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Ammonium Sulfide Surface Treatment of Electrodeposited *p*-Type Cuprous Oxide Thin Films

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The effects of ammonium sulfide surface treatment on electrodeposited *p*-type polycrystalline cuprous oxide (Cu_2O) thin films deposited on Ti substrates were studied. The structural and morphological properties of the films were investigated using scanning electron microscopy, x-ray diffraction, and energy-dispersive x-ray spectroscopy. The changes in the conductivities and photocurrents of the films after the ammonium sulfide treatment were determined. Films that had undergone the ammonium sulfide treatment showed reduced resistivities, enhanced spectral photoresponses, and enhanced current-voltage characteristics. The results showed that ammonium sulfide treatment improved the peak output current of the *p*-type Cu_2O films by about 400% compared with those of bare Cu_2O films. This improvement is attributed to the passivation of defects in the films by sulfur, showing that sulfur passivation provides a good method for improving of Cu_2O-based devices.

Keywords: cuprous oxide, thin films, electrodeposition, defects, passivation, spectral response

1. INTRODUCTION

Solid-state devices based on cuprous oxide (Cu_2O) semiconductors have been known for more than 80 years, even before the era of Si devices. Rectifier diodes based on these semiconductors were used industrially as early as 1926,[1] and development of the theory of semiconductors was mainly based on Cu_2O devices.[2-4]

However, there have been relatively few attempts to fabricate practical Cu_2O-based devices. The optimization of Cu_2O-based devices has been hindered by lack of a clear understanding of their electronic, optical, and thermodynamic properties, and by doping difficulties. Nevertheless, Cu_2O is still considered to be an attractive material because of its high availability and straight-forward processing properties, and the associated low costs. Cu_2O is a native *p*-type semiconductor, with a band gap of 2 eV and a relatively high absorption coefficient in the visible region.[5-8] Cu_2O has a very long excited lifetime (about 10 μs), which can be used for photoluminescence.[9] Numerous recent studies of Cu_2O thin films have shown that these have potential applications in many areas such as solar cells,[7,10] electronic and magnetic devices, sensors, and catalysis.[11-14]

Among many fabrication methods, electrodeposition is one of the simplest and most convenient methods of obtaining Cu_2O thin films. Electrodeposition has several advantages such as a low processing temperature, high deposition rate, and large-scale production, and the ability to control the morphologies, compositions, and doping of deposited materials. It has been demonstrated that electrodeposition is an effective method for growing uniform Cu_2O thin films on various substrates.[7,15,16]

Normally, the resistivity of an electrodeposited Cu_2O film is of the order of 10^9 - 10^{12} Ω cm, which is very high compared with the resistivity of bulk Cu_2O, which is in the range 10^2 - 10^4 Ω cm.[17] The high resistivity and defects at metal-Cu_2O junctions reduce the reliability and performance of the resulting Cu_2O-based devices, and there are few reports on their practical applications because their electrical and optical properties are difficult to control.

Surface passivation is a crucial step in the fabrication of electronic and optoelectronic devices. The modification of the surface properties of GaAs and InP by exposing them to a sulfur-containing agent (H_2S) was reported in 1981 by Massies *et al.*[18,19] and Montgomery *et al.*.[20] In 1985, Waldrop[21,22] reported the effect of exposing a GaAs surface to sulfur, selenium, and tellurium on the properties of metal-GaAs contacts. The breakthrough in modification of the surface properties of Group *III-V* compounds occurred in 1987 with the discovery that the passivation of Group *III-V* compound semiconductor surfaces by inorganic sulfides such as $(NH_4)_2S$ and $Na_2S.9H_2O$ significantly altered the electrical properties of devices made from these compounds.[23]

Recent work by Ishizuka *et al.*[24,25] demonstrated the

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passivation of Cu_2O thin films using treatment with hydrogen and cyanide. However, there have been no reports on the passivation of Cu_2O thin films using sulfur-containing agents. In this study, it was found that sulfur passivation by treatment with $(NH_4)_2S$ is very useful for modifying the surface of a *p*-type Cu_2O thin film. The results show that passivation significantly increases the photocurrent and decreases the resistivity of the Cu_2O thin film.

2. EXPERIMENTAL PROCEDURE

p-Type Cu_2O thin films were deposited on Ti substrates by electrodeposition,[26] performed in a three-electrode electrochemical cell containing a mixed aqueous solution of lactic acid (3.25 M), cupric sulfate (0.45 M), and sodium hydroxide. Cu_2O thin films were prepared at pH 9.5 and a bath temperature of 60°C at a deposition potential of –0.45 V versus a saturated calomel electrode (SCE). The deposition times were controlled using current versus time measurements to obtain films of thickness ~1 mm. It is well known that for GaAs,[21,22] sulfur passivation in a sulfur-containing solution is an etching process, during which a chemical reaction and dissolution alternately take place. In the case of Cu_2O thin films, the reaction rates are uncontrollable, so a similar mechanism cannot be proposed for sulfur passivation of Cu_2O thin films. $(NH_4)_2S$ vapor treatment was therefore used. This was accomplished by simply holding the Cu_2O film face down above a beaker containing 50 vol. % $(NH_4)_2S$ solution at 27°C, followed by rinsing immediately with distilled water. The front contacts to the films were then made using Ni.

The resistivities of the Cu_2O thin films were measured using the conducting probe technique. The surface morphologies of the films were studied using scanning electron microscopy (SEM; Philips XL40). The thin film structures were studied by energy-dispersive x-ray spectroscopy (EDS) and x-ray diffraction (XRD), using a Shimadzu SSX-550 analyzer and a Shimadzu (XD-D1) x-ray diffractometer respectively. The current-time measurements during deposition and the current-voltage (*I-V*) characteristics were measured using a Keithley 2100 multimeter. Spectral response measurements were made in a three-electrode photoelectrochemical cell (PEC) containing 0.1 M sodium acetate solution.[16]

3. RESULTS AND DISCUSSION

Figure 1(a) shows SEM images of a bare Cu_2O thin film; the polycrystalline Cu_2O grain size is typically in the range 0.1 - 1 μm. There are therefore many dangling bonds, which act as non-radiative recombination centers or carrier traps, on the surfaces of the polycrystalline grains. Figure 1(b) shows SEM images of the same thin films after treatment with 50 vol. % $(NH_4)_2S$ vapor for 5 s at 27°C. Figure 1(b) clearly shows that the surface is covered by a film, resulting from sulfur passivation of dangling bonds by Cu_xS formation.

Figure 2(a) shows the XRD patterns of the Cu_2O film before and after sulfur passivation. No peaks arising from Cu or CuO were detected, suggesting that the Cu_2O thin films were of high quality. From Fig. 2(a)(ii), it can be seen that sulfur passivation has no effect on the structural quality of the Cu_2O film.

The most likely scenario is the formation of amorphous Cu_xS,[27] which will not contribute to the x-ray diffraction of the passivated film. Furthermore, the appearance of a sulfur peak in the EDS spectrum shown in Fig. 2(b)(ii) after 50 vol. % sulfur passivation of the film is indicative of the incorporation of sulfur into the film.

The effect of the $(NH_4)_2S$ exposure time on the electrical resistivity of the Cu_2O film is shown in Fig. 3(a). It can be seen that increasing the exposure time reduces the film resistivity by several orders of magnitude.

Figure 3(b) shows the photoactivity of the film as a function of exposure time. It can be seen that the photoactivity peaks at an exposure time of around 5 s, and there is no photoactivity at exposure times longer than 20 s, indicating that the effect of the Cu_2O layer has been lost. It was found

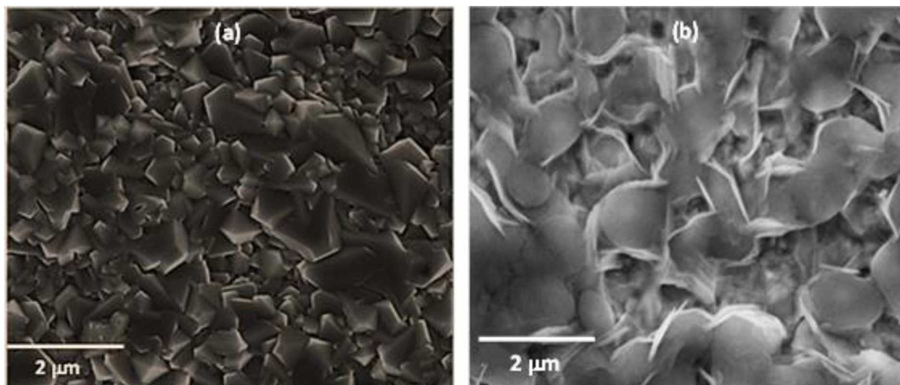

Fig. 1. SEM images of (a) unpassivated *p*-Cu_2O thin film and (b) *p*-Cu_2O thin film passivated using 50 vol. % sulfur for 5 s at 27°C.

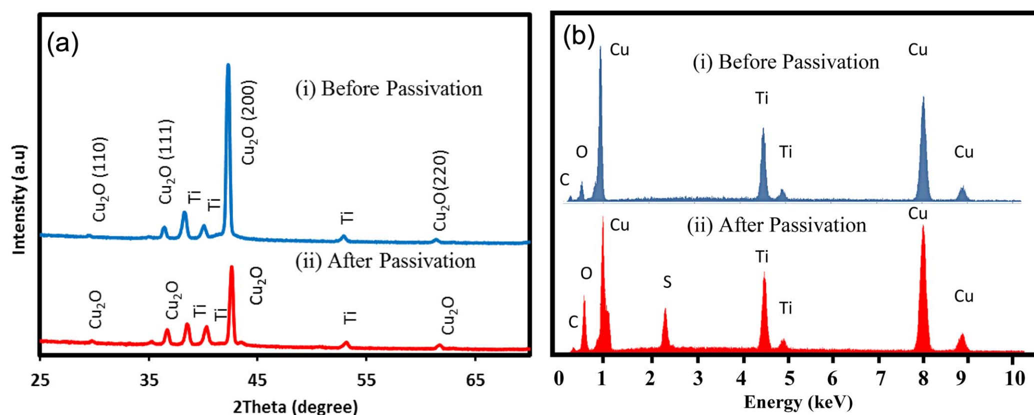

Fig. 2. (a) XRD spectra and (b) EDS spectra of (i) unpassivated and (ii) sulfur-passivated *p*-Cu_2O thin films.

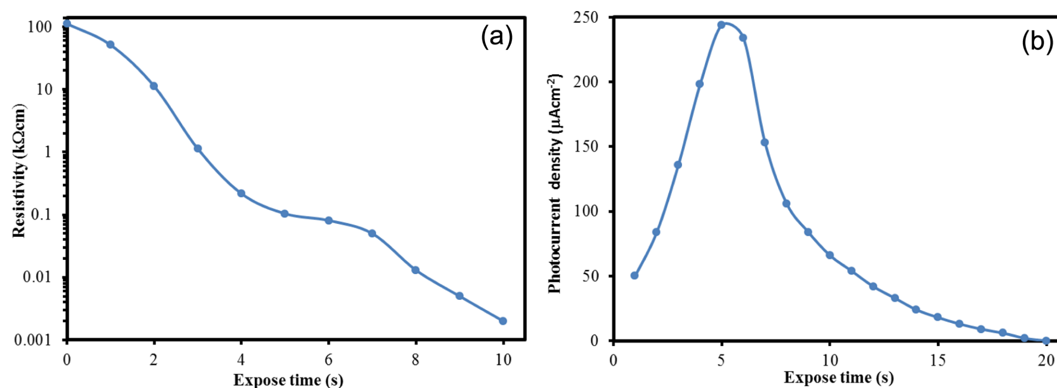

Fig. 3. (a) Resistivity and (b) photocurrent density of *p*-type Cu_2O as a function of passivation exposure time with 50 vol. % sulfur at 27°C.

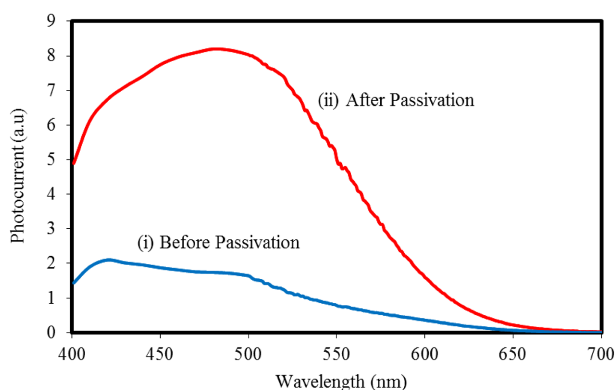

Fig. 4. Photocurrent spectral responses in PEC of unpassivated *p*-type Cu_2O thin film and film passivated using 50 vol. % sulfur for 5 s.

that a passivation time of 5 s, an $(NH_4)_2S$ concentration of 50 vol. %, and a temperature of 27°C gave the best photocurrent.

It was expected that sulfur passivation would minimize the effect of defects arising from non-radiative recombination centers or carrier traps present on the surface of the polycrystalline Cu_2O film. This is confirmed by the spectral response measurements shown in Fig. 4, which clearly shows that there is a significant improvement in the photocurrent, with a fourfold increase in the peak current, for the sulfur-passivated Cu_2O thin film compared with the unpassivated thin film.

Figure 5(i) and (ii) show the *I-V* characteristics of the unpassivated film and the film passivated by $(NH_4)_2S$ treatment, respectively. It can be seen that in the case of the unpassivated film, the current does not change much with changing voltage. The enlarged view in the inset in Fig. 5 shows variations consistent with formation of a Schottky contact between the *p*-type Cu_2O layer and the Ti substrate. Ni, which has a work function of 5.15 eV, forms an ohmic contact with a *p*-Cu_2O film, whereas Ti, which has a work function of 4.33 eV,[28] forms a Schottky barrier, because *p*-type Cu_2O has a work function of ~4.8 eV.[29] The *I-V* characteristics are significantly improved by sulfur passivation. The non-linear *I-V* relationship indicates deviation from the ohmic behavior, associated with non-ideal metal-semiconductor contacts. The much improved performance of the passivated Cu_2O film is attributed to the reduced resistivity, which is

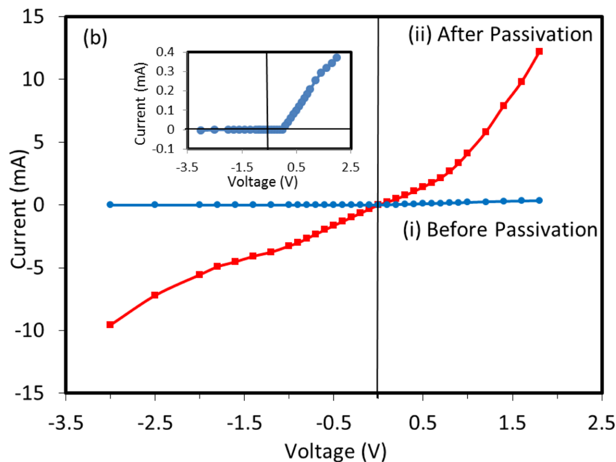

Fig. 5. *I-V* curves of unpassivated *p*-type Cu_2O thin film and film passivated using 50 vol. % sulfur for 5 s.

caused by the passivation of defects.

4. CONCLUSIONS

It was found that under the optimum conditions, i.e., $(NH_4)_2S$ concentration 50 vol. %, 27°C, and a passivation time of 5 s, sulfur passivation reduced the resistivity of electrodeposited *p*-type Cu_2O thin films by four orders of magnitude, resulting in a significant improvement in the spectral response characteristics. This is attributed to sulfur passivation of film defects. The results suggest that $(NH_4)_2S$ treatment is an effective method for the passivation of *p*-type Cu_2O thin film surfaces without changing their structural integrity.

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