Effect of conductive substrate (working electrode) on the morphology of electrodeposited Cu_2O

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Abstract

Cu_2O thin films were electrodeposited from a Cu(II) acetate solution containing 0.02 M Copper(II) acetate (Cu(OAc)_2) and 0.1 M sodium acetate (NaOAc) at pH 5.6, using three different working conductive electrodes with approximately the same square resistance—indium doped tin oxide glass (ITO/Glass), fluorine-doped tin oxide glass (FTO/Glass), and Indium doped tin oxide Polyethylene terephthalate (ITO/PET)—under identical conditions using a common growth condition. The Cu_2O thin films were characterized by means of scanning electron microscopy (SEM), x-ray diffraction (XRD), current density versus growth time for Cu_2O films, and electrochemical impedance spectroscopy (EIS). The results showed that the choice of substrate materials has a crucial role in controlling of Cu_2O growth. The charge transfer resistance (R_{ct}) of FTO/Glass- Cu_2O exhibits the lowest value; this means that FTO/Glass- Cu_2O possess the highest electron transfer efficiency. All Cu_2O films showed n-type semiconductor characteristic with charge carrier densities varying between 1.4×10^{18} – $1.2 \times 10^{19} \text{ cm}^{-3}$.

Keywords: morphology, Cu_2O thin films, electrodeposition

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AQ1 (Some figures may appear in colour only in the online journal)

1. Introduction

Current advances in materials have almost every fundamental to modern science and technology. On the nano-/micro-scale, dominion over structure, size, and morphology of a material enables control of its properties and enhancement of its utility for a given application. Among various metal oxide materials, cuprous oxide (Cu_2O) semiconductors remarkably are an interest area of research for a several fields. Nowadays, the promising applications of Cu_2O mainly focus on chemical sensors, photocatalysis, lithium

ion batteries and catalysis. Also, there are nascent applications that demand optical transparency and mechanical flexibility for a variety of optoelectronic and photovoltaic application [1–4].

It has increasingly attracted attention due to its widespread availability, environmental safety, low costs and compatibility with diverse substrates [5]. Cu_2O has been developed using various techniques—for example, sputtering [6], chemical oxidation [7], thermal oxidation [8], electrodeposition [9], chemical vapor deposition [10], etc.—but the growth of Cu_2O thin film using electrodeposition has been noted as remarkable

achievement, becoming a worldwide topic of interest. This technique has the strengths and advantages compared to other semiconductor growth technique. This preference due to its simplicity, scalability, manufacturability, and as a low cost deposition technology that can easily be carried out in normal laboratory conditions [11].

In the past decades, many efforts were used to innovate the crystallization of cuprous oxide thin film with different aspects including morphology, size, and structure using electrodeposition has attracted much attention. Because fascinating properties might be accomplished, Cu_2O can be tuned into various morphologies, such as cubes [12], truncated, octahedral, facets, polyhedral [13], flowerlike [14], etc. By focusing on synthesis of cuprous oxide thin film using the electrodeposition technique, authors tried to control the morphology of the deposited thin film depending on the applied potential [15], additives [16], temperature, pH [15], concentration, and type of electrolyte [17]. To the best of our knowledge, there are a few articles working on investigating the effect of conductive substrate—electrode on which the Cu_2O deposited, Oshero *et al* studied the Influence of ITO Electrode Surface Composition on the Growth of Electrodeposited Cu_2O Thin Films [18]. Also Liu *et al* reported the effect of the substrates include indium tin oxide film coated glass, n-Si wafer with (001) orientation and Au film evaporated onto Si substrate on the structural and optical properties of electrodeposited Cu_2O films [19].

Therefore, it is highly desirable to study the effect of the transparent and/or flexible working conductive substrate on the fabrication and the physical properties Cu_2O metal oxide.

In this paper, Cu_2O thin films are electrodeposited on three different working conductive substrates: indium doped tin oxide glass (ITO/Glass), fluorine-doped tin oxide glass (FTO/Glass), and Indium doped tin oxide Polyethylene terephthalate (ITO/PET), under identical conditions using a common growth solution. We investigated how the surface morphology of the deposited film was affected by the type of conductive substrate.

2. Experimental

2.1. Materials

Copper(II) acetate ($\text{Cu}(\text{OAc})_2$, 99% purity), sodium acetate (NaOAc , >98%), and acetic acid (HOAc , used to adjust solution pH value., 99% purity) were obtained from Sigma Aldrich, and used as purchased. The solutions used in this research were prepared with deionized water further purified with a Millipore Milli-Q purification system.

2.2. Deposition of Cu_2O films

The electrodeposition was performed with a standard three electrode system (CHI-660D; CH Instruments, Shanghai, China). Three different conductive substrates with approximately the same resistivity—Indium doped tin oxide glass (ITO/Glass; $13.4 \Omega/\square$), fluorine-doped tin oxide glass (FTO/

Glass; $13.4 \Omega/\square$), and Indium doped tin oxide Polyethylene terephthalate (ITO/PET; $15 \Omega/\square$)—were used as working electrodes. A platinum sheet and Ag/AgCl were respectively used as a counter and reference electrodes. All of the chemicals were used without further purification. Before electrodeposition, the substrates were rinsed with distilled water and then cleaned with ethanol in an ultrasonic set for about 10 min. In our work, Cu_2O films were electrodeposited in 0.1 M sodium acetate (NaOAc) and 0.02 M $\text{Cu}(\text{OAc})_2$ aqueous solutions [20], with pH adjusted to 5.6 using acetic acid.

2.3. Characterization

X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 5° to 65° with a x-ray diffractometer (X'Pert PRO; PANalytical B. V., Almelo, Netherlands), where a $\text{Cu K}\alpha$ ($K\alpha = 1.5406 \text{ \AA}$, 40 kV, 200 mA) was used as an x-ray source. ~~Micro-images for all films were obtained from a scanning electron microscope (SEM, Sirion 200, FEI, Hillsboro, Oregon, USA).~~ Field emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM- 6700 scanning electron microscope operated at 8.0 kV. Electrochemical impedance spectroscopy (EIS) measurements of the prepared films were performed in an acetonitrile solution of 0.1 mol L^{-1} lithium perchlorate electrolyte. The (EIS) measurements were performed with a standard three electrode system (CHI-660D; CH Instruments, Shanghai, China) at perturbation potential of 20 mV with frequency range from 10^{-1} – 10^5 Hz. Measurements were typically performed with respect to the open-circuit potential (OCP). Measurements were performed at room temperature and repeated at least three times. Finally, the type of conductivity and doping concentration of films were obtained through capacitance measurements represented in a Mott–Schottky plot using an amplitude of 20 mV and a frequency of 1 kHz.

3. Results and discussion

3.1. Structure and morphology of Cu_2O films

3.1.1. XRD. Electrodeposition of Cu_2O involves two steps: reduction of Cu^{2+} ions to Cu^+ ions (equation (1)) and precipitation of Cu^+ ions to Cu_2O due to the solubility limitation of Cu^+ ions (equation (2)) [15].

In order to select the appropriate potential for Cu_2O , electrodeposition of Cu_2O on the three electrodes was performed for 60 min at room temperature under different deposition potential conditions: -100 , -200 , -300 , -400 and -500 mV versus Ag/AgCl electrode. As shown in figure 1, it can be verified by the x-ray diffraction (XRD) spectra obtained from the films electrodeposited on PET/ITO at various potential.

Figure 1. XRD patterns for films electrochemically deposited under different applied potential: (●) Reflections of ITO/PET substrate.

At deposition potential -100 mV, XRD spectra shows peaks at 2θ values of 29.58° , 36.43° , 42.32° and 61.39° corresponding to the diffraction from (110), (111), (200) and (220) crystal plans of Cu_2O in addition to the PET/ITO peaks. With the potential increasing up to -500 mV, XRD spectra exhibits additional peaks at 2θ values of 43.40° and 50.55° corresponding to the reflection from (111) and (200) atomic plans of Cu in addition to the peaks corresponding to the Cu_2O and PET/ITO substrate. Thus, the appropriate potential for Cu_2O deposition is -100 mV versus Ag/AgCl electrode.

The prepared Cu_2O films grown on ITO/Glass, ITO/PET and FTO/Glass substrates were examined by x-ray diffraction. Their diffraction patterns as shown in figures 2(a)–(c) respectively indicates the presence of single-phase crystalline Cu_2O films. All diffraction peaks (at $2\theta = 29.58^\circ$, 36.43° , 42.32° , and 61.39° that correspond to the (110), (111), (200), and (220) planes of cubic Cu_2O , respectively) are indexed to the standard structure of Cu_2O , JCPDS card No. 05-0667. There are no impurity peaks from copper metal or cupric oxide present in these patterns. The XRD peak intensity ratio of $I(111)/I(200)$ for the two strongest peaks is plotted as a function of the conductive substrate (working electrode), as shown in figure 2(d), since the standard diffraction intensity ratio of the (111) peak to the (200) peak is 2.88. For Cu_2O films grown on ITO/Glass, the XRD spectra indicates an intensification of preferred (111) orientation with intensity ratio (4.29) [21]. Cu_2O films grown on ITO/PET shows relatively (111) preferred crystal plane than (200) orientation with intensity ratio (2.23) [17]. But in the case of prepared Cu_2O films grown on FTO/Glass substrates, it has good crystallinity with (200)-preferred orientation with intensity ratio (0.21) [22, 23]. According to the XRD

results, the substrate materials play a crucial role in the formation of Cu_2O [19].

3.1.2. SEM. Figure 3 shows SEM images of Cu_2O thin films grown on different (conductive substrates) working electrodes at -100 mV. As can be seen, the working electrode plays an important role on the morphology of the deposit [18, 19]. Using these identical conditions described here, three distinct morphological manifestations were observed: (i) figure 3 (A₂) and (A₃) show Fernlike Stellar Dendritic growth of Cu_2O crystals on ITO/Glass substrate; there are six branches and side branches structure spread along the ≥ 110 directions where the crystal plane (111) is parallel to the ITO/Glass substrate surface. Herein, the lateral growth to dendrite branches is more favored than new nucleation site [15], (ii) another typical dendrite-like-crystal grow on FTO/Glass substrate as shown in figure 3 (B₂) and (B₃); Four branched dendritic formed the crystal body. Moreover, each branch divaricated as dendrite branches and these branched dendrites linked together to form the crystal [24]. Dendritic crystals are developed to truncated octahedral crystals due to the acetate ions in the buffer preferentially adsorbing {111} planes slowing down crystal growth along the (111) directions normal to the substrate [24]. In summary, for ITO/Glass and FTO/Glass substrates, the lateral growth Cu_2O film is preferable over increasing thickness. This was mainly due to fact that the FTO & ITO/Glass are much more conductive than the semiconductive Cu_2O , resulting in the electrodeposition on the conductive substrate being faster than the growth out of the substrate [17]. (iii) For ITO/PET substrate, figure 3 (C₂) and (C₃) showed Cu_2O growth as {100} facets truncated octahedral grained structure film with complete surface coverage, this mean that the deposited Cu_2O

Figure 2. XRD patterns of (a) ITO/Glass & ITO/Glass- Cu_2O , (b) ITO/PET & ITO/PET- Cu_2O , (c) FTO/Glass & FTO/Glass- Cu_2O , (d) Plot of relative peak intensity of $I(111)/I(200)$ as a function of working electrode and (e) reflections of Cu_2O according to the JCPDS card No. 05-0667.

ad-atoms have good contact with the surface. This influences the final shapes of the crystals. As such, the growth mechanism is proposed as follows. When the Cu_2O crystal is electrodeposited on ITO/PET, nuclei with different orientations may form in adjacent sites on the polycrystalline surface. Then, all nuclei competitively grow, leading to interpenetration and suppression of growth. This leads to the production of crystalline structure with irregular shapes [23]. These changes observed in cuprite Cu_2O film morphology with different (conductive substrate) working electrode can be explained on the basis of growth and nucleation; Fleischmann and Thirsk proposed that a majority of the nucleation process can be divided into two categories: (a) progressive nucleation and (b) Instantaneous nucleation [25]. This is closely stratified by the current density as a function of film growth time given below. (see the online supporting information, figures S1–S3 (stacks.iop.org/000/000/000)).

Figure 4 shows the current density for a constant growth potential is plotted as a function of time. The behavior of current transient curves illustrates the two main regimes which were used to grow the crystals. The ITO/PET substrate leads to a continuously rising current and hence slow growth of the crystals (kinetically limited growth). ITO/Glass, FTO/Glass show also rising current but a decrease thereafter this

mean progressive nucleation followed by diffusion limited growth [25]. the current density– t characteristics of the Cu_2O growth also showed that the current densities decreased with changing the substrate in this order ITO/PET, FTO/Glass and ITO/Glass respectively, the morphology of Cu_2O tuned from facet shaped to branched, which is consistent with the results reported by [18, 24]. For FTO/Glass and ITO/Glass substrates a mode of sparse Cu_2O nucleation and lateral growth is dominant, as indicated by a lower current density during the nucleation stage (see figure 4, inset) and reflected by the branched film morphology (figure 3). This is due to Cu^{2+} ions near the Cu_2O nuclei are consumed, forming a concentric diffusion field at the initial stage of deposition [18]. A depletion zone is formed around the growing Cu_2O crystal when the deposition rate is faster than the diffusion rate of the nutrient Cu^{2+} ions. Once the depletion zone is formed, the apexes of a polyhedral crystal grow faster than the central parts of the facets and thus, branches are formed. Therefore, branched crystals are produced at low currents because of the limitation of the transportation of Cu^{2+} ions [24]. For ITO/PET, substrate Cu_2O deposited at high current density, the transportation of Cu^{2+} is enhanced and the possibility of branching decreases by a more-pronounced filling-in process to seal the gaps between

Figure 3. Top view SEM images of Cu_2O films electrodeposited from copper (II) acetate/sodium acetate solutions at pH = 5.6 for different working electrode (A₁) ITO/Glass, (A₂, A₃) ITO/Glass- Cu_2O , (B₁) FTO/Glass, (B₂, B₃) FTO/Glass- Cu_2O and (C₁) ITO/PET, (C₂, C₃) ITO/PET- Cu_2O .

the branches and thus, the greater density of faceted crystal nucleation sites is favorable resulting in a more compact, dense Cu_2O morphology [24].

3.2. Electrochemical impedance spectroscopy (EIS)

The EIS analysis was carried out for the cell within the frequency range of 10^5 – 10^{-1} Hz at the perturbation potential of 20 mV. Figure 5 shows the results of EIS measurement in this study including the Nyquist plot (Z imaginary [Z''] versus Z real [Z'], figure 5(a), phase angle ($-\psi$ versus $\log f$, figure 5(b)), bode plot ($\log|Z|$ versus $\log f$, figure 5(c)) and admittance plot (Y imaginary [Y''] versus Y real [Y'], figure 5(d)) for prepared samples. The impedance spectra were fitted with two-time constant parallel model (2TP) equivalent circuit [$R_s(\text{CPE1}(R_{\text{SEI}}(\text{CPE2}(R_{\text{ct}}W))))$] shown in figure 5(e), which represents the modified model originally proposed by Meyers *et al* [26] for porous electrodes. Here, R_s , R_{SEI} and R_{ct} represent the high frequency limit series impedance, usually respectively associated with the electrolyte resistance, the

resistance of the film and the charge transfer resistance. The use of a CPE is required due to the distribution of the relaxation times as a result of inhomogeneities present at a micro or nano (atomic/molecular) level, such as the surface roughness/porosity [27]. The CPE approach was used to fit EIS experimental spectra, the capacitance of double layer represented by constant phase element CPE2 (C_{dl}), while the fitting procedure showed that the exponent of CPE1 element gave the value of unity. Hence, in this case the CPE1 element was replaced by the pure capacitance, C_{SEI} . In the low frequency region, linear spike modeled by Warburg impedance (w) was related to the resistance against the diffusion of supporting electrolyte ions through the pores of the oxide film in the electrolyte/ Cu_2O layer/electrode configuration [28].

In figure 5(a) and the inset, the Nyquist plot consisted of (i) the higher frequency region, a very small semicircle corresponding to the capacitance and the resistance of the solid–electrolyte interface layer (SEI). This capacitance and resistance are formed due to the reaction between the electrolyte and the surface of the electrode, (ii) the mid-low

Figure 4. Current density versus film growth time for Cu_2O films electrodeposited on; FTO/Glass, ITO/Glass and ITO/PET.

frequency region; a large semicircle corresponding to double layer capacitance and the charge transfer resistance, which is followed by a straight line. The linear portion (with approximately 45 angle) observed in the low-frequency range, implies a mass-transfer limited process, where the double layer capacitance (C_{dl}) is impermeable and the current flows exclusively *via* the Faradaic branch of the circuit (see the online supporting information, figures S4 and S5 (stacks.iop.org/000/000/000)). The diffusion is the slowest event and therefore the Warburg impedance W , which represents the diffusion of a redox species, dominates the impedance at low frequencies [29].

From The values of the electrochemical impedance parameters obtained from the fitting procedure listed in table 1, it is observed that the semicircle diameter of FTO/Glass- Cu_2O electrode is shorter than that of the other electrodes, implying the charge transfer resistance (R_{ct}) of FTO/Glass- Cu_2O exhibits the lowest value, This means that FTO/Glass- Cu_2O possesses the highest charge transfer efficiency [30]. Figure 5(b) shows the relation between the frequency and phase angle plot. At low frequency region; the minimum phase angle ranges from 65–80°, which is less than the expected 90° of an ideal capacitive behavior. The slopes of the Bode plots ($\log Z$ versus $\log f$, figure 5(c) are less than unity, indicative of pseudocapacitive behavior [31].

Furthermore, figure 5(d) shows the admittance plot of ITO/PET- Cu_2O , ITO/Glass- Cu_2O and FTO/Glass- Cu_2O , which is generally characterized by knee frequency. The observed knee frequencies are 0.82, 8.1 and 14.6 KHz, respectively. The knee frequency defines the maximum frequency at which the resistive behavior becomes negligible and the capacitive behavior

becomes dominant. It can be seen that the FTO/Glass- Cu_2O displays higher knee frequency than the others which further substantiates the lower charge transfer resistance [32].

The capacitance versus potential ($C-V$) measurement was also employed to determine the conduction type of the cuprous oxide films, the flat band (E_{fb}) and carrier density (N_A), which can be obtained in a Mott-Schottky (MS) plot with $1/C^2$ Versus potential at a fixed frequency of 1 kHz. The capacitance-potential measurements are presented as a MS plot in following the equation:

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$$\frac{1}{C^2} = \frac{2}{N_A e \epsilon_0 \epsilon} \left[(E - E_{fb}) - \frac{KT}{e} \right] \quad (4)$$

In equation (4), C is the interfacial capacitance, ϵ is the dielectric constant of Cu_2O (taken as 7.5 [33]), ϵ_0 is the permittivity of free space, N_A is the number density of acceptors in Cu_2O (doping level), E is the applied potential, E_{fb} is the flat band potential, T is the absolute temperature (298 K), k is the Boltzmann constant, and e is the electron charge. Apparently, the conduction type may be identified by the sign of its Mott-Schottky plot ($1/C^2$ versus V plot); a positive slope indicates an n -type semiconductor, while a negative slope points to a p -type semiconductor [34]. The Mott-Schottky plots are presented in figure 6. As shown, the samples show positive slopes, indicating that these cuprous oxide films are n -type semiconductors. From the slope $= 2/\epsilon\epsilon_0 e N_A$ and intercept at $1/C^2 = 0$, the donor density (N_A) and the flat-band potential (E_{fb}) of an n -type semiconductor can be obtained, respectively. For the Cu_2O film deposited on ITO/PET, ITO/Glass and FTO/Glass conductive substrates, the measured flat band potentials and charge carrier densities were -0.36 , -0.44 and -0.55 V

Figure 5. Nyquist plot, Bode plots and admittance plot for Cu₂O thin film growing on (ITO/PET, ITO/Glass and FTO/Glass); (a) Nyquist plots; (Z imaginary versus Z real), (b) Bode phase plots; ($-\psi$ versus $\log f$), (c) Bode modulus plots; ($\log|Z|$ versus $\log f$), (d) admittance plot; (Y imaginary versus Y real) and (e) Equivalent electric circuits.

Table 1. The parameters obtained from the fitting of the equivalent electric circuit to the experimental impedance data obtained for different substrates.

	R_s ($\Omega \cdot \text{cm}^2$)	C_{SEI} (Fcm^{-2})	R_{SEI} ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\text{S} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	n	R_{ct} ($\Omega \cdot \text{cm}^2$)	W ($\text{S} \cdot \text{s}^{0.5} \cdot \text{cm}^{-2}$)
G/ITO	19.14	1.08×10^{-7}	12.66	9.66×10^{-5}	0.8582	0.58×10^4	14.49×10^{-5}
G/FTO	13.05	0.66×10^{-7}	12.94	9.00×10^{-5}	0.8082	0.40×10^4	12.46×10^{-5}
P/ITO	13.13	2.92×10^{-7}	46.56	4.64×10^{-5}	0.7567	1.74×10^4	9.584×10^{-5}

Figure 6. Mott-Schottky plots of Cu_2O films deposited on (a) ITO/PET, (b) FTO/Glass and (c) ITO/Glass.

versus Ag/AgCl and 1.4×10^{18} , 7×10^{18} and $1.2 \times 10^{19} \text{ cm}^{-3}$ respectively. These values, although high for a typical semiconductor, agree with the previously reported values for Cu_2O films synthesized through different methods [35, 36].

4. Conclusions

In summary, we have examined the fabrication of Cu_2O films with electrochemical deposition by selecting different conductive substrates as working electrodes and successfully found that the choice of substrate materials has a crucial role in controlling the Cu_2O growth without any additives or buffers. The morphology of the Cu_2O films deposited on (ITO/Glass, FTO/Glass and ITO/PET) was investigated. Fernlike Stellar Dendrites of preferred (111) orientation formed on ITO/Glass substrate, another typical dendrite like-crystal has good crystallinity with (200)-preferred orientation deposited on FTO/Glass and faceted, more dense and truncated polyhedral grained structure with different relatively (111) preferred crystal plane than (200) when it was grown on ITO/PET. The Electrochemical impedance spectroscopy (EIS) implies that the impedance results reveal frequency dispersion fitted with the two-time constant parallel model (2TP). From the values of the electrochemical impedance parameters obtained from the fitting procedure, the charge transfer resistance (R_{ct}) of FTO/Glass- Cu_2O exhibits the lowest value confirmed with high knee frequency than the others in the admittance plot. This means that FTO/Glass- Cu_2O possesses the highest electron transfer efficiency. Finally, The Mott-Schottky plot shows that all the films are n -type semiconductors.

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