMS, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

<sup>5</sup> Research and Utilization Division, Japan Synchrotron Radiation Research Institute/SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

<sup>6</sup> Department of Physics and Astronomy, Uppsala University, Box 516, S-75120 Uppsala, Sweden

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\* Corresponding author: e-mail [sumedhajayanetti@gmail.com](mailto:sumedhajayanetti@gmail.com), Phone: +94 112584777, Fax: +94 9112584777

The n-type and p-type cuprous oxide thin films were electrodeposited potentiostatically in acetate and lactate baths, respectively. Sulfur treatment of n-type and p-type cuprous oxide surfaces were achieved using gaseous (NH<sub>4</sub>)<sub>2</sub>S. Sulfur-treated Cu<sub>2</sub>O films were annealed in air at 100, 150, 200, 250, 350, and 450 °C for unique times to obtain the best photocurrent. Unannealed and annealed samples of sulfur-treated and untreated cuprous oxide were then investigated using high-energy X-ray diffraction (HEXRD). The HEXRD

measurements and the pair distribution function (PDF) analysis revealed that the sulfur treatment leads to the formation of crystalline CuS on Cu<sub>2</sub>O film surfaces. The present study also shows that the sulfur treatment causes minor structural changes in Cu<sub>2</sub>O samples due to the formation of CuS. It was observed that the sulfur-treated cuprous oxide samples retarded the formation of CuO at higher temperatures showing good thermal stability and enhancement of the photoactivity of the n-type and p-type cuprous oxides.

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**1 Introduction** Solar energy harvesting technologies, such as photovoltaics, have received wider attention in recent times among alternative clean energy sources due to the year round availability of solar energy. The nontoxicity and abundance of solar energy materials in the earth are among the key requirements to solar energy conversion technologies. In addition to their toxicities, some of the materials such as CdTe and CIGS (CuInGaSe<sub>2</sub>), may not be abundant enough for large scale use in energy conversion technologies involving conventional thin films. From this point of view, copper and zinc-based materials like Cu<sub>2</sub>O, Cu<sub>x</sub>S, ZnO, ZnS are of special interest both in the form of thin films and nanostructures as active layers, electron and hole transporting layers, or transparent contacts [1, 2]. Ability to fabricate these materials and related devices using less expensive techniques has made them even more suitable for such applications. Cuprous oxide (Cu<sub>2</sub>O),

a nontoxic material, can be synthesized with relative ease using scalable methods such as electrodeposition. Cu<sub>2</sub>O has a direct band gap of 2 eV. Extensive efforts have been made over the last decades to develop efficient Cu<sub>2</sub>O-based solar cells [2–6]. Due to the continuous efforts in research on thin film Cu<sub>2</sub>O-based devices, earlier recorded efficiencies that were stagnating around 1–2% have reached upto 6.1% recently where Cu<sub>2</sub>O has been used as the active layer in a p-Cu<sub>2</sub>O/n-Ga<sub>2</sub>O<sub>3</sub> heterostructure. Therefore, studies show the promise of Cu<sub>2</sub>O as a good solar cell material of which the theoretical efficiency is about 20% [3, 5, 6].

Some of the key issues that need to be addressed in Cu<sub>2</sub>O thin film solar cell development is the associated high resistivity and defects of the Cu<sub>2</sub>O thin films. For device applications, especially, the minimization of surface defects such as those due to dangling bonds and nonradiative recombination centers in the Cu<sub>2</sub>O films is of utmost

importance because it causes to reduce resistivity and enhance the electrical and optical properties [7–10]. An obvious approach to modify surface and interface properties of semiconductors is to make the surface interact with foreign atoms, e.g., sulfur [11], selenium [12], chlorine [13], or simple radicals, e.g., cyanides [14]. Such an approach leads to a significant reduction of non-radiative surface recombinations for many compound semiconductors and their solid solutions resulting in improved device performance. Studies conducted by us on passivation of n-Cu<sub>2</sub>O and p-Cu<sub>2</sub>O thin films using ammonium sulfide have demonstrated that the film resistivity can be lowered while increasing the photoactivity of the related thin film solar cell structures. It was shown that the increase in the peak photocurrent was approximately a 50-fold and 4-fold, respectively, compared to the untreated n-type Cu<sub>2</sub>O and p-type Cu<sub>2</sub>O films [9, 10]. The passivation along with annealing was successfully used to improve the efficiency of Ti/p-CuO/n-Cu<sub>2</sub>O/Au solar cell. The cell yielded a power conversion efficiency of 0.64%, which to the best of our knowledge is the highest reported efficiency for a CuO-based solar cell [15]. Further studies with regard to structural and thermal stability of passivated and annealed Cu<sub>2</sub>O thin films will provide important information for improving the performance of such devices. Previously, it was verified that the sulfur passivation of both n-Cu<sub>2</sub>O and p-Cu<sub>2</sub>O thin films using ammonium sulfide led to the formation of Cu<sub>x</sub>S. However, the nature of the so formed Cu<sub>x</sub>S was not able to be examined by laboratory X-ray diffraction [9, 10] which has limitations in providing complete information when the thin films consist of species in the form of very thin layers or dilute quantities. This can be circumvented by the use of high-energy X-ray diffraction (HEXRD) in which the diffraction data of high signal to noise ratio is capable of divulging structural information in a more accurate manner. In this work, impact of the ammonium sulfide-based passivation process on n-type and p-type Cu<sub>2</sub>O thin films was investigated using HEXRD. Structural changes of both untreated and ammonium sulfide-treated Cu<sub>2</sub>O samples were monitored at room temperature (30 °C) and at 450 °C.

**2 Experimental** Cu<sub>2</sub>O thin films were deposited on Ti substrates that were cleaned with detergent, diluted HNO<sub>3</sub>, in an acetone bath, and finally with distilled water prior to electrodeposition. The n-type Cu<sub>2</sub>O films were electrochemically deposited on a Ti substrate in an aqueous solution containing 0.01 M copper acetate and 0.1 M sodium acetate at solution pH of 5.6, a deposition potential of –200 mV versus saturated calomel electrode (SCE) and at a temperature of 60 °C. p-Cu<sub>2</sub>O films were deposited on Ti substrates in an aqueous solution containing 0.4 M copper sulfate and 3 M sodium lactate at a solution pH of 12, the deposition potential of –450 mV versus SCE and at a temperature of 60 °C. In order to obtain Cu<sub>2</sub>O thin films of similar thicknesses, different deposition times were used. To passivate the film surfaces, (NH<sub>4</sub>)<sub>2</sub>S vapor treatment was

used by simply holding the Cu<sub>2</sub>O film face down above a beaker containing 20 vol% (NH<sub>4</sub>)<sub>2</sub>S solution for n-type and 50 vol% (NH<sub>4</sub>)<sub>2</sub>S solution for p-type at 27 °C, followed by rinsing immediately with distilled water. Detailed experimental procedure has been discussed elsewhere [9, 10]. In order to make the spectral response measurements, all sulfur-treated Cu<sub>2</sub>O thin films were investigated in a three electrode photoelectrochemical cell containing a 0.1 M sodium acetate solution. Detailed experimental procedure has been discussed elsewhere [16]. During the measurements, the applied potential was maintained at 0 V versus SCE. The HEXRD experiments were performed using two-axis diffractometer at the beamline BL04B2 of SPring-8, Japan. The Si (220) monochromator was used to obtain an incident X-ray of wavelength of 0.20095 Å (energy ≈ 61.7 keV), and the intensity of the incident X-ray beam was monitored by an ionization chamber filled with Ar gas of 99.99% purity. The samples were held in a vacuum bell jar to avoid scattering of X-rays in air, and the diffracted X-rays were collected using three CdTe detectors in transmission geometry with the angle from 0.3° to 48° (corresponding  $Q = 0.2–25 \text{ \AA}^{-1}$ ). In order to perform HEXRD, electrodeposited sulfur-treated Cu<sub>2</sub>O thin films were peeled off from Ti substrates and filled in to silica capillary tubes of 1 mm internal diameter × 0.2 mm thickness × 70 mm length. Thermal stability of untreated and sulfur-treated Cu<sub>2</sub>O samples were investigated using HEXRD measurements after heating the Cu<sub>2</sub>O-filled capillaries at 450 °C on a hot plate for 2 h.

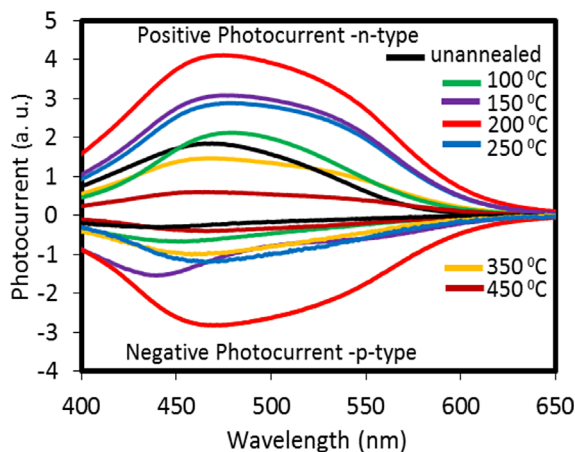
**3 Results and discussion** The sulfur-treated Cu<sub>2</sub>O films were annealed in air at 100, 150, 200, 250, 350, and 450 °C for a specific time at each temperature as shown in Table 1 to produce the best photocurrent. Optimization of the above annealing time duration was achieved by measuring the photoactivity of the sulfur-treated films in a photo electro chemical (PEC) cell.

Figure 1 shows the spectral response characteristics of n-type and p-type sulfur-treated Cu<sub>2</sub>O thin films for different annealing temperatures. The positive photoresponse shown in Fig. 1 corresponds to the n-type conductivity and the negative photoresponse corresponds to the p-type conductivity of the Cu<sub>2</sub>O thin films. It can be clearly seen that there is an improvement of the photoresponse with annealing temperature up to around 200 °C for both the n-type and p-type Cu<sub>2</sub>O films. Optimum results revealed that the annealing of Cu<sub>2</sub>O samples

**Table 1** Optimum annealing time to produce highest photocurrent for different annealing temperatures of n-type and p-type sulfur-treated Cu<sub>2</sub>O samples.

| annealing temperature (°C) | 100 | 150 | 200 | 250 | 350 | 450 |
|----------------------------|-----|-----|-----|-----|-----|-----|
| optimum time (h)           |     |     |     |     |     |     |
| n-type                     | 5   | 4   | 2   | 1   | 0.5 | 0.1 |
| p-type                     | 8   | 6   | 3   | 1   | 0.5 | 0.1 |



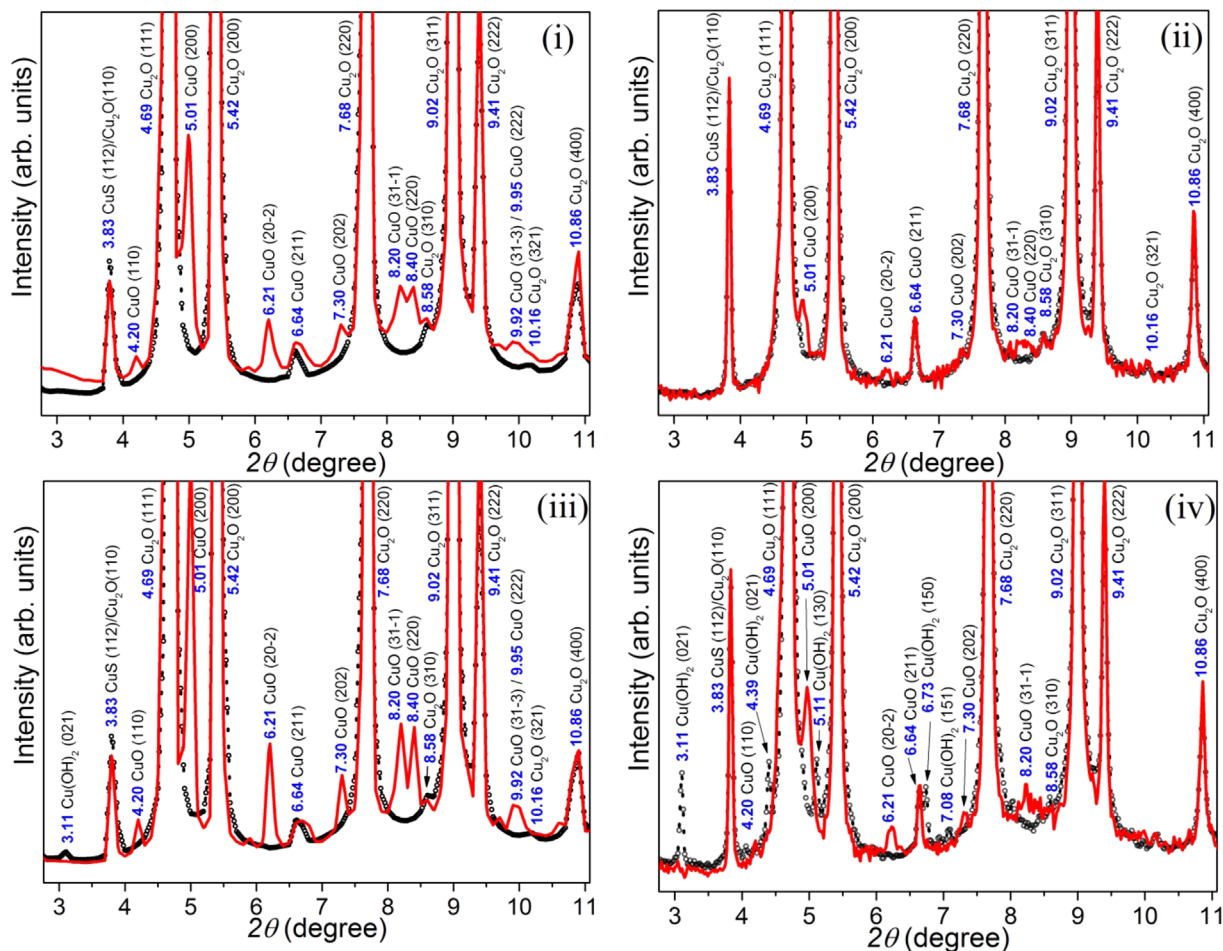


**Figure 1** Spectral response of sulfur-treated n-type  $\text{Cu}_2\text{O}$  and p-type  $\text{Cu}_2\text{O}$  films in a PEC as a function of annealing temperature.

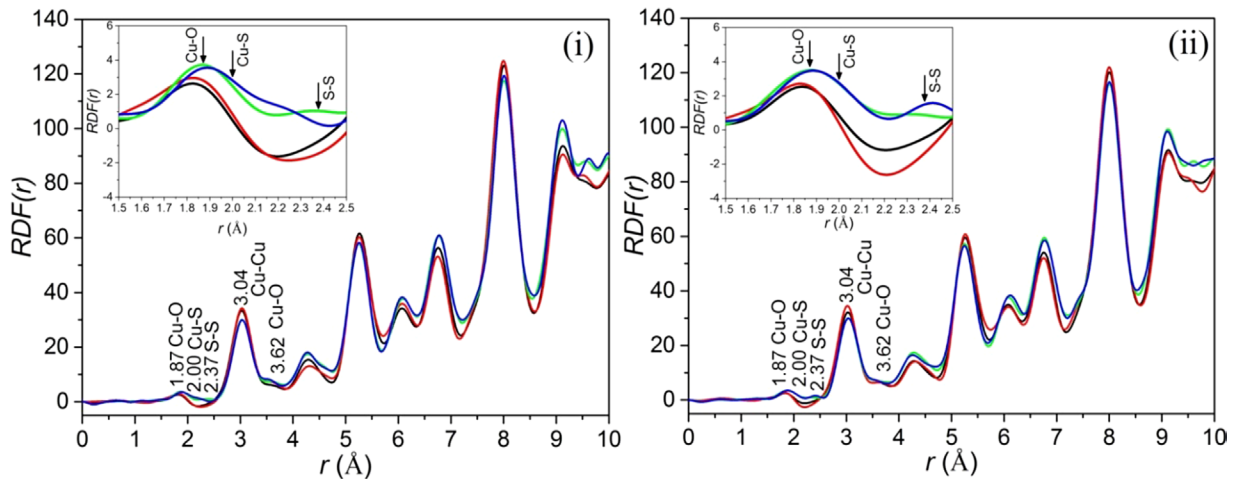
improves the peak photocurrent performance compared to that of unannealed samples by about 2-fold and 8-fold for sulfur-treated n-type  $\text{Cu}_2\text{O}$  and p-type  $\text{Cu}_2\text{O}$  films, respectively.

Figure 1 shows that further increase in the annealing temperature has resulted in a reduction in photoresponse. This is attributed to the possible formation of an amorphous  $\text{TiO}_2$  layer on Ti substrate which causes resistance of the substrate to increase. The decrease in photocurrent after annealing at higher temperatures (400 and 450 °C) can be attributed to the formation of  $\text{CuO}$  by oxidation of the  $\text{Cu}_2\text{O}$  layer.

Figure 2 shows the HEXRD measurements of (i) n-type  $\text{Cu}_2\text{O}$ , (ii) sulfur-treated n-type  $\text{Cu}_2\text{O}$ , (iii) p-type  $\text{Cu}_2\text{O}$ , and (iv) sulfur-treated p-type  $\text{Cu}_2\text{O}$  at room temperature (black circles) and annealed at 450 °C (red line). An XRD peak that was absent in previously reported XRD patterns [9, 10] could be observed using the HEXRD experiments. It was found to be due to the formation of an orthorhombic crystalline  $\text{CuS}$  phase after the sulfur treatment. As a result, the (110)  $\text{Cu}_2\text{O}$  diffraction peak at  $2\theta$  value of  $3.82^\circ$  has shifted slightly while increasing the intensity of the overall diffraction profile in which overlapped peaks of both  $\text{CuS}$  (at  $2\theta = 3.83^\circ$ ) and  $\text{Cu}_2\text{O}$  (at  $2\theta = 3.82^\circ$ ) are present. Calculations showed that the intensity ratio of (110)/(111)  $\text{Cu}_2\text{O}$  peaks of untreated n- $\text{Cu}_2\text{O}$  (0.025) and



**Figure 2** HEXRD patterns of (i) n-type  $\text{Cu}_2\text{O}$ , (ii) sulfur-treated n-type  $\text{Cu}_2\text{O}$ , (iii) p-type  $\text{Cu}_2\text{O}$ , and (iv) sulfur-treated p-type  $\text{Cu}_2\text{O}$  at room temperature (black circles) and annealed at 450 °C (red line).



**Figure 3** RDF profiles of (i) n-type Cu<sub>2</sub>O and (ii) p-type Cu<sub>2</sub>O, untreated at room temperature (black) and annealed at 450 °C (red), as well as sulfur-treated at room temperature (green) and annealed at 450 °C (blue).

p-Cu<sub>2</sub>O (0.024), respectively, had increased up to 0.055 after the sulfur treatment. Thus, these measurements confirm that the ammonium sulfide surface treatment causes to form very thin crystalline CuS films on the surface of the Cu<sub>2</sub>O films. It has been found that CuS shows a metal-like character [17–19], and therefore it is very useful to make devices with ohmic contacts. In Fig. 2, a comparison of the HEXRD patterns of untreated n-type and p-type Cu<sub>2</sub>O samples unannealed (room temperature 30 °C) (black circles) and annealed at 450 °C (red line) clearly shows that several CuO peaks have evolved after annealing at 450 °C due to the oxidation of Cu<sub>2</sub>O into CuO phase. However, it can be seen that the intensity of the CuO peaks of the annealed sulfur-treated Cu<sub>2</sub>O samples (blue line) are smaller compared to those of annealed untreated Cu<sub>2</sub>O samples (red line). Therefore it is clear, that the sulfur treatment helps to retard the formation of CuO phase at higher temperatures providing more thermal stability to the Cu<sub>2</sub>O samples.

In order to understand and to exploit the properties of materials better, a detailed knowledge about the atomic-scale structure is needed. However, it is not possible to obtain the crystallinity of thinner materials by using the laboratory X-ray diffraction, due to the effect of low signal to noise ratio. Lattice environments of such situations are derivable from HEXRD by mathematically converting the polarization, absorption, and background-corrected HEXRD data into a total structure factor  $S(Q)$  and radial distribution function (RDF) by a Fourier transformation of  $S(Q)$  [20]. Figure 3 shows the radial distribution functions of unannealed and annealed samples of sulfur-treated and untreated (i) n-type and (ii) p-type Cu<sub>2</sub>O. The figure clearly indicates that both n-type and p-type Cu<sub>2</sub>O have closely matched lattice parameters and the bond distances agree well with the previously reported data [21]. It can be seen that the peak of the first nearest neighbor Cu–O bond distance at 1.83 and 1.84 Å observed for untreated

n-Cu<sub>2</sub>O and p-Cu<sub>2</sub>O films, respectively, has increased up to 1.87 Å after the sulfur treatment. On the other hand, for the sulfur-treated Cu<sub>2</sub>O films, the shape of the RDF at 1.5–2.5 Å (see the insets) has substantially changed from the RDF profile of the untreated Cu<sub>2</sub>O sample due to the formation of Cu–S bond at 2 Å and S–S bond at 2.37 Å, the bond distances corresponding to orthorhombic CuS phase [22].

**4 Conclusions** These measurements confirm that the ammonium sulfide surface treatment causes to form very thin crystalline orthorhombic CuS layers on the surface of the Cu<sub>2</sub>O films providing a better thermal stability to them. Thus these results suggest that the annealing after sulfur treatment can have positive effects on the optical properties of Cu<sub>2</sub>O-based devices.

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