Effects of substrate temperature on the growth of CuO nano/micro rods by ion beam sputter deposition

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Abstract

CuO nano/micro rods were deposited on Si substrates by ion beam sputter deposition at substrate temperatures 300 °C, 350 °C, 400 °C and 450 °C. The effects of changing substrate temperature on the structural properties and surface morphology of the deposited CuO nano/micro rods were studied. Field Emission Scanning Electron Microscopy micrographs showed that at substrate temperature of 300 °C and 350 °C, tiny nanoparticles were observed on the surface of CuO thin films and at substrate temperature of 400 °C and 450 °C, CuO nano/micro rods of lengths (100 nm to 1 μm) and diameters (25 nm to 30 nm) observed in a periodic arrangement. X-Ray Diffraction (XRD) analysis showed that all the diffraction peaks of the samples were single-crystalline CuO corresponded to (111) orientation. From the crystallographic analysis using XRD data, crystallite sizes of the samples increased (18 to 32 nm) with the increase of substrate temperature. The Micro-Raman spectroscopy investigation shows that all the Raman peaks observed were phonon modes of CuO and as the substrate temperature increased, the intensities of the Rama peaks increased. Hence, by changing substrate temperatures, it is possible to deposit high quality CuO nano/micro thin films with tunable structures, morphologies and sizes for different optoelectronic applications through ion beam sputter deposition.

1. Introduction

Both p and n-type nano/micro-structured transitional metal oxides (TMOs) are recently essential materials for manufacturing of several novel functional and smart pn-junction based optoelectronic devices, such as transistors [1], supercapacitors [2–4], light emitting diodes (LEDs) [5, 6], photo electrodes [7, 8], etc. These TMOs nano/micro crystals have been attracting much attention not only for fundamental scientific research, but also for several practical applications because of their unique physicochemical properties [9–11]. These physicochemical properties are strongly dependent on the sizes, shapes, compositions, and structures of the nano/micro crystals. Especially, quasi–unidimensional (Q1D) nanostructured materials have higher surface area to volume ratio [12–15] offering better crystallinity, higher integration density, lower power consumption and decrease of the recombination process for designing of different optoelectronic devices due to the less distance that the photogenerated charge carriers must travel to attain the interface [16].

Cupric oxide (CuO) is one of the well-known p-type TMO materials with relatively narrow band gap (1.2–1.9 eV) [2–4]. CuO has took substantial consideration in recent years as a result of its smart optoelectronic properties [17] and wide applications in solar cells [18], catalysts [19, 20], lithium ion batteries [21–23], gas sensors [24, 25], biosensors [26, 27], etc. CuO is an interesting semiconductor material due to its advantages and the source elements such as: low cost, the occurrence of the source element in large amount, non-toxicity, and low-cost production processing [28]. Several work have been made to deposit different nano/micro structured CuO thin film, such as nanowires [29, 30], nano-flowers [31], nanorods [32], and nanoparticles [28, 33, 34] to improve the performances of CuO based devices. In recent years, well-controlled fabrications of nano/micro structured TMOs with different sizes, shapes, chemical compositions, and structures is essential for the
advancement of nano-science and nanotechnology because of the new and novel chemophysical and optoelectronic properties [17, 35, 36]. Accordingly, various nanostructured CuO thin films have been deposited by many deposition methods, including chemical methods [32], hydrothermal synthesis [37], solution methods [6, 35], sol-gel method [1, 7, 38], DC magnetron sputtering [36, 39], spray pyrolysis [40], etc. As compared with other physical vapor deposition (PVD) techniques, Ion Beam Sputter Deposition (IBSD) is more preferable method because; it is high energetic deposition, it helps to have intense material densities in deposition of high quality thin films, it gives better adherence of thin films, it is a preferable deposition with better hardness and structural stability, it helps us to make very smooth and sensitive coatings and it has low scattering loses of deposition [41–44].

In IBSD, several deposition parameters play vital roles in deposition of thin films and thus these parameters determine the quality, structure, morphology and the entire properties of thin films. The properties of thin films deposited by IBSD are strongly depended on the Substrate Temperature (ST) since the mobility of the adatoms on the substrate surface during deposition increases and the nucleation changes as the temperature changes.

Many research works have been conducted focusing on the investigation of various deposition parameters in different PVD methods of copper oxide thin films. Ogwu et al. [45] investigated the influence of rf power and oxygen flow rate on the optical transmittance of copper oxide thin films prepared by reactive magnetron sputtering. In this study, they reported that the optical transmission was found to increase from 10% to above 80% as the rf power was reduced from 800 to 200 W and the optical band gap value also increased from 2.05 to 2.4 eV. This tunable behavior of the band gap is very essential for many applications [46]. According to a very recent study reported by Jhansi et al. [47], CuO thin films deposited by pyrolysis method at various substrate temperatures, ranging from 300 to 600 °C showed that the ST has strong influence on the crystallite sizes and optical transmission and band gaps clearly rely upon the growth temperatures.

In recent times, no research works have been reported on the influence of substrate temperature on the growth of CuO thin films particularly by PVD. Hence, the main objective of study was to investigate the influence of ST on growth of CuO (structural & morphological) nanorods by keeping the other deposition parameters constant.

2. Experimental

CuO thin films were deposited on SiO₂/Si substrates at 300 °C, 350 °C, 400 °C and 450 °C ST by reactive IBSD [48, 49] for 1.5 h applying a discharging voltage of 1 kV. All the samples were deposited with constant argon/oxygen flow rate of (Ar:O₂ = 1.8/0.6) standard cubic centimeters per minute (sccm). The samples were referred as 300 °C, 350 °C, 400 °C and 450 °C. In the deposition process, a metallic copper target (99.99%) was placed at the center of the sputtering module as indicated in the schematic drawing of the deposition chamber in figure 1 [50].

Both the sputter and reactive gases (argon and oxygen) were passed into the ion source using the individual mass flow controllers. In conducting experiments, a metallic copper target (99.99%) was positioned 35 mm downstream of the ion source and the prepared substrates were placed at 65 mm upstream of the copper target. The chamber was evacuated down to a pressure of 3 × 10⁻⁵ torr using mechanical and diffusion pumps. The main reason for making all the sputtering parameters same except the ST in this study was, the research work was aimed at investigating the influence of ST on the structural & morphological properties of CuO nano/micro rods. The surface morphologies of the thin films were investigated by Field Emission Scanning Electron Microscopy (FE-SEM) of model JEOL JSM-6500F with an accelerating voltage of 15 keV. X-ray diffraction (XRD) patterns were collected with a Bruker, D2 Phaser x-ray diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å) in the θ–2θ mode. Micro-Raman spectra measurements were recorded in backscattering modes at room temperature in a PTT RAMaker micro-Raman system utilizing a green laser at 532 nm.

3. Results and discussion

3.1. SEM analysis

The surface morphologies of CuO nano/micro structures deposited by IBSD on SiO₂/Si at 300 °C, 350 °C, 400 °C and 450 °C are presented in figures 2(a)–(d).

The cross-sectional SEM images of the samples deposited at different substrate temperatures are shown in figure 3. As it can be observed from figure 3, when the substrate temperature increases from 300 °C to 450 °C, thickness of the deposited thin films measured from the cross-sectional SEM images also increases (changed from 210 nm to 690 nm).
When the ST = 300 °C, a CuO thin film (TF) surface of thickness ~210 nm (figure 3(a)) was achieved where very tiny nanoparticles (NPs) homogeneously appeared on the top of it (figure 3(a)).

When the ST = 350 °C, some of the tiny nanoparticles became larger in size and rod like structures were observed randomly on the top of the CuO (TF) with thickness ~408 nm. While the ST increased again to 400 °C, many nano/micro rods of lengths (100 nm to 1 μm) and diameters (25 nm to 30 nm) were observed in a periodic arrangement on the top of the CuO TF with thickness ~500 nm. When ST reached at 450 °C, the morphology observed at ST = 400 °C became smooth and the rods became rarely distributed across the surface of the CuO TF with thickness ~690 nm. This may be due to the last stage of nucleation. The morphology of the CuO TF were dramatically changed from tiny NPs to highly ordered CuO nano/micro rods as ST changes from 300 °C to 450 °C indicating that ST played a vital role on the morphology of the growth of CuO nano/micro structures by IBSD.

When we see the growth mechanism of the CuO nano/micro rods, first the CuO TF thickness deposited on the surface of the SiO₂/Si substrates. After a while, the growth favored to nucleate to small clusters on the CuO TF and grown to nano/micro rods. Therefore, the formation mechanism for the nano/micro rods is the Stranskei Karastanov (SK) mode.

**Figure 1.** Schematic drawing of the reactive integrated ion beam sputter module. 1: upper cathode, 2: anode, 3: gas inlet, 4: outer shielding, 5: permanent magnets, 6: lower cathode, 7: ion beam. During deposition, the anode is biased at $V_a$, while all other components were grounded to earth.

**Figure 2.** Top-view FE-SEM micrographs of CuO nanostructured samples deposited with Ar:O₂ ratio of 3:1 at different substrate temperatures.
3.2. XRD analysis
As it is well-known, XRD is a powerful and commonly used technique for structural characterization of materials since the structural properties of materials strongly depend on the crystallinity degree. In this study, the XRD patterns of CuO nano/micro structures deposited at different substrate temperatures on SiO$_2$/Si are shown in figure 3. The XRD diffraction peaks are well indexed to CuO and are matched with JCPDS #720629, #050661, #800076 and #801916 for diffraction peaks appeared at 2$\theta$ values of 35.56°, 35.55°, 35.53°, and 35.50° respectively. All the diffraction peaks of the samples of this study correspond to the (111) plane of CuO and the XRD analysis indicates that samples are composed of CuO only without the presence of Cu$_2$O or metallic Cu demonstrating that the material is pure single-crystalline CuO.

As presented in figure 4, the intensity of the XRD diffraction peak of samples increased with the increase of ST from 300 °C to 450 °C, which indicates the improvement of crystallinity of the CuO thin film.

From table 1, it can be evidently observed that the position of the XRD diffraction peak (2$\theta$) is slightly shifted towards the lower angle when the substrate temperature changed from 300 °C to 450 °C with an increment of 50 °C. The shift of XRD diffraction peak positions as the substrate temperature increases indicates that samples suffered from tensile strain which is attributed to the thermal expansion mismatch between SiO$_2$ and CuO. The XRD spectra shown humps between 2$\theta$ values of 25° and 35° are due to the amorphous nature of silicon (a-Si).
The crystallite size \(D\) of the sample at different substrate temperature was calculated employing the known Scherrer formula \(51\) presented in equation \(1\).

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]  

(1)

In equation \(1\), \(\lambda\) is the x-ray wavelength \(0.15406\ nm\), \(\beta\) is the FWHM and \(\theta\) is the Bragg angle. The Scherrer constant \(k\) is most often cited in the literature as having a value of about 0.94. The crystallite sizes \(D\) of the deposited CuO TF at different ST were calculated using the Scherrer equation employing the full width at half maximum (FWHM) of the XRD diffraction data. The FWHM of CuO thin films in this study decreased from 0.44 to 0.26° upon increasing the substrate temperature from 300 °C to 450 °C as presented table 1. This indicates that the crystallite size of CuO thin films increases (18 to 32 nm) when the ST increased. It could be observed from these results that the films grown at higher ST showed narrower diffraction peaks (table 1) due to the increase in crystallite size. The change of crystallite upon change of ST shows the crystallite size of thin films deposited through IBSD can be controlled by changing the ST.

### 3.3. Raman spectroscopy analysis

Figure 5 shows micro-Raman spectra of CuO thin films deposited with Ar:O\(_2\) ratio of 3:1 at ST of 300 °C, 350 °C, 400 °C and 450 °C. From the figure, at a ST of 300 °C only a week Raman peak is observed at 297 cm\(^{-1}\). At ST of 350 °C and 400 °C two Raman peaks are observed at 297 and 626 cm\(^{-1}\). When ST reached at 450 °C, three Raman peaks are found at 297, 343 and 626 cm\(^{-1}\). All the three Raman peaks (297, 343 and 626 cm\(^{-1}\)) observed here are Ag, B1g and B2g phonon modes of CuO [52] respectively demonstrating that the samples are pure CuO. At ST of 300 °C, Ag and B2g phonon modes with very weak peak intensities were detected. When the ST increased to 350 and 400 °C, the two Raman peaks (297 and 626 cm\(^{-1}\)) detected with stronger intensities as presented in figure 5A. When the ST reached at 450 °C, an additional Raman peak at 343 cm\(^{-1}\) is observed. When closely observed the natures of the Raman peaks, it shows the following properties. Firstly, the intensities of peaks increased as ST increased, secondly, the broadness of the peaks decrease as ST increased, and thirdly an

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**Figure 5.** Micro-Raman spectra of CuO thin film samples deposited with Ar:O\(_2\) of 3:1 at different substrate temperature.

| Sub. temperature (°C) | 2θ (degree) | d-spacing (Å) | FWHM (°) | D (nm) |
|-----------------------|-------------|---------------|----------|--------|
| 300                   | 35.56       | 2.522         | 0.44     | 18     |
| 350                   | 35.55       | 2.523         | 0.36     | 23     |
| 400                   | 35.53       | 2.525         | 0.31     | 29     |
| 450                   | 35.50       | 2.527         | 0.26     | 32     |

**Table 1.** Crystallographic properties of mono-crystalline CuO nano/micro structures deposited by IBSD at different substrate temperature (300 °C to 450 °C).

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additional peak is observed when ST reached at 450 °C. These three behaviors illustrate that the crystallite of the CuO films improved as the as the ST increased.

4. Conclusions

CuO nano/micro rods have been successfully deposited on Si substrate at a substrate temperature of 300 °C, 350 °C, 400 °C and 450 °C with an Ar:O₂ ratio of 3:1 by IBSD. The FE-SEM micrographs show that the films deposited at substrate temperatures of 300 °C, 350 °C are tiny nano particles while at substrate temperatures of 400 °C & 450 °C, nano/micro rods of lengths (100 nm to 1 μm) observed in a periodic arrangement. The XRD analysis showed all the diffraction peaks of the samples corresponded to (1 1) plane of CuO only without the presence of Cu₂O or metallic Cu demonstrating that the material is pure single-crystalline. Micro-Raman spectroscopy shows that all Raman peaks observed are phonon modes of CuO and as the ST increases, the intensities of the Raman peaks increased indicating that the improvement of crystallite of the CuO films as the as the ST increases.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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