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Preparation of Cu_2O Films with Preferred Crystal Orientations by Electrodeposition Method†

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Cuprous oxide (Cu_2O) films were electrodeposited by potentiostatic method on the indium tin oxide conductive glass substrate. The films were characterized by XRD and SEM. The electrodeposition process conditions for the preparation of Cu_2O films with preferred orientations of (111) or (200) lattice plane were investigated. According to the result of experiments, the preferred crystal orientations of the obtained Cu_2O films were related to electrodeposition potential and the molar ratio of $CuSO_4$ *vs*. lactic acid in plating solution.

Keywords: Electrochemisitry, Cathodic deposition, Cuprous oxide film, Structure, Appearance.

INTRODUCTION

Cuprous oxide (Cu_2O), is one of the most important semiconductor materials with a narrow band gap (E_g = 2.17 eV)[1], widely used as gas sensors, solar cells and photocatalysis[2]. It can be used as the absorption layer material of solar cell that theoretical photoelectric conversion efficiency is as high as 20 %[3]. In addition, as a effective photocatalyst, the successful application of Cu_2O photodegradation technique to remove methylene blue from dyeing wastewater has been reported[4]. Today, there were many methods to prepare Cu_2O film[5]. Electrodeposition method is a low-temperature and environment-friendly soft chemical method which has many advantages, such as simple preparation process, low cost, high purity and large area thin film products[4]. Furthermore, the structure and thickness of the electrodeposited film are easy to control by adjusting electrodeposition process parameters. Many researches proved the temperature, current density and pH value of plating solution were the process parameters which influence the morphologies and quality of electrodeposited films[6]. However, there were few reports about the effect of electrode potential on preferred crystal orientations of Cu_2O films prepared by electrodeposition method. In this paper, the films with different preferred crystal orientations were electrodeposited by potentiostatic method and proper process parameters, such as electrodeposition potential and the molar ratio of $CuSO_4$ *vs*. lactic acid in plating solution would be discussed.

EXPERIMENTAL

All reagents were of analytical grade and used without further purification. The Cu_2O thin films were electrodeposited on commercial indium tin oxide glass (HYSTN80, Huayi Conductive Glass Co. Ltd., Anhui, PRC) substrates in potentiostatic mode. All electrodeposition experiments were carried out by three-electrode cell[7], using Cu foil (3 cm × 3 cm), indium tin oxide glass substrate (1 cm × 2 cm) and saturated calomel electrode (SCE) as the counter electrode, working electrode and reference electrode, respectively. The cell was powered by a potentiostat (DJS-292, Shanghai REX Instrument Factory, Shanghai, PRC).

Before deposition, the substrate was cleaned by ultrasonic treatment in toluene, acetone and ethanol in turn, rinsed by distilled water and washed with deionized water, then dried in air. Afterward, it was immersed in plating electrolyte. There were two plating solutions, named after 1#, 2# in this paper, containing 0.2 and 0.64 mol/L lactic acid, respectively. Two plating solutions all contained 0.1 mol/L $CuSO_4$. Therefore, the molar ratio of $CuSO_4$ *vs*. lactic acid in 1# and 2# plating solution were 1:2 and 1:6.4, respectively. Before been using, the solutions' pH value was raised to 10 by dropwise adding 15 mol/L NaOH solution, under constant stirring; A pH meter (pHS-2C, Shanghai REX Instrument Factory, Shanghai, PRC) was used as a pH detector.

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Deposition potential was varied in the range -0.4 to -3.0V (*vs*. SCE) and the time of deposition[4] was 25 min. The electrodeposition temperature was at 75 ºC. After deposition, the working electrode with Cu_2O films was taken from the cell and washed with deionized water, then dried in air at room temperature.

The structure and overall crystallinity in Cu_2O films was characterized through θ-2θ scans operated on a X-ray diffractometer (Y-2000, Dandong radiative instrument group Co. Ltd. Liaoning, PRC) with CuK_α radiation (λ = 1.5406 Å). The surface morphology of the prepared film was investigated through scanning electron microscopy on a field-emission SEM (Sirion200, FEI Company, USA) operated at 5 kV voltage value.

RESULTS AND DISCUSSION

Effect of deposition potential on preferred crystal orientations of Cu_2O films

Cu_2O films deposited in 1# plating solution at different potential series: Fig. 1 shows the X-ray diffraction patterns of the different Cu_2O films electrodeposited at different potential from -0.2 to -2.2 V (*vs*. SCE) in 1# plating solution in which the molar ratio of $CuSO_4$ vs. lactic acid is 1:2. Fig. 1 shows the deposited Cu_2O films are grown along preferred (111) crystal plains when deposition potential is from -0.6 to -2.2 V (*vs*. SCE) and the Cu_2O films is preferred (200) crystal growth when the potential is from -0.2 to -0.4 V (*vs*. SCE). Comparing XRD patterns in Fig. 2, it can be observed that the films prepared with electrode potential of -1.6 V (*vs*. SCE) has the most strong (111) reflection peak than the others. Commonly, the strong reflection peaks imply the good degree of crystallinity[8]. According to the diffraction intensity of (111) plane, the films deposited at -1.6 V (*vs*. SCE) have the best degree of crystallinity and optimal deposition potential is -1.6 V (*vs*. SCE).

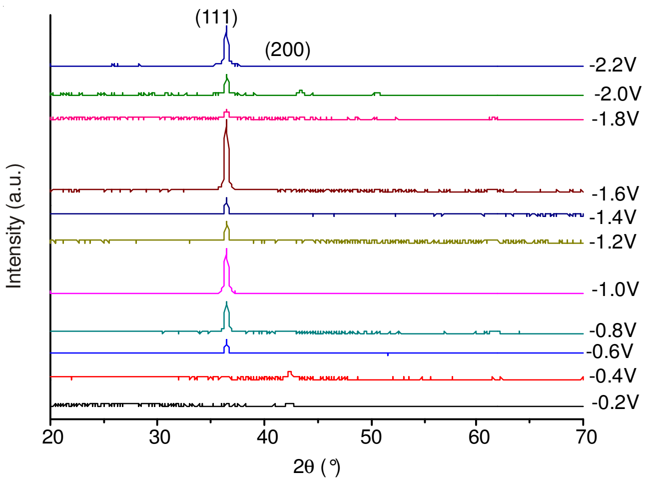


Fig. 1. Effect of potential on preferred crystal orientations of Cu_2O films deposited in 1# plating solution in which the molar ratio of $CuSO_4$ vs. lactic acid is 1:2

Cu_2O films deposited in 2# plating solution at different potential series: Fig. 2 shows the X-ray diffraction patterns of the different Cu_2O films electrodeposited at different deposition potential from -0.4 to -3.0V (*vs*. SCE) in 2# plating solution in which the molar ratio of $CuSO_4$ *vs*. lactic acid is 1:6.4. The films have preferred (200) crystal orientation when deposition potential is from -0.6 to -2.6 V (*vs*. SCE). According to the (200) peaks' intensity, the films deposited at -1.8 V (*vs*. SCE) have the best degree of crystallinity and optimal deposition potential is -1.8 V (*vs*. SCE).

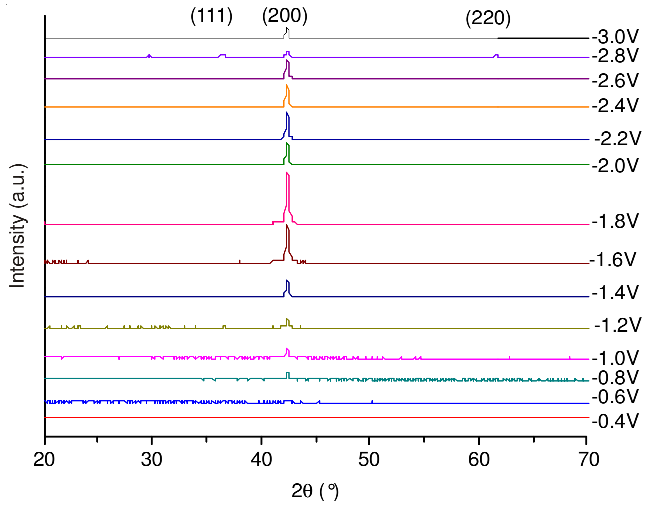
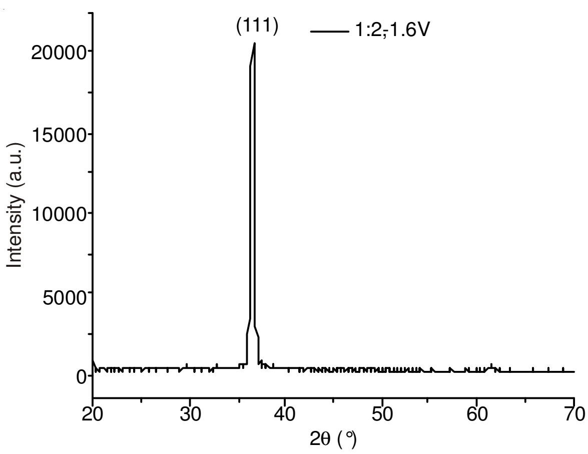


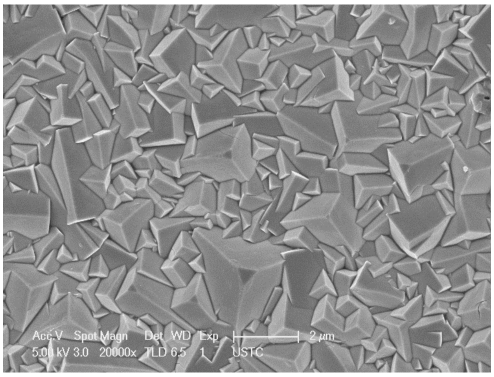
Fig. 2. Effect of potential on preferred crystal orientations of Cu_2O films deposited in 2# plating solution in which the molar ratio of $CuSO_4$ *vs*. lactic acid is 1:6.4

Characterization of Cu_2O films prepared at optimal deposition potential: XRD patterns and SEM images of two films prepared at optimal deposition potential are as follows. One film was deposited in 1# plating solution at -1.6V (*vs*. SCE), which has (111) preferred crystal orientation. Another was deposited in 2# plating solution at -1.8V (*vs*. SCE), which has (200) preferred crystal orientation.

Cu_2O film with (111) preferred crystal orientation: Fig. 3 shows the X-ray diffraction pattern and SEM image of the Cu_2O film deposited at -1.6V (*vs*. SCE) in 1# plating solution in which the molar ratio of $CuSO_4$ *vs.* lactic acid was 1:2. According to Fig. 3(a), peaks on the XRD pattern are accurately accorded with the standard PDF card No. 77-0199 pattern. It is obvious that the film is of cubic lattice system (a = 4.258 Å). Fig. 3(b) shows the top-view SEM image of the film. The crystal grains are simple and regular cubic shape and are of high degree of crystallinity.



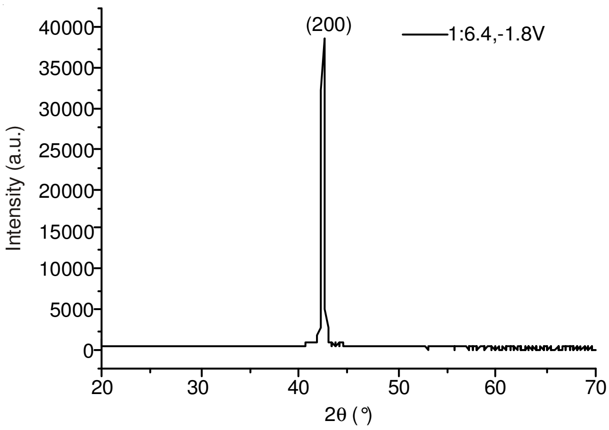
(a) XRD pattern



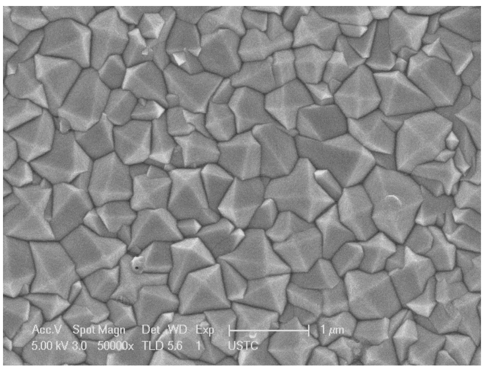
(b) SEM image

Fig. 3. XRD pattern and SEM image of Cu_2O film with (111) preferred crystal orientation

Cu_2O film with (200) preferred crystal orientation: Fig. 4 shows the X-ray diffraction pattern and SEM image of the Cu_2O film deposited at -1.8V (*vs*. SCE) in 2# plating solution in which the molar ratio of $CuSO_4$ vs. lactic acid was 1:6.4. According to Fig. 4(a), peaks on the XRD pattern are accurately accorded with the standard PDF card No. 05-0667 pattern. It is obvious that the film is of cubic lattice system (a = 4.27 Å). Fig. 4(b) shows the top-view SEM image of the film. The crystal grains are octahedral shape and also have high degree of crystallinity.



(a) XRD pattern



(b) SEM image

Fig. 4. XRD pattern and SEM image of Cu_2O film with (200) preferred crystal orientation

Conclusion

In summary, a low-temperature and environment-friendly soft chemical electrodeposition technique had been successfully applied to fabricate Cu_2O thin films with preferred orientations of (111) or (200) lattice plane. Because of controllability, the potentiostatic mode was applied to deposition process. The time and temperature of deposition process were 25 min and 75 ºC, respectively. According to the result of experiments, the films' preferred crystal orientations were related to electrodeposition potential and the molar ratio of $CuSO_4$ *vs*. lactic acid in plating solution. Cu_2O thin film with preferred crystal orientation of (111) can be deposited at electrode potential arranging from -0.6 V ~ -2.2 V (*vs*. SCE) in 1# plating solution in which the molar ratio of $CuSO_4$ *vs.* lactic acid was 1:2. Cu_2O thin film with preferred crystal orientation of (200) can be deposited at electrode potential arranging from -0.6 V ~ -2.6 V (*vs*. SCE) in 2# plating solution in which the molar ratio of $CuSO_4$ *vs.* lactic acid was 1:6.4. The deposition potential arrangement of Cu_2O thin film with (200) preferred crystal orientation was wider than the films with (111) preferred crystal orientation.

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