

RESEARCH ARTICLE

Effect of pre-surface treatments on p-Cu₂O/Au Schottky junctions

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Submitted: 22 March 2019; Revised: 13 October 2020; Accepted: 23 October 2020

Abstract: Cuprous oxide (Cu₂O) is a suitable semiconducting material for fabrication of low-cost, eco-friendly semiconductor junction devices. Besides the parameterization of the growth conditions of Cu₂O, formation of metal contacts impact the overall performance of these type of devices. The existence of unavoidable dangling bonds and/or dislocated surface atoms could lead to form imperfect contacts with metals, for example in Cu₂O/Au junction devices. Nevertheless, modification of the Cu₂O thin film surfaces prior to make contacts with Au has shown the capability to alter the junction properties. Here we report that, the application of surface treatments; annealing and/or sulphidation on specifically the electrodeposited p-Cu₂O thin film surfaces, where p-Cu₂O thin films were grown in low cupric ion concentrated acetate bath, has influenced the interfacial properties of particular p-Cu₂O/Au Schottky junctions compared to the untreated p-Cu₂O/Au Schottky junction. This has been well-established by the results of SEM and C-V characterizations of p-Cu₂O/Au Schottky junctions. The subsequent annealing and sulphidation of p-Cu₂O thin film surfaces have lowered the built-in potential value by 121 mV compared to the untreated Schottky junction. This result reveals the possibility of employing surface treatments on electrodeposited Cu₂O thin films in fabrication of high efficient Cu₂O based junction devices.

Keywords: Annealing, cuprous oxide, electrodeposition, pre-treatments, Schottky junction, sulphidation.

INTRODUCTION

As a feasible, eco-friendly, affordable, photosensitive semiconductor, Cu₂O is found in applications in photovoltaics (Camacho-Espinosa *et al.*, 2018), photocatalysts (Singh *et al.*, 2018), water splitting

systems (Ma *et al.*, 2015), gas sensors (Jayasingha *et al.*, 2017), glucose sensors (Yu *et al.*, 2018), supercapacitors (Wang *et al.*, 2018) and magnetic storage devices (Hu *et al.*, 2016).

It is known that extracting output of a semiconductor through a proper metallic contact enhances the device performance. Therefore, it is useful to have knowledge on how a semiconductor works with a metal interface. Basically, the work functions of a semiconductor and the metal in contact tell whether it is an ohmic or Schottky junction (Sze & Ng, 2006). The Schottky nature of Cu₂O/metal junction is useful in fabrication of Schottky barrier solar cells and making ohmic contact is important in other type of solar cell configurations (i.e., homo-, hetero- or multi-junctions), transistors, Peltier modules etc.

In 1979s, Olsen *et al.* have reported the theoretical and experimental results related to Cu₂O in contact with variety of metals such as, Yb, Mg, Mn, Al, Cu, Cr and Au (Olsen *et al.*, 1979). Practically, the reported ohmic nature of the Cu₂O/Au contact is not observed in electrodeposited Cu₂O thin films (Kafi *et al.*, 2018a; b). However, the other attractive properties of electrodeposition method such as ability to grow Cu₂O on different substrates (Abdelfatah *et al.*, 2015; Mohra *et al.*, 2016; Bouderbalaet *et al.*, 2018) or different orders in a cell configurations (Jayathileke *et al.*, 2008; Wijesundera *et al.*, 2016) and uses of Au contact such as, low resistivity, high mobility and durability (Mayer, 1984) tell us the importance of formation of low resistive p-Cu₂O/Au junctions.

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Detailed interfacial studies on surface treated p-Cu₂O/Au Schottky junction, where p-Cu₂O thin films grown in acetate bath, are not available in the literature. Semiconductor surface reconstruction and modification change the surface properties where it is useful in optimisation of the overall junction performance (Morrison, 1977; Jayathilaka *et al.*, 2014; Wijesundera *et al.*, 2016)

In this study, the effect on the surface properties of p-Cu₂O thin films grown in aqueous acetate electrolyte, by changing the surface properties; annealing and/or sulphidation, in contact with Au Schottky junction has been investigated microscopically and the interfacial properties were studied with the aid of Mott-Schottky analysis. The study has shown that these pre-treatments on Cu₂O thin film surfaces modify the interface properties not only by protecting its surfaces from corrosion and passivating the surface reactivity, but also by improving the photocurrent collection via Au contact. This result is well-established by the values obtained from the built-in potential and doping density profiles of the Cu₂O thin films. Further, the built-in potentials relative to the Fermi level of Au have diminished for the surface treated p-Cu₂O thin films compared to the as-grown p-Cu₂O thin film. Thus, the reduction of the Schottky barrier height is feasible by applying surface pre-treatments. This understanding is a very important in fabrication of junction devices to minimize power losses.

METHODOLOGY

p-Cu₂O thin films were potentiostatically electrodeposited on titanium (Ti) substrates by using a three electrode electrochemical system consisting of a reference electrode of Ag/AgCl, a counter electrode of platinum plate and a working electrode of Ti. Hokuto Denko Hub-151 potentiostat/galvanostat was used for this purpose. Table 1 represents the essential parameters of p-Cu₂O thin film deposition used here (Jayathileke *et al.*, 2008; Wijesundera *et al.*, 2016). Note that, a few drops of diluted 0.01 M NaOH was used to adjust the pH of the film deposition bath.

In order to study the effect on the pre-treatments of the p-Cu₂O thin film surfaces, one set of as-grown p-Cu₂O thin films was annealed at 175°C for 10 min in a Carbolite heavy duty box furnace (Wijesundera *et al.*, 2016) and another identical set of as-grown p-Cu₂O thin films was exposed to 20 vol% of ammonium sulphide solution for 8s at room temperature (Kafi *et al.*, 2018b; Jayathilaka *et al.*, 2014). Also, a third identical set of

as-grown p-Cu₂O thin films was subsequently annealed and sulphided using the above pre-treatment conditions. Then, the desired Schottky junctions; as-grown p-Cu₂O/Au, annealed p-Cu₂O/Au, sulphided p-Cu₂O/Au and annealed and sulphided p-Cu₂O/Au were fabricated using the Cressington sputtered coater.

The structure and the surface morphology of the p-Cu₂O thin films were studied using Rigaku Ultima IV X-ray diffractometer and ZESIS EVO scanning electron microscope respectively. Further, the capacitance-voltage (C-V) characterization was used for all of the above surface treated and untreated p-Cu₂O/Au Schottky junctions using Gamry series G300 potentiostat/galvanostat/ZRA instrument.

RESULTS AND DISCUSSION

Well-adhered qualitative p-Cu₂O thin films were successfully electrodeposited on Ti substrates by applying the growth conditions stated in the Table 1. The thickness of the films was calculated by monitoring the current passing through the electrodeposition process (Wijesundera *et al.*, 2016) and the calculated thickness of the film was in the order of 1–2 μm. The optimum growth conditions were used to grow the p-Cu₂O thin films (Jayathileke *et al.*, 2008). Since the same growth conditions were used to grow thin films, the thickness of the thin films can be assumed the same for all the films. In this study, the effect of surface properties on the surface pre-treatment to the films was explored.

Table 1: The best conditions of the p-Cu₂O thin film bath deposition

Parameter	Best condition
Ion concentration	0.1 M sodium acetate 0.001 cupric acetate
Deposition potential	-200 mV vs. Ag/AgCl
Deposition time	40 min
Temperature of the bath	55 °C
pH of the bath	7.2

XRD characterisation of the p-Cu₂O thin films grown in the acetate bath revealed its qualitative structure. Figure 1 represents the XRD spectrum of an as-grown p-Cu₂O thin film. Clearly, observed XRD pattern represents single phase polycrystalline Cu₂O peaks corresponding

to the reflections from (110), (111), (200), (220) and (311) planes. There are no any other peaks (from impurity phases) except the peaks corresponding to the Ti substrate. Similar XRD for electrodeposited Cu₂O thin films has been reported by Jamali *et al.*, (2017). Therefore, it can be concluded that this XRD pattern describes the bulk properties of p-Cu₂O thin films.

SEM images in Figure 2 visibly illustrate the changes of the p-Cu₂O thin film surfaces under pre-described surfaces treatments. According to the Figure 2 the sharpness of the grain boundaries of the as-grown p-Cu₂O thin films in the acetate bath is very low compared to the Cu₂O thin films that have undergone pre-treatments. With the effect of low temperature annealing and sulphidation, the grain arrangement of p-Cu₂O thin films on titanium substrates has reconstructed the thin films surfaces into sharp grain arrangement (Kafi *et al.*, 2018b). Thus, it is observed as sharp pyramid shaped grains on their surfaces. The observed pyramid shaped grains may due to the orientation of cubic shaped micro grains. i.e., application of pre-treatments on the Cu₂O film surfaces have qualitatively changed the surface properties.

In order to make a quantitative analysis on these surface-treated or untreated p-Cu₂O/Au Schottky junctions Mott-Schottky analysis is the obvious choice. The interfacial behaviour of p-Cu₂O/Au Schottky junctions can be easily analysed through the built-in potentials and the doping densities obtained from the

C-V measurements (Mott-Schottky analysis). A Mott-Schottky plot is the linear variation of the inverse square of the capacitance of the space charge layer ($1/C^2$) versus the applied potential (V), which is explained by the Mott-Schottky theory (Sze & Ng, 2006). According to equation 1, the V-intercept and the gradient of the Mott-Schottky plot give the built-in potential and the doping density of the particular film respectively.

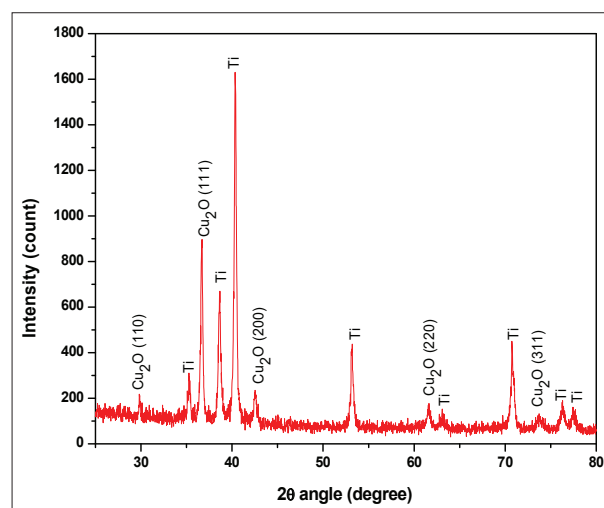


Figure 1: XRD spectrum of the electrodeposited p-Cu₂O thin films grown at bath pH value 7.2 in acetate bath

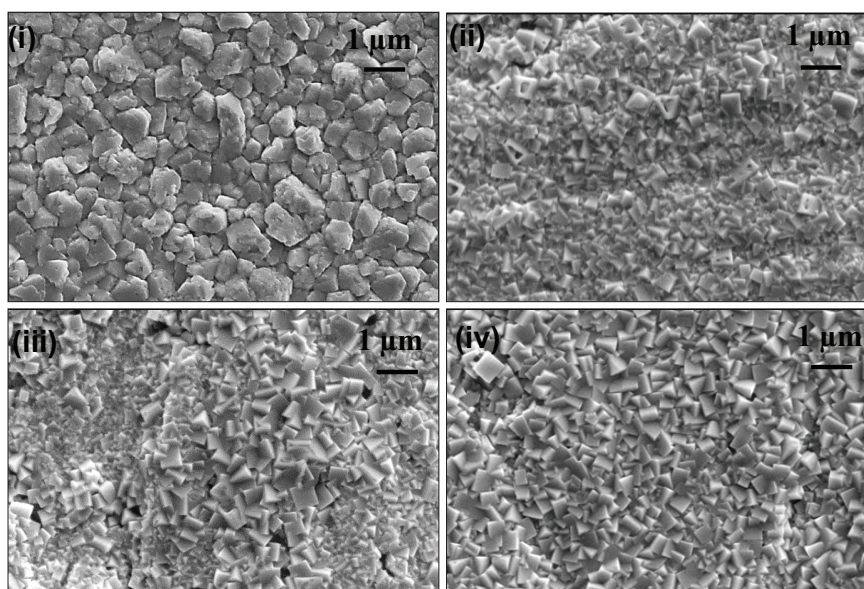


Figure 2: SEM image of (i) as-grown (ii) annealed (iii) sulphidated and (iv) annealed and sulphidated p-Cu₂O thin film surfaces

$$\frac{1}{C^2} = - \frac{2}{e\epsilon\epsilon_0 A^2 N_A} \left(V - V_{bi} + \frac{kT}{e} \right) \quad \dots(01)$$

where C , ϵ , ϵ_0 , A , N_A , V , V_{bi} , k , T and e represent the capacitance of the space charge region, dielectric constant of the semiconductor which is 6.6 for Cu_2O (Heltemes, 1966), the permittivity of the free space, area in contact of the junction, acceptor density, applied potential, built-in potential, Boltzmann constant, temperature and the charge of an electron respectively.

Further, the Fermi level (E_F) positions relative to the valence band edge (E_V) of p- Cu_2O was calculated using the following equation (2) (Sze & Ng, 2006).

$$E_F - E_V = \frac{kT}{e} \ln \left(\frac{N_V}{N_A} \right) \quad \dots(02)$$

Where N_V is the effective density of states in valence band and for p- Cu_2O this value is $1.1 \times 10^{19} \text{ cm}^{-3}$ when it is calculated with an effective hole mass of $0.58 m_0$ (Hodby *et al.*, 2001); Here the m_0 is the electron mass and all other symbols have their usual meaning.

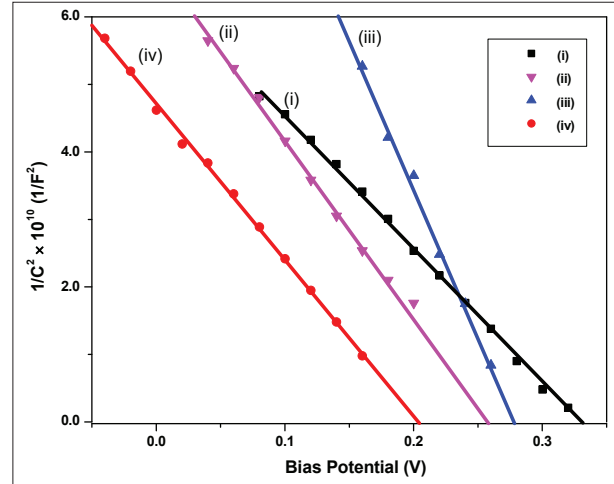


Figure 3: Dark C-V characteristics of the depletion of the (i) as-grown, (ii) annealed (iii) sulphided and (iv) annealed and sulphided p- $\text{Cu}_2\text{O}/\text{Au}$ Schottky junctions

Table 2 represents the estimated values for the built-in potentials, acceptor densities and ($E_V - E_F$) values of the

Table 2: Comparison of the built-in potential, acceptor density and $E_V - E_F$ values of the Schottky junctions under consideration.

Schottky junctions	Built-in potential (V)	Acceptor density (10^{17} cm^{-3})	$E_V - E_F$ (eV)
As-grown p- $\text{Cu}_2\text{O}/\text{Au}$	0.329	9.58	0.084
Annealed p- $\text{Cu}_2\text{O}/\text{Au}$	0.256	7.33	0.091
Sulphided p- $\text{Cu}_2\text{O}/\text{Au}$	0.275	4.38	0.104
Annealed & sulphided p- $\text{Cu}_2\text{O}/\text{Au}$	0.208	2.82	0.116

surface treated and untreated p- Cu_2O thin films. These values are calculated with the aid of the Figure 3, equations (1) and (2). According to the Table 2, it is clear that the built-in potential and doping density of the surface treated p- $\text{Cu}_2\text{O}/\text{Au}$ Schottky junctions have diminished in values compared to as-grown p- $\text{Cu}_2\text{O}/\text{Au}$ Schottky junction. It is well-known that the p- and n-type nature of the Cu_2O is due to the lattice defects. Cu_2O thin film surfaces are very reactive in the absence of surface passivation. Presence of dangling bonds and chemisorption of the Cu_2O thin film surfaces lead to formation surface states in the Cu_2O thin film surfaces. Thus, the bulk properties of Cu_2O thin films will not

be same at the surface. One possible explanation to the observed result is that, annealing and/or sulphidation of p- Cu_2O thin films have modified/reconstructed the incompletely coordinated surface atoms and the dangling bonds at the interface of the p- $\text{Cu}_2\text{O}/\text{Au}$.

Further, the built-in potentials relative to the Fermi level of Au have diminished for the surface treated p- Cu_2O thin films at $\text{Cu}_2\text{O}/\text{Au}$ Schottky junction compared to the as-grown p- Cu_2O thin films implying that the energy band position of Cu_2O relative to the Fermi level of Au is lowered by surface reconstruction/modification of the interface surface layer. Furthermore,

in comparison with the E_V-E_F values with the surface treatments, it is clear that the observed negative shift of the built-in potential relative to the Fermi level of Au is resulted due to the shift of its valence band edge itself. Evidently, similar result was reported for the p-Cu₂O thin films grown in lactate bath (Kafi *et al.*, 2018b).

CONCLUSION

SEM and C-V characterisations have revealed that the pre-treatments on the p-Cu₂O thin film surfaces prior to the Au contacts have the ability to alter the interface properties of the p-Cu₂O/Au junctions. This is due to the surface modification and/or reconstruction of the dislocated atoms at the interface layer of the Schottky junctions. Thus, the information on the negative shift of the built-in potential at the surface treated Cu₂O/Au interfaces relative to the Fermi level of Au implies the reduction of Schottky barrier height. This result is very useful in fabrication and designing of efficient Cu₂O based junction devices.

Acknowledgement

Financial assistance by National Research Council of Sri Lanka (Under NRC research grant: 15-41) is gratefully acknowledged.

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