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Surface treatment of electrodeposited n-type Cu$_2$O thin films for applications in Cu$_2$O based devices

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In this Letter, we report the effects of ammonium sulfide [(NH$_4$)$_2$S] surface treatment on electrical and optical characteristics of the electrodeposited n-type Cu$_2$O thin films on Ti substrates. Films characterized structurally and morphologically before and after the surface treatment were compared using conductivity, spectral photoresponse and current–voltage (*I–V*) measurements. The ammonium sulfide surface treatment time showed an impact on optical and electrical characteristics of the films. Treated Cu$_2$O films exhibited enhanced conductivity giving rise to a 50-fold increase in the photocurrent and improved *I–V* characteristics. It was found that the sulfur passivation resulted in a nearly ohmic behaviour for Au or Ni contacts made with n-type Cu$_2$O whereas Ag or Cu contacts showed nearly Schottky behaviour. The results showed that ammonium sulfide treatments were very effective to passivate defects and improve the optical and electrical properties of polycrystalline n-type Cu$_2$O thin films that may provide a solid platform for Cu$_2$O based devices of enhanced quality.
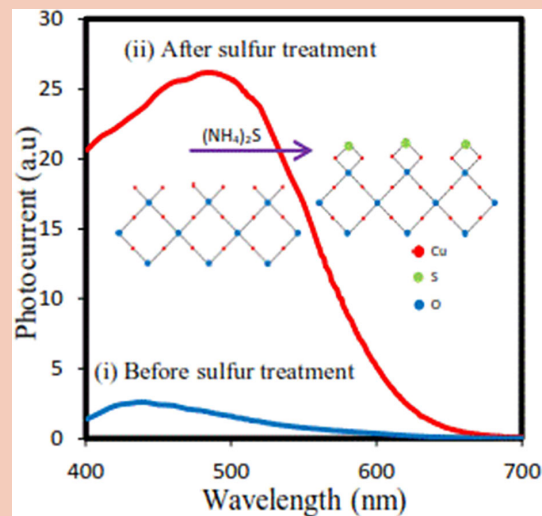
1 Motivation As an important functional optoelectronic semiconductor, cuprous oxide (Cu$_2$O) has shown great potential in applications such as electronics, gas sensors, energy, due to its unique electronic and optical properties. The nontoxicity, the low processing cost and the abundance of its component elements in the Earth's crust make Cu$_2$O even more suitable for such applications [1–3].

Several methods including thermal oxidation, chemical oxidation, anodic oxidation, vacuum evaporation and electrodeposition have been used to prepare Cu$_2$O films. Among these, electrodeposition is considered the simplest and one of the most convenient fabrication methods. Achievability of higher deposition rates at low processing temperatures and the controllabilty of conductivity type are its added advantages. While electrodeposition does not re-

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Phys. Status Solidi RRL **8**, No. 6 (2014)   593

Rapid
Research Letter

quire expensive equipment, it is capable of fabricating uniform films on various substrates of complex geometries. The ability of electrodeposition to control the conductivity type is especially important for the fabrication of Cu_2O thin films as this is normally considered a p-type material [4, 5]. Previous work shows that the electrodeposition can be used effectively to fabricate n-type Cu_2O films, which arises due to oxygen vacancies and/or additional copper ions [6–8].

However, the resistivity of the electrodeposited films is of the order of 10^9–10^{12} Ω cm, which is very high, compared to the values 10^2–10^4 Ω cm observed in bulk Cu_2O [9]. This is attributed to the high densities of defects inherent in electrodeposited Cu_2O thin films that cause difficulties in the fabrication of devices of good quality. For example, over the last few decades, the energy conversion efficiency of Cu_2O based thin film solar cells has improved very slowly.

Despite a number of studies have been carried out to improve the efficiency of the Cu_2O based thin film solar cells, the highest reported energy conversion efficiency up-to now is 5.38% [10]. This value is significantly lower compared to the theoretical limit of the energy conversion efficiency of ~20%, predicted by Shockley–Queisser photobalance calculations [5, 10].

The surface properties of Cu_2O thin films have a significant effect on their electronic and optical properties. Surface atoms and grain boundaries usually have unsaturated or dangling bonds and defects. These induce extra electronic states within the bandgap and act as electron/hole trapping centers that potentially quench the photoactive and charge transport properties of the film. The modification of the Cu_2O surface is thus considered an important step for obtaining enhanced electronic and optical properties. Therefore, the surface treatment remains a crucial processing step for the fabrication of Cu_2O based electronic and optoelectronic devices. In the past, the sulfur treatment has been widely used to passivate the surface states of group IV, III–V, and II–VI semiconductors. This process has effectively improved the surface properties, including the dependence of barrier height on the metal work function for Schottky contacts and the reduction of surface leakage currents etc. [11]. Cu_xS is a promising p-type absorber semiconducting material which has a high electrical conductivity [12]. Cu_xS has been studied until the early 1980s as a potential thin-film solar cell material. Major interest in the synthesis of a Cu_xS phase has largely been due to its applications in the Cu_xS/CdS solar cells. An excellent summary on Cu_xS solar cells has been made by Fahrenbruch and Bube [12]. Fabrication of Cu_xS layers by reacting Cu_2O thin films with aqueous Na_2S has previously been reported by Briskman [3].

However, evidence of using sulfur treatment to passivate the Cu_2O film surfaces is not available in literature even though cyanides and hydrogen have been used for the passivation of p-type Cu_2O film surfaces [13, 14]. Recently, we have demonstrated the use of $(NH_4)_2S$ assisted sulfur

treatment for the enhancement of optical and electrical properties of p-type Cu_2O thin films [15]. Similar experiments were carried out in order to study the effect of sulfur treatment on n-type Cu_2O thin films fabricated using electrodeposition. In this Letter, the effect of $(NH_4)_2S$ treatment on the optical and electrical properties of electrodeposited n-type Cu_2O thin films is discussed. While the results are consistent with those obtained for p-type Cu_2O films, it was found that the $(NH_4)_2S$ treated n-type films show much better electrical and optical characteristics.

2 Experimental and results Electrodeposition of n-type Cu_2O thin films on Ti substrates was accomplished in a three-electrode electrochemical cell containing aqueous solutions of 0.1 M sodium acetate and 0.01 M cupric acetate. The detailed experimental procedure has been discussed elsewhere [4]. The deposition times were monitored using current versus time measurements to control the film thicknesses to ~1 μm. $(NH_4)_2S$ vapor treatment was accomplished by simply holding the Cu_2O film face down above a beaker containing 20 vol% $(NH_4)_2S$ solution at 27 °C, followed by rinsing immediately with distilled water. By varying the exposure time, the optimum treatment time was determined. The surface morphologies of the films were studied using scanning electron microscopy (SEM). Figure 1(a) shows the SEM view of a bare Cu_2O thin film where there is a uniform coverage of polycrystalline grains of size which is typically in the range 0.5–1 μm. The high degree of polycrystallinity is indicative of the density of defects that exist on the film which may be in the form of dangling bonds that act as recombination centers or carrier traps etc. Figure 1(b) shows an SEM image of the thin film after $(NH_4)_2S$ vapor treatment carried out for 8 s. In Fig. 1(b), the formation of a nonuniform additional layer is clearly visible on the surface of the Cu_2O film after the $(NH_4)_2S$ vapor treatment. Figure 1(c)
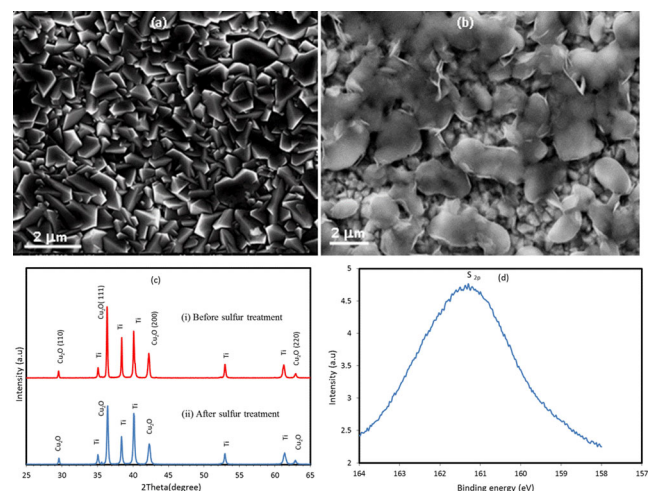

Figure 1 SEM picture of an (a) untreated and (b) sulfur treated n-type Cu_2O thin film. (c) XRD spectra of (i) untreated and (ii) sulfur treated film. (d) XPS scan of the S_{2p} region core-level peak of sulfur treated n-type Cu_2O thin film.
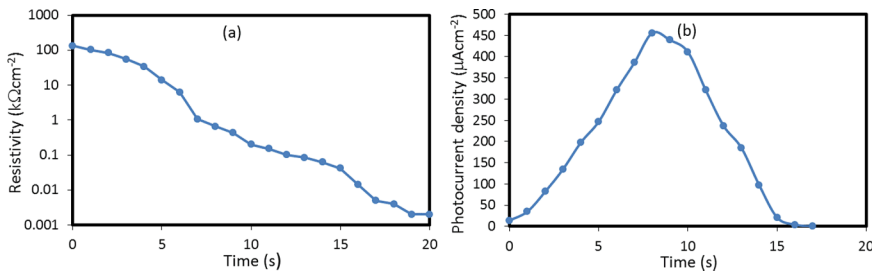
Figure 2 (a) Resistivity and (b) photocurrent density of Cu_2O as a function of sulfur treatment time.

shows the X-ray diffraction (XRD) patterns of the above samples before and after $(NH_4)_2S$ vapor treatment. All the XRD peaks are due to Cu_2O and the Ti substrate. The $(NH_4)_2S$ vapor treated sample does not show any Cu_xS peaks indicating that Cu_xS on the surface of the film possibly exists in amorphous form. However, the slight decrease in the XRD peak intensities after $(NH_4)_2S$ vapor treatment is indicative of the possible formation of Cu_xS on the film surface. In order to confirm the sulfidation, XPS measurements were performed on sulfur treated samples and the Cu_{2p}, O_{1s}, and S_{2p} core levels were analyzed. A C_{1s} core-level peak observed at 284.6 eV was recorded as reference peak for the spectrum. As shown in Fig. 1(d), an XPS scan made on sulfur treated n-type Cu_2O film shows the S_{2p} core-level peak at ∼161.5 eV indicating that sulfur in the sample exists in the sulfide form confirming the formation of Cu_xS. The position of this Cu_xS peak was found to be consistent with the values reported in Ref. [16]. An additional weaker XPS peak at 168.4 eV could also be seen and was attributed to the formation of $CuSO_4$ due to the interaction of Cu_xS with air [17] (data not shown here). Figure 2(a) shows the the effect of the $(NH_4)_2S$ exposure time on the electrical resistivity of the Cu_2O films measured using the conducting probe technique. It can be seen that the increasing exposure time reduces the film resistivity by several orders of magnitude. Figure 2(b) displays the photocurrent of the film as a function of exposure time. It shows that a photocurrent density of ∼10 μA cm^{-2} produced by the bare Cu_2O film has risen up to ∼460 μA cm^{-2} after an $(NH_4)_2S$ exposure time of 8 s. Further increase in the exposure time reduces the photocurrent density which

diminishes beyond ∼15 s indicating that the effect of the Cu_2O layer has been lost.

The films were investigated in a three-electrode photoelectrochemical cell containing a 0.1 M sodium acetate solution for their spectral responses as previously reported [4]. Figure 3 shows the normalized spectral response data before and after the sulfur treatment of the Cu_2O thin films. The spectral response measurements made for the bare Cu_2O thin film show the onset of photocurrent at 620 nm matching the bandgap of Cu_2O of ∼2 eV [4]. The sign of the photocurrent (positive photocurrent) accounts for the n-type conductivity before and after treatment. Measurements repeated on the $(NH_4)_2S$ vapor treated Cu_2O thin film showed a significantly improved n-type photocurrent signal with the same onset at ∼620 nm indicating that the response was still coming from the Cu_2O film. Figure 3 also shows the absence of long-wavelength response that could be expected if the absorption in p-type Cu_xS (band gap ∼1.2–1.5 eV) layer is present [18]. This result is consistent with the SEM data of the $(NH_4)_2S$ vapor treated sample that shows a very thin, degenerate Cu_xS layer which makes an insignificant contribution to the absorption of light. Thus, the charge separation at the Cu_2O/Cu_xS interface becomes insignificant making this junction ohmic.

The significantly improved spectral response characteristics justify the minimization of defects present on the surface and the grain boundaries of the polycrystalline Cu_2O film due to $(NH_4)_2S$ vapor treatment. It is interesting to note the behavior of the M (= Ag, Cu, Au, Ni)/n-Cu_2O/Ti system when the films are subjected to I–V measurements before and after the $(NH_4)_2S$ vapor treatment. Figure 4 shows the I–V characteristics of the electrodeposited bare n-Cu_2O thin film on a Ti substrate for which the front contacts are made with silver (work function $\Phi_{Ag} = 4.26$ eV), copper ($\Phi_{cu} = 4.65$ eV), gold ($\Phi_{Au} = 5.1$ eV) and nickel ($\Phi_{Ni} = 5.15$ eV) [19]. The estimated work function of n-Cu_2O is ∼4.28 eV [5, 9]. Thus, the front contacts would result in Schottky junctions of which the barrier heights would decrease with the decreasing work function of the contact metal. Available literature reports that the work function of Ti, the back contact metal, is in the range of 3.9–4.33 eV [19, 20] making the back contact also rectifying even though the Schottky barrier height would be smaller compared to those of front contacts. Thus, the overall I–V characteristics shows a rectifying behavior as shown in Fig. 4(a) where the characteristics are mainly expected to be dominated by the nature of the front contact.
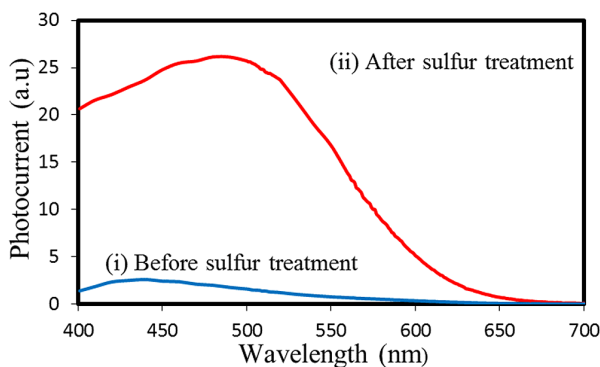

Figure 3 Photocurrent spectral responses of the (i) untreated and (ii) sulfur treated n-type Cu_2O thin film in PEC.

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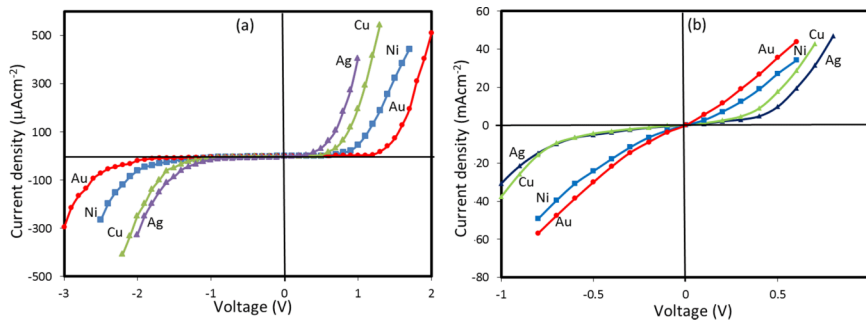
Rapid
Research Letter

Figure 4 *I–V* curves of the (a) untreated and (b) sulfur treated n-type Cu_2O thin film with Ag, Cu, Au, Ni front contact.

The relatively large reverse leakage currents that can be observed in Fig. 4(a) are also typical of Schottky junctions. Figure 4(b) shows the *I–V* characteristics of the n-Cu_2O thin films electrodeposited on a Ti substrate on which the front contacts have been made with the same metals above after the $(NH_4)_2S$ vapor treatment which has formed p-type Cu_xS on the surface of the n-Cu_2O film. It can be clearly seen that the resulting M/p-Cu_xS junctions have altered the *I–V* characteristics in which the current has been increased by several orders of magnitude after the $(NH_4)_2S$ vapor treatment that has enhanced the conductivity of the film. Especially, the variation of the onset values of the forward currents with the work functions of the metal clearly indicates the change in barrier heights. It should also be noted that there is a reversal in the onset values of currents in the four metals. Simultaneously, the *I–V* characteristics show a transition from rectifying to ohmic behavior which is more pronounced for samples with Au/Cu_xS and Ni/Cu_xS front contacts. These *I–V* characteristics can be well understood considering the work function of p-type Cu_xS, Φ_{Cu_xS}, which lies in the range of 4.15–5.03 eV depending on the value of x $(1 \leq x \leq 2)$ [21]. When $\Phi_{Cu_xS} = 4.15$ eV, all the metal work functions associated with the front contacts become larger than Φ_{Cu_xS} giving rise to ohmic contacts. When $\Phi_{Cu_xS} = 5.03$ eV, the Au/Cu_xS and Ni/Cu_xS contacts would give rise to ohmic contacts while rectifying type behaviour can be expected from the Ag/Cu_xS and Cu/Cu_xS contacts. The less dramatic ohmic behavior that is shown in Fig. 4(b) for Ag/Cu_xS and Cu/Cu_xS contacts suggests that the formed Cu_xS layer has a work function larger than 4.15 eV and a moderate x value between 1 and 2. Thus, it can be seen that the role of the p-Cu_xS layer that is formed upon $(NH_4)_2S$ vapor treatment is twofold, i.e., by minimization of defects it enhances the conductivity of the n-Cu_2O layer by several orders of magnitude while influencing the nature of the front contact depending on the selected metal.

3 Conclusions In summary, we have investigated the influence of sulfur treatment on the electrical and optical properties of the electrodeposited n-type Cu_2O surface. An enhancement in the photocurrent and spectral responses and a significant reduction of resistivity have been observed after the $(NH_4)_2S$ surface treatment which causes the reduction of defect density. It can be seen that the photocur-

rent peaks at an exposure time of around 8 s with approximately a fifty-fold increase compared to the untreated Cu_2O film sample. The *I–V* characteristics of sulfur treated n-type Cu_2O show nearly ohmic behavior with Ni and Au and a less dramatic rectifying behavior with Cu and Ag contacts.

The study provides valuable insights into the effect of surface properties on the characteristics of Cu_2O based devices when different contacts are used.

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