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Research Article

Growth of Cu_2O Nanopyramids by Ion Beam Sputter Deposition

Assamen Ayalew Ejigu

Department of Electrical Engineering, Wollo University, Kombolcha Institute of Technology, P.O. Box 208, Kombolcha, Ethiopia

Correspondence should be addressed to Assamen Ayalew Ejigu; assamen2002@gmail.com

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In this study, we have successfully deposited n-type Cu_2O triangular nanopyramids on Si by employing ion beam sputter deposition with an $Ar:O_2$ ratio of 9 : 1 at a substrate temperature of 450°C. Scanning electron microscopy measurements showed attractively triangular nanopyramids of ~500 nm edge and height lengths. Both X-ray diffraction and Raman spectroscopy characterizations showed the structures were single-phase polycrystalline Cu_2O, and the room-temperature photoluminescence investigation showed interestingly green and blue exciton luminescence emissions. All Mott—Schottky, linear sweep voltammetry, and photocurrent measurements indicated that the conductivity of the Cu_2O pyramids is of n-type.

1. Introduction

Recently, cuprous oxide (Cu_2O) nanostructures are drawing great attention due to their smart optoelectronic characteristics such as nontoxic, naturally abundant, inexpensive market price, and high absorption coefficient. Cu_2O nanostructures have extensive applications in water splitting [1], photosensing [2], electrode material for lithium-ion batteries [3], photocatalysis [4], low-cost solar energy conversion [5], etc. On the other hand, the use of Cu_2O as an initial study material to understand the basic principles is indispensable since excitons in Cu_2O were suggested as noble candidates for understanding of Bose–Einstein condensation [6] because of their unique combinational properties. However, there are few reports on room-temperature exciton emission due to optical quenching and domination of copper vacancy (V_{Cu}) related luminescence. As a result, there is no sufficient information about room temperature (RT) excitons to explore the optoelectronic applications of Cu_2O comprehensively. To overcome these problems, one possible way is to deposit Cu_2O with suppressed copper vacancies, and this leads to the realization of n-type Cu_2O since p-type conductivity is due to the existence of copper vacancies.

So far, different methods such as chemical bath deposition, solution-phase epitaxial growth, magnetron sputtering, and electrodeposition [7–10] have been employed to deposit Cu_2O nanostructures with different shapes such as nanowires, nanorods, nanocubes, nanopyramids, and polyhedrons. However, most of the methods utilize different precursors and surfactants for control synthesis with relatively high oxygen flow rates. As a result, most of the methods yield p-type Cu_2O. There are only few reports on the preparation of n-type Cu_2O nanostructures using physical methods with suppressed copper defect-related luminescence. In this paper, we report the growth and characterization of novel n-type Cu_2O triangular nanopyramids (TNPs) using ion beam sputter deposition (IBSD), and the experimental results show that attractively high structural quality n-type Cu_2O TNPs can be fabricated that exhibit RT green exciton photoluminescence (PL).

2. Experimental

A copper target was placed at 35 mm downstream of the ion source and a Si substrate was placed at 65 mm upstream of the copper target. Argon and oxygen gases were used as sputter and reactive gases [11], respectively with a flow rate of 9 : 1. The deposition was performed applying a discharging voltage of 1 kV at a temperature of 450°C for 1.5 hours. Field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F, and 15 keV) was used to take images. X-ray diffraction (XRD) was measured with a Bruker, D2 Phaser X-ray diffractometer using the Cu Kα, radiation ($\lambda = 0.15406$ nm) in the θ–2θ

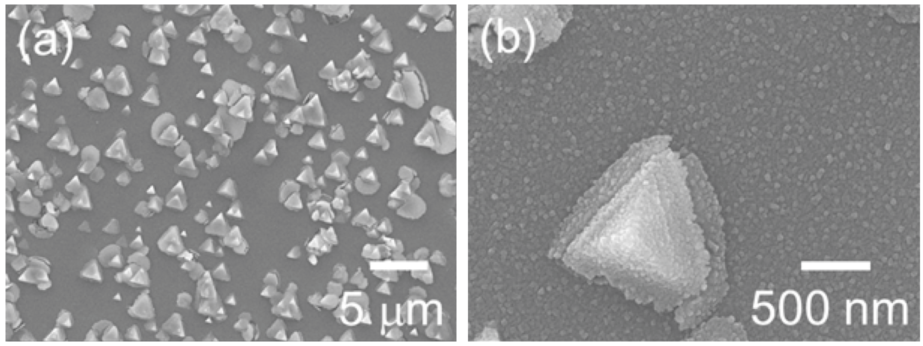

Figure 1: FE-SEM micrographs of Cu_2O TNPs.

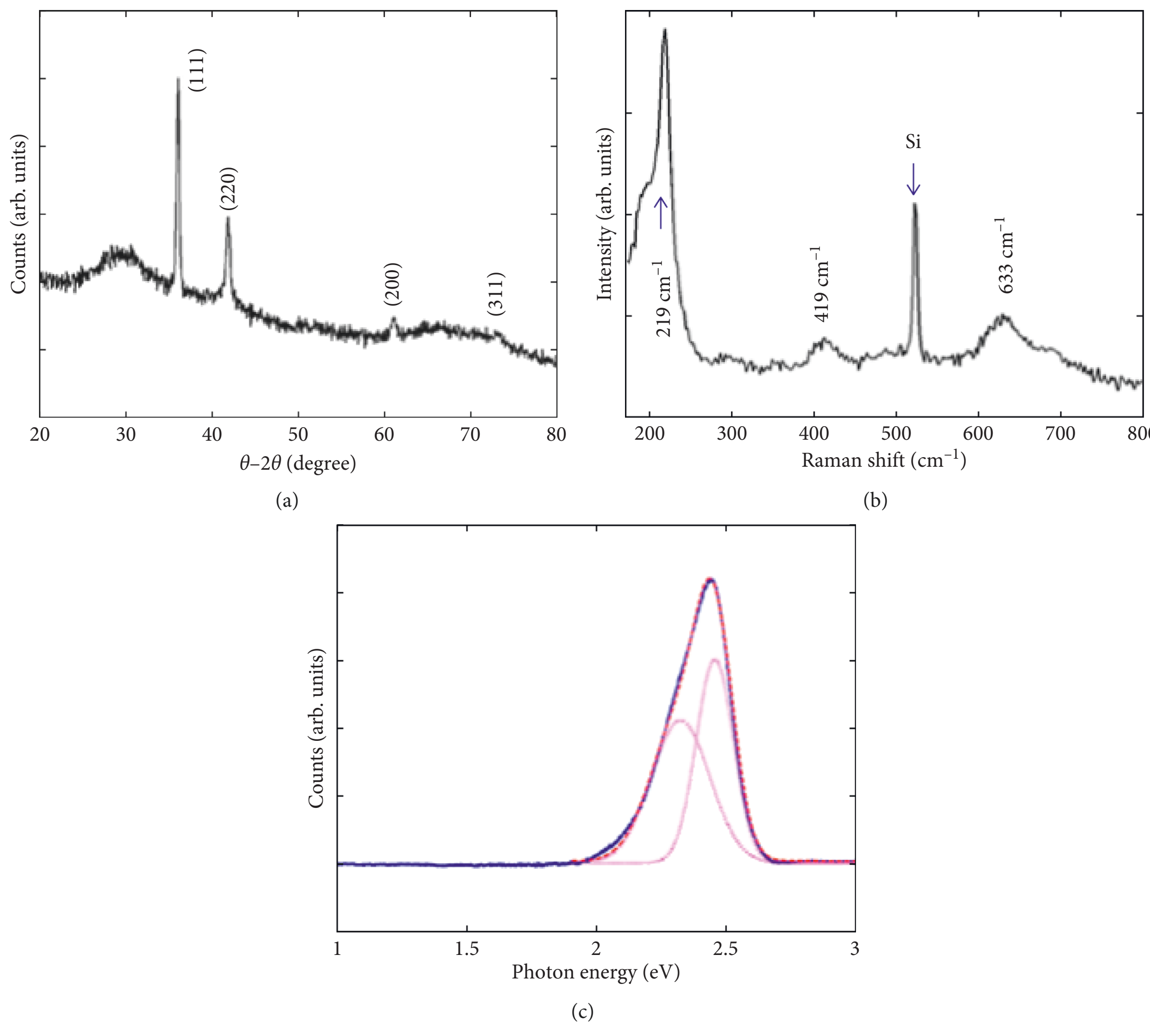

Figure 2: (a) XRD diffraction patterns (b) Raman spectra of Cu_2O TNPs and (c) PL spectra of Cu_2O TNPs.

range. Raman spectroscopy measurements were taken in a PTT RAMaker micro-Raman system utilizing a green laser at 532 nm with a power of 10 mW. The RT PL measurement was taken at 300 K using a 405 nm wavelength laser source with a power of 5 mW. The spectra were dispersed by a Triax 550 spectrometer and detected by a CCD detector cooled to −71 K. Photo-electrochemical measurements were done by a Gamry G300 potentiostat with Ag/AgCl, Pt, and Cu_2O sample as reference, counter, and working electrodes, respectively, using a customized electrochemical cell filled with 0.5 M K_2SO_4 electrolyte, employing xenon lamp for illumination.

3. Results and Discussion

Figures 1(a) and 1(b) denote the FE-SEM micrographs of Cu_2O TNP samples with different magnification values. The

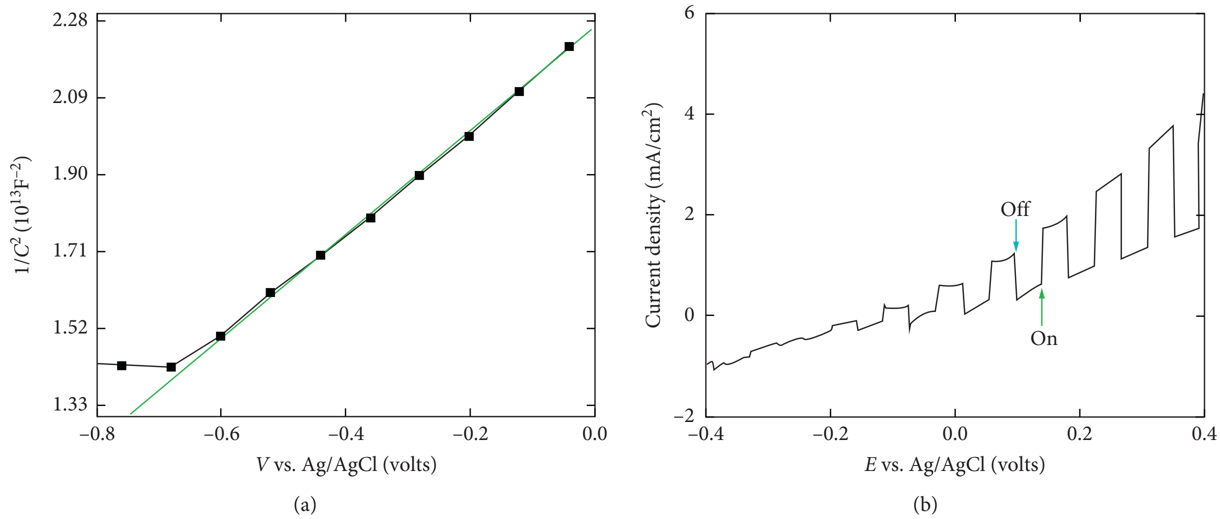

FIGURE 3: (a) Mott–Schottky plot and (b) linear sweep voltammetry measurement of Cu_2O TNPs.

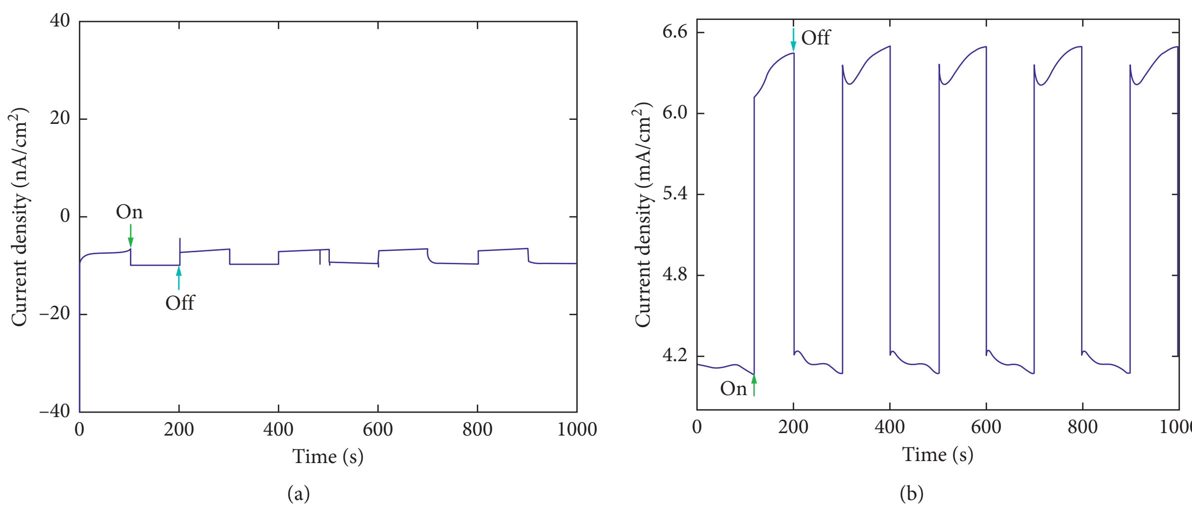

FIGURE 4: (a) −0.3 V and (b) 0.3 V biased transient photocurrent graphs for Cu_2O TNPs.

images indicate uniform, vertically aligned Cu_2O TNPs with an edge length of ~500 nm, and the images exhibit smooth morphologies. The cross-sectional view of the FE-SEM micrograph (not presented) shows that the Cu_2O TNPs are on the top of a ~180 nm thick Cu_2O thin film, and the height of the TNPs is ~500 nm. This demonstrates that the growth mechanism of the Cu_2O TNPs is due to the Stranski–Krastanov (SK) mode of growth.

Figure 2(a) demonstrates the XRD patterns of the Cu_2O TNP samples, and it shows all the diffraction peaks matched with Cu_2O phase (JCPDS #78-2076) and are indexed as the (111), (200), (220), and (311) planes. As it can be seen from Figure 2(a), the (111) peak is the largest compared with the other peaks, and it shows the growth of the Cu_2O TNPs is along the (111) plane. The sample was further investigated using Raman spectroscopy (Figure 2(b)). The measurement shows all the peaks are the characteristic Raman peaks of Cu_2O [12–15], and the result is consistent with the XRD measurements. Moreover, the strongly defined Raman mode at 219 cm^{-1} proves the structural quality of the sample.

Photoluminescence (PL) characterization of Cu_2O TNPs was carried out at room temperature. Figure 2(c) demonstrates the PL response of the Cu_2O TNP sample at RT, and the result shows a strong PL exciton emission of 2.451 eV. This strong PL band can be fitted into two Gaussian peaks: the green exciton (2.3 eV) and blue exciton (2.451 eV) [16] of Cu_2O. Mostly, exciton emission of Cu_2O is observed at low temperature (~5 K), but this study clearly shows a promising RT exciton emission. According to Ito et al., the green exciton emission of cuprous oxide can be observed at 2.304 eV at a temperature of 4.2 K, which is similar to our result (2.3 eV) attributed due to transition from Γ_8^+ to Γ_6^+. Furthermore, the PL peak at 2.451 eV is closer to the blue luminescence emission E_{oC} (2.6 eV) observed during the transition from Γ_8^+ to Γ_8^-. The detection of these significantly strong RT exciton emissions from the sample is a very encouraging result, and it has extensive potential applications in fabrication and engineering of photonic and optoelectronic devices working in the green and blue light spectrum.

As shown from Figure 3(a), the value of slope of the Mott–Schottky plot of the Cu_2O TNPs is positive, demonstrating a typical behavior of n-type conductivity with a linear increase of C^{-2} when the voltage becomes larger and larger. Figure 3(b) shows the linear sweep voltammetry measurement of the Cu_2O TNP sample carried out in a custom-built system, which includes a light source, an illumination switch, and a three-electrode cell system to investigate the conduction type of the sample recorded in 0.5 M of K_2SO_4 electrolyte. Figure 3(b) shows that as the potential becomes negative, the anodic photocurrent drops. On the other hand, as the voltage becomes positive, the anodic photocurrent increases, which proves the nature of n-type photoelectrodes.

Figure 4 designates the photocurrent response of Cu_2O TNPs under −0.3 V (Figure 4(a)) and 0.3 V (Figure 4(b)) bias with respect to the Ag/AgCl reference electrode. The figures show anodic photocurrent appeared dominantly even though there is negligible catholic photocurrent density (Figure 4(a)) when biased negatively compared with the positively biased. The magnitude of the anodic photocurrent for the positively biased (Figure 4(b)) one is very huge, indicating that the carrier type is of n-type, and the value of the photocurrent density (~2.1 mA/cm^2) is very huge and promising for the Cu_2O semiconductor material.

4. Conclusion

In this work, n-type Cu_2O TNPs with high structural quality and excellent optical properties have been grown successfully by IBSD with an Ar : O_2 ratio of 9 : 1 at a temperature of 450°C using metallic copper as a target. The FE-SEM investigation shows that Cu_2O TNPs of edge length ~500 nm have been grown across the sample on the top of the Cu_2O thin film (TF), following the SK mode of growth. Both XRD and Raman spectra measurements reveal with good agreement that the sample is a single-phase Cu_2O. Strong exciton PL bands observed at 2.3 eV and 2.45 eV attributed from green exciton and blue PL emissions. In this study, the observation of the exciton luminescence in the green and blue regions of the spectrum of light is very useful for further understanding of the optical properties of Cu_2O nanostructures and for the fabrication of optoelectronic displaying devices working at RT using Cu_2O TNPs. Besides, the high structural quality and the n-type conductivity of the sample ascertain that the grown pyramids are of novel quality and can be used in low-dimensional semiconductor researches and helpful to improve the efficiency of the solar cell using Cu_2O.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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