Highly improved hydration level sensing properties of Copper Oxide films with Sodium and Potassium doping

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Abstract

In this study, un-doped, Na-doped, and K-doped nanostructured CuO films were successfully synthesized by the successive ionic layer adsorption and reaction (SILAR) technique and then characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Current-voltage (I-V) measurements. Structural properties of the CuO films were affected from doping. The XRD pattern indicates the formation of polycrystalline CuO films with no secondary phases. Furthermore, doping affected the crystal structure of the samples. The optimum conductivity values for both Na and K were obtained at 4M % doping concentrations. The comparative hydration level sensing properties of the un-doped, Na-doped, and K-doped CuO nanoparticles were also investigated. A significant enhancement in hydration level sensing properties was observed for both 4M % Na and K-doped CuO films for all concentration levels. Detailed discussions were reported in the study regarding atomic radii, crystalline structure, and conductivity.

Keywords: Artificial Sweat, Biosensor, Hydration, CuO

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I. Introduction

In recent years, nanoscaled metal oxide thin films have attracted researcher's interest extensively in various fields including but not limited to electronics, optoelectronics, and sensors [1, 2]. Nanostructured copper oxide (CuO), in particular, has been one of the most explored metal oxides thanks to their non-toxicity and excellent chemical stability. CuO is a p-type semiconductor with a narrow band gap of 1.3 eV [3].

Physical properties of CuO films rely on their morphology, crystallite size, and distribution which are strongly dependent on the preparation method. A broad variety of techniques have been utilized for the deposition of nanostructured CuO films such as molecular beam epitaxy [4], chemical vapor deposition [5], pulsed laser deposition [6], sol-gel [7], ultrasonic spray pyrolysis [8], and SILAR (Successive Ionic Layer Adsorption and Reaction) [3]. SILAR is cheaper and easier and done at low-temperature comparing to traditional approaches that require advanced processing. Furthermore, SILAR method offers simplicity, reproducibility, environment friendly and safe manufacturability, and large area deposition suitability [3, 9].

Besides preparation methods, physical properties of CuO films can also be altered by addition of dopants. Doping, in general, is a powerful technique for optimizing the sensing properties of metal oxide semiconductors. Indeed, researchers have recently focused on the investigations of un-doped and doped nanostructured metal oxide films. For example, doping with alkali metals such as Sodium and Potassium enhances the conductivity, sensitivity and selectivity of humidity sensors [10-12]. It was reported that doping thin films with alkali metals affects luminescence and electrical properties of films [13, 14]. Also, alkali metals are highly reactive hence can easily be oxidized which makes them even more suitable dopant for metal oxide nanostructures

[15]. In the case of sweat sensing applications, Sodium and potassium can be considered as viable dopants as they are major components in human sweat [11, 16-20].

Excessive sweating is the major reason for dehydration during physical activities, especially in hot and humid conditions [17]. Sweating is a natural as well as an effective way of regulating the body temperature, but causes water and electrolytes (mainly Na^+ , Cl^- and K^+) loss from the body [18]. Dehydration and electrolyte imbalance have vital importance to particularly endurance athletes [19, 20]. Therefore, continuous and real-time analysis of sweat may be used to detect changes in sweat composition as a warning indicator [21].

Metal doped CuO thin films have yet to be investigated for their hydration level detection properties except some preliminary studies on partially artificial sweat doped films [16]. In this study we focused on incorporating sodium and potassium ions as dopants and investigated the effect on sweat sensing properties of CuO films. A detailed investigation has been carried out on the structural, morphological, electrical, and sensing properties of sodium and potassium doped CuO films prepared by SILAR technique.

2. Experimental details

2.1. Preparation of Artificial Sweat and Film deposition

It is known that sweat pH is regulated by the human body and ranges between 5 and 7. Consistent with the human physiology, the standard for the artificial sweat preparation (European standard EN1811: 2012 [22]) suggests to adjust the pH to 5.4. Therefore, the pH of the prepared artificial sweat solutions were adjusted accordingly with a maximum deviation of 0.3. Although sweat consists hundreds of components, as the standard depicted, only four ingredients were used which are 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). These solutions were prepared in deionized water in weight/volume ratios. pH value was adjusted to 5.4 ± 0.3 by adding 0.001M ammonium hydroxide (Fisher Scientific). EcoTestr PH2 pH meter was used for pH measurements.

Un-doped and doped nanostructured CuO films were grown on glass slides by using SILAR method. The glass substrates were cleaned using dilute sulfuric acid solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}$, 1:5 by volume) followed by acetone and double distilled water rinse [2,15]. Deionized (DI) water was used in all solution preparations. A DI water with a double distillation filtration system was used where the resistivity is set at 18.2 MOhm cm. Using DI water ensures that the prepared solutions only contain the compounds that are added such as ions. Un-doped CuO films were prepared as the following: In order to obtain 0.1M Copper Chloride solution, 1.7 g of copper (II) chloride dihydrate (chemical symbol given as $\text{CuCl}_2 \cdot \text{H}_2\text{O}$) were weighed and mixed with 100 mL of DI. ~~0.1 M Copper Chloride solution was prepared by using a magnetic stirring hot plate at room temperature with copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and 100 ml double distilled water (18.2 MOhm).~~ pH value of the solution was then adjusted to around 10.0 by adding aqueous ammonia and the solution was heated up to 90 °C. Temperature was kept constant during the film growth process. The cleaned glass substrates were immersed into the solution containing Cu^{+2} and kept there for 20 s. They were then taken out from the bath and immediately dipped into hot water (90 °C) for another 20 s. This cycle was repeated 12 times. Same procedure was followed for the doped CuO films with the exception of addition of Na^+ and K^+ into copper chloride solutions. Various ion dopant concentrations were prepared in molar percentages of 2, 4, 6 and 8 M%.

2.2. Characterization of the films

A Hitachi 3400 N-II scanning electron microscope (SEM) was used for morphological imaging of un-doped and doped CuO films. Crystal structures of the samples were examined by X-ray diffractometer (XRD) (Rigaku Miniflex II). Resistivity values of the CuO films were determined by using room temperature I-V measurements with Keithley 617 electrometer. Sweat sensing properties of un-doped and doped CuO films were investigated by dropping 15 μ l of artificial sweat solution with different concentrations on the surface. Resistivity measurements were used to determine the performance of the sensors. Concentrations of artificial sweat were selected to be 13.10, 20.96, 26.20, 52.40 and 104.8 mM.

3. Results and discussion

3.1. Morphological and microstructural analyses

The surface topographies of un-doped and doped CuO films were investigated by examining the SEM results (Figs. 1 and 2). Fig. 1 shows SEM images of the un-doped CuO film for two different magnifications. It is clear from Fig. 1 that the film is highly dense with uniform surface and the nano-sized structure are well dispersed on the substrate without any cracks. There are plate-like CuO nanostructures which cover the substrate homogenously.

The SEM micrographs of doped films in Fig. 2 show that the surfaces are homogenous and densely packed similar to Fig. 1. We observed from Fig. 2 that surface properties of the CuO films with different doping levels of Sodium and Potassium were slightly modified comparing to the un-doped film. The changes in morphologies can be attributed to the difference in ionic radius of dopant elements (Na: 116 pm and K: 152 pm) and copper (Cu: 97 pm), which affect the

growth process of crystal structure. The larger ionic radius of K as compared to ionic radius of Cu, would induce an expansion in lattice parameters of doped CuO. Thus, the presence of K and Na accelerates the phase of CuO peak [23]. As seen in our results, incorporation of Na and K in CuO films had a clear effect on surface morphology. The change in particle size can be attributed to the significant increase in ionic radius (from 97 pm to 152 pm) between Cu and K. These results are also supported with XRD observations below. The density as well as the length of the nano-plates were observed to be increasing with doping. Length change, in particular, is more apparent for potassium doping. These changes combined affected the crystalline structure and electrical properties of the CuO films.

Structural properties of CuO films such as structural identity and crystallinity quality were investigated by XRD and given in Fig. 3 and Fig. 4. All the diffraction peaks can be indexed to the monoclinic phase of CuO crystals [JCPDS 01-080-0076]. Fig. 3 shows the XRD pattern of Na-doped CuO films with different concentrations of sodium. The XRD pattern of un-doped CuO film was also included in Fig. 3 for comparison. Un-doped CuO samples indicate the diffraction angles at 2θ value of 32.4° , 35.4° , 38.5° , 48.8° , 53.4° , 66.4° , and 68.0° corresponding to (110), ($\bar{1}11$), (111), ($\bar{2}02$), (020), (113), and (022) CuO crystal planes, respectively. There are no secondary phases observed. The peak intensities of CuO films slightly increased with Na doping that could perhaps be due to the occupation of oxygen vacancies by Sodium anions [24]. XRD results in Fig. 3 showed strong preferential orientation in (111) and ($\bar{1}11$) directions. XRD peaks narrow down with Sodium doping which indicates higher crystallinity quality compared with the un-doped CuO film.

Fig. 4 shows the XRD pattern of K-doped CuO films with un-doped CuO film as the baseline. Similar to Sodium doping, no extra peaks (i.e. phases) were detected with potassium doping. As doping concentration increases, the peak intensities become more intense and sharper indicating a good crystallinity quality. Figs. 3 and 4 prove that Na and K atoms scatter homogenously in the CuO lattice because no peaks belonging to other oxide forms of Cu, Na and K are observed. Although there is not a clear shift of 2θ in $(\bar{1}11)$ diffraction was observed from Figs. 3 and 4, obtained diffraction data showed a slight shift towards higher Bragg angle from 35.495 (for un-doped CuO) to 35.554 (for Na-doped) and 35.754 (for K-doped). These peak shifts towards the higher angle appears due to the created structural strain from doping [25]. Doping causes a shift in the peak due to the decrease in crystal lattice constant. This change is perhaps due to the occupation of Na and K atoms on the CuO site [26].

3.2. Electrical Characterization

It is known that doping levels significantly affect the electrical properties of metal oxide films [27-29]. Therefore, we studied different doping levels (from 2M% to 8M%) in order to determine the optimum doping concentration to obtain better sensitivity of CuO films to artificial sweat. Fig. 5 shows the sheet resistance values of the un-doped and doped CuO films as a function of Na and K molar ratios of 2, 4, 6 and 8M%. Here, the concentration values are calculated as a function of the molarity of the dopant. It is clear from Fig. 5 that the resistivity values of the films strongly depend on the doping levels. For both Na and K doping, resistivity values seem to be reaching a local minimum at 4M %. Besides this concentration, there is an increasing trend in resistivity with higher dopant levels. It must be noted here that this observation is done with 4 data points, hence the trends might be slightly different with a full

spectrum of dopant analysis, which is outside the scope of this paper. Regardless, ~~It must also be noted that~~ the resistivity values for all the doped films are much lower than the un-doped CuO film, which is expected.

It is expected that the resistivity values decrease with higher doping concentrations as a result of increased density of free electrons coming from the dopant. However, Fig. 5 shows that this expectation has not been satisfied after 4M % for CuO films. This is mainly due to the creation of carrier traps in the lattice that reduced the mobility [30-32]. For low concentrations, these traps do not exist because dopant ions are effectively replaced with Cu ions in the films which can enhance the carrier concentration. Moreover, higher concentration of doping levels cause ionized impurity scattering centers in CuO films which is another reason in resistivity increase after 4M % of doping [33, 34].

Another important observation from Fig. 5 is that K-doped CuO films have consistently higher conductivity than Na-doped CuO films for the same doping concentration. It is known that the lattice parameter is dependent on the atomic radii of the dopant and the doped material [35]. In our case, atomic radius difference between K and Cu ($243 - 157 \text{ pm} = 86$) is bigger than Na and Cu ($190 - 157 = 33$). Previous research showed that the electron conductivity enhances as the lattice parameter expands [36-38].

In order to evaluate the sensing performance of doped and un-doped CuO films, the sensing response, S , to different artificial sweat concentrations is defined using the equation below [39]:

$$S = \frac{R_{nom} - R_i}{R_{nom}} \times 100 \quad (1)$$

where S is the percentage change in resistivity of CuO films after the artificial sweat is dropped, (labeled as R_i) with respect to the nominal resistivity (R_{nom} , no solution application). Fig. 6 shows the sensing response for 2M% and 4M% Na- and K-doped CuO films for artificial sweat concentrations from 13 mM to 105 mM. This range was chosen to cover low and high concentration values of artificial sweat with respect to an average concentration which is around 60 mM. 2M% Na-doped CuO film does not improve the sensing response significantly. Although 2M% K-doped CuO film shows an improvement in sensing response in higher artificial sweat concentrations, lower concentrations of artificial sweat does not result in a consistent improvement in sensing response. Both 4M% Na- and K-doped CuO films showed significant enhancement in sensing response. This enhancement is more apparent for K-doped films. Sensing response increases 1.7 ± 0.4 times on average and 2.4 ± 0.4 times on average for 4M% Na- and K-doped CuO films, respectively, over a range of artificial sweat applications. Another important observation from Fig. 6 is that all CuO films respond the most at mid-range artificial sweat concentration, i.e. around 50 mM. As the added artificial sweat concentration increases, the CuO films reach a saturation due to the limited active sensing area thus decreasing the sensing response [39]. Overall, doping CuO films with Na and K ions increased the sensing response, which is consistent with previous studies [24, 40].

4. Conclusions

In this study, we have investigated the hydration level sensing characteristics of un-doped and Na- and K-doped CuO films at room temperature. Un-doped and Na- and K-doped nanostructured CuO thin films were deposited on glass substrates by using SILAR technique. Various doping concentrations were experimented in order to optimize the sensing properties of doped CuO films. The SEM images revealed that the length and density of nano-plates were affected by doping. The XRD results confirmed that all the films show CuO crystalline structure and the influence of Na and K-doping on the peak intensity and peak position. The electrical conductivity was found to be increased with Na and K doping with reaching a maximum at 4M %. The sensing response of the films were investigated by drop casting artificial sweat solutions on the CuO films. The sensing response of doped films showed a significant improvement with respect to the un-doped CuO film, particularly for high artificial sweat concentrations. It is concluded that Na- and K-doped CuO films show a great promise to be used for sweat sensing applications.

Acknowledgements

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 and Dr. Gabriel Caruntu helped with XRD measurements.

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SEM images of un-doped CuO films

Resistivity

Sensing Response

Figure 1: SEM photos of un-doped CuO films for two magnifications. Films are uniformly dispersed and nanostructured plate-like CuO morphology is observed.

Figure 2: SEM photos of various doping concentrations for Na and K. The scale bars are 2 μm in length. For both metal doped films, increasing doping caused denser films. Also, length of the nanoplates increased particularly for K.

Figure 3: XRD patterns for Na-doped CuO films. The peak intensity increases with doping suggesting better crystallinity. The XRD pattern of the un-doped CuO film is also included for comparison.

Figure 4: XRD patterns for un-doped and K-doped CuO films. The peak intensity slightly increases with doping suggesting better crystallinity.

Figure 5: Resistivity values of CuO films for un-doped and Na- and K doping. The decrease in resistivity from 2M % to 4M% is due to the additional dopants in the films. The increase after 4M % for resistivity is potentially due to the carrier traps that are introduced due to high level of doping.

Figure 6: The sensing response of undoped and Na- and K-doped CuO films were investigated for various artificial sweat concentrations. The sensing response significantly improves with 4M% Na or K doping. There is a consistent improvement with all doped CuO films with respect to the un-doped CuO film.