Optical analyses of annealed copper films by a method based on Bruggeman homogenization formalism: Influence of deposition angle and annealing temperature

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ARTICLE INFO

Keywords:
Oblique angle deposition
Bruggeman homogenization
Optical spectra
Cu thin films
Annealing process
Copper nitride

ABSTRACT

Normal and oblique angle depositions were used to produce copper thin films which were subsequently annealed with flow of nitrogen gas at different temperatures (100, 180 and 350 °C). Optical responses of these samples obtained at near normal incidence angle using both s- and p-polarized lights. Field emission scanning electron microscope (FESEM) analyses of the samples provided the physical structure and morphology of the samples. Bruggeman homogenization formalism calculations were used to propose a method for prediction of the reflection spectra which were compared and fitted to the experimental results. The most effective factors in this type of work were found to be the film thickness, the material inclusion (void fraction) and the thickness ratio of copper nitride layer formed on top of copper layer to the thickness of copper layer which was estimated from comparison of theoretical optical spectra with those of experimental results. Results showed that the latter ratio increases with annealing temperature and the highest temperature of 350 °C caused a drastic change in the optical spectra of the samples.

1. Introduction

Design and engineering of nano-structured thin films are performed using oblique angle deposition (OAD) or glancing angle deposition (GLAD). These thin films are of high interest to both scientists and industrialists due to their various physical properties and are called sculptured thin films [1–8]. These techniques provide facilities for fabrication of layers with different predesigned geometries. The optical properties of these sculptured thin films strongly depend on their deposited material and the structure and smallest change in their structure can cause a variation in their optical responses [9–16]. The response of different materials exposed to light is different and in summary with regards to metals (conductors) it can be said that a considerable part of the incident light is absorbed and reflected and a negligible part of it is transmitted from metallic samples. However, weak semi-conductors and insulators are transparent materials and transmit a considerable amount of the incident light while absorbance and reflectance by these materials are very small. In the previously reported works [13,10–16] the influence of different parameters such as type of material and the structure of thin film on the optical properties was investigated. In the present work our aim is to make changes in the nature of material (i.e., different states (metal and non-metal)) in presence of each other and investigate their properties. Hence, copper thin

https://doi.org/10.1016/j.ijleo.2019.02.021
Received 5 December 2018; Received in revised form 6 February 2019; Accepted 9 February 2019
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films were produced using two different deposition angles of 0° and 40° and post-annealed with flow of nitrogen at different annealing temperatures. Under these conditions it is expected that the fabricated thin films consist of a structure combined copper nitride (top layer of the thin film) and copper (conductor) (bottom layer of the thin film) as experimentally reported by Khojier and Savaloni [17].

Theoretical and experimental investigations of optical spectra of the produced samples showed that the optical properties of these layers are intermediate between conductors and semi-conductors (insulators). The influential factors on the optical properties of such thin films are the film thickness, ratio of the thickness of the nitride layer to the thickness of the copper layer and the material inclusion (void fraction) in the structure of the thin film. These parameters are estimated from comparison of the results obtained from Bruggeman homogenization simulation method [9–11] and the experimental results.

2. Fundamental concepts

Bruggeman homogenization method [9–11] is a powerful technique that is used for investigation of optical properties of thin films with voids in their structure. In our earlier works it was used for investigation of optical properties of zinc sulfide (semi-conductor) [15] and metals such as manganese [14,16] and silver [13]. The detailed theory is explained in [9–11]. Here, a brief version which includes those concepts that are used in this work are explained.

In Bruggeman formalism the well-known electromagnetic relation between electric field $E$ and the electric displacement vector $D$ appears in the form of the tensor equation:

$$D(r, \omega) = \varepsilon_0 \varepsilon_{TF}^* E(r, \omega),$$

where, $\varepsilon_{TF}^*$ is the tensor for the dielectric constant related to the inhomogeneous layer and $\varepsilon_0$ is the electrical permittivity constant in vacuum, $r$ is the position vector in space and $\omega$ is the angular velocity of electromagnetic wave propagation. The form of dielectric constant tensor depends on the localized orientations of the layer.

In Fig. 1 the deposition geometry of the thin film and the mechanism implemented in the Bruggeman homogenization method as well as the procedure used in the present work are illustrated.

In Fig. 1(a) the thin film deposition mechanism is briefly given. The thin film is formed from deposition of material’s vapor on the substrate. Hence, it may include both the material and voids between them. The fraction of material may be assigned as $f_s$ and the fraction of voids as $f_v$. Let the incident vapor make an angle $\alpha$ with the surface normal and the columnar structures growth at an angle $\beta$ then $\chi$ is the angle of columnar structure with the substrate surface. The relationship between these angles are given by two experimental rules, namely tangent rule ($\tan(\beta) = \frac{1}{2} \tan(\alpha)$) [18] and Tait rule ($\beta = \alpha - \sin^{-1}\left(\frac{1 - \cos(\alpha)}{2}\right)$) [19]. The former is valid up to 60° deposition angle while the latter applies on angles greater than 60°. In Fig. 1(a) each of the columnar structures and each of the void parts between them may be considered as an assembly of ellipsoids as shown in Fig. 1(b). These ellipsoids are initially considered as standard ellipsoids which are shown in Fig. 1(c) whose characteristic is the ratio of its principal axes, $1/\gamma_b$ are dimensionless half the length of the principal axes of the ellipsoid. The ellipsoids are initially oriented in the x-axis direction and with
a dielectric constant tensor:

\[
\varepsilon_{ref} = \begin{pmatrix}
\varepsilon_0 & 0 & 0 \\
0 & \varepsilon_r & 0 \\
0 & 0 & \varepsilon_e
\end{pmatrix}.
\]

(2)

In order to obtain the dielectric constants \(\varepsilon_{in}, \varepsilon_{b},\) and \(\varepsilon_c\) (Eq. (2)) called Bruggeman epsilons, the following three tensor equations should be solved in an iterative process.

\[
f_{\alpha}A_{\alpha} + (1 - f_{\alpha})A_{\alpha} = 0,
\]

(3)

\[
A_{\alpha,\gamma} = \varepsilon_0 (\varepsilon_{\alpha,\gamma}I - \varepsilon_{ref}), [I + i\omega\varepsilon_0 D_{\alpha,\gamma}, (\varepsilon_{\alpha,\gamma}I - \varepsilon_{ref})]^{-1},
\]

(4)

\[
D_{\alpha,\gamma} = \frac{2}{i\omega\varepsilon_0} \int_0^{2\pi} \int_0^\pi \sin \theta \times \left( (\sin \theta \cos \varphi)^2 u_{\alpha,\gamma} + \left(\frac{\cos \theta}{\gamma_{\alpha,\gamma}^2}\right)^2 u_{\alpha,\gamma} + \left(\frac{\sin \theta \sin \varphi}{\gamma_{\alpha,\gamma}^2}\right)^2 \varepsilon_c \right) \right) d\theta d\varphi.
\]

(5)

where \(A_{\alpha}(v)\) is the polarizability density tensor corresponding to material (void), \(D_{\alpha}(v)\) is the depolarization tensor of material (void), \(I\) is the identity tensor, \(\varepsilon_{\alpha}\) is the dielectric constant of material (void), \(\gamma^{(v)}\) is half the diameter of material (void) ellipsoids and \(\theta\) and \(\varphi\) are the polar and azimuthal angles of the spherical coordinate, respectively.

The final tensor of the dielectric constant of ellipsoids in form of Fig. 1(b) may be obtained as:

\[
\varepsilon^{TF}_c = S_{c}(\chi).\ v_{ref}, \ S_{c}^{T}(\chi).
\]

(6)

where, \(S_c(\chi)\) and \(S_c^T(\chi)\) are rotation matrix about y-axis and its transpose matrix, respectively [11].

At this stage the well-known Maxwell equations will be solved for the thin film and by introducing the boundary conditions a transfer matrix can be obtained which is the characteristic of the said thin film. This matrix is used to obtain the intensities of reflected and transmitted lights. If the thin film consists of a few layers (i.e., multilayer) then the transfer matrix can be obtained from consecutive multiplication of the transfer matrices of these layers.

The simulation procedure for the thin films produced in this work is shown in Fig. 1(d) where the film is considered as two materials (i.e., copper and copper nitride) and void (vacuum) fraction. The thickness of the thin film, \(L\), consists of a number of sub-layers and by increasing the thickness of the material inclusion in these sub-layers decreases. This is consistent with the structure of sculptured thin films where a dense bottom layer forms and then on top of this bottom layer the structure of sculptured thin film forms with increasing void fraction [20,21]. The thickness of film \(L\) in Fig. 1 is divided into two sections \(L1\) and \(L2\) where \(L1\) (top part of the film) consists of first material (copper nitride) and the void fraction and \(L2\) (bottom part of the film) is made of second material (copper) and the void fraction.

It is worthwhile to mention that when using Bruggeman homogenization method for metals one should be aware that the real part of the dielectric is negative (< 0). Hence, calculation of the total dielectric constant may result in unphysical values if the material (metal) inclusion in the wavelength region of interest is not chosen carefully.

3. Experimental details

Copper sculptured thin films were deposited on glass substrates (microscope slide) by electron beam evaporation. An Edwards (Edwards E19 A3) coating plant with a base pressure of \(2 \times 10^{-7}\) mbar was used. The deposition angle (vapor incident angle) \(\alpha\) was selected at 0° and 40°. A deposition rate of 0.2 Ås\(^{-1}\) was used for production of the thin films. The deposition rate was measured by a quartz crystal deposition rate controller (Sigma Instruments, SQM-160,USA) positioned close to the substrate and at almost the same azimuthal angle as that of the substrate. This was corrected by obtaining the film thickness using the field emission electron microscope. Prior to deposition, the substrates were ultrasonically cleaned in heated acetone, then ethanol. The distance between the evaporation source and the substrates was 30 cm.

Post-annealing of the Cu/glass thin films was performed in a horizontal tube furnace (Exciton, 1200-30/6, T.H, Iran equipped with a Shinko temperature programmable controller PCD 33 A) at three different temperatures of 100°C, 180 °C and 350 °C, with 250 sccm flow of nitrogen. The samples reached the selected annealing temperature with a thermal gradient of 7 °C/min \(^{-1}\) and were kept at the annealing temperature for 5 h, then gradually cooled down to room temperature in the annealing environment (i.e., flow of nitrogen).

The film thicknesses and column shapes and sizes were measured by a field emission scanning electron microscope (FESEM) (Hitachi S-4100 SEM, Japan). The FESEM samples were coated with a very thin layer of gold to prevent the charging effect. The reflectance and transmittance spectra of the samples were obtained using a single-beam spectrophotometer (Aquila nk-8000) in the spectral range of 400–1100 nm and both s- and p-polarizations in steps of 5 nm wavelength at different incident light angles.

4. Experimental results

Fig. 2 shows the FESEM images of the samples produced in this work at two different deposition angles of 0° and 40° after
annealing process. In Fig. 2 it can be seen that by increasing the annealing temperature the columnar structure is changed to nonsymmetrical (disordered) structure. This change is not an abnormal process in the structure of the film through annealing as it can be the result of diffusion process as well as impregnation of the grains with the annealing gas and change of crystallographic structure.

The optical responses of the produced samples were obtained at 10° incidence angle using both s- and p-polarizations. Considering that these spectra were taken at near normal incidence angle no considerable change was observed between s- and p-polarizations behavior [15]. Also the intensity of the transmitted spectra due to presence of copper metal in the structure of the films was negligible (about 0.1 percent). Hence, we only discuss the reflection spectra of p-polarized light which were normalized to unity.

Fig. 3 shows the reflection spectra for the samples deposited at 0° and 40°. A small decrease of reflection intensity can be distinguished between the spectrum of unannealed sample and those annealed at lower temperatures of 100 °C and 180 °C. However, further increase of annealing temperature to 350 °C caused a drastic change in the spectrum. This is true for both deposition angles (α = 0° and α = 40°). This observation shows that at higher temperatures the structure undergoes a large change which can be due to different processes involved during annealing of the sample, such as enhanced diffusion effect and embodiment of nitrogen molecules in the structure of the film as well as change of chemical structure of the film. These observations are also consistent with the results of FESEM shown in Fig. 2 and discussed in the preceding section.

5. Bruggeman homogenization results

In references [13,14] it is shown that the most effective factors on the intensity of reflection from a thin film is the void fraction
(material inclusion) in the structure of the film. The influence of the film thickness and material inclusion on the intensity of the transmitted light is also reported in [13,14]. Hence, in order to carry out the calculations the film thickness was chosen so that a negligible transmittance (0.1 percent) may result. This provides the condition that all other parameters can be obtained from the reflection spectra. Considering the experimental processes carried out on the samples and the results of annealing process reported in [17] in which the annealing gas penetrates into a limited thickness of the film, it was expected that the final samples consist of copper nitride film at the top of the sample and copper at the bottom of the sample. Hence, in order to analyze the experimental spectra of Fig. 3 the Bruggeman calculations were carried out for two materials (i.e., copper and copper nitride) each with presence of void (vacuum). Calculations were carried out for a fixed thickness and different void fractions. The required optical constants for copper and copper nitride were obtained from [22] and [23], respectively and are depicted in Fig. 4. In Fig. 4, n and k subscripts of the assignment of the symbols correspond to real and imaginary parts of the refractive index, respectively. Fig. 5 shows results of these calculations from which the following observations may be made:

i) Generally, the intensity of the reflection spectra of copper (Fig. 5(a)) increases with wavelength while it decreases with material inclusion. Their behavior within the wavelength region of 400–600 nm is relatively linear and by increasing the wavelength a sharp increase occurs in their spectra. The spectra become gradually oscillatory by decreasing the material inclusion.

ii) The intensity of the reflection spectra of copper nitride (Fig. 5(b)) on the whole decreases with increasing the wavelength with an exception that within the wavelength region of 400–650 nm a minimum is observed which undergoes blue shift by decreasing the material inclusion.

From comparison of Figs. 3 and 5 it can be deduce that the unannealed sample and those annealed at lower temperatures of 100 °C and 180 °C are not affected by nitrogen gas and have kept their metallic structure. However, those annealed at higher temperature of 350 °C show bimodal behavior between metal and nitride: the intensity of their spectra at short wavelengths show decreasing behavior then there exist a minimum and at long wavelengths the intensity increases.

![Fig. 4. Variations of the real (n subscript) and imaginary (k subscript) of the optical constants of copper [22] and copper nitride [23] versus wavelength of the incident light.](image)

![Fig. 5. Results of Bruggeman homogenization calculations for reflection spectra using different material inclusions. a) Copper thin films, b) copper nitride thin films. Film thickness $L = 200 \text{ nm}$ and for normal incident light ($\varepsilon, \varphi = 0$).](image)
In order to investigate these phenomena the film is considered to be formed in shape of two layers on top of each other. The lower film being copper and the top layer is copper nitride. This is experimentally confirmed by Savaloni and co-workers [17,24] who studied the penetration depth of oxygen in titanium films of different thickness at different annealing temperatures and found that films with thickness less than 70 nm can be recognized as Ti-oxide films while thicker films are only surface oxidized Ti films.

In our earlier work [14] a multilayer method was proposed for investigation of optical properties of thin films. The important conclusions of that work may be summarized here:

i) In thin films the material inclusion decreases from bottom to top and layer becomes more porous.

ii) It was found that the best way to investigate the thin film is to consider it as very thin layers on top of each other and their material inclusion decreases from bottom to the top (Section 1).

iii) The most effective parameter on the reflection spectrum is the material inclusion and the most important factors in transmittance spectrum are film thickness and the material inclusion. The rest of parameters are used for obtaining a better fit to the experimental results.

iv) The most important part of this type of work is to introduce a function in which the variation of material inclusion with increasing the film thickness is precisely included. This investigation in ref [14] showed that the best function is an exponential one.

In order to carry out this investigation it was first assumed that the variation of the material inclusion in the film structure is linearly decreasing from bottom to top. Fig. 6 shows the results of these calculations. In Fig. 6 the thickness and average material inclusion of copper nitride layer and copper layer are assigned as \( L_1 \), \( f_{\text{i,1}} \) and \( L_2 \), \( f_{\text{i,2}} \), respectively.

In Fig. 6 the influence of different parameters on the spectra can clearly be observed while the bimodal behavior mentioned before for copper nitride and copper structure is also vividly observable. As the films annealed at 350 °C were most affected by the annealing process the fitting process was concentrated on the results of these samples. An exponential function in form of \( f_i = c_1 e^{c_2(z-L)} \), \( f_i = 1 - c_1 e^{c_2(z-L)} \) was used to obtain the best fit to the experimental results, where \( L \) is the whole film thickness, \( c_1 \) and \( c_2 \) are coefficients that depend on the minimum and the maximum values of material inclusion and \( z \) varies from the bottom to the top of the film (Fig. 1). The results for the best fit are shown in Fig. 7.

In Fig. 7 it can clearly be observed that the technique used in this work is a powerful method for prediction of the structure of thin film. The parameters used for the fitting process are included inside the figures. The other intriguing point about Fig. 7 is the reduced material inclusion in the film deposited at 40° vapor incident angle relative to the film deposited at 0° which can be due to initial higher porosity of this film [25–27].

"It is worthwhile to mention that in all calculations the number of sub-layers for the simulation process presented in Fig. 1(d) was 30. In order to obtain simulated spectrum for each sub-layer, calculations were carried out over the wavelength region of 400–1100 nm for 71 times (intervals of 10 nm). Hence, to obtain and plot the spectrum for each sample (thin film) discussed in this work \( 30 \times 71 = 2130 \) times calculations were performed.

6. Conclusion

It is shown that the structure of thin films undergone annealing process have a bimodal behavior which show gradual transition from the initial material to the expected material due to the annealing condition. This phenomenon affects the optical response of the film and becomes more pronounced at higher annealing temperatures. A method for prediction of the optical response of such thin films based on the Bruggeman homogenization formalism is proposed. Comparison of the results of this method with experimental observations proved to be a powerful technique for investigation of the structure of thin films. The gas molecules penetration in the structure of metals leads to formation of compositional structures consisting of metals and semi-conductors with intermediate metal-semi-conductor properties. Engineering of penetration depth and the percentage of gas molecules penetration in the structure of thin films during the annealing process is of high importance which is undergone investigation in this work using both theoretical and
Fig. 7. Column I) Best fits to the experimental results of annealed samples at 350 °C temperature. Column II) form of the function for material inclusion in the annealed samples at 350 °C temperature.

experimental approaches.

Data availability

All the data presented in this work can be obtained from the authors.

Acknowledgements

This work was carried out with the support of the University of Tehran, University of Mohaghegh Ardabili and Islamic Azad University.

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