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Original Research article

Permutation Entropy as a Parameter fo Characterizing the Surface of a Thin Film

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ABSTRACT

In this work, silver thin films were prepared using sputtering at different deposition times with the nanoscale thickness. To investigate their surface morphology, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were employed. The surface topography of the samples studied using the AFM. The results revealed that, the roughness of the thin films enhanced by increasing the sputtering time. The permutation entropy (PE) was introduced as an interesting parameter to characterize the surface morphology. At the best of our knowledge, it is the first time one uses the PE for characterizing the thin films. Although the roughness might always enhance by increasing the film thickness, it was not the case for PE. The PE was found to be an independent parameter for characterizing the surface of thin film.

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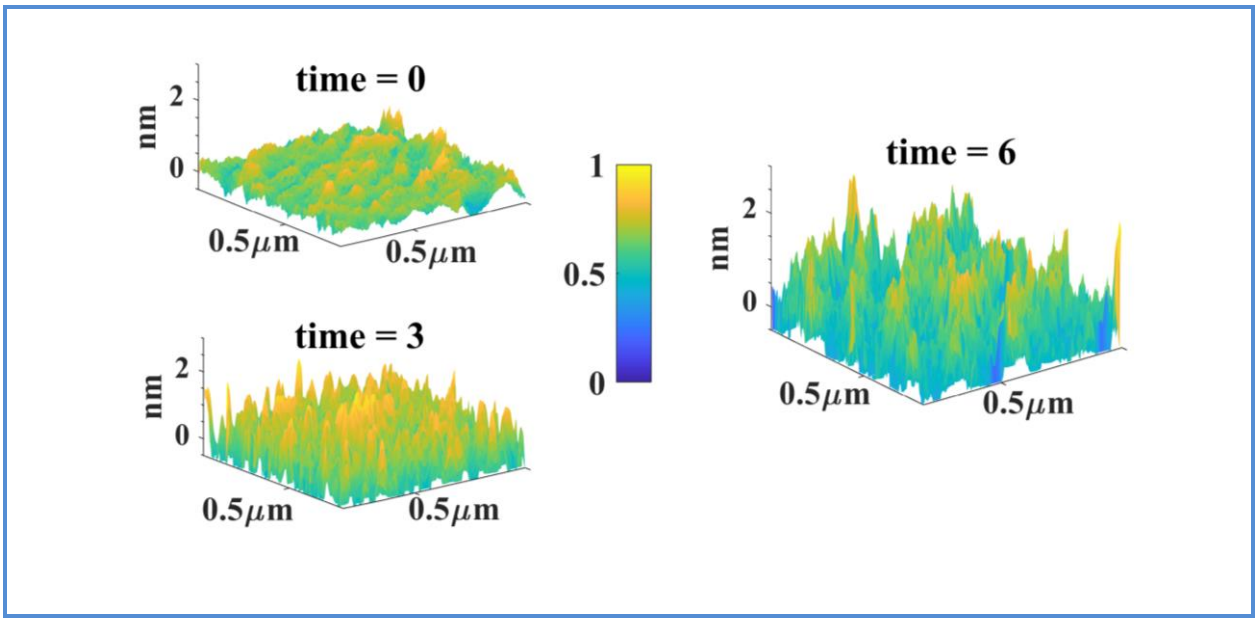
Graphical Abstract



Introduction

The height-height correlation function is a method used for characterizing a surface. One of the most important parameters within this function is the roughness of the surface [1, 2]. Although the roughness is an important property of the surface morphology, it does not measure the height fluctuation's complexity. There may be different materials with the same roughness but different properties. Permutation entropy (PE) is a parameter, characterizing the time series and distinguishes between random, chaotic and periodic time series and even its dynamic properties [3, 4]. It can also detect dynamical changes quantitatively [5]. In this research study, the PE was used to measure the complexity through the surface of the prepared thin films and characterize them.

Silver is a very important metal in science and technology. It also has the highest electrical and thermal conductivity and optical reflectivity of all metals [6]. Some of its applications include optics [7-9], nanophotonic [10], flexible transparent electrodes [11], antioxidant [12-14], solar cells [15] protein sensors [16], biosensors [17], and fluorescence imaging of single molecules [18]. There are distinct techniques explaining the surface growth of the silver thin films. They cover molecular-beam epitaxy (MBE) method, physical vapor deposition (PVD), electrophoretic deposition (EPD), and sputtering [1, 19-23].

In this study, we introduced a new parameter to characterize the silver thin film morphology as follows. After introducing the model and theory, we present the details of our experiments in

section 2. Then reports and analysis of our results are presented in section 3. Finally, the main conclusions of our study was recapped in conclusion.

Experimental

Roughness and scaling

One of the most important factors in characterizing surface morphology is its roughness. The roughness of the surface is defined as root mean square of the (RMS) or variance of the height over a box of size L:

$$W(L,t) = \langle h^2(t) - \langle h(t) \rangle_L^2 \rangle_L \quad \text{(Eq. 1)}$$

In which W (L, t) is roughness of the sample at time t and over boxes of size L. (χ) is the mean of the parameter x over boxes of size L [1].

Surface roughness, W, will increase by increasing the box size L until a saturation amount called W_s. This saturation takes place at a special size and time denoted by L_s and t_s respectively. According to normal Family-Vicsek scaling in small time scales (less than t_s), roughness scales with time as: $W \sim t^{\beta}$ [24]. The exponent β is called the growth exponent, which shows the growth regimes. Rough exponent α is defined as: $W_s \sim L_s^{\alpha}$. Moreover, there is another exponent z, which is defined by $t_s \sim L_s^z$ and named dynamic exponent. These exponents are related by scaling law: $z=\alpha/\beta$. These relations lead us to the following scaling equation:

$$W(L,t) \sim L^{\alpha} f(t/L^z) \quad \text{(Eq. 2)}$$

In which $f(x) \sim x^{\beta}$ for $x \ll 1$ and is a constant for $x \gg 1$.

Permutation entropy

Permutation entropy (PE) is a measure for arbitrary time series based on analysis of permutation patterns. It measures the complexity through a time series which enables us to distinguish between periodic, random and/or chaotic systems [3-5]. PE compares the successive numbers in a time series and measures their fluctuation as follows. To calculate the PE of a time series with n dimension, one must extract all *n*-component successive subsets and compare their number. Afterward, all the subsets with the same rise and fall pattern π will be counted note that there is n! pattern for *n*-component subsets. For example, in the 3-component case, there is 6 different pattern such as: $x_1<x_2<x_3$, $x_3<x_1<x_2$ and so on. Then one should calculate the entropy using the well-known Shannon entropy.

$$PE_3 = -\sum_{\pi} p(\pi)\log(p(\pi)) \quad \text{(Eq. 3)}$$

Where p (π) = n (π)/N_{tot} is probability of finding the pattern π. Here, the natural logarithm has been used in place of base 2 for simplicity. As a result the maximum entropy for 3-component subsets becomes $PE_{3,max} = 6\times1/6\times\log(6) \cong 1.79$

Here one-dimensional PE of time series has been generalized to the two-dimensional matrix. In order to calculate the PE, one should compare each data to its four nearest neighbors in its up, down, right and left. The maximum of the PE in this 5-component case becomes log (5!) ≅ 4.79. Measuring the PE, helps one to estimate the small size fluctuations in the sample surface.

Experiment

In this section, our experimental details including sputtering, XRD, AFM, and SEM images were presented.

Sputtering

A glass lam of size 15×25 mm^2 was used as the substrate. Then a DC magnetron device applied with discharge current of 110 mA (model DST3 from Nanostructured Coatings Co.) to construct Ag thin films. The chamber vacuum has a base pressure of 1.6×10^{-4} Torr and after inserting the argon the working pressure became 6×10^{-2} Torr. A silver target with a purity of 99.999% employed. The substrate is cleaned using cleanser-distilled water solution in an ultrasonic bath for 10 min. Ethanol and acetone used for better cleaning. Then all of the samples dried in nitrogen flow. Two Ag thin films were grown by the sputtering time of 3 and 6 min.

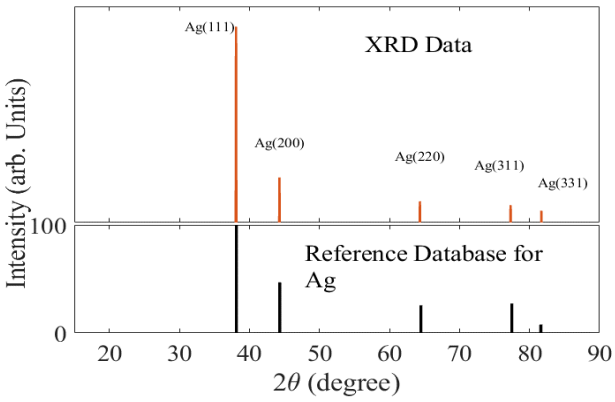


Figure 1. Intensity of the X-ray diffraction versus beam position in 2θ for the 6 minutes sample has been compared to the reference of JCPDS card number of 01-089-3722

Results and discussion

X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM) is used for analyzing the structure and morphology of the samples.

XRD

The XRD structure of the sample (taken from Philips model: PW1730) confirms that the sample layer must be silver and it has a crystal structure (Figure 1). As shown, the images were taken from angles between 2θ=14.7 and 2=89.95 with a resolution of 0.05 degrees in room temperature of 25 °C. The international centre for diffraction data (ICDD) card number of the XRD pattern was 01-089-3722. It can be seen that the ratio of peak intensity is slightly different from that shown in the reference graph. The lack of clarity is due to the small size of the thin film. In addition to *d*-spacing and atomic structure, the first at peak angle and the other in the peak intensity of X-ray images are effective, other important factors such as thin films thickness have an effect on the quality and success of X-ray measurements. If the thickness of the thin film is less than a micrometer, then much of the X-ray spectrum is inserted into the substrate and the resulting images give little information about the thin layer.

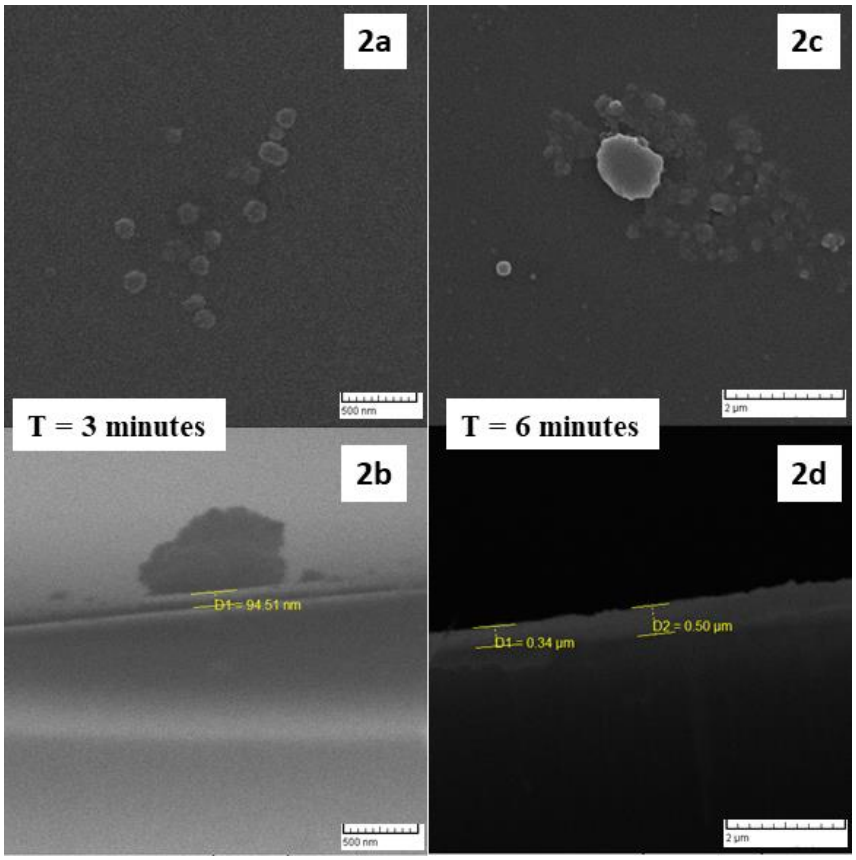


Figure 2. The image from the surface and cross SEM images of the prepared samples with deposition time of 3 and 6 min

SEM analysis

The SEM images were taken from Vega 2 model of Tescan Co. Surfaces and cross-section of the samples were evaluated by SEM. (Figures 2a and 2b) show the images from the surface and the cross SEM images of the prepared samples after 3 min of sputtering. Moreover, the image from the surface and the cross SEM images of the 6 min sample are indicated in (Figures 2c and 2d), respectively. The SEM measurements indicate that the average size of the particles in a 3-minute sample is from about nanometer to 150 nm, and for a 6-minute sample of a few nm to 400 nm. As (Figure 2) shows, by doubling the sputtering time from 3 to 6 min, the film thickness increased, approximately, up to about five times. It also causes the grains sizes on the surface to grow. It is seen that the thickness dependence with the duration of the sputtering in this device is not linear and can be due to the instability and uniformity of the plasma, fluctuating of current and voltage or flows of the input argon gas along with the sputtering.

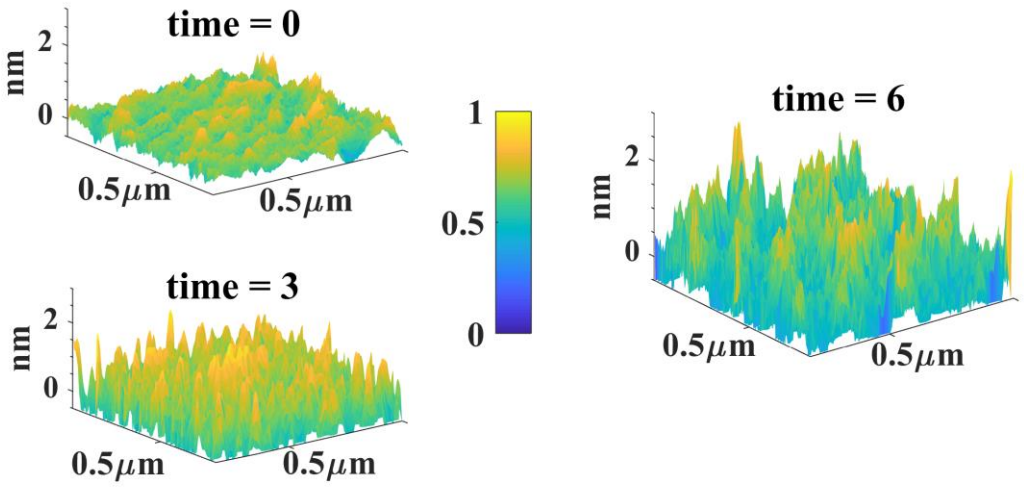


Figure 3. Surface height of the substrate and two samples with sputtering times of 3 and 6 minutes obtained from AFM images. Roughness increases by increasing the sputtering time as expected.

AFM analysis

To obtain the surface morphology of the data, an atomic force microscopy images in boxes of size 5 μm and with the resolution of 256×256 was used. The device model was full plus from Ara Nanoscope Iran Co. The image was also taken in contact mode.

Roughness

(Figure 3) compares the AFM images of the 3 and 6 min thin film samples by the glass substrate. The insets plotted the AFM images of boxes with sizes of 0.5 μm×0.5 μm which show the roughness in more details. As can be seen in Figure 3, the roughness of the thin films will increase by increasing the sputtering time. (Figure 4) illustrates that the roughness of the computational box will also increase by increasing the box sizes until its saturation amount. This saturation amount itself also increases by increasing the sputtering time from 3 min to 6 min. The sputtering times have been doubled and the roughness has been increased much more than just doubling. Moreover, it was found that the sputtered silver thin films are rougher compared with that of the glass substrate.

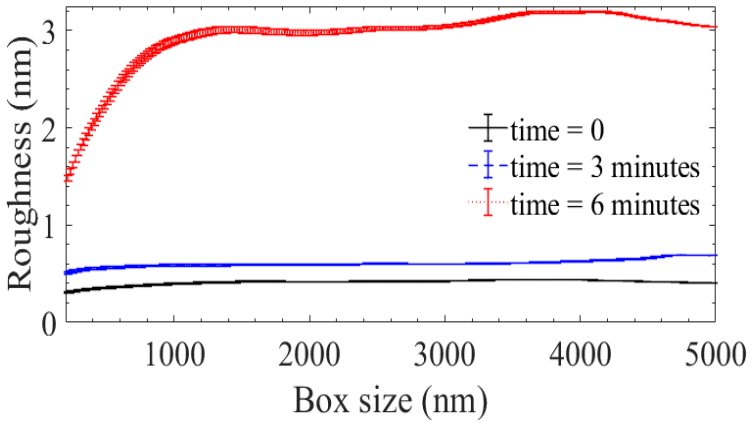


Figure 4. Roughness of the height data with respect to computational box sizes in nanometers. The roughness is calculated by equation 1

Permutation entropy (PE)

The PE was calculated using the Eq. 3. The results are demonstrated in Figure 5. It demonstrates the PE of the glass substrate and silver thin films constructed by different deposition times of 3 min and 6 min. (Figure 5) confirms our expectation that increasing the box size may enhance the PE. Comparing these results by the roughness shown in (Figure 3) is very promising. Although the roughness is increased by increasing the sputtering time, it is not the case for permutation entropy. In this case, the fluctuations measured by PE for the Ag thin film from the sputtering time of 6 min are well below the fluctuations of even the glass lam itself. These results show that the permutation entropy can be used for characterizing the thin film surfaces independent of the roughness and one could characterize in more detail and more accurately by reporting both the roughness and permutation entropy of a thin film sample.

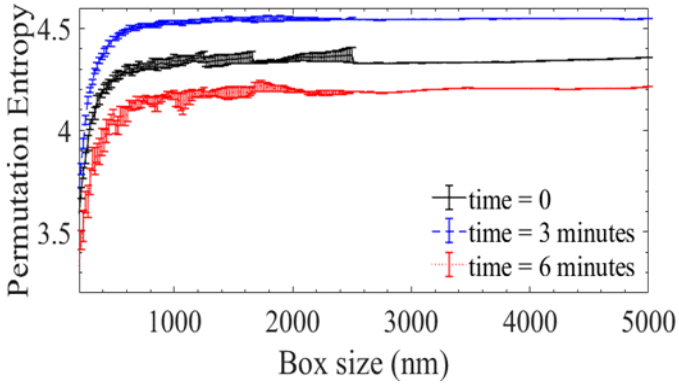


Figure 5. Permutation entropies of different surfaces of the substrate and thin films prepared by the sputtering time of 3 and 6 minutes are compared. The permutation entropies are calculated by Eq. 3 in distinct computational box sizes

Conclusion

Permutation entropy measures the fluctuations in a time series. It has been generalized to a 2-dimensional matrix. It was found that the permutation entropy for a thin film surface is independent of roughness in general and could be used as a separate parameter for characterizing the details of surface morphology of thin films. Our results pave the way for improving the understanding of the surface morphology. It also helps us to improve the surface characterization by introducing a new independent parameter to be measured. Furthermore, the SEM results showed that the film thickness is increasing much faster than the slope of one versus sputtering time.

Conflict of Interest

We have no conflicts of interest to disclose.

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