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Nanostructured copper and copper oxide thin films fabricated by hydrothermal treatment of copper hydroxide nitrate

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ABSTRACT

Metallic copper and copper oxide thin films were fabricated on surface of glass slide substrates. Copper oxide thin films were prepared by a hydrothermal method using an α-phase layered hydroxide, copper hydroxide nitrate as a precursor. Morphology, thickness and crystallite size of the obtained copper oxide thin films changed by changing the time of hydrothermal treatment. Accordingly, the copper oxide thin films showed various water contact angles and optical band gaps. As, the optical band gap of the nanostructured copper oxide thin films increased with an increase in hydrothermal time from 1.85 to 2.95 eV. Moreover, the water contact angles changed from 16.4 to 38.8° by changing the hydrothermal time. By a reductive hydrothermal-treatment route, the copper oxide thin film was reduced to metallic copper thin film without any particle growth.

1. Introduction

In recent years, numerous studies have been carried out on the topic of surface coatings. It is due to the fact that various fields of new technologies from electronic devices to surface catalysts, self-cleaning, solar and fuel cells and even biology and environment phenomena depended on thin films [1–7]. To this end, a variety of organic and inorganic materials such as polymers, pure and doped metal oxides/hydroxides and carbon materials have been successfully coated onto different substrates for specific purposes. Accordingly, copper oxide (CuO) (a p-type semiconductor with band gap energy of 1.4 eV in its bulk form) is a good candidate to be fabricated as a thin film due to its potential applications as gas sensors, batteries, solar cells as well as photocatalysts [3–5,8,9]. On the other hand, copper (the reductive product of copper oxide) is one of the most important metals in modern technologies [7,10]. For instances, in fabrication and packaging the microelectronics, especially in integrated circuits (ICs) and mechanical/electrical micro systems (MEMSs), copper thin films as the excellent conductors are extensively used. So far, for fabrication of thin films on various substrates, several methods such as chemical vapor deposition (CVD), sol–gel, pulsed-laser deposition, electro-deposition, magnetron sputtering of a target, wet chemical routes and other methods were used [11–17]. It is well known that the surface properties such as adhesion, wettability, surface reactivity and catalytic activity are related to the development of a homogeneous thin film on the base material surface.

Copper hydroxide nitrate (CHN) is an α-phase layered hydroxide with its formula — $Cu_2(OH)_3NO_3$ whose layers are formed in the monoclinic lattice [18,19]. One-fourth of the hydroxide ions within each layer are replaced by nitrate anions. The nitrate ions are located between the layers and are coordinated with copper cations via one oxygen atom [18]. The α-phase layered hydroxides have been precursors to produce diverse upcoming products such as metal oxides, metallic particles, catalysts and various carbon materials [18].

Herein, we report the results obtained in the synthesis and characterization of nanostructured thin films of SiO_2/CHN, SiO_2/CuO and metallic copper (SiO_2/Cu), which were prepared by using a wet chemical hydrothermal route. First, CHN was synthesized and then, nanostructured SiO_2/CuO was obtained by hydrothermal treatment of CHN onto SiO_2 glass slide and finally SiO_2/Cu thin film was observed by reductive hydrothermal treatment of SiO_2/CuO. Results from X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), contact angle measurement (CA) and also optical measurement studies are discussed.

2. Material and methods

2.1. Synthesis of copper hydroxide nitrate, CHN

CHN was synthesized by our previous work [19]. Briefly, an aqueous solution of 0.2 M $Cu(NO_3)_2$ was brought to pH = 5.5 ± 0.05 by dropwise additions of 0.5 M NaOH solution with vigorous stirring under nitrogen

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atmosphere. The precipitate was filtered, washed with water and acetone and dried in an oven, overnight at 80 °C.

2.2. Fabrication of CHN on glass slide

First, glass slides as the substrates were washed with dish cleaners and were then treated in a piranha solution for 4 h at 90 °C. For this sample, the glass slide was placed in the solution that was used for CHN preparation and the sample was labeled as SiO_2/CHN.

2.2. Fabrication of copper oxide on glass slide

0.2 g of CHN was dispersed into 30 mL of distilled water to make a suspension by ultrasonic water bath for 30 min. Afterward, a piece of glass slide and 30 mL of the suspension were placed into a Teflon-lined stainless steel autoclave (45 mL capacity) and the coating process was carried out in an oven for 4, 8 and 12 h at 200 °C. The products were labeled as $SiO_2/CuO^4/CuO^8/CuO^{12}$. Here, CHN particles were calcined in this condition and were coated on the surface of glass slide as copper oxide. For comparing, the SiO_2/CuO^8 thin film was heat-treated in air atmosphere at 400 °C at a rate of 5 °C/min for 1 h holding time (labeled as SiO_2/CuOh).

2.3. Fabrication of metallic copper on glass slide

For preventing particle growth and glass slide melting due to necessary high temperatures for heating the metal oxides in a reduction atmosphere to get metallic materials, a wet chemical method was applied to reduce the SiO_2/CuO precursor to obtain the SiO_2/Cu, where the coated particles on the slide surface keep their initial size and shape. Accordingly, the SiO_2/CuO^8 slide and a solution containing 10 mL of *N*,*N*-dimethylformamide (DMF) and 20 mL of ethanol (96%) were placed into the Teflon-lined stainless steel autoclave and were then heated to 200 °C in a furnace for 20 h at a rate of 10 °C/min. The hydrothermal-treated product was labeled as SiO_2/Cu^8.

2.4. Material characterization

X-ray diffraction patterns (XRD) were collected on a JEOL-JDX-8030 diffractometer unit using CuK_α ($\lambda = 1.54$ Å) at 30 kV and 20 mA. FTIR spectra were recorded using a Bruker (Vector 33) spectrophotometer in the range of 400–4000 cm^{-1}. The optical absorption measurements were performed using a Perkin-Elmer UV–visible spectrophotometer, Lambda 20. A scanning electron microscope (KYKY, EM3200) was used to study the surface morphology of some thin films. The contact angles (CA) were measured by a Dataphysics (OCA 15 Plus) static dynamic contact angle instrument, after dropping several water drops on the film surface of each sample.

3. Results and discussion

3.1. XRD of CHN and thin films

XRD patterns for the as-prepared CHN, its resultant $SiO_2/CuO^4/CuO^8/CuO^{12}$ and SiO_2/Cu_8 thin films are shown in Fig. 1. As shown in the figure, CHN with high crystallinity (card no, 15-0014) has a brucite-like structure with the narrow width and intense reflection of the basal spacing peak around 6.9 Å [19,20]. The average thickness (D_{001}) and the average brucite-like-layer number of crystallites were 15.5 nm and 21, respectively, estimated by the Debye–Scherrer's formula [21]. Fig. 1 also shows XRD patterns for the copper oxide thin films with the presence of three new peaks at 36, 39 and 49° (2θ) (card no, 45-0937) and the lack of the peak at 12.85° due to the parent material, CHN. That is, the hydrothermal treatment at 200 °C (for 4–12 h) with high vapor pressure converted the layered

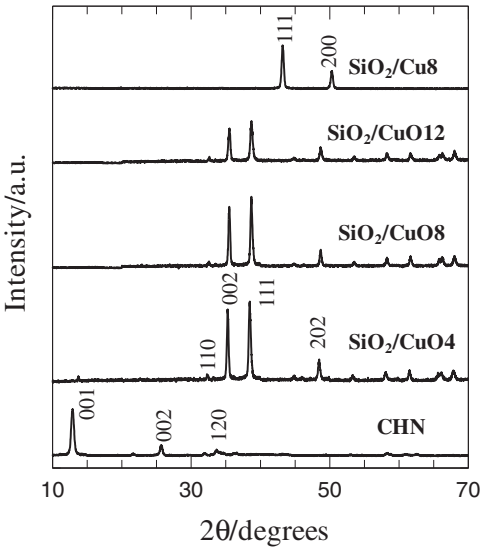

Fig. 1. XRD patterns for CHN and its resulting SiO_2/CuO and SiO_2/Cu thin films.

hydroxide material into copper oxide according to the following equation [19]:

$$4Cu_2(OH)_3NO_{3(s)} \rightarrow 8CuO_{(s)} + 6H_2O_{(v)} + 4NO_{2(g)} + O_{2(g)}. \quad (1)$$

The average crystallite sizes for SiO_2/CuO^4, SiO_2/CuO^8 and SiO_2/CuO^{12} thin films were 24.48, 24.36 and 19.85 nm, respectively. This reveals that with an increase in the contact time, the crystallites are shrunk gradually due to the high vapor pressure condition of the hydrothermal process. Fig. 1 also shows XRD pattern of SiO_2/Cu^8, the reductive hydrothermal product of SiO_2/CuO^8. As observed, no any oxide-related peaks can be seen in the pattern. The pattern is consistent with card no. 04-0836. This confirms that the reductive hydrothermal process was really effective to the formation of the metallic copper from its copper oxide phase. Herein, DMF acts as a weak reducing agent in the process, and a small amount of water which is needed for the process can be obtained via ethanol as the following [22].

$$HCON(CH_3)_2 + H_2O \rightarrow HCOOH + NH(CH_3)_2 \quad (2)$$

$$CuO + HCOOH \rightarrow Cu + H_2O + CO_2. \quad (3)$$

The average crystallite size of copper thin film for SiO_2/Cu^8 was 16.21 nm. This decrease in the crystallite size of metallic copper compared with that of the initial copper oxide (SiO_2/CuO^8) is probably due to the shrinkage of the copper oxide unit cells by the removal of oxide from the CuO structure, resulting in less volume of metallic copper unit cell (cubic) compared with that of copper oxide (monoclinic).

3.2. FTIR study of CHN and thin films

Fig. 2 shows FTIR spectra for CHN, SiO_2/copper oxide and SiO_2/Cu^8 thin films. In the CHN sample, lattice vibrations of Cu–OH and Cu–O metal–oxygen bonds are observed at 507 and 427 cm^{-1} [19,20]. The band at 675 cm^{-1} is ascribed to the δ-mode of the O–H groups [19,23]. The υ_2 and υ_3 vibrational modes of the nitrate anions between the layers of CHN are observed at 877 and 1383 cm^{-1}, respectively [18,19]. The band at 1045 cm^{-1} is attributed to the bending vibration of Cu–O–H. Finally, the band at 1421 cm^{-1} is a characteristic of well crystallized copper hydroxide nitrate [19,20].

The FTIR spectra of the hydrothermal-treated copper oxides are also shown in Fig. 2. As shown in the figure, there are three intense bands in the range of 440–600 cm^{-1} which are attributed to Cu–O (metal–oxygen) vibrations for all the SiO_2/CuO samples. For SiO_2/CuO^4 sample,