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Study of CuS Thin Films Deposited by PLD Simulated for Prism Based SPR Sensor

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A B S T R A C T

Copper Sulfide CuS thin film was prepared using pulsed laser deposition PLD technique and characterized by X-ray and SEM. The optical, structural, and morphological properties are examined at different energies 500 mJ, 600 mJ, 700 mJ, and 800 mJ. The best result was 600 mJ which annealed at various annealing temperatures 300°C, 350°C, 400°C, and 450°C. The effect of thermal annealing on CuS thin film was examined X-ray and SEM. CuS Film was simulated using a prism-based SPR optical sensor. This paper introduces the optical test study of CuS thin film deposited by pulsed laser deposition technique on the quartz substrate and supported by theoretical application study under the effect of surface plasmon resonance (SPR). In this research field, the optical and morphological characteristics of the CuS thin film were deposited by PLD at different laser energies. The annealing process was applied for better-deposited thin-film; the XRD results, SEM images, transmittance T%, and energy gap Eg were analyzed thoroughly and compared to evaluate the thin-film. This effort was made in an in-depth analysis of CuS thin film deposited by PLD on the quartz substrate and applied theoretically in surface plasmon application.

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1. Introduction

There has been a growing interest in the last few decades using semiconductor chalcogenide thin-film such as Copper sulfide (CuS). Due to the wide range of applications in most science and technology like commercial applications, Photo-thermal conversion applications, and Photovoltaic applications, CuS has significantly been interested [1].

Copper sulfide can quickly form a series of nonstoichiometric compounds, depends on the exact composition Cu_xS (x=1-2) with a crystal structure varying from orthogonal to hexagonal. The high absorbance of the CuS thin films used for photo-thermal solar energy conversion [2].

The high electrical conductivity and low cost (in price) preparation CuS is considered a perfect semiconductor material. Single crystal and simple thin-film forms related to its structural and electrical properties made it an excellent choice in sensor applications such as pH sensors. These characteristics are fully controlled or dependent on the preparation method and the deposition conditions dominating thin film growth [3].

Copper sulfide exhibits a different type of compositions ranging from Cu2S (Chalcocite) at copper-rich sites to CuS2 at the copper-deficient sites such as CuS (covellite). Copper sulfide (CuxS) forms five stable phases at room temperature: Covellite (CuS), anilite (Cu1.75S), digenite (Cu1.8S), and chalcocite (Cu2S) [4]. CuS becomes an essential candidate for the solar cell industry [5] or an optical sensor using surface plasmon resonance [6].

Surface Plasmon Resonance (SPR) is an optical phenomenon where the charges at the plasmonic layer are excited by incident photons of a light beam [7]; at a certain angle of incidence, the plasmonic waves propagate parallel to the metal surface [8]. Therefore, any small variation in the sensing environment's reflective index (RI) will shift the SPR resonance dip, leading to analyte sensing accurately [9, 10].

PLD is considered one of the most confident processes for thin-film synthesis [5]. The unique advantages include controlling the films' growth rate, high reproducibility, the possibility of using large substrates, different materials, crystallinity, uniformity, and low impurity of the deposited film. Moreover, the PLD technique permits a stoichiometric material transfer from the target towards the substrate surfaces in the case of multicomponent marks [11]. Our choice of the laser energies used to bomb the target in the deposition process to excite the material atoms from the target and their ability to stick together as a thin film is mainly deposited and regularly, and this is what indicated and confirmed by previous studies. Since the composition's annealing temperature was successful and good optical properties, the composition needs enhancement, so we chose variable annealing temperatures.

2. Guidelines for Preparation

The primary material in this experiment is Copper sulfide (CuS) powder. This material (commercial) was compressed into a uniform solid disk (2.1 cm diameter, 0.4 cm thickness) using a mechanical piston device (university of technology - Iraq) work at high pressure, as shown in Figure 1. CuS is used to build a Nano-crystalline CuS photonic thin-film, representing binary chemical compounds of Sulfur (S) and copper (Cu).

Figure 1: CuS solid disk.

Solid-state Q-switch Nd:YAG pulsed laser (neodymium-doped yttrium aluminum garnet) was used to ablate the CuS material, which deposits CuS on the quartz substrate to form CuS thin film. Pulse duration: 10 nsec, substrate temperature: - 250°C, the number of pulses is 150 on the CuS disc target to make each sample surface of CuS thin film on the substrate, frequency: 3 Hz, wavelength

1064 nm, pulsed energy 500 mJ,600 mJ,700 mJ, 800 mJ as shown in Table I. Four samples of CuS thin-film were gained from four laser energies [12]. The setup of the PLD technique is shown in Figure 2.

TABLE I: Nd:YAG pulsed laser parameters

Laser properties	Data
Pulse duration	10 nsec
substrate temperature	250°C
number of pulses	150
frequency	3 Hz
wavelength	1064 nm
pulsed energy	500 mJ,600 mJ,700 mJ, 800 mJ.

Frequency (3 Hz) is excellent and suitable for laser energies, and hence it is included in the energy band gap calculation. Figure 3 shows the diagram for the preparation and properties of CuS films.

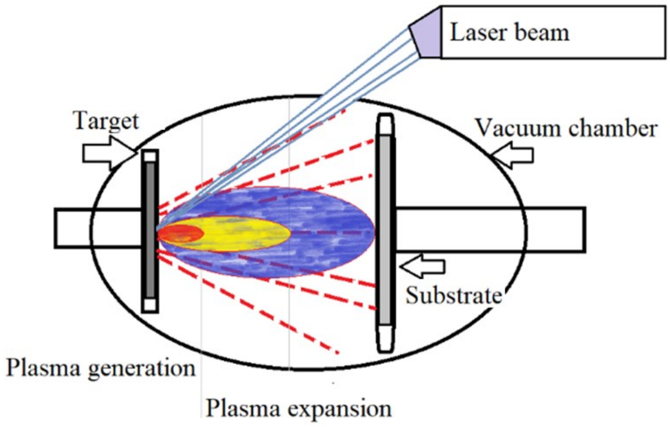

Figure 2: PLD technique for the preparation of CuS thin film.

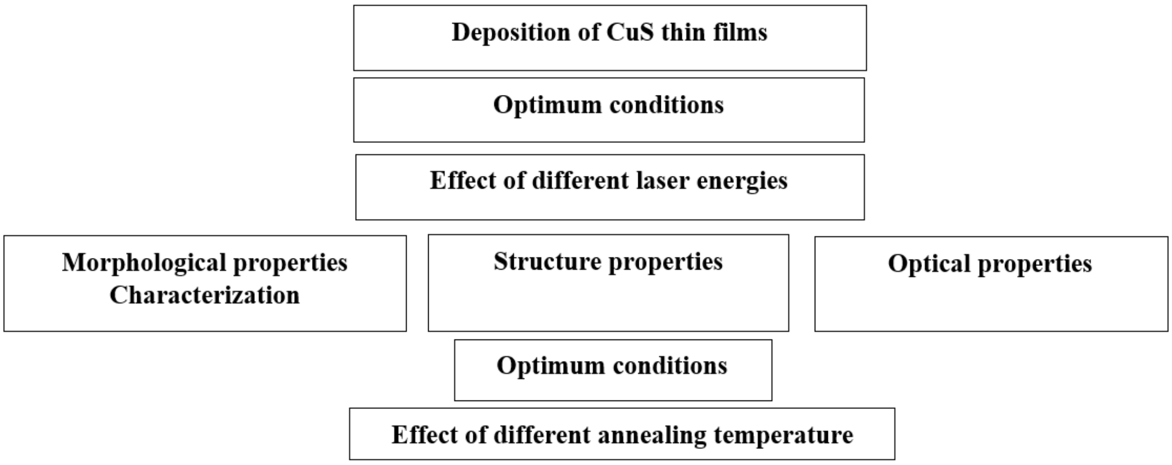

Figure 3: Diagram for the preparation of CuS films

SPR sensor results depend on the refractive index (n) and extinction coefficient (k) parameters. To specify the CuS n and k, both values were calculated using Eq.(1) [13]

$$\alpha = (1/d)\ln(1/T) \quad (1)$$

d is the thickness of thin-film, and T is the CuS thin film's transmittance [14]. It is widely known that α is used to specify the optical band gap, α is related to the photon energy to calculate optical absorption or absorption coefficient. So to find the value of k, this found from Eq. (2) [15]

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

We calculated R practically through theoretical R values extracted from the known law A+T+R=1 [13] depending on the practically extracted A, T. Also, rely on the error ratio of R values of previous studies.

n value (refractive index) of the CuS deposited thin film was measured directly from reflectance value using simple Eq.(3) below [16]

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{3}$$

The estimated real part n values of CuS deposited thin films, the n value of the CuS thin film is shown in Eq.(4) [13],

$$N = n - ik \tag{4}$$

The magnitude of n=1.12 and the magnitude of k=0.05 before the annealing process; these two magnitudes represent the CuS thin film's refractive index was measured at 600 nm. These two magnitudes were measured theoretically by using equations depending on practical values of A and T.

The annealing process was applied to CuS thin films at 300°C, 350°C, 400°C, and 450°C and kept for 30 minutes at the processed temperature. To crystallize the thin film, reduce the internal surface defects, and remove the organic material layer from the CuS film. Then samples were tested using the XRD and SEM to characterize the thin film. All measurements were applied to the CuS thin film before and after annealing treatment.

Finally, the CuS was applied in the SPR sensor method. The n and k values were deduced from the group equations 1 to 4. The theoretical approach of SPR was based on the set of input data, 1.77861 RI of the Prism, 632 nm laser wavelength, 40 nm gold layer thickness, and last layer 10-50 nm thicknesses for CuS chemical compound, and water was 1.33 RI. The simulation program was built using MATLAB software. The data that was collected is the relation between resonance wavelengths and absorption.

3. Rustles and discussion

I. Before Annealing Process

A. XRD test

The X-ray diffraction test for the CuS thin film was recorded in the position 2θ (degree) of different laser energies 500mJ, 600mJ, 700mJ, and 800 mJ, as shown in Figure ٤. A sharp rise occurred at (2θ=22˚) for all four samples, but it shows different intensity values. The samples in this Figure radiated by 500 mJ, 600mJ, 700 mJ, and 800 mJ laser energies. The sample of 600 mJ has an intensity value higher than other tested samples' intensity values, so it was chosen for the next process of annealing the CuS thin film at different temperatures.

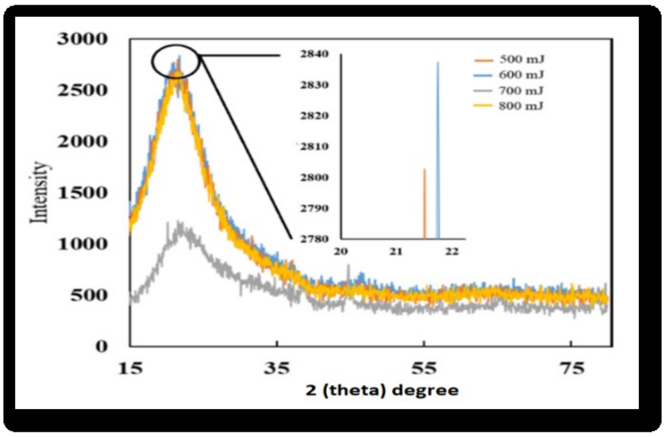

Figure 4: XRD patterns of CuS thin film at different laser deposition energies (500, 600, 700, and 800) mJ before the annealing process.

B. SEM Test

A scanning electron microscopy (SEM) was used to study CuS thin films' surface morphology fabricated on the quartz substrates. The particle size was measured and found between 29 nm to 53 nm, as shown in Figure ٥. Particle size has a considerable effect on optical properties. SEM image of CuS thin film formed by radiated the CuS target by 600mJ. The surface topography consists of multiple -columns and islands and low and high walls that affect the absorbed light's properties and may lead to unwanted light scattering and even broadening of the plasmonic absorption curve due to the inhomogeneous of the deposited surface.

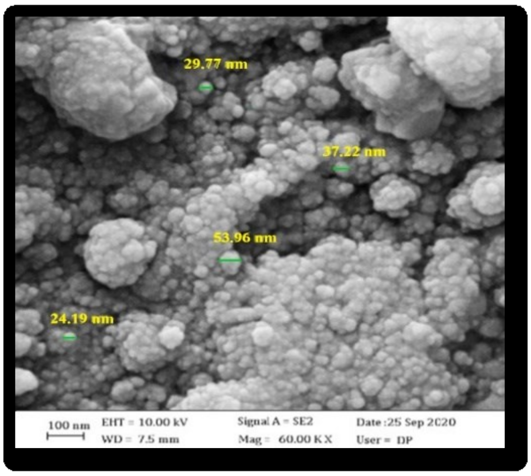

Figure 5: SEM image of the CuS thin film deposited using 600 mJ.

C. Optical Transmittance (T)

Studying the transmittance characteristics of any deposited film is of most interest due to its essential scientific relation with other characteristics. The transmittance spectra directly depend on the chemical compound, crystal structure, energy of the photon, film surface morphology, and thickness. Figure ٦ shows the effect of laser energies on the transmittance spectra. The transmittance increases with increasing wavelength for before and after annealing.

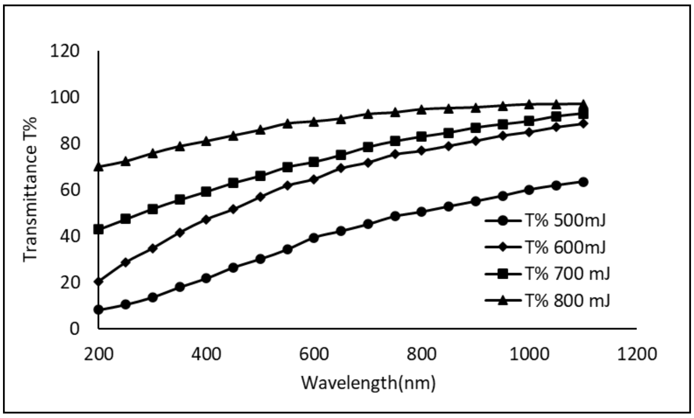

Figure 6: Optical transmission spectra of thin films of different laser energies E= (500Mj, 600mJ, 700mJ, 800mJ).

D. Optical Bandgap (Eg)

The direct band gaps of the CuS thin films before annealing were obtained from the $(\alpha h\nu)^2$ vs. hν graphs as shown in Figure ٧. Values are in the range of 3.4 to 4.1, and the band gap decreases with the increment of the coating thickness.

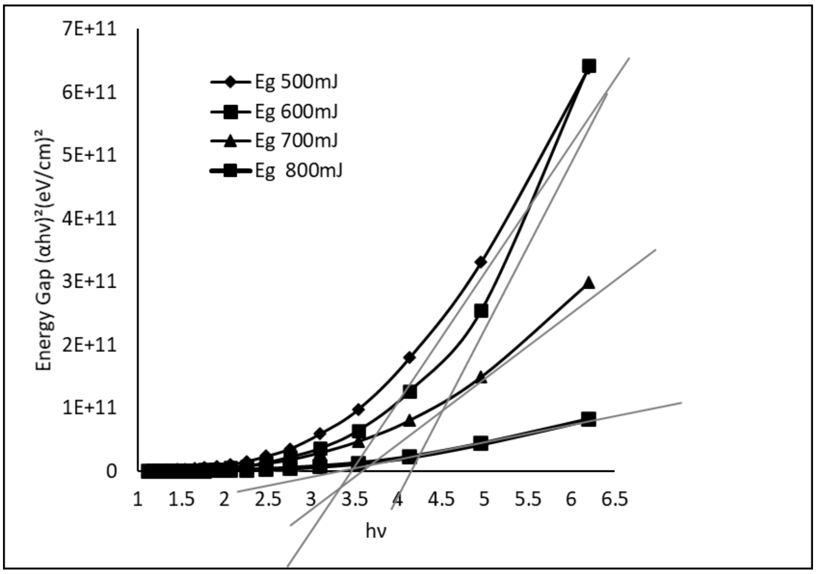

Figure 7: Energy band gap of the CuS thin film after different laser energies (500mJ, 600mJ, 700mJ, and 800mJ)

II. After Annealing Process

A. XRD Test

Figure 8 shows the effect of annealing temperatures 300°C, 350°C, 400°C, and 450°C on the intensity using X-Ray—the annealing process for the best PLD result of 600 mJ. The most substantial diffraction peaks (102) are observed at degrees of 2θ=12.4°. A small indefinite peak is observed at 2θ=25.45, as shown in Figure ٨. It is determined as the plane (008) corresponding to this peak. It is observed that these calculated values are compatible with standard lattice parameter values of hexagonal copper sulfide [17]. From those conclusions, it is determined that the CuS deposited thin films grew in hexagonal phase and having a polycrystal structure. It is found out that the best crystallization for the CuS thin films that are obtained at 400°C was derived from PLD.

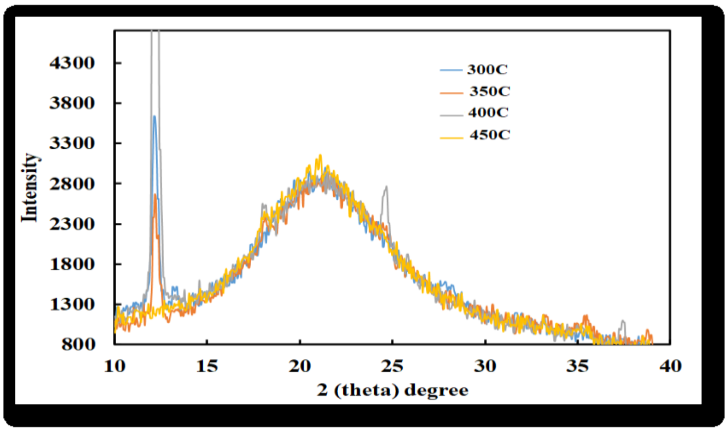

Figure 8: XRD of the CuS thin film at different annealing temperatures 300°C, 350°C, 400°C, and 450°C

B. SEM Test

Morphology, structure, physical and chemical properties can be altered easily due to the thermal annealing process. Therefore, it is commonly used to tailor the characteristics of CuS chemical compounds. The SEM images of the annealed CuS thin film are presented in Figure ٩. In this Figure, three different annealing temperatures were done (300°C, 350°C, and 400°C). The SEM image after annealing temperatures shows a substantial variation in particle size as well as the proportional intensity of X-Ray's work.

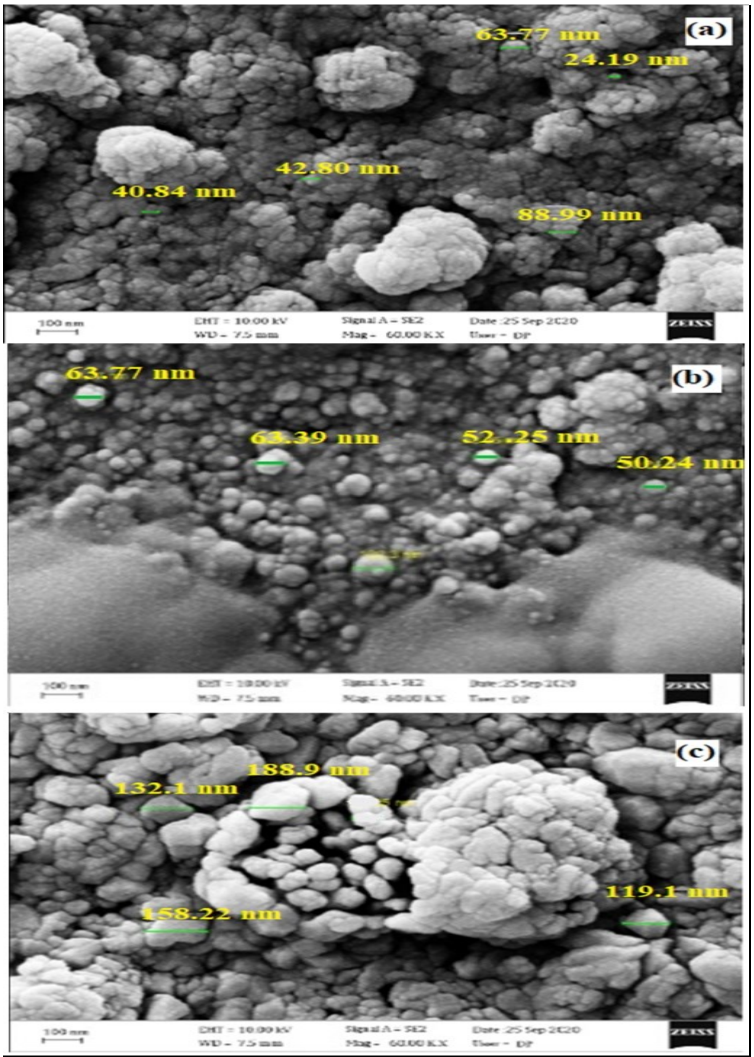

Figure 9: SEM images of the CuS thin film at the different annealing temperatures

C. Optical Transmittance (T)

Figure ١٠ shows the optical transmittance of the CuS thin films after annealing. The annealing process of the deposited films increases the optical transmittance, and this increase could be attributed to the decreasing and rearrangement of the films' defects. Besides, the annealing leads to an improvement in the crystallinity of the film's structure.

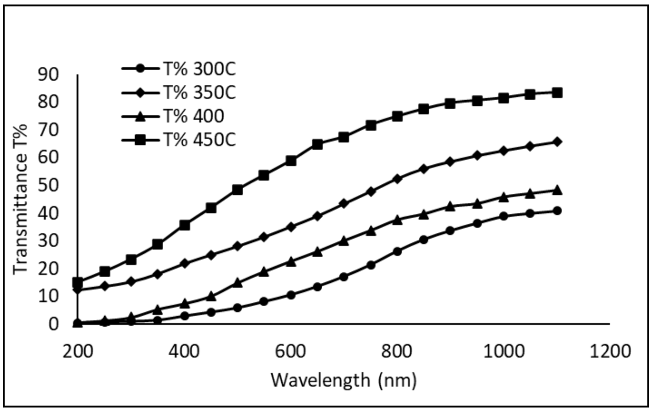

Figure 10: Optical transmission spectra of thin films of different annealing temperatures T= (300°C, 350°C, 400°C, 450°C)

D. Optical Bandgap (Eg)

Figure 1١ shows the direct band gaps of the CuS thin films that were annealed at different temperatures. Values are in the range of 3.2 to 3.8, and the band gap decreases with the increment of the coating thickness.

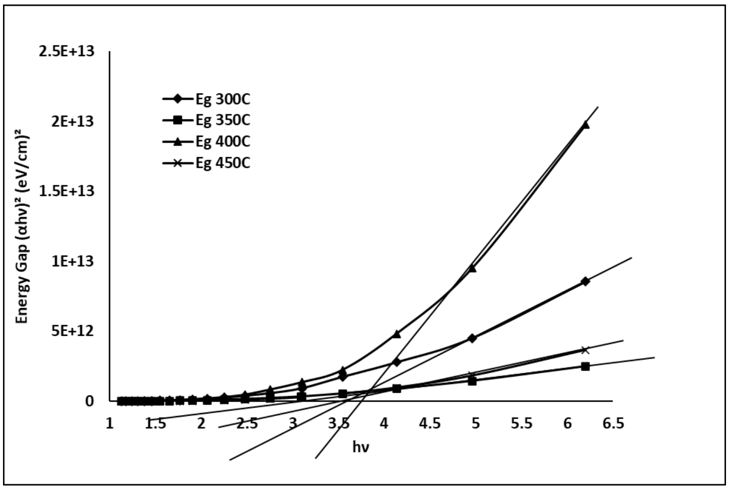

Figure 11: Energy band gap of the CuS thin film at different annealing temperatures (300°C, 350°C, 400°C, and 450°C)

4. SPR SIMULATION RESULTS

The surface plasmon phenomenon can be used for sensing applications by depositing the sensing layer above the plasmonic material. In this part, CuS thin film in Nano-shape was simulated as a second layer above the gold layer, as shown in Figure 1٢(a). By changing the thickness of the CuS layer between 10 and 50 nm, the SPR curve and the resonance angle shift were straightforward and easy to read. Compared to other sensing layers of different kinds of literature [18] [19] [20], this range of thickness variation in the SPR curve looks very interesting, even at 50 nm thickness, which is very difficult to get with other types of material. In Figure 1٢(b), the shift can be recognized toward redshift by changing the refractive index at 50 nm thickness of the CuS. This indication can put the CuS thin film in many sensor applications that need to increase the sensitivity or quality of the SPR sensor. The refractive index values are varied according to the base of preparation [16]; In our research, the n and k are found according to the PLD-based method.

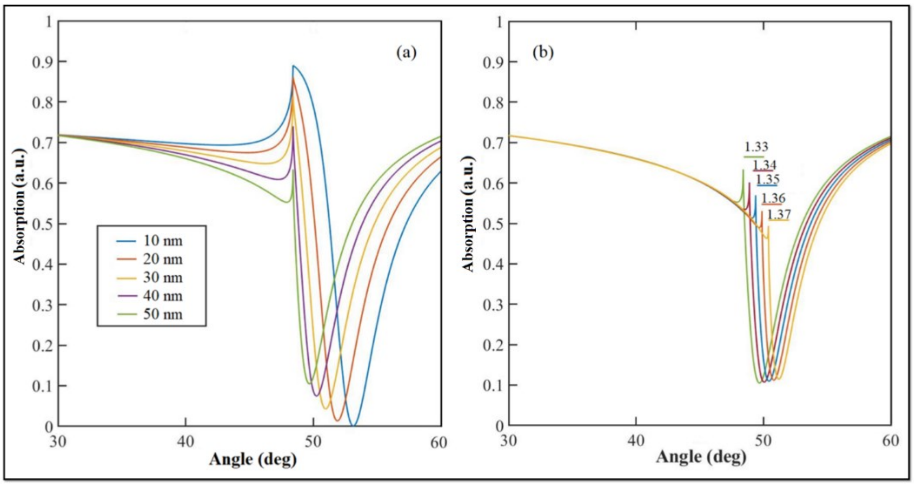

Figure 12: CuS thin film applied theoretically for SPR a) thickness variation b) refractive index variation

5. CONCLUSION

The PLD method showed an easy, fast, and controllable way to deposit CuS thin film using multiple pulsed lasers, followed by annealing processes to 600 mJ specimens. The results show transmittance increased with increasing wavelength before and after the annealing process. The optical band gap is decreased from (3.4 - 4.1) eV before annealing to (3.2 to 3.8) eV after annealing because annealing affects CuS films and makes them flatter. The results show X-Ray from the maximum value at 600 mJ. The SEM image after annealing temperatures shows a substantial variation in particle size and the proportional intensity of X-Ray's work. This result made the CuS (chemical compound) is a suitable material for the SPR sensor application. The thickness and shift were tested under the surface plasmon effect; thickness variation can be distinguished even at 10 nm layer thickness. This test outcome shows a recognizable change in resonance angle with changing refractive index.

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