Hydration detection through use of artificial sweat in doped-and partially-doped nanostructured CuO films

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Hydration detection through use of artificial sweat in doped- and partially-doped nanostructured CuO films

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Received 9 January 2015; received in revised form 26 February 2015; accepted 27 February 2015

Abstract

A new method of sweat sensing based on nanostructured Copper Oxide (CuO) films is presented. Films were developed by the Successive Ionic Layer Adsorption and Reaction (SILAR) method. The morphological, structural and electrical properties of the CuO films were investigated by scanning electron microscopy, X-ray diffraction analysis, and room temperature current–voltage measurements, respectively. We doped CuO films with artificial sweat during the film growth process. We also drop cast the surface of the intrinsic CuO films with artificial sweat to investigate the effect of partial doping. Our results showed that partial doping indeed gave results consistent with those of actual doping. The resistivity of the partially doped films was decreased with increasing artificial sweat concentrations.

Keywords: Biosensor; CuO; Artificial sweat; Hydration detection

1. Introduction

In the past decades, nanostructured materials based metal-oxide semiconductors have been investigated for their sensing capabilities [1,2]. Copper oxide (CuO) nanostructures, in particular, have been actively studied in a very broad range of electronics applications due to their good electrical conductivity, low cost and non-toxicity [3]. CuO-based sensors exhibit high sensitivity and selectivity [4,5]. CuO has potential applications in solar energy conversion, catalysis and gas sensors [2,3,6].

CuO has a monoclinic crystal structure and a p-type semiconductor, which are well utilized in sensor applications [7,8]. CuO films have been produced by the electro-deposition method [9], wet chemistry [10], sol–gel dip-coating [11] and successive ionic layer adsorption and reaction (SILAR) [12]. As compared to other methods, SILAR offers a very easy, cheap, and efficient strategy which can be performed in low temperatures [13].

Sweating is a biological mechanism used to adjust body temperature via evaporative heat loss [14]. Sweat contains electrolytes such as Na\textsuperscript{+}, Cl\textsuperscript{−}, K\textsuperscript{+}, lactate, and urea [15,16]. The normal sweat rate for humans is approximately 0.5 L/day, which can increase to up to 2 L/h during extreme physical activities such as running [17,18]. However, in cases in which the sweat rate is high, reabsorption is slow, resulting in electrolyte loss from the body, and dehydration [19]. Correct and immediate determination of dehydration level in the body is vital because any change from normal levels may induce health problems. Developing highly sensitive and selective sweat sensors has attracted much attention due to its importance in areas of biotechnology and clinical diagnostics [20–23].

The aim of this study is to investigate the use of CuO thin films as a potential sweat sensing material. We hypothesize that adding a drop of sweat solution on to the CuO thin film will have an effect similar to doping the film initially. Therefore, we prepared two types of CuO films: intrinsic and...
2. Experimental details

Artificial sweat was prepared using the European standard EN1811: 2012 [24]. The following components were added into deionized water (weight/volume ratio): 0.5% of sodium chloride (VWR); 0.1% of potassium chloride (VWR); 0.1% of lactic acid (VWR); and 0.1% of urea (Fisher Scientific). Various artificial sweat concentrations were prepared by simply increasing the ratios in concert with each other. The pH value of artificial sweat was adjusted to 5.4 ± 0.3 by adding 0.001 M ammonium hydroxide (Fisher Scientific) using an EcoTestr PH2 pH meter. Nanostructured CuO films were deposited on glass substrates using SILAR technique: Cleaning of the glass substrates occurred in three steps: (1) immersion in dilute sulfuric acid solution (H₂SO₄:H₂O, 1:5 by volume); (2) immersion in acetone; and (3) immersion in DI water, each for 5 min in an ultrasonic bath [25,26]. Thin film growth solution was prepared by stirring 100 ml of 0.1 M CuCl₂·2H₂O solution (double distilled water, resistivity of 18.2 MΩ cm). After stirring, the pH value of the solution was adjusted to ~10.0 by adding aqueous ammonia. The solution was then heated to 90 °C and kept at this temperature during the film growth. Glass
substrates were dipped into the solution vertically for 20 s and then into hot water (90 °C) for another 20 s. This cycle was repeated 12 times. In order to investigate the effect of artificial sweat as a dopant, three different concentrations of artificial sweat (low, medium, and high) were added to the growth baths (3 ml of artificial sweat solution). Intrinsic (no treatment) CuO film surfaces were also treated with three different concentrations of artificial sweat to see the effect of partial doping. This was performed by dropping 10 μl of solution on the surface. Concentrations of artificial sweat for both doping and partial doping were selected as 1.4 mM (low concentration), 1.9 mM (medium concentration), and 5 mM (high concentration).

The surface morphology of CuO films was investigated with scanning electron microscopy (SEM, Hitachi 3400N-II). The accelerating voltage was 5 kV. The present phases and orientations of the nanostructures were examined by a Rigaku Miniflex II X-ray diffractometer (XRD) over the range of 2θ=20–70°. Room temperature I–V measurements were performed using a Keithley 617 electrometer that was computer controlled via LABVIEW. Resistivity values of the CuO films were determined considering the Ohmic region of the measurement. Silver paste was used to create two electrodes for the I–V measurements. It is important to note that the measured resistivity values are not bulk resistivity but surface resistivity since electrodes were placed on the sides of the CuO film. Therefore, we used the sheet resistance concept, which is given per square, i.e., Ω/□ or Ω/sq.

3. Results and discussion

3.1. Surface morphology

The surface morphology of CuO films was investigated by SEM. Fig. 1 shows the SEM images of intrinsic, DI water treated, artificial sweat doped, and artificial sweat partially doped CuO films. SEM images show that substrates are almost fully covered with nano-sized CuO plates. This uniform and dense morphology is important for electronic and optical applications [27]. Surfaces of CuO films were also treated with water as control (Fig. 1b) and no differences were observed compared to the intrinsic CuO films (Fig. 1a). Fig. 1d, f, and h reveal that the width and length of the nanoplates were reduced with partial doping of artificial sweat compared to doped films (Fig. 1c, e, and g). Additionally, increases in the artificial sweat concentration caused non-uniform film morphologies. Overall, SEM images reveal that the films are homogeneous and well adhered to the substrate. The surface properties of the CuO films remained nearly unchanged with increasing dopant concentrations. On the other hand, artificial sweat doped CuO films have some voids but partially doped CuO films did not have similar voids.

3.2. X-ray characterization

XRD studies were carried out to investigate the crystallographic properties of the films. Fig. 2 shows the XRD patterns of the intrinsic and artificial sweat doped CuO films deposited on glass substrates for different artificial sweat concentrations. XRD characterization illustrated that CuO films did not show any additional impurity phase indicating that there were no new chemical phases related to artificial sweat doping. These peaks can be assigned to the (1 1 0), (1 1 1), (2 0 2), (1 1 3), and (1 1 3) planes of the monoclinic structure of CuO nanoparticles according to the Joint Committee on Powder Diffraction Standards (JCPDS) international diffraction database [28].

The recorded peak intensities for intrinsic and artificial sweat doped CuO films are summarized in Table 1. It can be deduced from Table 1 that the peak intensity of CuO films generally increases with the level of doping. This result indicates that artificial sweat doping contributes to the crystallinity of CuO films.

The average crystallite size value (D) can be calculated from the full width at the half maximum (FWHM) of the peak (β) by using Scherrer’s formula [25]:

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where λ is the wavelength of the X-ray radiation and θ is the Bragg’s angle of the peaks. The average crystallite size of the CuO films was calculated by taking into account all the peaks’ planes throughout the 2θ range. Intrinsic CuO film has the average (and the lowest among all the films) crystallite size of 26 nm. The calculated crystallite size values are listed in Table 1. As seen from the table, average crystallite size of CuO films mostly increase with the level of doping.
The diffraction peak of 2θ in the (1 1 1) plane shifted towards a higher Bragg angle from 35.47° (for intrinsic CuO) to 35.53° (for artificial sweat doped CuO films). This slight shift is due to the composed structural strain [29]. This effect is caused by doping the CuO film with artificial sweat that includes several ions (Na⁺, K⁺, lactate⁻ and urea⁺) that have different radii than that of the Cu²⁺ ion.

Fig. 3 shows the XRD patterns of the intrinsic and partially doped CuO films for different artificial sweat concentrations. Similar to Fig. 2, XRD results of CuO films did not show any other impurity phases. Because partial doping was accomplished by adding the dopant after the film growing process, the peak position did not change as much as it did in doped films. However, the recorded peak intensities and the average crystallite sizes did indeed change with partial doping as shown in Table 2.

3.3. Electrical measurements

Resistivity measurements can provide significant information about the correlation of resistivity to the concentration of certain biological materials. In order to assess the feasibility of CuO films as a sweat sensing material, partially doped films were further investigated for their electrical characteristics. Although doping of CuO films gives more significant changes in the peak shift and intensity, sweat sensing can be carried out only by dropping the sweat solution on a film. The IV measurements were performed on partially doped films where the measurements were taken as soon as the artificial sweat was dropped and while the device was still wet. For comparison, the same devices were also measured after complete drying over the course of 1 day. Room temperature resistivity values of CuO films were obtained considering the Ohmic region of the measurement.

Fig. 4 shows resulting resistivity measurements of the CuO films. The horizontal dashed line represents the resistivity value of the intrinsic CuO film which was calculated to be 315 MΩ/cm. As the concentration of the artificial sweat increases, the resistivity values decrease from 315 to 102 MΩ/cm while the samples were still wet. The specific values of the calculated resistivity are listed in Table 3. This result is apparent since higher concentrations of artificial sweat consists of more ions that contribute to the conductivity. Once the films were dried, the resistivity values increased significantly due to evaporation of water. Since the surface morphology of partially doped films is not as uniform as that of intrinsic or doped CuO films, the resistivity values of dried samples are much bigger. Furthermore, precipitation of ions on the surface after drying affected the surface quality, degrading the conductivity.

Additionally, Fig. 4 shows the resistivity of doped CuO films for different artificial sweat concentrations. These values are also given in Table 4. Contrary to the case of partially doped CuO films, the resistivity increases with concentration. This is perhaps due to the deformation of the electron structure of the film during doping, causing a decrease in free electron density [30,31].

4. Conclusions

For decades, researchers have been investigating new technologies for detecting physiological conditions of humans via sweat analysis. In this work, we have successfully employed...
nanostructured CuO films as potential sweat sensing materials. Analysis of the results led to the following conclusions:

(a) SEM: The morphology of CuO films was investigated and we found that direct doping of the film causes the nano-plates to become thinner. This method also introduces additional voids. On the other hand, the size of the nano-plates of partially doped films remained the same as that of the intrinsic films. However, partial doping resulted in less homogenous surface structure.

(b) XRD: The size of the crystallinity and the recorded peak intensity increased with both doped and partially doped CuO films as the artificial sweat concentration increased. The average crystallite size of the intrinsic CuO film was measured around 26 nm.

(c) I–V: Resistivity measurements clearly showed that there is a strong correlation between resistivity and the concentration of the artificial sweat. This result is apparent particularly for the partially doped films. Since instantaneous sweat sensing can be performed only by adding the newly collected sweat on a sensor, our “partial” doping is a viable and feasible method.

We strongly believe that the novel method of partial doping can be a new way of exploring sensing techniques particularly for biological monitoring systems.

Acknowledgments

Partial funding was provided by the National Science Foundation (EEC-1201095) and the Scientific and Technological Research Council of Turkey (TUBITAK Grant 2219). Dr. Axel Mellinger provided experimental guidance on IV measurements. Tommaso Costanzo helped with XRD measurements. Dr. Janis Voegle proofread the manuscript and provided significant insights.

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