Materials Chemistry and Physics 147 (2014) 987–995

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Influence of thermal annealing on microstructural, morphological, optical properties and surface electronic structure of copper oxide thin films

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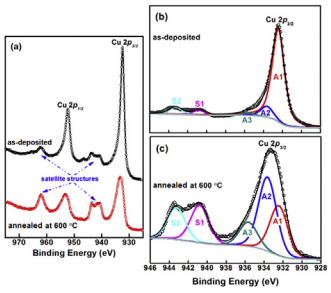
HIGHLIGHTS

- Effect of post-deposition annealing on copper oxide thin films was investigated.
- Structural, optical, and electronic properties of the thin films were determined.
- Oxidation states of copper oxide thin films were confirmed by XPS analysis.
- Mixed phases of CuO and Cu_2O were found to coexist in copper oxide thin films.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 March 2013
Received in revised form
27 May 2014
Accepted 19 June 2014
Available online 8 July 2014

Keywords:
A. Thin films
B. Sol-gel growth
C. X-ray photo-emission spectroscopy (XPS)
D. Electronic structure

ABSTRACT

In this study, effect of the post-deposition thermal annealing on copper oxide thin films has been systemically investigated. The copper oxide thin films were chemically deposited on glass substrates by spin-coating. Samples were annealed in air at atmospheric pressure and at different temperatures ranging from 200 to 600°C. The microstructural, morphological, optical properties and surface electronic structure of the thin films have been studied by diagnostic techniques such as X-ray diffraction (XRD), Raman spectroscopy, ultraviolet–visible (UV–VIS) absorption spectroscopy, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The thickness of the films was about 520 nm. Crystallinity and grain size was found to improve with annealing temperature. The optical bandgap of the samples was found to be in between 1.93 and 2.08 eV. Cupric oxide (CuO), cuprous oxide (Cu_2O) and copper hydroxide ($Cu(OH)_2$) phases were observed on the surface of as-deposited and 600 °C annealed thin films and relative concentrations of these three phases were found to depend on annealing temperature. A complete characterization

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http://dx.doi.org/10.1016/j.matchemphys.2014.06.047
0254-0584/

reported herein allowed us to better understand the surface properties of copper oxide thin films which could then be used as active layers in optoelectronic devices such as solar cells and photodetectors.

1. Introduction

CuO (tenorite) and Cu_2O (cuprite) are the two stable oxide forms of copper. CuO has a monoclinic crystal structure and a bandgap of 1.2–1.9 eV [1,2]. This metal oxide has black color and high absorptivity and low thermal emittance [3]. On the other hand, Cu_2O with a brownish-red color has cubic crystal structure and a bandgap of 2.0–2.2 eV [2]. Both of these oxides are semiconducting in nature and exhibit p-type characteristic due to copper vacancies in the structure. The advantages of copper oxides include their non-toxic nature, abundance of their precursor materials, and cost-effective synthesis routes. CuO attracted significant interest due to its great potential for hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and nitrogen oxide (NO_2) gas sensor applications [4–7]. Its high-temperature superconductivity properties have also been investigated which is believed to result from the specific coordination between Cu and O atoms [8]. In addition, this compound has been employed for the fabrication of glucose sensors [9,10], lithium-ion batteries [11,12], magnetic storage [13], and catalysts [14]. Cu_2O, on the other hand, is one of the first semiconductors to be discovered. Cu_2O exhibits several attractive characteristics for optoelectronic devices due to its high absorption coefficient and reasonably good majority carrier mobility.

The copper oxides have also attracted interest due to their potential applications in solar cell technology. High optical absorptivity in the visible or near infrared region due to its direct bandgap structure [15,16], non-toxicity and most particularly cost-efficient production routes could make copper oxides alternative to silicon which is predominantly used in conventional solar cells. Therefore, CuO and Cu_2O can potentially be used to fabricate thin film solar cells and photodetectors. In particular, a heterojunction structure with a complementing n-type semiconductor could lead to high performance devices [17–19]. In such applications, there are many factors that can affect the heterojunction formation, the efficiency and performance of devices. Optical and microstructural properties of copper oxide thin films are only two of them, which should be carefully optimized for a decent device performance. It is then crucial to determine these properties under different processing conditions. Moreover, post-deposition treatments might be useful to control and improve the microstructural, optical and electrical properties of thin films. A detailed study of copper oxide thin films is then of scientific and technological interest. Gaining a deeper understanding of the properties of copper oxide films will allow optimization of the processing conditions required to fabricate highly efficient optoelectronic devices.

Copper oxide thin films can be prepared using a wide range of methods including reactive evaporation [20], chemical deposition [1,2], thermal oxidation [21–23], chemical vapor deposition (CVD) [3], and sol–gel [4,24]. The deposition method and conditions including the post-deposition treatments play an important role in the determination of the physical and chemical properties of copper oxide thin films. Among these methods, sol–gel is the most widely used one due to its low cost, simplicity and controllability. It is also possible to deposit films over large areas under atmospheric conditions.

In this paper, we report on the variation of the microstructural, morphological, optical properties and surface electronic structure of the copper oxide thin films during the post-deposition heat treatment, and showed that the copper oxide thin films with required chemical compositions and physical properties can be tailored using post-deposition annealing treatments.

2. Experimental

The solution for the deposition of thin films was prepared by dissolving copper acetate [$Cu(CH_3COO)_2 \cdot H_2O$, Merck, 99,98%] in ethanol. Afterwards, lactic acid ($C_3H_6O_3$) and triethylamine ($C_6H_{15}N$) was added to the prepared solution. The pH of the acquired solution was approximately 5.5. The thin films were deposited by spin-coating technique on soda-lime silicate glass substrates. Prior to deposition, the substrates were ultrasonically cleaned in consecutive acetone, ethanol, and de-ionized water (18.3 MΩ) baths for 15 min. Then, they were dried with nitrogen gas. The spin-coating was applied at 2000 rpm. At the end of a coating cycle, thin films were dried on a hot plate at 200 °C for 2 min in air under ambient conditions. Relative humidity of air environment was less than 30%. To avoid cracking in thin films and inhomogeneous coverage, multiple coatings were made with drying in between each successive coating step. Fifteen coatings were carried out and a film thickness of about 520 nm was obtained. Finally, as-deposited films were annealed in a muffle furnace under atmospheric pressure conditions in air at five different temperatures (200, 300, 400, 500 and 600 °C) for 30 min to investigate the effect of annealing temperature on the microstructural, morphological, optical properties and surface electronic structure of the thin films. First, the furnace temperature was elevated to post-deposition annealing temperature with a heating rate of 20 °C min^{-1}. Once the temperature reached the desired value, thin film samples were placed inside the furnace. Although the annealing temperature was set to the indicated value, due to our furnace, temperature dropped to much lower levels (depending on time of loading, sometimes to low 200 °C's). It then takes some time to get back to the indicated temperature. The samples annealed for 30 min after reaching the set temperature. Then the furnace was turned off and thin film samples were allowed to cool down to room temperature naturally to prevent film cracking by thermal stress. An as-deposited sample was used as a reference.

In order to determine the crystal phase(s) of the deposited thin films, a Rigaku miniflex XRD system equipped with Cu K_α radiation ($\lambda = 0.154$ nm) was used. The XRD patterns were recorded in the range of 10–80° with a scan speed of 2°/min. The surface morphology and roughness of the thin films were characterized by FESEM (Nova NanoSEM 430-operated at 10 kV) and AFM (Vecoo MultiMode V), respectively. Optical properties of the samples have been analyzed using an optical setup consisting of an 8-inch integrating sphere with 1-inch ports (Newport, 70679NS), a monochromator (Newport, 74100), a UV-enhanced Si photodiode detector (Newport, 70356), and a collimated beam from a 100 W halogen lamp. The samples were mounted at the front side of the integrating sphere for transmittance measurements and at the back side of the integrating sphere for reflectance measurements. The wavelength range for both the reflectance and transmittance measurements was varied between 400 and 1100 nm. The surface electronic structure and chemical states of the atomic species in the thin films were examined via XPS using a monochromatic Al K_α X-ray source (1486.6 eV) (PHI 5000 VersaProbe). The XPS