Journal of Ceramic Processing Research. Vol. 12, No. 5, pp.606~609 (2011)

J O U R N A L O F
Ceramic Processing Research

Effect of thermal annealing on the structural and optical properties of CuO nanocrystals formed on Al_2O_3 substrates using spin coating

Chan Ho Yoo and Tae Whan Kim*

Department of Electronics and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Cupric oxide (CuO) nanocrystals were formed on Al_2O_3 substrates by spin-coating and thermal treatment methods. X-ray photoelectron spectroscopy profiles showed that the CuO nanocrystals were formed on the Al_2O_3 substrates and that the binding energy of the peak corresponding to the Cu $2p_{3/2}$ decreased with an increase in the annealing temperature. X-ray diffraction (XRD) patterns showed that the XRD peak intensity corresponding to the (200) K_α diffraction peak for the CuO nanoparticles on the Al_2O_3 substrates increased with an increase in the annealing temperature. Scanning electron microscopy images showed that the average diameter and the density of the CuO crystalline nanoparticles formed on Al_2O_3 substrates increased with an increase in the annealing temperature due to the coalescence of the CuO nanoparticles. Photoluminescence spectra at 300 K showed that a peak position related to the band edge emissions shifted to the small energy side with an increase in the annealing temperature.

Key words: CuO nanocrystal, Structural property, Optical property, Al_2O_3, Thermal annealing.

Introduction

Cupric oxide (CuO) semiconductors have attracted a great deal of interest because of their potential applications in electronic and optoelectronic devices, such as electrochemical cells [1], gas sensors [2, 3], magnetic storage media [4], solar cells [5], field emitters [6], and nanodevices for catalysis [7, 8]. Because CuO materials are non-toxic and their constituents are available in abundance [9], they have emerged as excellent candidates due to interest in promising applications in environmentally-friendly electronic and optoelectronic devices. CuO semiconductors have been currently of interest for solar cell applications due to their optical properties of a high solar absorbency and a low thermal emittance [10]. The potential applications of CuO nanostructures have driven extensive efforts to form various types of nanostructures [11, 12]. CuO nanostructures have been formed by using several techniques, such as precursors [13], hydrothermal decomposition [14], self-catalytic growth [15], and solvothermal [16] routes. Among these CuO nanostructures, CuO nanoparticles were formed using a sol-gel technique [17], a one-step solid state reaction [18], an electrochemical method [19], and a colloid-thermal synthesis process [8]. Even though some studies concerning the various formation methods of CuO nanoparticles have been reported [8, 17-19], systematic studies on the effect of thermal annealing on the structural and optical properties of CuO nanocrystals formed on Al_2O_3 substrates using a spin-coating method are necessary to enhance device performance.

This paper reports data on the effect of thermal annealing on the structural and optical properties of CuO nanocrystals formed on Al_2O_3 substrates using spin coating. X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the stoichiomery of the CuO nanocrystals. X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements were carried out to investigate the structural properties of the CuO nanocrystals, and photoluminescence (PL) measurements were performed to investigate the optical properties of the CuO nanocrystals.

Experimental Details

The samples used in this study were formed on Al_2O_3 substrates using spin-coating and a thermal treatment method. Copper (I) acetate ($CuCO_2\ CH_3$) was used as a starting material, and ethanol solution was used as a solvent. After the mixed solution was formed by dissolving copper (I) acetate (5 wt%) in a 30 ml ethanol solution at 300 K, the saturated solution was stirred at 60 °C for 20 minute to obtain a homogeneous solution. The solution prepared was dropped onto the Al_2O_3 substrate, and then rotated by a spin coater at 7000 rpm for 30 s. After the solution of the copper (I) acetate powder was deposited on the Al_2O_3 substrates by spin-coating, the samples were dried on a hot-plate for 5 minute in order to remove the solvent and organic residuals. The samples were then inserted into a furnace and annealed in air at 300, 500, and 700 °C for 1 h. CuO nanoparticles were formed by the

*Corresponding author:
Tel : +82-2-2220-0354
Fax: +82-2-2292-4135
E-mail: twk@hanyang.ac.kr

thermal treatment resulting from the vaporization of the acetic acid. The cryatalline quality and size of the CuO nanoparticles could be controlled by changing the annealing temperature and time.

The XPS measurements were performed using a VG Multilab ESCA 2000 system equipped with a monochromated Mg K_α X-ray as an excitation source. The XRD measurements were performed using a Rigaku D/Max-IV diffractometer with Cu-$K_{\alpha1}$ (λ = 1.54056 Å) radiation. The SEM measurements were performed using a SUPRA 60 made by Carl Zeiss. The PL measurements were carried out using a 50 cm monochromator equipped with an RCA 31034 photomultiplier tube. The excitation source was the 3250 Å line of a He-Cd laser, and the sample temperature was kept at 300 K.

Results and Discussion

Fig. 1 shows the XPS spectra for CuO nanocrystals grown on Al_2O_3 substrates at (a) 300, (b) 500, and (c) 700 °C. All the spectra obtained were calibrated to a C 1 s electron peak at 284.5 eV. The XPS peaks at 933.9, 933.7, and 933.4 eV for CuO nanocrystals annealed at 300, 500, and 700 °C correspond to the Cu $2p_{3/2}$ shown in the upper spectra of Fig. 1, which is in reasonable agreement with bulk CuO [20]. The binding energy of the peak corresponding to the Cu $2p_{3/2}$ decreases with an increase in the annealing temperature. The broad peaks between 529 and 532 eV for the XPS spectrum are related O 1s [18], as the lower spectra of Fig. 1. The peak at 529.2 eV is attributed to O^{2-} in CuO nanoparticles, and the peak at 531.4 eV is related to the oxygen adsorbed onto the surface of the CuO nanoparticles. The XPS spectra demonstrate that the materials formed are CuO nanocrystals.

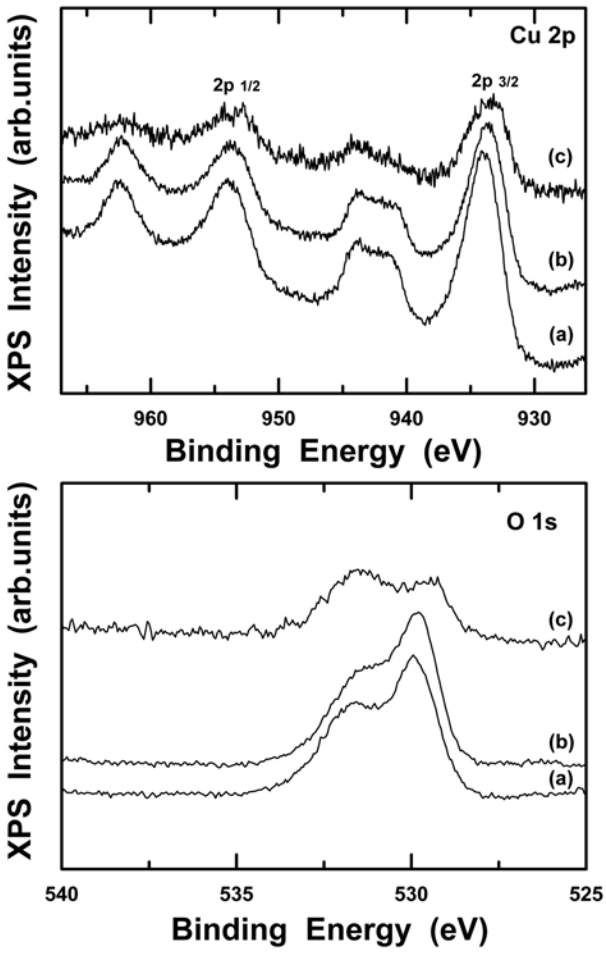

Fig. 1. X-ray photoelectron spectroscopy Cu 2p and O 1s spectra for CuO nanoparticles grown on Al_2O_3 substrates at (a) 300, (b) 500, and (c) 700 °C.

Fig. 2 shows XRD data for the CuO nanoparticles on the Al_2O_3 substrates annealed at 300, 500, and 700 °C. The XRD curves for the CuO nanoparticles on the Al_2O_3 substrates show that the (200) and (400) K_α diffraction peaks corresponding to the CuO nanoparticles are clearly observed in Fig. 2, indicative of the formation of strongly-aligned CuO (100) nanoparticles. The CuO nanoparticles with a single crystalline structure are well aligned on the Al_2O_3 substrates. The XRD peak intensity corresponding to the (200) K_α diffraction peak for the CuO nanocrystals on the Al_2O_3 substrates increases with an increase in the annealing temperature, resulting in the enhancement of the sample qualities.

Fig. 3 shows SEM images of CuO nanocrystals formed on Al_2O_3 substrates annealed at (a) 300, (b) 500, and (c) 700 °C. The SEM images show that CuO nanocrystals are formed on Al_2O_3 substrates using the spin-coating method and subsequently annealed at 300, 500, and

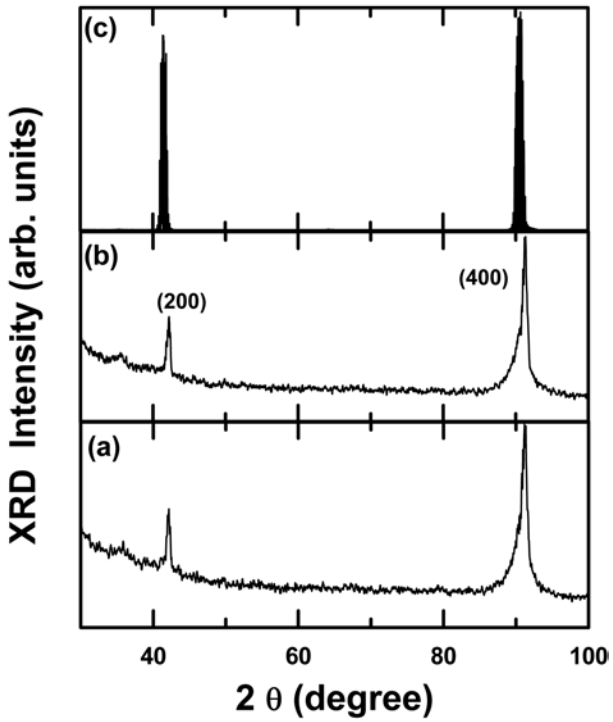

Fig. 2. X-ray diffraction patterns of the CuO nanoparticles formed on the Al_2O_3 substrates annealed at (a) 300, (b) 500, and (c) 700 °C.

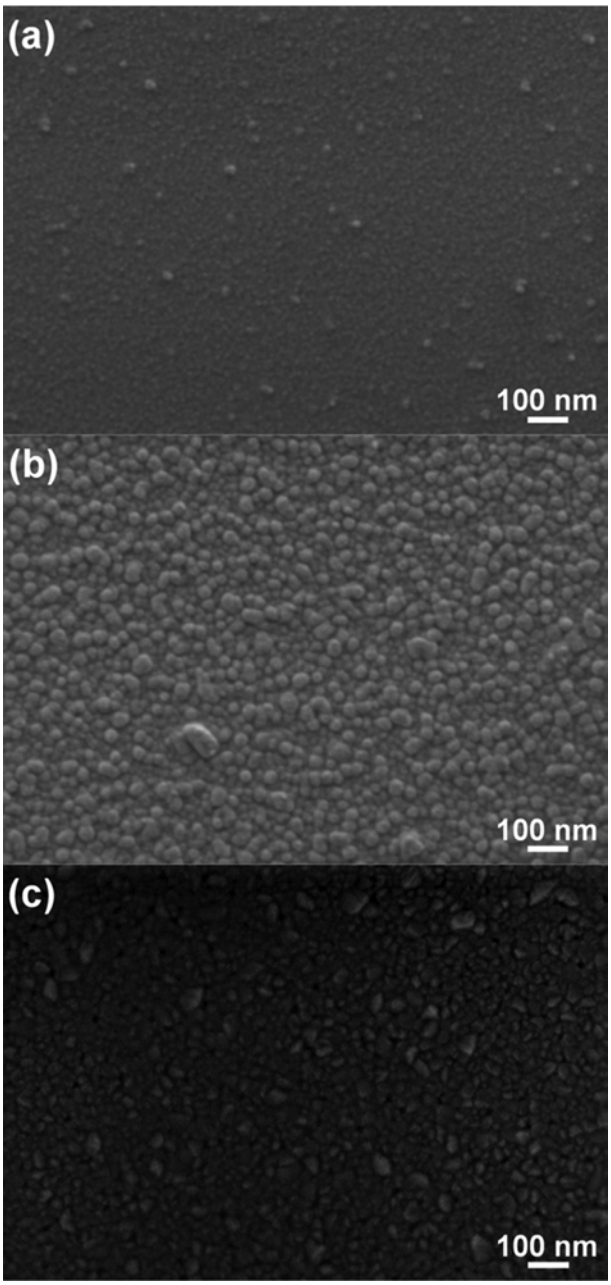

Fig. 3. Scanning electron microscopy images of the CuO nanoparticles formed on the Al_2O_3 substrates annealed at (a) 300, (b) 500, and (b) 700 °C.

700 °C for 1 h. The average diameters of the annealed CuO nanocrystals formed on Al_2O_3 substrates are between approximately 10 and 100 nm. The average diameter and the density of the CuO nanocrystals formed on Al_2O_3 substrates increase with an increase in the annealing temperature due to the coalescence of the CuO nanoparticles resulting from a higher thermal energy.

Fig. 4 shows PL spectra at 300 K for CuO nanocrystals formed on the Al_2O_3 substrates annealed at (a) 300, (b) 500, and (c) 700 °C. A dominant emission peak around 3.15 eV of the PL spectrum for CuO nanocrystals grown on Al_2O_3 substrates at 300 °C is observed in the blue

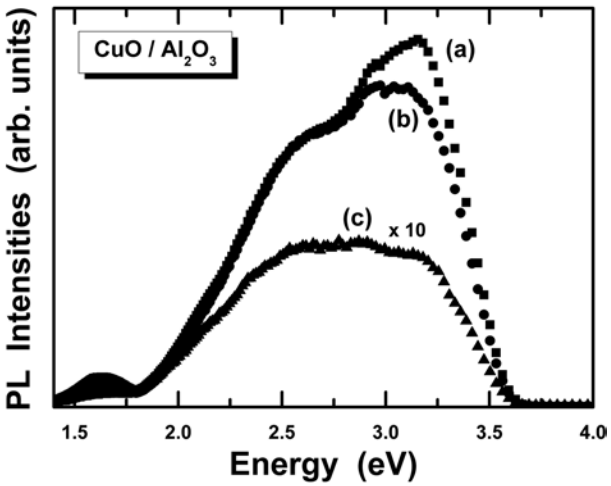

Fig. 4. Photoluminescence spectra of the CuO nanoparticles formed on the Al_2O_3 substrates annealed at (a) 300, (b) 500, and (c) 700 °C.

region, as shown in Fig. 4(a). The large blueshift of the PL peak position corresponding to the band edge emission for the CuO nanocrystals in comparison with bulk CuO is attributed to the enhancement of the quantum confinement effect resulting from the decrease in the dimensional structure. This result is in reasonable agreement with the band-gap of CuO nanocrystals prepared using a microwave irradiation process [21]. The peak position related to the band edge emissions shifts to the small energy side with an increase in the annealing temperature resulting from an increase in the size of the CuO nanocrystals, as shown in the SEM images of the Fig. 3. The peak intensities of the band-edge emission for CuO nanocrystals decrease with an increase in the annealing temperature. This behavior might originate from an increase in the dislocation density with an increase in the annealing temperature.

Summary and Conclusions

CuO nanocrystals were formed on Al_2O_3 substrates using a spin-coating process. XPS data indicated that CuO nanocrystals were formed on Al_2O_3 substrates and that the binding energy of the peak corresponding to the Cu $2p_{3/2}$ decreased with an increase in the annealing temperature. XRD patterns showed that the XRD peak intensity corresponding to the (200) K_α diffraction peak for the CuO nanoparticles on the Al_2O_3 substrates increased with an increase in the annealing temperature, resulting in an enhancement of the sample crystallinity. SEM images showed that the average diameter and the density of the CuO crystalline nanoparticles formed on Al_2O_3 substrates increased with an increase in the annealing temperature due to the coalescence of the CuO nanoparticles resulting from a higher thermal energy. PL spectra at 300 K showed that a peak position related to the band edge emissions shifted to the small energy side with an increase in the annealing temperature resulting from an increase in the

size of the CuO nanocrystals. A dominant emission peak in the blue region of the PL spectra for CuO nanocrystals was observed. These results can help to improve an understanding of the effect of thermal annealing on the structural and optical properties of CuO nanocrystals formed on Al_2O_3 substrates using spin coating.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0018877).

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