Cuprous oxide thin films electrodeposited under conditions of different temperatures and pH values

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Cuprous oxide films were prepared by electrodeposition using copper dichloride and sodium citrate as raw materials on the conductive SnO_2 glass substrates. The effects of pH value and deposition temperature on electrochemical performance and phase formation of cuprous oxide thin films were investigated. The electrochemical performance of the bath was tested by the electrochemical workstation. The phases of product samples were analyzed by X-ray diffraction (XRD) and the morphology of the product films were observed using scanning electron microscope (SEM). Experimental results show that, when pH=1 Hydrogen evolution phenomena were quite serious with more intense ionic discharge, while the more stable reactions with pH=2 and small polarizability are conducive to formation of the cuprous oxide film. When pH=1 and 2, only XRD peaks for Cu_2O as a product phase can be seen except those of SnO_2 conducting layer on the glass substrates. The higher temperature promotes crystallization of the cuprous oxide film while the obvious shedding phenomena occurred at the deposition temperature higher than 60 ^oC. The morphology of the product films varied greatly with the deposition temperature rising. Irregular shape, feathery shape and cubic crystal particles can be occurred in the product films obtained at 20 ^oC, 40 ^oC and 60 ^oC respectively. Well crystallized, dense and uniform cuprous oxide film can be prepared when pH=2 at 60 ºC.

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1. Introduction

The cuprous oxide with a direct band gap of 1.95-2.2 eV has a high absorptivity since the exciton can be continuously transported in its single crystal. It has become important materials of making photoelectric converters [1]. It has potential applications in solar conversion, electronic, magnetic storage devices, biosensors and catalysis for its unique optical and magnetic properties [2,3]. Especially it has good prospects in photovoltaic applications due to its advantages of innocuity, high efficiency and low cost. There are many methods for preparing cuprous oxide films, such as thermal oxidation [4], radical oxidation method [5], magnetron sputtering [6], pulsed laser deposition [7] and electrodeposition techniques [8]. In these methods electrodeposition has many advantages of low temperature, low-cost and high productivity, moreover, it can be easily used to prepare films on substrates with complex morphology and to control the morphology, composition and doping of films. In addition N-type and P-type semiconductor thin films can be prepared respectively under different deposition conditions. It was found that N-type Cu_2O semiconductor thin films can be prepared by the electrodeposition in the weak acid solution [9] and granular Cu_2O films with cubic or various dendritic morphologies can be obtained by controlling the deposition potential. Cu_2O thin films can also be obtained by electrodeposition in alkaline solution [10]. In addition, there are few works about the effect of complexing agents on the morphology of Cu_2O film. Currently three deposition systems can be selected to prepare Cu_2O films as follows: (1) The system of copper nitrate: in copper nitrate solution the morphology of Cu_2O crystals can be controlled by adjusting the amount of different additives [11]; (2) The system of copper acetate and sodium acetate: In mixed solution of copper acetate and sodium acetate with a certain concentration the pH value can be adjusted by adding glacial acetic acid according to the need of depositing film [12]; (3) The system of copper sulfate and acid: In a mixed solution of copper sulfate and acid such as anhydrous acid, the electrolyte was keep at about 60 ºC and its pH value can be adjusted between 9~12 by adding NaOH. Currently the system of copper salt and lactic acid is mainly used for electrodeposition of Cu_2O thin films [13]. The cuprous oxide cell model was constructed by Mcshane et al and their results show that the conductivity of cuprous oxide films limits the conversion efficiency of the cell [14]. Electrodeposited p-Cu_2O film has the acceptor density varied from 10^{17} cm^{-3} on the surface to 10^{13} cm^{-3} in the bulk [15]. Kunhee Han et al studied the effect of doping on preparation of cuprous oxide thin films and found that relatively large crystal particles of cuprous oxide can be obtained with bromine doped on surface [16]. The substrate has an influence on the thickness of cuprous oxide film prepared by I.S. Brandt et al using lactic acid and copper sulphate as raw materials [17]. In this work, cuprous oxide thin films were prepared by the electrodeposition method using copper chloride and sodium citrate, the effects of pH value on the electrochemical performance of the bath and phase formation and the effect of deposition temperature on phase formation and microstructure of the product films were investigated.

2. Experimental

Pretreatment processes: Cuprous oxide thin film samples were fabricated on 20mm×10mm× 4mm glass substrates with conductive SnO_2 layer. The selected reagents are analytical grade. The cleaning processes of conductive glass substrates are as follows: Slicing, Cleaning in deionized water, ultrasonic cleaning in ammonia (t=15min), Cleaning in deionized water, ultrasonic cleaning in acetone (t=15min), Cleaning in deionized water, ultrasonic cleaning in alcohol (t=15min), Cleaning in deionized water and drying (at 60~70 ºC).

The cyclic voltammetry curves, chrono- amperometry curves and cathodic polarization curves of the bath were tested by three-electrode system with a platinum electrode as an auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, tin oxide conductive glass substrate as the working electrode. The tests were carried out on the PARSTAT 2273 electrochemical workstation produced by Princeton Applied Research Company with the scan rate of 10 mV/s and a range of -1～0V. Cuprous oxide thin films were prepared in a solution containing 0.03 mol/L $CuCl_2·2H_2O$ and 0.015 mol/L citric acid trisodium salt dehydrate (pH=2) under -1.0V for 30min by HDV-7C potentiostat transistors provided by radio Plant production of Sanming City, Fujian.

The phases of product samples were analyzed by X-ray diffraction (XRD) on the Bruker D8 Advance XRD system with Nifiltered Cu-Kα (λ=1.5059 Å). The size and morphology of the product films were observed using scanning electron microscope (SEM) with a model of JSM-6380LA made by Japan Electronics Co., Ltd.

3. Results and discussion

3.1 The effect of pH values on electrochemical characteristics of the bath for depositing cuprous oxide films

3.1.1 The effect of the bath pH values on the chronoamperometry curves

According to the current knowledge, in electrodeposition the current starts to increase with the formation, activation and growth of crystal nucleus until the crystal nucleus finally covered the substrate part in electrolyte, then the crystal grains began to grow and the product film became more and more thick, at the same time the resistance increased while the current decreased and approached gradually to stable values. Fig. 1 shows the chronoamperometry curves of the bath with different pH values at room temperature in a range of -1～0V. It indicates that when pH=1 it has relative large reactive current with large changes in magnitude and begin to stabilize after 35s. When pH=2 the reaction is relatively slow and gradually to be stabilized after 38s. When pH=3 the reaction is relatively unstable and the changing amplitude is relatively large. In addition the current values of other curves gradually decrease. According to the reaction formula (1) and (2) as follows, the higher the H^+ concentration was the more violent the reaction was at the beginning. As the reaction was carried out to a certain extent, the reaction of formula (1) toward right was inhibited with the H^+ concentration increasing continuously.

$$2Cu^{2+}+2e^-+H_2O\rightarrow Cu_2O+2H^+ \quad (1)$$

$$Cu^{2+}+2e^-\rightarrow Cu \quad (2)$$

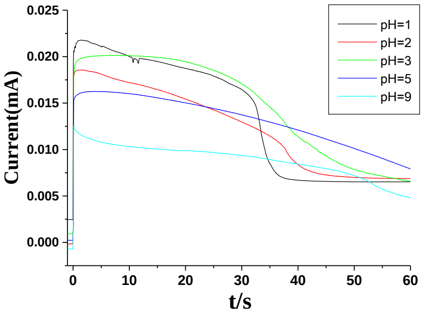

Fig. 1. The chronoamperometry curves of the bath with different pH values at room temperature

3.1.2 The effect of the bath pH values on cyclic voltammetry curves

Fig. 2 shows the cyclic voltammetry curves of the bath with different pH values at room temperature in a range of -1～0V. It can be known that the starting and peak reduction potentials on these curves are different and correspond to different bath pH values. The cyclic voltammetry curves that pH=1 and pH=2 have similar trend while most current densities for the bath with pH=2 are relatively larger, with the scanning potential moving toward negative direction the current increased dramatically, which can make ions move faster and the plasma discharge greater. It is conducive to formation of cuprous oxide. As the pH value increases to 3, 5 and 9 the cyclic voltammetry curves of the bath tend to smooth and have unobvious ion reaction and no reduction peak, which is unfavorable to form cuprous oxide.

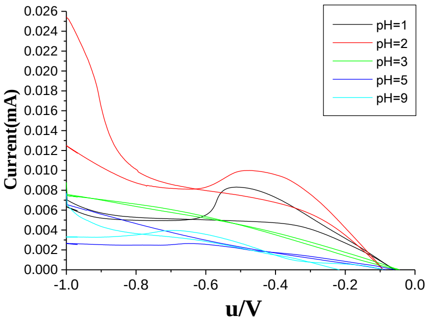

Fig. 2. The cyclic voltammetry curves of the bath with different pH values at room temperature

3.1.3 The effect of the bath on cathodic polarization curves

The slope of a point on the polarization curve is called as polarizability for its current density. The greater the polarizability of the bath is, the greater the polarizing tendency is, the electrode process will be harder to carry out due to the relative large resistance. Fig. 3 shows the cathodic polarization curves of the bath with different pH values at room temperature. It demonstrates that the static potentials are varied for the bath with different pH values. With the current density increasing the electrode potential is gradually moving toward negative direction. It can be seen that the trend of the curve with pH=1 is close to that for pH=2. The polarizability increases first to a large value and then decreases as the current density increases. When the potential is near -1.0V the polarizability sharply reduced from the maximum. The most current densities for pH=2 are larger than those for pH=1, which is more conducive to form homogeneous and dense thin films of cuprous oxide. The polarizabilities of pH=3 and 5 have little change with the current density increasing. The polarizability of pH=9 increases with the current density increasing, which makes the resistance in electrode process increases.

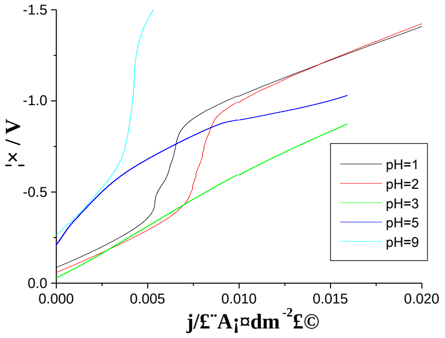

Fig. 3. The cathodic polarization curves of the bath with different pH values at room temperature

3.1.4 The effect of the bath pH values on phase formation of product films

Fig. 4 shows XRD patterns of the product films deposited in the bath with different pH values at room temperature under -1.0V for 30min. It can be seen that the pH value of the bath has a great impact on phase formation of product films. When pH=5, 9 and 11, no XRD peaks of Cu_2O can be found except those of SnO_2 conducting layer and Cu. As the pH value decreases to 3, Cu_2O phase appears in the product film while Cu still exists. When pH=1 and 2, only Cu_2O peaks as product phase can be seen except those of SnO_2 conducting layer on glass substrates.

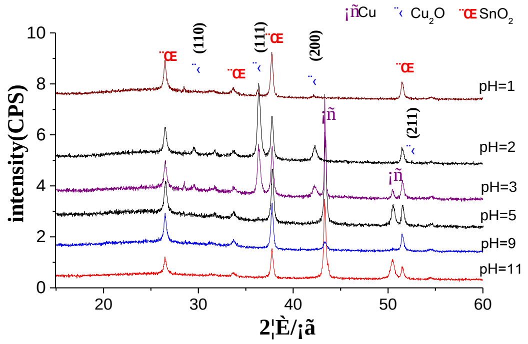

Fig. 4. XRD patterns of the product films deposited in the bath with different pH values under -1.0V for 30min

3.2 The effect of deposition temperature on the on phase formation and morphology of product films

Fig. 5 shows XRD patterns of the product films deposited at different temperatures on glass substrates with SnO_2 conducting layer. It can be seen that, the Cu_2O peaks in the product film obtained at 60 °C are more high and sharp than those obtained 40 °C and 20 °C, which indicates that the higher temperature promotes crystallization of the cuprous oxide film. However, obvious shedding phenomena occurred when the deposition temperature was higher than 60 °C, so the deposition temperature should be not more than 60 °C.

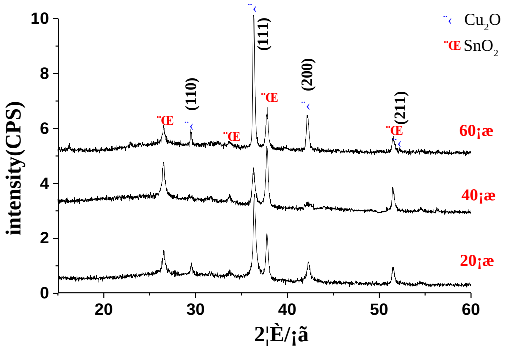

Fig. 5. XRD patterns of the product films deposited at different temperatures under -1.0V for 30min

Fig. 6 shows SEM images of the product films deposited at different temperatures. It indicates that the morphology of the product films varied greatly with the deposition temperature rising. The product film obtained 20 °C consists of irregular shape particles with sizes of about 0.5 μm or less. When the deposition temperature is 40 °C, feathery shape crystal particles arrange symmetrically along growth orientation. The product film deposited at 60 °C consists of many cubic particles with relative uniform sizes of about 1 μm or less.

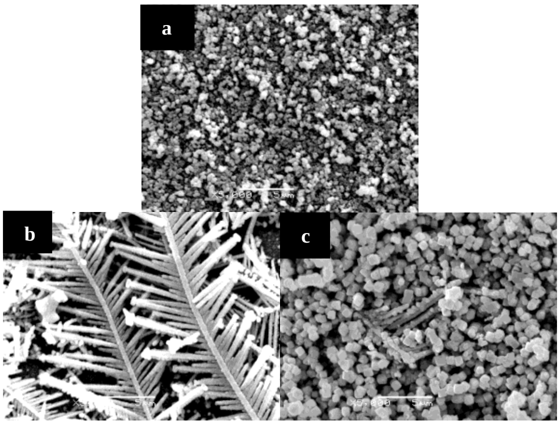

Fig. 6. SEM images of the product films deposited at different temperatures a) 20 ºC, b) 40 ºC, c) 60 ºC

4. Conclusions

The cuprous oxide thin films were prepared by potentiostatic electrodeposition under conditions of different pH values and temperatures using copper citrate and sodium chloride as raw materials. The electrochemical curves indicate that when pH=1 Hydrogen evolution phenomena were quite serious with more intense ionic discharge, while the more stable reactions with pH=2 and small polarizability are conducive to formation of cuprous oxide film. As the pH value decreases from 11 to 3, Cu_2O phase appears in the product film with Cu phase. When pH=1 and 2, only XRD peaks for Cu_2O as product phase can be seen except those of SnO_2 conducting layer on glass substrates. The higher temperature promotes crystallization of the cuprous oxide film, but obvious shedding phenomena occurred at the deposition temperature higher than 60 ^{o}C. The morphology of the product films varied greatly with the deposition temperature rising. The product film obtained 20 ^{o}C consists of irregular shape particles with sizes of about 0.5 μm or less. When the deposition temperature is 40 ^{o}C, feathery shape crystal particles arrange symmetrically along growth orientation. The product film deposited at 60 ^{o}C consists of many cubic particles with relative uniform sizes of about 1 μm or less. Well crystallized, dense and uniform cuprous oxide films can be prepared when pH=2 and at 60 ºC.

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