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Characterization of ZnO, Cu and Mo Composite Thin Films in Different Annealing Temperatures

Rouhollah Haji Abdolvahab*, Mohammad Reza Zamani Meymian, Noura Soudmand

Physics Department, Iran University of Science and Technology (IUST), 16846-13114, Tehran, Iran

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ABSTRACT

In this research study, we prepared different thin films of ZnO:Cu, ZnO:Mo, and Zno:Mo:Cu using a magnetron co-sputtering method. At the best of our knowledge, it is the first time that one prepared co-sputtered Zno:Mo:Cu thin films. We also annealed the samples at 100, 200, 400, and 800 °C. The samples were both theoretically and experimentally. We investigate the AFM results of the samples in the above-mentioned temperatures and compare different parameters of saturation roughness, height density function, and permutation entropy.
The results demonstrated that the height density function became wider and the roughness decreased at higher temperatures. Moreover, the plot of permutation entropy versus roughness enabled us to distinguish between our samples.

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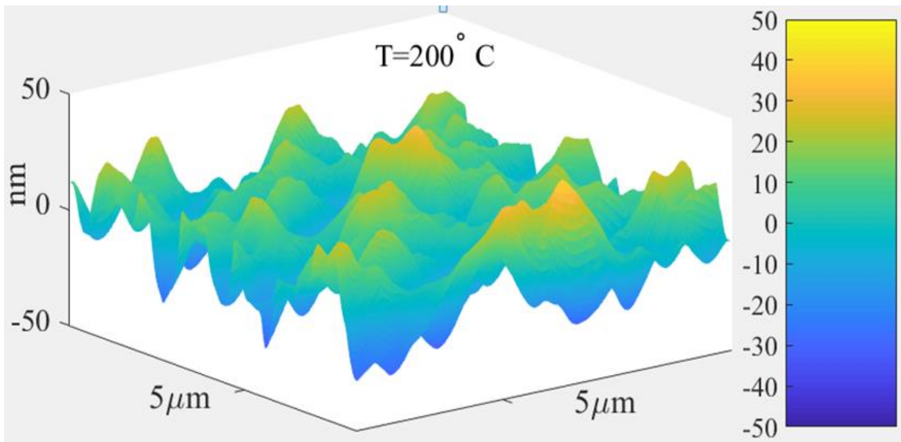
*Corresponding author: E-mail: rabdolvahab@gmail.com, Physics Department, Iran University of Science and Technology (IUST), 16846-13114, Tehran, Iran, Tel: +982173225887; Fax: +982173021661

Graphical Abstract



Introduction

ZnO thin films are sound recognized wide-gap semiconductors [1]. They have been used in transparent conductive contacts [2]. Furthermore, their characteristics presented them properly suitable for various applications in areas such as optoelectronics, piezoelectric, and surface acoustic wave devices [2-4]. Film crystalline structure is very important in determining the working parameters and decreasing the stability of them. The crystalline structure is determined by the deposition technique and preparing process [5]. Many experimental and theoretical investigations have been conducted on the diverse aspects of this semiconductor at the presence of other contaminations. This supports us to have a deeper understanding of both microscopic and macroscopic properties of these thin films [6-10].

After introducing the theoretical model and empirical process in the theoretical model, we will go directly to our results. The probability density function of the height, roughness, and permutation entropy of the ZnO:Cu, ZnO:Mo, and Zno:Mo:Cu thin films in various annealing temperatures were compared, as well. We also analyzed our theoretical results based on AFM images.

Experimental

Theoretical model

Height probability density function

The probability density function (PDF) of the heights is an overall parameter, demonstrating how the height sizes are distributed through the whole box. It does not provide any information about the places of the heights. To obtain a better PDF, we changed the origin of the heights to their means. Thus, the mean of the heights now was zero and the heights were both positive and negative.

Thin film roughness

The roughness, W, is defined as the square root of the mean square of deviation from the mean.

$$W(l,t)= <h^2(t)-<h(t)>^2 > \qquad (1)$$

Where $<h(t)>$ is the mean of height, over boxes of size l×l [11]. It enhanced by increasing the box size, l. This behaviour continued until a saturation amount, Ws, was observed. The roughness reached to this saturation amount at the box size of ls, which is known as saturation size.

Permutation entropy

Permutation entropy (PE) can evaluate the complexity of data [12, 13]. It counts the subsets of different patterns π and measures its Shannon information entropy:

$$PEn(x)=-\Sigma\pi P(\pi)\ln(P(\pi)) \qquad (2)$$

Experimental methods

DST3-A magnetron sputtering system (nano-structured coatings Co) was employed to create composite thin films of ZnO:Cu, ZnO:Mo and ZnO:Cu:Mo on the quartz and silicon substrates. The substrates were placed on a rotating holder. At first run, we mounted the ZnO and the Cu targets at RF and DC sputtering guns, respectively. In the second run, the ZnO and the Mo have been mounted in the same way. In the final run, we mounted the ZnO target at RF and both Cu and Mo targets at DC. The detail of the sputtering is summarized in Table 1.

Table 1. The deposition conditions (sputtering time for each sample was 90 minutes, their DC current was 10 mA and the RF power for all the sample was 300 W)

Sample	Base pressure	Deposition pressure	DC voltage	Argon flow current
ZnO:Cu	7.80×10^{-5} Torr	2.60×10^{-2} Torr	279 V	27sccm
ZnO:Mo	5.50×10^{-5} Torr	2.46×10^{-2} Torr	284 V	27sccm
ZnO:Cu:Mo	8.00×10^{-5} Torr	2.40×10^{-2} Torr	288 V	29sccm

We cleaned both the silicon and quartz substrates in cleanser-distilled water solution. Afterward, the same procedure was conducted in ethanol and acetone. Finally, all the samples were dried at the presence of nitrogen flow [14]. All the sputterings were done at room temperature.

To examine the annealing effect on thin films, different temperatures of 100, 200, 400, and 800 °C were selected. Then we annealed each sample for 90 min. The exiton oven of model dicon 500 with the ability to program the temperature gradient was used in this experiment. We increased the temperature steadily and uniformly. At the end of the experiments, the temperature decreased to room temperature.

Atomic force microscopy

The topology of the co-sputtered ZnO and Cu and Mo thin films were gathered using atomic force microscopy (AFM). The AFM images were taken in its contact mode and boxes of sizes 0.5, 1, 2 and 5 μm, each with 512×512 pixels resolution. We also changed the temperature from 23 °C to 100, 200 and 800 °C. The AFM device model was a full plus from Ara nanoscope, Co. Figure 1. demonstrates an example of the sample ZnO:Mo.

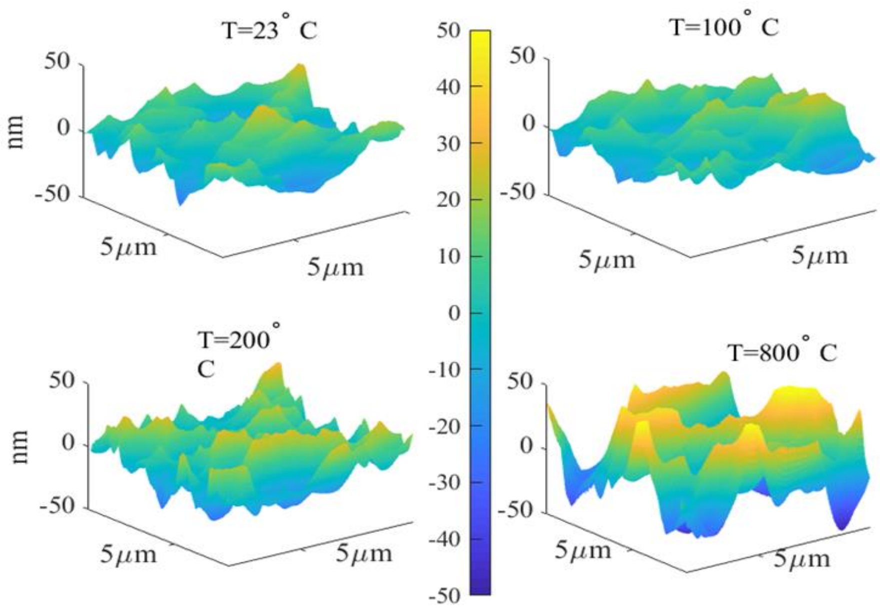


Figure 1. Comparison between ZnO:Mo composite thin films in room temperature and annealed temperatures of 100, 200 and 800 °C. The scale of the color bar which is demonstrated in the middle of the figure is in nm. The size of the AFM boxes is $ 500 nm×500 nm with the resolution of 512×512 pixels

Energy-dispersive X-ray spectroscopy (EDS)

Before annealing, an EDS analysis was used to ensure that the sputtering process was performed well. Moreover, the atomic percentage was determined using EDS (see Table 2).

Table 2a. EDS results; ZnO:Cu

ZnO:Cu	W%	A%
Zn	91.43	91.21
Cu	8.57	8.79

Table 2b. EDS results; ZnO:Mo

ZnO:Mo	W%	A%
Zn	97.38	98.20
Cu	2.62	1.80

Table 2c. EDS results; ZnO:Cu:Mo

ZnO:Cu:Mo	W%	A%
Zn	88.83	89.26
Cu	8.94	9.21
Mo	2.23	1.53

Results and discussion

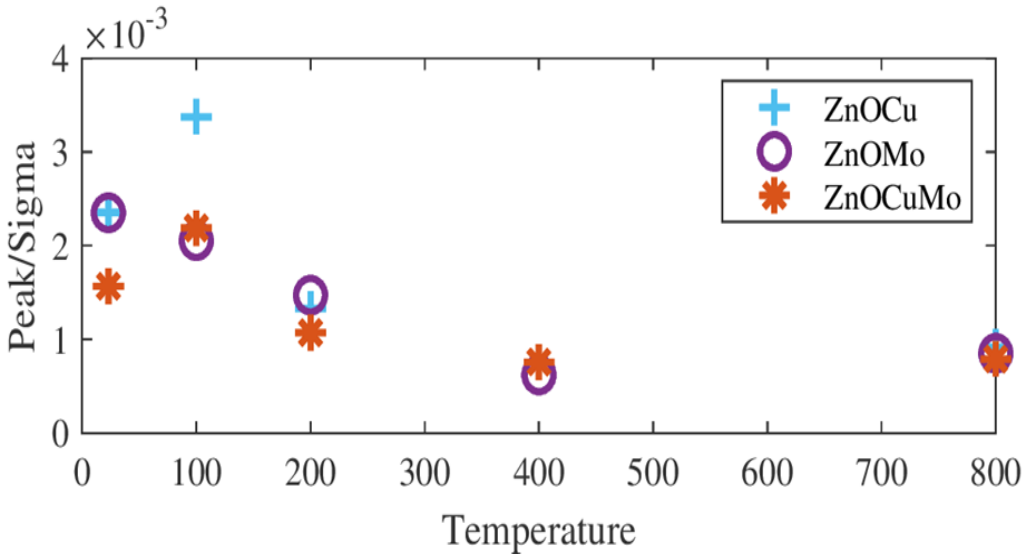


Figure 2. Peak per width of the probability density function of the heights of ZnO:Cu, ZnO:Mo and ZnO:Mo:Cu thin films versus temperature for different temperatures of 23, 100, 200 and 800 degrees of centigrade. The heights are in nm

Height distribution function

We derive the height distribution of the samples of our prepared composite thin films taken from AFM data. The results of the peak per variance of the distributions for different thin films were plotted versus temperature (Figure 2). Generally, increasing the temperature improved the distributions.

Surface roughness

We used the AFM images of ZnO:Cu, ZnO:Mo, and ZnO:Mo:Cu thin films at different annealing temperatures. The resolution was 512×512 pixels and their box sizes were 5 µm×5 µm. The saturation roughness, Ws, versus annealing temperature is shown in Figure 3. As can be seen in Figure 3, the Ws was increased by enhancing the annealing temperature. Moreover, it was reached a plateau in higher temperatures.

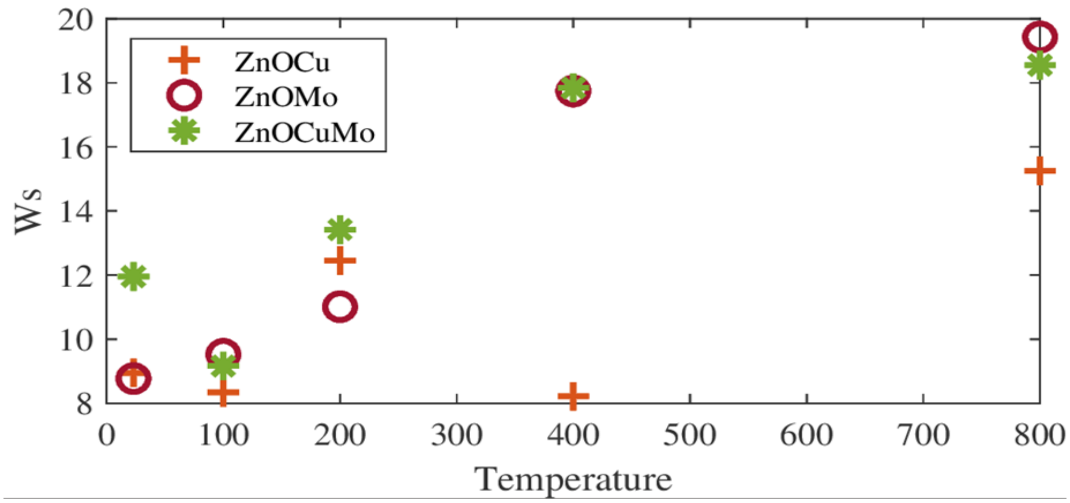


Figure 3. The roughness of the AFM data, W, according to equation 1, is plotted against box sizes l for different samples, S1 to S6

As Figure 4. demonstrates, the PE versus Ws figure is a rather good plot for distinguishing between our samples.

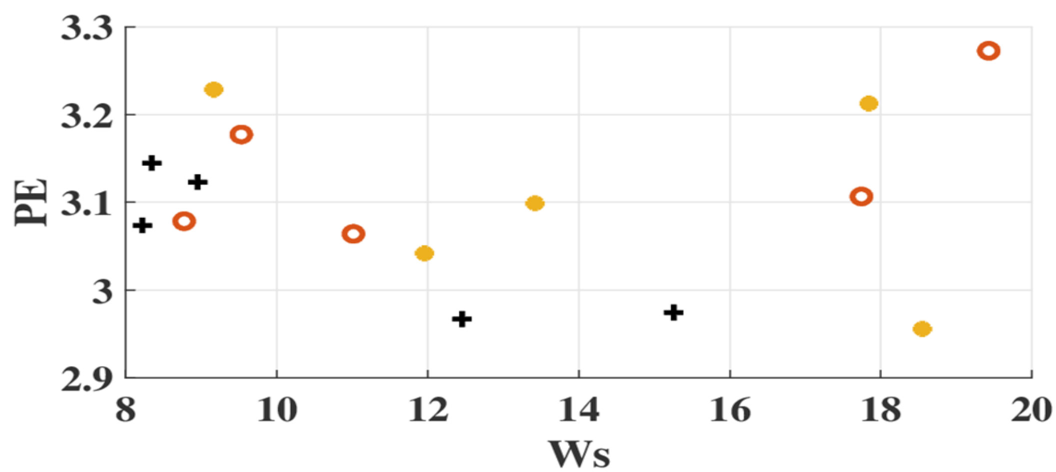


Figure 4. Permutation entropy is plotted against box sizes in nm. Different plots are for prepared thin film samples of ZnO:Cu in different temperatures of 23, 100, 200 and 800 °C

Topology of co-sputtered thin films

We prepared three different composite samples of the co-sputtered thin films of zinc oxide and copper and molybdenum (ZnO:Cu, ZnO:Mo, and ZnO:Cu:Mo) by magnetron sputtering. Figures 5 and 6 present the height of the composite thin films ZnO:Cu and ZnO:Cu:Mo respectively, obtained from AFM images of boxes of size 5 μm×5 μm with the resolution of 512×512 pixels. As demonstrated in Figure 5, increasing the temperature enhanced the roughness of the composite sample.

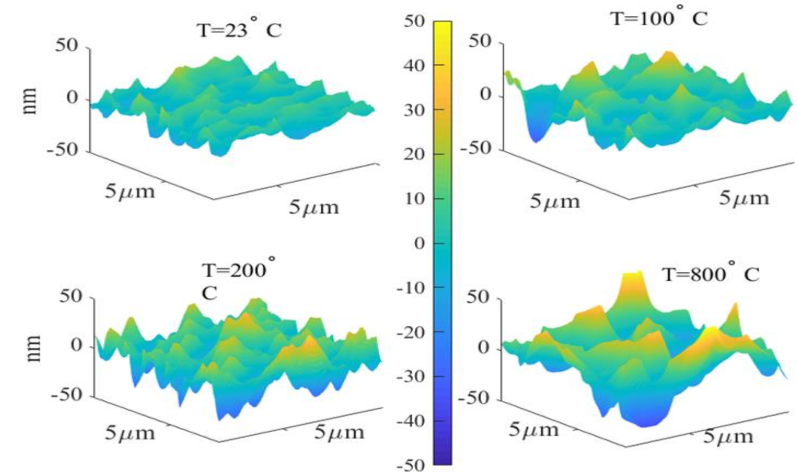


Figure 5. Comparison between ZnO:Cu composite thin films in room temperature and annealed temperatures of 100, 200 and 800 °C. The scale of the color bar which is demonstrated in the middle of the figure is in nm. The size of the AFM boxes is 500 nm×500 nm with the resolution of 512×512 pixels

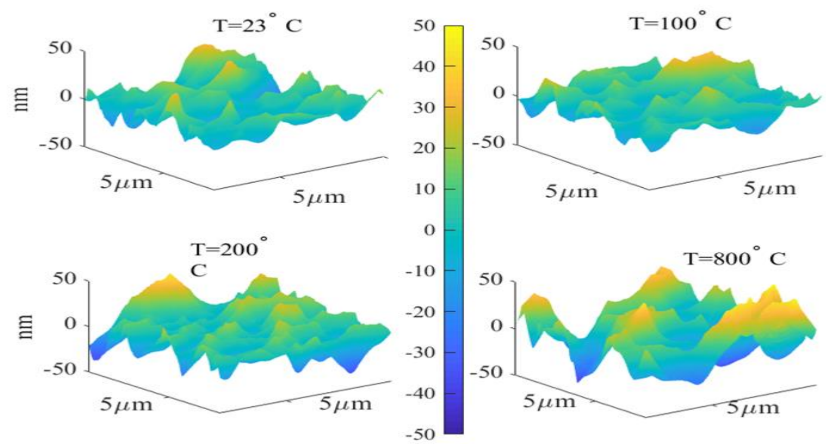


Figure 6. Comparison between ZnO:Mo:Cu composite thin films in room temperature and annealed temperatures of 100, 200 and 800 °C. The scale of the color bar which is demonstrated in the middle of the figure is in nm. The size of the AFM boxes is 500 nm×500 nm with the resolution of 512×512 pixels

Conclusions

We developed three distinctive thin film samples of ZnO:Cu, ZnO:Mo, and Zno:Mo:Cu using a magnetron co-sputtering arrangement. It is noteworthy to mention that, at the best of our knowledge it is the first time the co-sputtering of three samples of Zno, Mo, and Cu is done simultaneously. Afterward, we annealed thin films at 100, 200, 400, and 800 °C. We assessed the AFM images of the samples and compared different parameters of the height probability density function, saturation roughness W_s, and permutation entropy.

The results revealed that the height's density function became broader by increasing the temperature. Saturation roughness although also decreased at higher temperatures. Besides, employing both permutation entropy and saturation roughness enables us to differentiate between our thin film samples.

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Conflict of Interest

We have no conflicts of interest to disclose.

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