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Optical characterization of Cu₃N thin film with Swanepoel method

Davoud Dorranian, Laya Dejam[*] and Gelareh Mosayebian

Abstract

Swanepoel method is employed for spectroscopic determination of optical properties of Cu₃N thin film using transmittance data. Investigated films have been deposited using reactive magnetron sputtering system. Deposition time was 9 to 21 min. Refractive index, absorption coefficient, and bandgap energy of the samples are determined. Thickness of the films is calculated by Swanepoel method, and result is compared with the thickness of the films measured by profilmeter. It is shown that Swanepoel method is a reliable way to calculate the optical constants of thin films when the transmittance spectrum of the film is influenced by wavelike patterns due to reflection of the probe beam from different interfaces.

Keywords: Copper nitride, Thin film, Magnetron sputtering, Energy gap, Swanepoel method.

PACs: 81.05.Je, 82.20.Fw, 78.20.Ci, 68.55.Jk.

Background

There is convenient method with using few known equations to determine the optical constants of semiconductor and insulator thin films based on their reflectance and transmittance spectrum [1]. However, when thickness of the film is in the range of micrometer, some wavelike patterns due to interaction of probe beam reflected from different interfaces appear in transmittance and reflectance spectrum. These patterns are a source of errors in calculating the optical parameters of thin film such as refractive index and absorption coefficient. Actually, this wavelike patterns which appeared in all results are not true. In this case, Swanepoel method can be used as a solution for this problem. In fact, Swanepoel method is a way to simulate the wavelike patterns in the transmittance spectrum with smooth curves. Other advantage of this method is that the reflectance of the sample is not required for calculating optical parameters. Because reflectance of the sample can be influenced by the roughness of the sample, it can be another source of error in calculating the optical parameters of the thin films.

Copper nitride (Cu₃N) with the structure of cubic anti-ReO₃, one kind of excellent semiconductors with many extraordinary properties due to its small indirect band gap, has obtained considerable attention in recent years as a new material applicable for optical storage devices and high-speed integrated circuits. At very low temperature (about 300 to 470°C), Cu₃N decomposes into Cu and N₂ and becomes a conductor from a semiconductor. So the low decomposition temperature and discriminating optical properties of the compound Cu₃N are applicable for optical read-only memory disks by generating microscopic Cu-metal spots on Cu₃N film by performing local laser heating. On the other hand, its optical reflectivity in visible and infrared range is far smaller than that of pure Cu [2-6].

In this work, with the goal of introducing the Swanepoel theory [7] as a precise method to characterize the optical parameters of thin films, the optical properties of Cu₃N thin films are investigated. The transmittance spectra of Cu₃N thin films over the wavelength range 200 to 2,000 nm at room temperature are measured. These films were deposited on glass substrate by reactive DC magnetron sputtering of a Cu target with 50% nitrogen contents in the working gas at different sputtering times. Optical transmission spectra of films are analyzed to determine their optical constants such as refractive index, absorption coefficient using Swanepoel method, and the effect of sputtering parameters on the optical properties of films are discussed. Details of the structure of films are reported in reference [6].

This manuscript is organized as follows: After this introduction, the experimental setup is presented in

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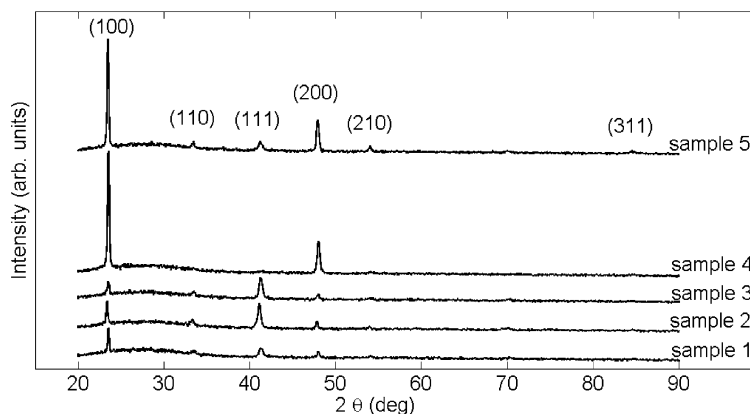
Figure 1 X-ray diffraction spectrums of the deposited films.

section 2. Section 3 is devoted to description of Swanepoel method, results, and discussion. All stages to extract refractive index, absorption coefficient, and band gap energy are explained in detail in this section; and finally, a discussion on the behavior of optical parameters of all deposited films is presented. Conclusion of the manuscript can be read in section 4.

Methods

Copper nitride thin films were sputtered on BK7 glass substrate, by using a cylindrical direct current reactive magnetron sputtering system. Before deposition, substrates were cleaned by ultrasonic waves in acetone and alcohol, and dried by blowing air. In the deposition process, no external heating was provided. The base pressure of the vacuum chamber just before sputtering was 2×10^{-4} mbar. During the sputtering experiment, the pressure was maintained at 6×10^{-2} mbar. A pure copper (99.99%), 30 mm diameter and 195 mm in height, was used as the target. The working gas was a mixture of 99.999% pure nitrogen and 99.999% pure argon with the same percent N_2/Ar (50%). The distance between the substrate and the target was 30 mm. The discharge current was 200 mA at the voltage difference of about 700 V, and deposition time was varied between 9 and 21 min. Uniform magnetic field of 400 Gauss was generated in the sputtering reactor parallel to the axis of cylindrical chamber by a solenoid.

After film deposition, X-ray diffraction (XRD) was performed on STOE-XRD diffractometer using Cu- K_α line (l = 0.15406 nm). Change in transmittance spectrum of the samples was measured by a Varian Cary-500 spectrophotometer (Varian Inc., CA, USA) at room temperature, and a Dektak3 profilmeter was employed to measure the thickness of the growth films.

## Swanepoel method, results and discussion

Films structure

The XRD patterns of Cu_3N films deposited on glass substrate are shown in Figure 1. The XRD analysis reveals that the films are polycrystalline of cubic Cu_3N structure with peaks at $2\theta = 23.54°$, $41.19°$, and $47.88°$ corresponding to $Cu_3N(100)$, $Cu_3N(111)$, and $Cu_3N(200)$ orientations, respectively. Grain size of the sputtered films is calculated by Scherrer's formula, and their thickness is measured by profilmeter which is between 360 and 770 nm as well as deposition rate of samples are presented in Table 1. The XRD patterns of samples show that the crystallinity of deposited films is increased with increasing the thickness of deposited films, i. e., deposition time. Optical transmittance spectra of deposited films are presented in Figure 2. Spectra show an increase at wavelengths between 600 and 800 nm, and the wavelike structures can be seen in all patterns due to the interaction of the beam transmitted from different interfaces.

Swanepoel method

The practical condition for a thin film on a transparent substrate is shown in Figure 3. In this figure, *d, n, α,* and *T* denote the thickness, refractive index, absorption coefficient,

Table 1 Sputtering time, film thickness, deposition rate, band gap energy, and grain size of samples

Sample	1	2	3	4	5
Sputtering time (min)	9	12	15	18	21
Film thickness (nm)	360	450	610	630	770
Deposition rate (nm/min)	40	37.5	40.6	35	36.6
Band gap energy (eV)	1.91	1.85	1.81	1.90	1.9
Grain size (100) planes (nm)	37.57	37.5	36.46	38.95	40.11
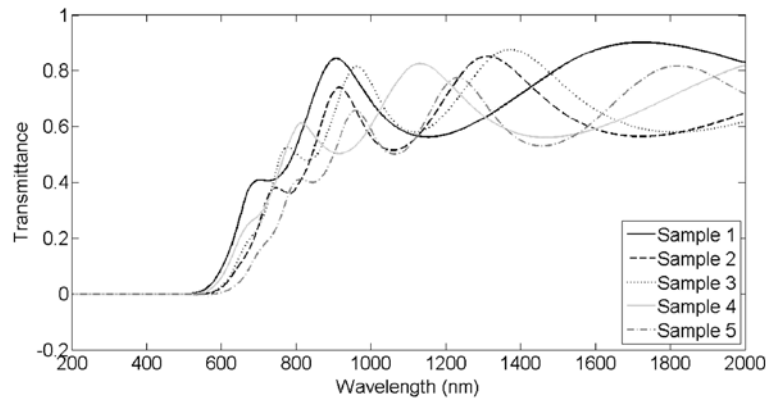
Figure 2 Transmittance of samples deposited on glass substrate.

and transmission of the film, respectively. The transparent substrate has a thickness of several orders of magnitude larger than d with index of refractions and absorption coefficient $\alpha_s = 0$ and transmittance T_s. The index of refraction for air is taken to be $n_0 = 1$. If the thickness d is uniform, interference effects give rise to the spectrum, shown by the full curve in Figure 4. The transmittance spectrum of sample 5 is presented in Figure 4. This sample is chosen to be described by Swanepoel method for extracting the optical parameters. These interference fringes can be used to calculate the optical constants of the film. For the sake of comparison, we have also included the transmittance spectrum of the bare substrate, which is shown by dotted line as T_s. Cu_3N thin film strongly absorbs the electromagnetic wave with wavelengths smaller than 600 nm. The basic equation for interference fringes is

$$2nd = m\lambda \tag{1}$$

where m is an integer for maxima and half integer for minima, n is refractive index, d is the thickness of the film,

and λ is wavelength. The transmission T for the normal incidence resulted from the interference of the wave transmitted from three interfaces can be written as [7]:

$$T = T(n, x) = \frac{Ax}{B - Cx\cos(\phi) + Dx^2} \tag{2}$$

where
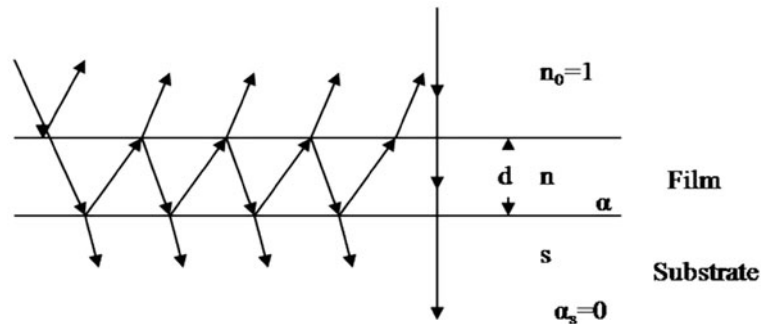
$$A = 16n^2 s \tag{3a}$$

$$B = (n+1)^3(n+s^2) \tag{3b}$$

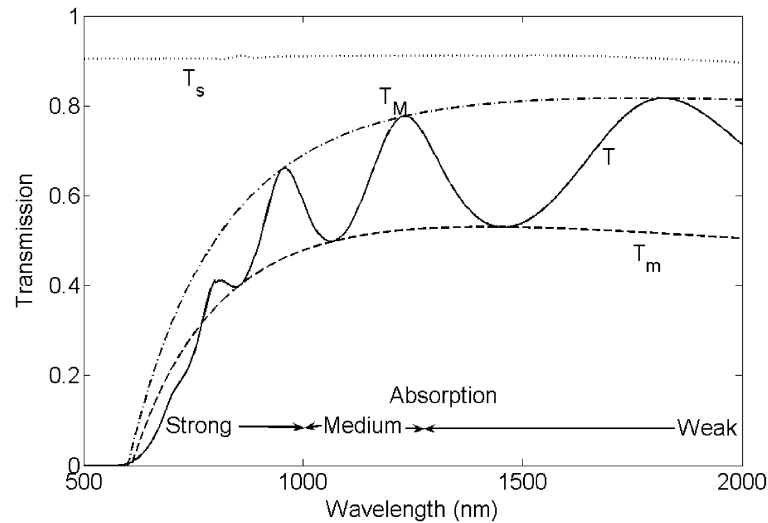$$C = 2(n^2 - 1)(n^2 - s^2) \tag{3c}$$

$$D = (n-1)^3(n-s^2) \tag{3d}$$

$$\Phi = 4\pi nd/\lambda \tag{3e}$$

$$x = \exp(-\alpha d) \tag{3f}$$

For maximum and minimum points of interferences $\cos(\phi) = 1$, so T_M and T_m curves as the upper and lower

Figure 3 Schematic view of substrate and thin film. Arrows indicate transmission and reflection at different interfaces.

Figure 4 T_s **is the transmittance of bare substrate and** T **is the transmittance of sample 5.** T_M and T_m are the fitted curves to the maxima and minima of T.

bounding functions of transmittance can be found by fitting the two below curves to these points as

$$T_M = \frac{Ax}{B - Cx + Dx^2} \qquad (4)$$

$$T_m = \frac{Ax}{B + Cx + Dx^2} \qquad (5)$$

If T_s is the maximum value of the transmission of substrate, then substrate refractive index s can be given by the following equation:

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2} \qquad (6)$$

The upper bounding function T_M passes through the maxima of the spectrum and T_m through the minima is shown in Figure 4, where the envelope for a simulated transmission curve is shown.

From Equations 4 and 5, we have

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A} \qquad (7)$$
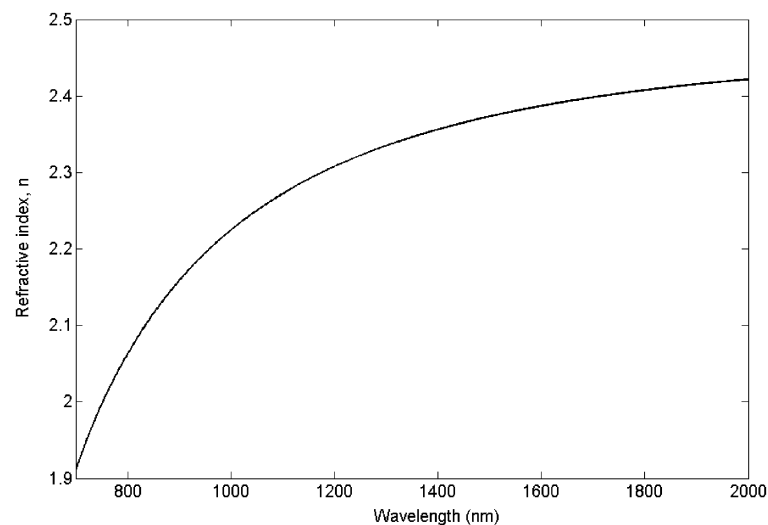
Figure 5 Refractive index of sample 5 calculated by Swanepoel method.

Table 2 Optical data which were used to calculate the thickness and refractive index of sample 5

λ	T_M	T_m	n_1	d_1 (nm)	m	d_2 (nm)	n_2
1,822	0.817	0.516	2.408		2	756.64	2.41
1,470	0.809	0.531	2.368		2.5	775.97	2.368
1,234	0.777	0.524	2.316	900	3	799.2	2.317
1,068	0.725	0.499	2.258	997			
954	0.616	0.460	2.197	1,179			
852	0.596	0.397	2.183	1,117			
Average				1,048.25		777.2	

The right hand side of Equation 7 is independent of the thickness of the film. Substituting C and A from Equation 3 into Equation 7 leads to

$$n = \left[N + \left(N^2 - s^2\right)^{1/2}\right]^{1/2} \tag{8}$$

where

$$N = 2s(T_M - T_m)/T_M T_m + \left(s^2 + 1\right)/2 \tag{9}$$

For the Cu_3N thin film which is shown in Figure 4, using the least square method the fitted curves are

$$T_M = -6.7595 \times 10^5/\lambda^2 + 0.007673 \times 10^5/\lambda + 0.6$$

$$T_m = -6.0382 \times 10^5/\lambda^2 + 0.008515 \times 10^5/\lambda + 0.231$$

By using these equations in Equations 8 and 9, taking $s = 1.5$, the refractive index of Cu_3N sample in the range of fitted curves can be obtained which is presented in Figure 5. With increasing of wavelength, the refractive index of Cu_3N thin film is increased from 1.9 to 2.4. We

attribute this to strong absorption of Cu_3N and nitrides films in this range. Obtained magnitudes for n are in good agreement with other reports [8,9]. The magnitudes of refractive index with the magnitudes of exact maxima and minima of transmission (Figure 4) of sample 5 are presented as n_1 in Table 2. A curve of the from

$$n(\lambda) \approx a_0 + \frac{a_1}{\lambda^2} \tag{10}$$

can be fitted to these points with $a_0 = 2.594$, and $a_1 = -1.845 \times 10^4$. This curve is the second order Cauchy dispersion relation. This empirical fit was derived by Cauchy based on a theory of light propagation later proven to be false. Nevertheless, it is often used by optical spectroscopists for its simplicity [10]. Extracted $n(\lambda)$ and its accompanying Cauchy fit are shown in Figure 6.

If n_1 and n^*_1 are the refractive indices calculated from two consecutive maxima or minima corresponds to two wavelengths of λ_1 and λ_2, then the thickness of the film d can be obtained from [7]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n^*_1 - n_1 \lambda_2)} \tag{11}$$

The thickness obtained from Equation 11 is very sensitive to the uncertainty in the value of the refractive index which is derived from Equation 8. The values of film thickness calculated from Equation 11 are shown as d_1 in Table 2.

If the dispersion of refractive index is negligible (which is usually the case well away from the absorption edge), the order of interference m at the maxima of transmission spectra for wavelength λ_1 is:
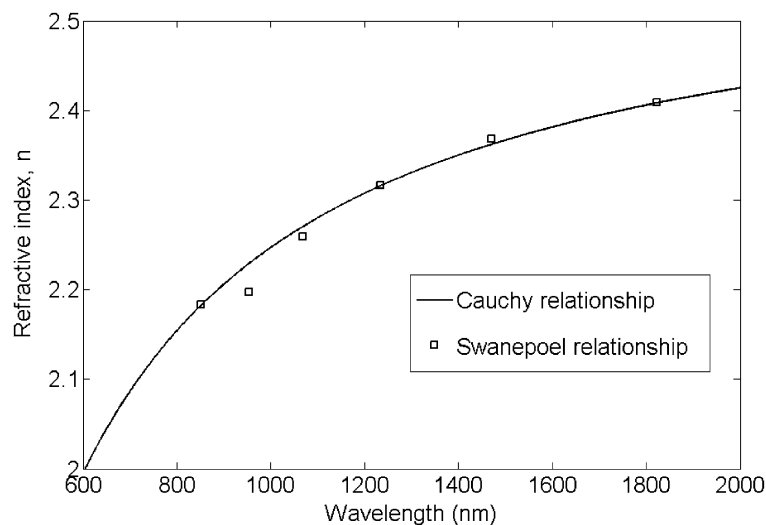
Figure 6 Extracted $n(\lambda)$ from exact magnitudes of T_M and T_m and its accompanying Cauchy fit.
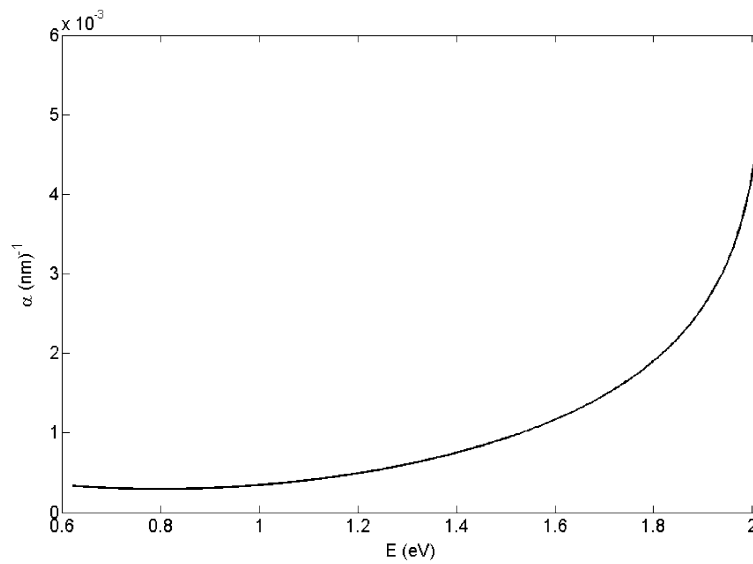
Figure 7 Absorption coefficient of sample 5 calculated by Swanepoel method.

$$m = \left[\frac{\lambda_2}{\lambda_1 - \lambda_2} \right] \tag{12}$$

Where λ_1 and λ_2 are the wavelengths of two adjacent transmission maxima $(\lambda_1 > \lambda_2)$, and the symbol (x) stands for nearest integer. Another magnitude for thickness can be found by using m from Equation 12 in Equation 1, which is indicated as d_2.

Different regions of strong, medium, and weak absorption are indicated in Figure 4. For the strong absorption region where interference fringes disappear, the absorption coefficient α, is given by [7].

$$\alpha = \frac{1}{d} \ln \left[\frac{16n^2 s}{(n+1)^3 (n+s^2) T_0} \right], \tag{13}$$

in which $T_0 = Ax/B$, and d is the film thickness. The n and s are the refractive indices of the film and substrate, respectively. In the spectral region of medium
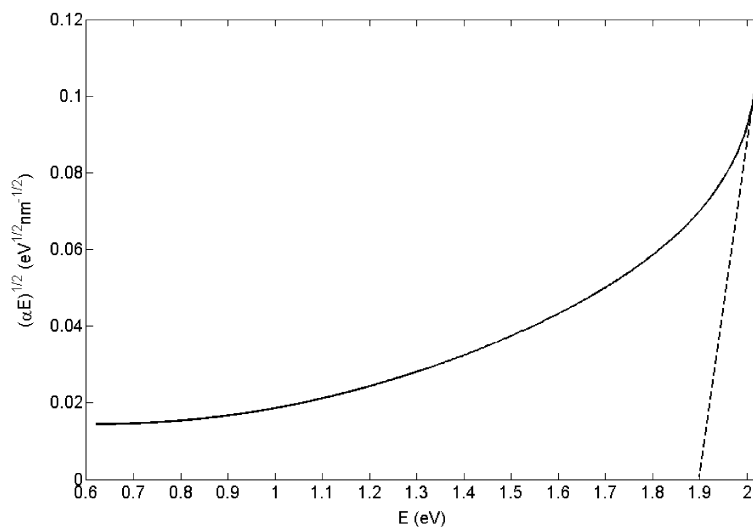
Figure 8 The $(\alpha E)^{1/2}$-E dependence of sample 5 to calculate the band gap energy.
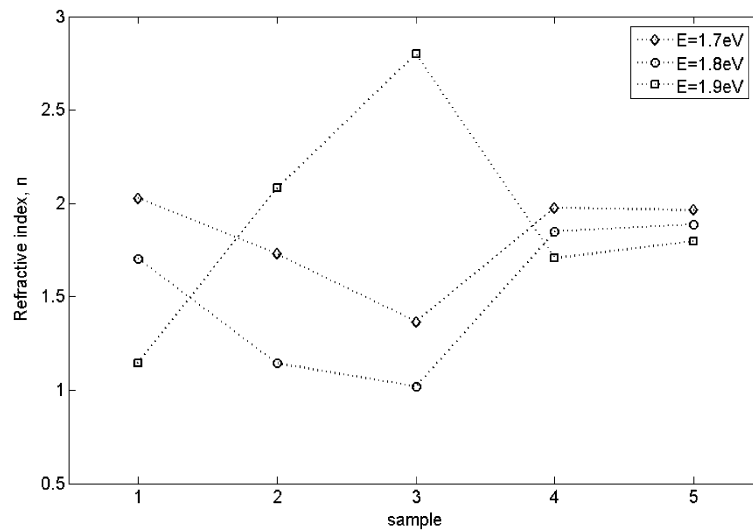
Figure 9 Refractive indxes of samples calculated by Swanepoel method.

absorption where interference fringes appear distinctly in the transmission spectra, α can be obtained by [7]

$$\alpha = \frac{1}{d} \ln \frac{(n-1)^3(n-s^2)}{E_m - \left[E_m^2 - (n^2-1)^3(n^2-s^4)\right]^{0.5}} \quad (14)$$

where $E_m = (8n^2s/T_m) - (n^2-1)(n^2-s^2)$.

Absorption coefficient of Cu_3N thin film for strong and medium regions is presented in Figure 7. It is noticeable that the wavelike patterns due to interaction of probe beam reflected from different interfaces will be appeared in the optical absorption coefficient which is evaluated from the transmittance data using the known relation $\alpha = (1/d)\ln(1/T)$. Of course, they cannot be true [6].

The optical energy gap E_g is another important quantity that characterizes semiconductors and dielectric materials since it has a paramount importance in the design and modeling of such materials [11]. An approximate functional dependency of α on the energy of photons is given by the expression [12]:

$$\alpha = A \sqrt[p]{E - E_g} \frac{}{E} \quad (15)$$

where A is a dimensional constant, E_g is the optical bandgap, and p is an index representing the transition order. For indirect optical bandgap, $p = 1/2$, and the curve $(\alpha E)^{1/2}$-E tends asymptotically towards a linear section; other values of p (generally 2) suggest a direct optical bandgap. The structure of Cu_3N prepared in this study has an indirect optical band gap, as is shown by the plot of $(\alpha E)^{1/2}$ versus E in Figure 8. Consequently, E_g is the intersection of E axis with a fit to the linear section of the $(\alpha E)^{1/2}$-E curve. Through this procedure, we found $E_g = 1.9$ eV for the Cu_3N thin film of sample 5 as is shown in Figure 8. The optical bandgap energy of all samples extracted by using the Swanepoel method data is exactly the same with the magnitudes extracted from the last data, which show that the interference in transmittance spectrum does not make noticeable changes in the absorption edge magnitudes.

Table 3 Optical data which were used to calculate the thickness and refractive index of sample 4

λ	T_M	T_m	n_1	d_1 (nm)	m	d_2 (nm)	n_2
1,992	0.8181	0.523	2.4				
1,478	0.853	0.5615	2.4				
1,134	0.826	0.557	2.4	548.5			
920	0.723	0.5016	2.2	651.47			
818	0.614	0.436	2.1	1,109	3	584.28	2.1
686	0.268	0.2683	1.9	1,321	3.5	631.84	1.9
Average				907.5		608.84	

Table 4 Optical data which were used to calculate the thickness and refractive index of sample 3

λ	T_M	T_m	n_1	d_1 (nm)	m	d_2 (nm)	n_2
1,842	0.746	0.581	2.1		1		2.1
1,376	0.877	0.596	2.4		2.5	716.6	2.4
1,126	0.890	0.581	2.4	504.3	3	703.75	2.4
964	0.818	0.543	2.4	670.7	4.5		
832	0.644	0.475	2.1	1,273.5			
782	0.529	0.433	1.9				
Average				816.167		710	

Table 5 Optical data which were used to calculate the thickness and refractive index of sample 2

λ	T_M	T_m	n_1	d_1 (nm)	m	d_2 (nm)	n_2
1,724	0.737	0.564	2.1		1		
1,314	0.851	0.556	2.4		2.5	684.37	2.4
1,064	0.842	0.515	2.5	441.8	3	638.4	2.5
916	0.739	0.453	2.4	630.03	4.5		
798	0.534	0.361	2.1				
746	0.381	0.300	1.9				
Average				535.9		661.38	

Table 6 Optical data which were used to calculate the thickness and refractive index of sample 1

| λ	T_M	T_m	n_1	d_1 (nm)	m	d_2 (nm)	n_2
1,702	0.902	0.600	2.4		1	354.58	2.4
1,168	0.665	0.564	2.6		1.5	336.92	2.6
902	0.845	0.498	2.5	367.23	3		
744	0.575	0.411	2.1	838.14	2.5		
690	0.406	0.363	1.7	1,624.16			
557	0.364	0.17	1.1	589.82			
Average				854.8375		345.75	

Results and discussion

Extracted refractive index and thickness of other sputtered Cu_3N samples by Swanepoel method are presented in Tables 3, 4, 5 and 6. The magnitudes of d_2 are closer to the magnitudes of thickness measured by profilmeter in comparison with d_1. The same results are also presented in reference 7.

Two methods for calculating the thickness are introduced. In the first method, thickness of the film can be determined by the use of corresponding wavelength at of Equation 8 maxima, and minima points occurs as introduced in Equation 11. In this case, refractive index should also take into account. In the second method, Equation 10 is used. As can be seen, the distribution of thickness deposited films calculated from Swanepoel method is very large and far from measured magnitudes. Error is more than 20%. One source of error is the first fitting procedure of T_M and T_m to transmittance curve. Especially, when the number of maxima or minima on transmittance curve is less than three, the error is larger. Calculated magnitudes for n are more accurate and usually $n_1 = n_2$. This is because for calculating the n, the exact maxima or minima on transmittance curve are used.

Variations of refractive indexes of samples calculated by Swanepoel method in the range of 500 to 2,000 nm wavelength of electromagnetic wave are shown in Figure 9. Extracted magnitudes for n between 2.06 and 2.28 confirm that deposited films on substrates are uniform. Change in refractive index of deposited films at 650, 690, and 730 nm, corresponds to 1.9, 1.8, and 1.7 eV which are related to the bandgap energy and thickness of the samples. Bandgap energy of samples is decreased from sample 1 to 3 and then is increased. Considering the magnitude of bandgap energy and thickness of films with their refractive index shows that the refractive index of samples is decreased and then is increased with their thickness when the photon energy is smaller than the bandgap energy. This behavior is reversed when the photon energy is larger
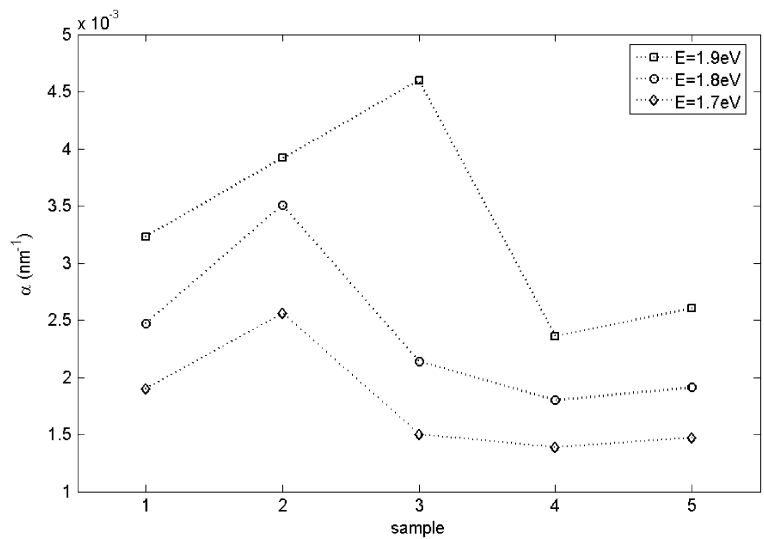
Figure 10 Absorption coefficient of Cu₃N samples. Absorption coefficient of Cu_3N samples for photons at 1.7 eV energy, 1.8 eV energy and 1.9 eV energy.

than the bandgap energy. The refractive index of deposited films is approximately constant for two last samples when the thickness of samples is larger than 620 nm. In fact, by increasing the thickness and crystallinity of thin films, absorption and dispersion in the layers will increase which leads to increasing the refractive index. This can be due to the density of deposited films. Increasing the crystallinity of films in (100) direction besides increasing the thickness of deposited films leads to increasing their density. Increasing the density of films increases their refractive index when the energy of photons is smaller than the bandgap energy of films. As is presented in Figure 9, when energy of photons is larger than the bandgap energy of films, the dispersion of refractive index occurs [1].

Absorption coefficient of Cu_3N samples for photons at 1.7, 1.8, and 1.9 eV energies which are applied energies for copper nitride thin films are plotted in Figure 10. As is expected, the absorption coefficient of samples is increased with increasing the photon energy. However, the rate of this change depends on whether the photon energy is larger or smaller than the energy of bandgap. For photons with energy larger than the band gap energy of film absorption, coefficient is increased noticeably. It is clear that α must be a strong function of the energy hv of the photons. For $hv < Eg$ (direct), no electron hole pairs can be created, the material is transparent, and α is small. For $hv \leq Eg$ (direct), absorption should be strong.

Conclusions

In this work, the Swanepoel method is introduced practically to determine the optical characteristics of Cu_3N thin films deposited on BK7 glass substrate. It is shown that when the transmittance spectrum of films is affected by the wavelike structure patterns due to interference of probe beam after successive reflections from different interfaces, using Swanepoel method for determination of optical constants of deposited films leads to reducing error significantly. Besides, measuring the film thickness by profilmeter, two other ways based on refractive index and interference pattern are presented for calculating the thickness. Results show that the magnitude calculated from the second way is closer to the measured magnitudes. It is observed that appeared wavelike patterns in the transmittance spectrum do not make error in calculating the magnitude of bandgap energy of the thin films. Some fluctuation can be observed in the magnitude of refractive index and absorption coefficient of samples which tends to zero when the thickness of the films is increased.

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