Enhanced hydration detection properties of nanostructured CuO films by annealing

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Abstract

This work reports the effects of annealing on the material properties and sweat sensing behavior of nanostructured CuO-based films. CuO films were grown on glass substrates via SILAR (Successive Ionic Layer Adsorption and Reaction) method. Films were annealed at 200 °C and 400 °C in ambient air for 45 minutes. Scanning electron microscopy analysis confirmed the plate-like morphology of CuO nanostructures with average plate thickness increasing from 30 nm to 70 nm with increasing annealing temperature. X-ray diffraction studies of the films revealed that the average crystallite sizes were around 17–22 nm. The bandgap values were calculated from the UV–visible absorbance spectrum and it was determined that the annealing process lowered the bandgap valued from 1.46 eV to 1.38 eV suggesting that the resistivity would also decrease. The prospect of sweat electrolyte sensing properties of CuO films was studied by drop cast application of different concentrations of artificial sweat solutions. We found that annealing process increases the sensitivity of sweat electrolyte level detection for particularly low concentration artificial sweat solutions.

Keywords: Sweat Sensing, CuO, Artificial Sweat, SILAR

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1. INTRODUCTION

Semiconductors fabricated from metal oxide nanostructured materials have been studied extensively due to their good electrical and optical properties in the fields of electronics, optoelectronics, and sensor applications [1]. In particular, Copper oxide (CuO) structures have drawn a significant interest thanks to their availability and wide applicability in optoelectronics, gas sensors, and transistors [2,3]. CuO is a p-type semiconductor with a bandgap of about 1.5 eV. Its physical properties mainly depend on the fabrication conditions and the growth processes [4,5]. The physical properties can further be manipulated by annealing [3].

Different deposition techniques have been used for growing nanostructured CuO films such as electro-deposition [6], sol-gel [7], thermal evaporation [8], reactive sputtering techniques [9], and successive ionic layer adsorption and reaction (SILAR) [10]. Among these methods, SILAR provides the following advantages: (a) SILAR does not require high quality target or substrates, (b) it does not require vacuum, which is a great advantage for industrial applications [11], and (c) it is a cheap, forgiving, and reproducible process. Recently, nanostructured CuO films have been used in sensing applications such as gases and glucose sensors [12,13]. However, CuO films have yet to be investigated in terms of their sweat sensing capabilities.

Human bodies use sweat to regulate the body temperature. On average, sweat production for healthy adults range between 300 and 700 mL/day during a normal daily life [14]. Sweat rates increase significantly with exercise, stress, and climate conditions. Monitoring human sweat electrolyte levels would be of particular interest for those who perform sports or other activities requiring endurance [15]. Excessive sweating can cause imbalances in electrolyte concentrations in the human body, which can lead to serious health problems[16]. Research showed that hydration levels can be monitored by observing the ion

concentrations (such as K^+ , Na^+ and lactic acid) in the sweat [17]. This information can be used to enhance athletic or even general daily life performance [18].

In this work, we changed the morphological, structural, and optical properties of CuO films with annealing in to order investigate the sweat sensing capabilities of the films. We conducted the experiment at two different annealing temperatures and compared the results with as-deposited (i.e., no annealing) films. The sweat sensing properties of CuO films were tested via resistivity measurements by incorporating different concentrations of artificial sweat solutions.

2. MATERIALS and METHODS

2.1. Preparation of Artificial Sweat and CuO Films

Various concentrations of artificial sweat solutions were prepared based on **previous work** [19]. 0.5% of sodium chloride, 0.1% of potassium chloride, 0.1 % of lactic acid, and 0.1 % of urea were added to deionized water in weight/volume ratios. Chemicals were purchased from VWR and Fisher Scientific (urea). 0.001M ammonium hydroxide (Fisher Scientific) were added to each solution to adjust the pH to 5.4 ± 0.3 . pH values were tested by using EcoTestr PH2 pH meter. As-deposited and annealed CuO films were grown on glass substrates by using SILAR technique. Thin film growth solution was prepared by stirring 100 ml of 0.1 M $CuCl_2 \cdot 2H_2O$ solution (double distilled water, resistivity of $18.2 \text{ M}\Omega\text{cm}$). After stirring, the pH value of the solution was adjusted to around 10 by adding aqueous ammonia. The solution was then heated to 90°C and kept constant during the growth process. The glass substrates were immersed into the solution vertically for 20 seconds and then into hot water (90°C) for another 20 seconds. This cycle was repeated 10 times. Then, CuO films were annealed at either 200°C or 400°C for 45 min in ambient air. As-deposited CuO films were not annealed.

2.2. Characterization of CuO films

Nanostructured CuO films were characterized by using SEM (Scanning Electron Microscopy), XRD (X-ray Diffraction), UV-vis (Ultraviolet-visible) spectrophotometer, surface profilometer, and I-V measurements. The surface morphology of as-deposited and annealed samples were investigated by SEM (Hitachi 3400 N-II). The film thickness was measured using Sloan Dektak Profilometer. The crystalline structure and crystallite sizes of films were characterized by XRD (Rigaku Miniflex II). The bandgap energies of samples were calculated from UV–Vis measurements (Beckman DU-640B Spectrophotometer). Resistivity values of the CuO films were determined by using room temperature I-V measurements (Keithley 617 electrometer). Sweat sensing properties as-deposited and annealed CuO films were investigated via resistivity measurements by dropping 10 μ l of artificial sweat solution on the surface. Concentrations of artificial sweat were selected to be 20, 80, 130 and 260 mM.

3. RESULTS and DISCUSSION

3.1 Surface Studies

The surface morphology and microstructure of the nanostructured CuO films were examined by SEM at two different magnifications. Figure 1 shows the SEM images of as-deposited (Figure 1a and b), annealed at 200 °C (Figure 1c and d) or 400 °C (Figure 1e and f) samples.

FIG. 1: SEM photos of CuO films with and without annealing. Photos on the right are higher magnification (50K) of same films of the ones on the left (20K). Scale bars for a, c, and e are 2 μm , whereas, b, d, f are 1 μm . (a) and (b) As-deposited CuO films, i.e., no annealing. Average plate thickness is around 30 nm. (c) and (d) CuO films annealed at 200 $^{\circ}\text{C}$. Average plate thickness is increased to around 45 nm. (e) and (f) CuO films annealed at 400 $^{\circ}\text{C}$ where plate thickness increased further up to 70 nm.

The average thickness of CuO nanoplates for as-deposited films (Figure 1a and b) were calculated to be 30 nm by using SEM's size analysis feature. After thermal treatment at either 200 $^{\circ}\text{C}$ or 400 $^{\circ}\text{C}$, the plate thickness of CuO films increased as shown in Figure 1c, d, e, and f. The surface morphology of the CuO films appear to change significantly as a function of annealing temperature values. It was found that average thickness of the plates

increased from an average size of 30 nm to almost 70 nm with annealing process. The increase in crystallite size is due to the increase on super saturation of the reaction products, which improve the crystal core forming reaction[120].

The thickness of CuO films were also measured and given in Table 1. The thickness of the films decreased from 1.37 to 0.76 μm with the increase of annealing temperature. The annealing process leads to removal of water inside the film structure causing a shrinkage of films hence decrease in the thickness[21].

3.2. XRD Studies

The crystallite structure of the CuO films obtained from XRD were presented in Figure 2. The XRD measurements indicated a strong preferential orientation in the $(\bar{1} 1 1)$ and $(1 1 1)$ directions, which demonstrates that the films are in the crystal planes of the CuO nanostructures. It can be seen from Figure 2 that the peak intensities increased with the annealing temperature.

FIG. 2: XRD measurements of as-deposited and annealed films. The peak intensity increases with the annealing temperature which leads to an increase in the crystallite size. Therefore, it can be said that the annealing process enhances the crystallinity quality.

The average crystallite size values (D) of the CuO films were calculated by using the Scherrer equation [22]:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where β is the angular width of peaks at FWHM (Full Width Half Maximum), λ is the wavelength of the X-ray radiation and θ is the Braggs angle of the peaks. The mean crystallite size of as-deposited CuO film is around 17 nm as shown in Table 1, whereas films annealed at 200 °C and 400 °C had average crystallite sizes of 20 and 21 nm, respectively. This size change is mainly due to the improved crystallinity and the decrease of defect density in the CuO films. These variations can further be explained with the change in the microstructure of the nanostructured CuO films due to the annealing treatment, which are in good agreement with literature [3,23,24]. XRD results are also consistent with the SEM measurements where the particle thickness increased with increasing annealing temperature.

Table 1: The average plate thickness, crystallite sizes, film thickness and bandgap values of as-deposited and annealed CuO films.

CuO Films	Average Plate Thickness (nm)	Crystallite Size (nm)	Film Thickness (μm)	Bandgap (eV)
As-deposited	30	17	1.37	1.46
Annealed at 200 °C	45	21	0.90	1.43
Annealed at 400 °C	70	22	0.76	1.38

3.3. Optical Studies

Absorption spectroscopy is an important process to reveal the optical properties of semiconductor nanomaterials. The absorption properties were measured at room temperature via UV–vis spectrometer. The optical bandgap values of the CuO films have been calculated by using Tauc's equation [10]:

$$(\alpha h\nu) = C(h\nu - E_g)^m \quad (2)$$

where α is the absorption coefficient, c is an energy independent constant, $h\nu$ is the photon energy, E_g is the optical bandgap of the material and $m = 1/2$ stands for the allowed direct

transitions. Figure 3 shows the bandgap plots of as-deposited and annealed CuO films. It can be seen from Figure 3 that the absorption edge shifts to higher wavelengths with annealing.

FIG. 3: UV-Vis observations of samples were plotted using Tauc's equation where $(ah\nu)^2$ was plotted with respect to the photon energy. Asymptotic lines were extended to the photon energy to determine the bandgap values of samples.

This shift demonstrates the decrease in E_g values of CuO samples. The E_g values were found to be 1.46, 1.43 and 1.38 eV for as-deposited or annealed at 200 °C or 400 °C, respectively. These variations of the optical bandgap values with annealing process are mainly due to the quantum confinement effect in nanostructured materials [25-27].

On the other hand, it is known that there is an inverse relationship between crystallite size and bandgap values. We plotted the crystallite size and bandgap values for different annealing temperatures in Figure 4.

FIG. 4: Crystallite size and the bandgap values were plotted in different axis for annealing temperature to show the inverse relationship. This phenomena arises due to the quantum confinement effect in nanoscale.

It can clearly be seen that there is an inverse dependence between the E_g values and the crystallite size [28].

3.4. Electrical Resistivity Studies

Sweat sensing properties of the CuO films were investigated via I-V measurements at room temperature. As observed in Table 2, the resistivity values of CuO films decreased with increasing annealing temperature values. Annealing processing helps reduce the size of the voids and the density of defects in the film which results in higher mobility of active species that ultimately decreases the resistivity [3]. This result has a good agreement with optical and structural characterization of the films.

Table 2: Resistivity values of as-deposited and annealed CuO films. Samples were tested immediately after dropping the solution.

CuO Films	Resistance ($M\Omega/\square$)				
	No Solution	19.65 mM	78.60 mM	131 mM	262 mM
As-deposited	11.60	9.96	8.65	6.75	6.35
Annealed at 200 °C	8.22	6.30	5.96	4.60	4.23
Annealed at 400 °C	3.20	2.42	2.30	1.75	1.55

Resistivity measurements are one of the most common techniques in sensor characterization. It is well known that the resistivity decreases after annealing process particularly for metal oxide nanostructures [29-31]. Resistivity values of different concentrations of sweat solutions were measured to investigate the sweat sensing properties of CuO films. Artificial sweat solutions were dropped on the as-deposited and annealed films and resistivity values were measured right after the drop application as shown in Figure 5. It is imperative that the resistivity values would decrease with increasing concentrations of artificial sweat and annealing temperature value.

FIG. 5: Resistivity values decrease with increasing artificial sweat concentration, as expected. Further drop on the resistivity is observed with increasing annealing temperatures.

It is vital to evaluate the sensing properties of sensors by looking at the various concentrations of the sensing analyte. In order to determine if the annealing process enhances the sensing properties of films, sensitivity values were calculated using the measurement data listed in Table 2. The sensitivity (S) here is defined as the percentage change in resistivity (R_i) with respect to the nominal resistivity (no solution application, R_{nom}) [32]:

$$S = \frac{R_{nom} - R_i}{R_{nom}} \quad (3)$$

Figure 6 shows the sensitivity values of as-deposited and annealed films with the drop application.

FIG. 6: Sensitivity of as-deposited and annealed CuO films with the application of different concentrations of artificial sweat solutions. Although annealing does not have much effect on higher concentrations, it is clear that the sensitivity values are significantly higher than as-deposited films for low concentrations.

It can be observed from Figure 6 that a significant increase in the response in terms of sensitivity at low concentrations of artificial sweat. However, sensitivity values reach to a saturation at higher concentrations. We believe this phenomenon occurs due to the limiting active sensing area. As the concentration increases, because the active sensing area remains the same, resistivity value reaches to a saturation minimum [33]. It can be concluded that higher sensitivities for hydration detection can be achieved with annealing. Annealed CuO films can thus be considered as potential sweat-based hydration detection sensors for particularly low concentration sweat solutions.

4. CONCLUSION

The SILAR method was successfully implemented in preparing CuO films. Nanostructured CuO films were modified by annealing in order to see its effect on material properties as well as the sweat electrolyte sensing. Characterization of CuO films included structural, morphological, optical, and I-V properties. Results showed that annealing process led to (1) an increase in the plate thickness, (2) an increase in the crystallite size, (3) a decrease in energy bandgap, and finally (4) a decrease in resistivity.

Sweat electrolyte sensing properties of as-deposited and annealed films were studied by calculating the sensitivity from resistivity measurements for different concentrations of artificial sweat drop casting on films. The main finding of this study was that annealing process increases (almost two times) the sensitivity to hydration level detection for particularly low concentration sweat solutions. It was also observed that sensitivity values reach a saturation maximum due to the fixed active area of the sensing device.

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References

- [1] A. Amlouk, K. Boubaker, M. Bouhafs, M. Amlouk, Optimization of transparent conducting oxide ZnO compound thickness in terms of four alloys thermo-physical performance aggregates, *Journal of Alloys and Compounds* 509 (2011) 3661–3666.
- [2] J. H. Kim, A. Katoch, S. W. Choi, S. Sub Kim, Growth and sensing properties of networked p-CuO nanowires, *Sensors and Actuators B* 212 (2015) 190–195.
- [3] D. Gopalakrishna, K. Vijayalakshmin, C. Ravidhas, Effect of annealing on the properties of nanostructured CuO thin films for enhanced ethanol sensitivity, *Ceramics International* 39 (2013) 7685–7691.
- [4] P. Chanda, A. Gaur, As. Kumar, U. Kumar Gaur, Structural and optical study of Li doped CuO thin films on Si (1 0 0) substrate deposited by pulsed laser deposition, *Applied Surface Science* 307 (2014) 280–286.
- [5] T. Terasako, T. Murakami, A. Hyodou, S. Shirakata, Structural and electrical properties of CuO films and n-ZnO/p-CuO heterojunctions prepared by chemical bath deposition based technique, *Solar Energy Materials & Solar Cells* 132 (2015) 74–79.
- [6] J. Yang, L.C. Jiang, W.D. Zhang, S. Gunasekaran, A highly sensitive non-enzymatic glucose sensor based on a simple two-step electrodeposition of cupric oxide (CuO) nanoparticles onto multi-walled carbon nanotube arrays *Talanta* 82 (2010) 25-33.
- [7] L. Armelao, D. Barecca, M. Bertapelle, G. Bottaro, C. Sada, E. Tondello, A sol–gel approach to nanophasic copper oxide thin films, *Thin Solid Films* 442 (2003) 48–52.
- [8] V.R. Katti, A.K. Debnath, K.P. Muthe, M. Kaur, A.K. Dua, S.C. Gadkari, S.K. Gupta, V.C. Sahni, Mechanism of drifts in H₂S sensing properties of SnO₂:CuO composite thin film sensors prepared by thermal evaporation *Sens. Actuators B: Chem.* 96 (2003) 245-252.

- [9] S. Ghosh, D. K. Avasthi, P. Shah, V. Ganesan, A. Gupta, D. Sarangi, R. Bhattacharya, W. Assmann, Deposition of thin films of different oxides of Copper by RF reactive sputtering and their characterization, *Vacuum* 57 (2000) 377–385.
- [10] F. Bayansal, B. Şahin, M. Yüksel, N. Biyikli, H.A. Çetinkara, H.S. Güder, Influence of coumarin as an additive on CuO nanostructures prepared by successive ionic layer adsorption and reaction (SILAR) method, *Journal of Alloys and Compounds*, 566 (2013) 78–82.
- [11] H M Pathan, C D Lokhande, Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method, *Bull. Mater. Sci.*, 27 (2004) 85–111.
- [12] H. J. Park, N. Choi, H. Kang, M. Y. Jung, J. W. Park, K. H. Park, D. Lee, A ppb-level formaldehyde gas sensor based on CuO nanocubes prepared using a polyol process, *Sensors and Actuators B* 203 (2014) 282–288.
- [13] K. Li, G. Fan, La. Yang, F. Li, Novel ultrasensitive non-enzymatic glucose sensors based on controlled flower-like CuO hierarchical films, *Sensors and Actuators B* 199 (2014) 175–182.
- [14] A. Mena-Bravo, M.D. Luque de Castro, Sweat: A sample with limited present applications and promising future in metabolomics, *Journal of Pharmaceutical and Biomedical Analysis* 90 (2014) 139–147.
- [15] R. Stewart, J. Reed, J. Zhong, K. Morton, T.L. Porter, Human hydration level monitoring using embedded piezoresistive microcantilever sensors, *Medical Engineering & Physics* 29 (2007) 1084–1088.
- [16] J. Webera, A. Kumarc, A. Kumara, S. Bhansali, Novel lactate and pH biosensor for skin and sweat analysis based on single walled carbon nanotubes, *Sensors and Actuators B* 117 (2006) 308–313.

- [17] M. Al-Omari, K. Sel, A. Mueller, A. Mellinger, and T. Kaya, The effect of Na⁺ and K⁺ doping on the properties of sol-gel deposited 2-hydroxy-1,4-naphthoquinone thin films, *J. Appl. Phys.* 113, (2013) 204901.
- [18] V. F. Curtoa, Co. Fay, S. Coyle, R. Byrne, C. O'Toole, C. Barry, S. Hughes, N. Moyna, D. Diamond, F. Benito-Lopez, Real-time sweat pH monitoring based on a wearable chemical barcode micro-fluidic platform incorporating ionic liquids, *Sensors and Actuators B* 171–172 (2012) 1327–1334.
- [19] M. Alomari, G. Liu, A. Mueller, A. Mock, R. Ghosh, K. Smith, and T. Kaya, “A Portable Optical Human Sweat Sensor,” *Journal of Applied Physics*, 116 (21), 183102, 2014.
- [20] C.C. Vidyasagar, Y. Arthoba Naik, T.G. Venkatesh, R. Viswanatha, *Powder Technology* 214 (2011), 337-343.
- [21] V.R. Shinde, C.D. Lokhande, R.S. Mane, S.H. Han, Hydrophobic and textured ZnO films deposited by chemical bath deposition: annealing effect *Applied Surface Science* 245 (2005) 407–41.
- [22] B. Sahin, F. Bayansal, M. Yüksel, H.A. Çetinkara. “Influence of annealing to the properties of un-doped and Co-doped CdO films”. *Materials Science in Semiconductor Processing*, 18 (2014) 135-140.
- [23] G. Caruntu, R. Rarig Jr, I. Dumitru, C. J. O'Connor, Annealing effects on the crystallite size and dielectric properties of ultrafine Ba₁₂xSr_xTiO₃ (0,x,1) powders synthesized through an oxalate-complex precursor, *Journal of Materials Chemistry*, 16 (2006) 752-758.
- [24] J.Y. Park, T.H. Kwon, S.W. Koh, Y.C. Kang, Annealing temperature dependence on the physic chemical properties of copper oxide, *Bulletin of the Korean Chemical Society* 32(2011)1331–1335.
- [25] K.E. Andersen, C.Y. Fong, W.E. Pickett, Quantum confinement in CdSe nanocrystallites, *Journal of Non-Crystalline Solids* 299–302 (2002) 1105–1110.

- [26] M. Beaudoin, M. Meunier, C.J. Arsenault, Blueshift of the optical bandgap: Implications for the quantum confinement effect in a-Si:H/a-SiN_x:H multilayers, *Physical Review B* 47 (1993) 2197-2202.
- [27] S. Furukawa, T. Miyasato, Quantum size effects on the optical bandgap of microcrystalline Si:H, *Physical Review B*, 38 (1988) 5726-5729.
- [28] B. Sahin, Improved optical performance of CdO films prepared with CTAB as surfactant, *Philosophical Magazine* 94, (2014), 2750–2757.
- [29] H.T. Hsueh, T.J. Hsueh, S.J. Chang, F.Y. Hung, T.Y. Tsai, W.Y. Weng, C.L. Hsu, B.T. Dai, CuO nanowire-based humidity sensors prepared on glass substrate; *Sensors and Actuators B* 156 (2011) 906– 911.
- [30] A.C. Nwanya, P.R. Deshmukh, R. U.Osuji, M. Maaza, C.D. Lokhande, F. I.Ezema, Synthesis, characterization and gas-sensing properties of SILAR deposited ZnO-CdO nanocomposite thin film, *Sensors and Actuators B* 206(2015)671–678.
- [31] M. A. Rahman , M. K. R. Khan, Effect of annealing temperature on structural, electrical and optical properties of spray pyrolytic nanocrystalline CdO thin films, *Materials Science in Semiconductor Processing* 24(2014)26–33.
- [32] J.Kim, A. Katoch, S. Choi, S. S. Kim, Growth and sensing properties of networked p-CuO nanowires, *Sensors and Actuators B* 212 (2015) 190–195.
- [33] M. Parmar , R. Bhatia , V. Prasad, K. Rajanna, Ethanol sensing using CuO/MWNT thin film, *Sensors and Actuators B* 158 (2011) 229–234

SEM images of CuO films

Sensing Response