Study and Prepared of CuS Thin Films by Ultrasonic Nebulizer Method

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Abstract:

Thin Film of copper sulfide with different thickness (100, 200 and 300) nm have been prepared on pre-heated glass substrates up to (330^{o}C) by Ultrasonic Nebulizer Deposition (UND). The effect of thickness on the structural, optical, and electrical properties of films has been investigated. The results of the XRD show that the film which deposited with thickness CuS phase with (103) orientation. Atomic force measurement showed the grain size increase with thickness in the range of (76.91-101.32 nm). The optical properties of the films have been studied over a wavelength (370-1100)nm. The calculated optical energy band gap values were between 2.55 and 2.62eV, depending on the film thickness and in which phase crystallized. The effect of thickness on the electric properties the films have a positive Hall coefficient (p-type), the hall effect increases as thickness increase this due to inversely depend RH on carrier concentration.

Keyword: CuS, Ultrasonic Nebulizer Deposition, electric properties.

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Introduction :

Copper sulfide is a chemical compound of copper and sulfur (I-VI) is an important aterial from the point of basic research, because it is low cost , ease of deposition of good quality films from these materials by a variety of growth methods, known to exist in several crystallographic and stoichiometric forms, special properties and potential applications [1].
Copper sulfide has excellent metallic properties at lower temperature, and readily transforms into superconductors at 1.6 K [2].

CuS generally exists in hexagonal crystalline phase and a primitive hexagonal unit cell with a = 3.8020 and c = 16.430 Å. Importance of CuS in semiconductor materials is because of its nonlinear optical properties [3], excellent solar radiation absorbing properties [4] and high capacity cathode material in lithium secondary batteries [5]. The band gap of CuS can be easily tuned by changing the morphology e.g. CuS microspheres have a band gap of 2.08 eV, CuS nanotubes have a band gap of 2.06 eV, CuS nano flakes have a band gap of 2.16 eV and CuS nanoparticles have a band gap of 1.88 eV, and provide different absorbance edges both in UV and visible region [2].

Experimental Details

Copper sulfide films were deposited onto preheated glass slides (330^{o}C) with different thickness by Ultrasonic Nebulizer Deposition (UND) technique. Copper Chloride salt ($CuCl_2 \cdot 2H_2O$, 134.45g/mol (99.98%) purity, BDH Chemical Ltd Pool England) and thiourea ($CS(NH_2)_2$) 76.33g/mol, 99% purity, BDH Chemical Ltd Pool England) were dissolved in distilled water. The precursor solution of copper sulfide films was prepared by mixed aqueous solution (1:1) of Chloride salt (0.2 M) and aqueous copper solution of thiourea (0.2 M) to make a 0.2 M solution of total metal content. The resulting solution was sprayed onto glass substrates by using an ultrasonic nebulizer system (Sonics). In order to get good quality films and complete combustion all the deposition parameters such as the distance between the substrate and the nozzle, gas flow rate, deposition temperature, and the concentration of the solutions were optimized.

Film thickness (t) measured by weight difference method and optical interferometer method. The optical method was based on interference of He-Ne laser light beam reflected from film surface and substrate bottom by using the known formula:

$$t = \frac{\Delta x}{x} \times \frac{\lambda}{2} \quad \ldots\ldots \quad 1$$

Where x is fringe width, Δx is the distance between two fringes and λ is wavelength of laser light (632.8 nm).

The structural properties of the films by X-ray diffraction (XRD) by PHILIPS PW 1840 diffractometer with Cu Kα radiation (λ= 1.5406 Å) operated by 40 kV and 30 mA. All samples were scanned in the range (20° to 70°) with a scan speed of 5°/min. Surface studies of the samples were done with the help of atomic force microscopy (AFM) type (SPM-AA3000 contact mode spectrometer, Angstrom).

Optical transmission and absorption spectra of the films were wavelength from (370- 900) nm by UV–VIS– NIR spectrophotometer (type Shimadzu).

Results and discussion

Figure (1) indicates that XRD pattern of thin films at different thickness (100, 200 and 300 nm). Films deposited with thickness 100, 200 and 300 nm, had predominantly CuS phase orientated along (103) plane at 2θ=31.7° the peak positions matched with those reported in JCPDS card No 6-464, and another peaks of CuS are (101) and (107). The average crystallite size (G) of the films calculated from the peak (103) for CuS phase using the following relation (Scherer formula) [5]:

$$G = \frac{0.9\,\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots \quad 2$$

Where, λ is the wavelength of x-rays which is equal to 1.5406 Å, β was the full width at half maximum (FWHM) measured in radians and θ is the Bragg angle. The result showed that all values are agreement with standard JCPDS Table (1).

Using d values for CuS phase for the cubic systems, lattice parameter (a_o), (c_o) are calculated with the help of eq. (3) and listed in Table (1).The result showed that the all values are agreement with standard JCPDS [5]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{---------- } 3$$

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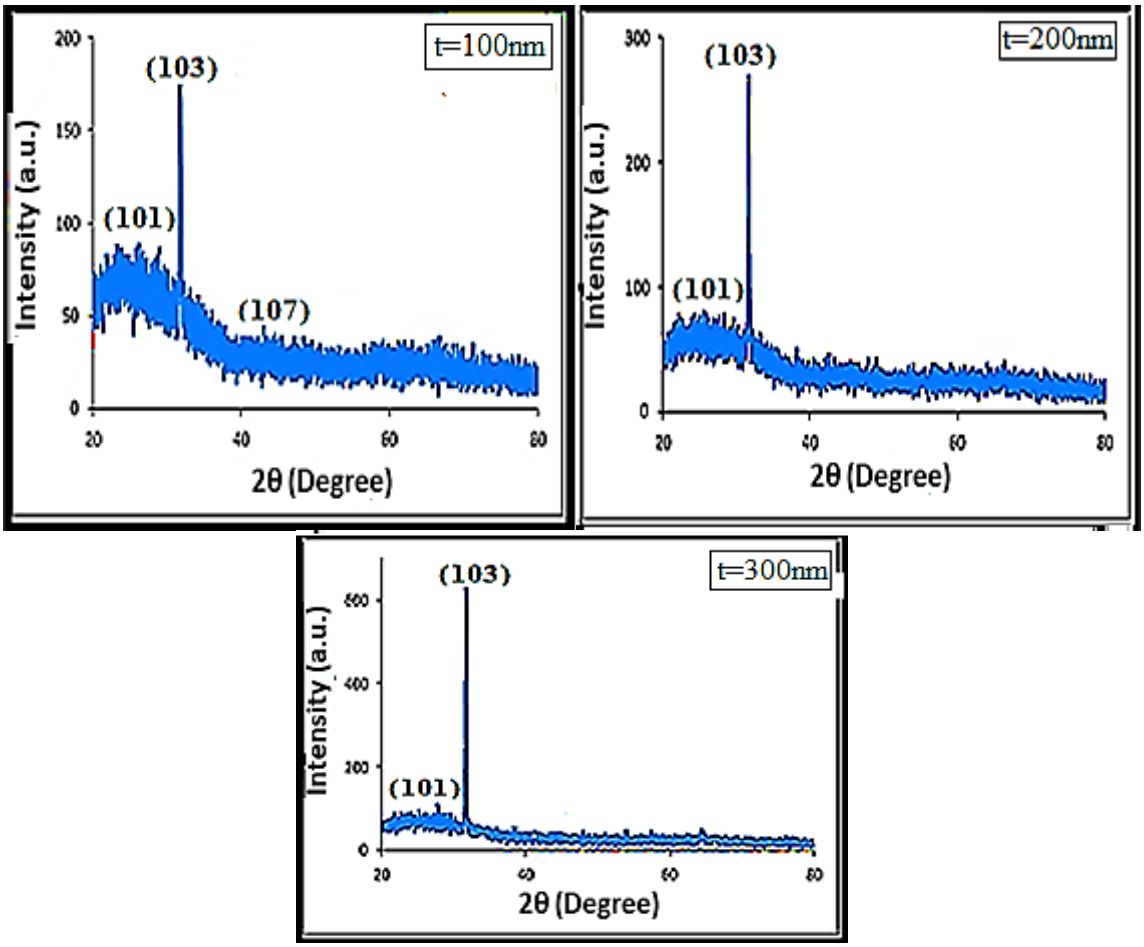

Figure (1) XRD of CuS Thin films at different thickness.

Table (1) The result from the X-Ray diffraction measurement for CuS different thickness.

parameters / Sample		JCPDS	100nm	200nm	300nm
2θ (deg)	**(103)**	31.784	31.745	31.757	31.822
$d_{(hkl)}$ (Å)	**(103)**	2.8100	2.816	2.8154	2.8098
FWHM	**(103)**	-	0.195	0.191	0.138
Lattice Constants	**a_o(Å)**	3.79	3.73	3.825	3.779
	c_o(Å)	16.344	16.9	16.076	16.44
G (nm)	**(103)**	-	42.35	43.2	59.86
Tc(hkl)	**(103)**	-	1.310	1.390	1.590

Atomic force microscopy (AFM)

The figure (2) shown the **images** of (AFM) concern with CuS thin films for different thickness on the glass substrate at temperature (330°C), the table (2) shown the Root mean square (RMS), Roughness and Grain size different with CuS Thickness. The range of grain size values between (78.65-101.32 nm) these values indicate of increase surface roughness comfort into increase the size of all crystalline[6].

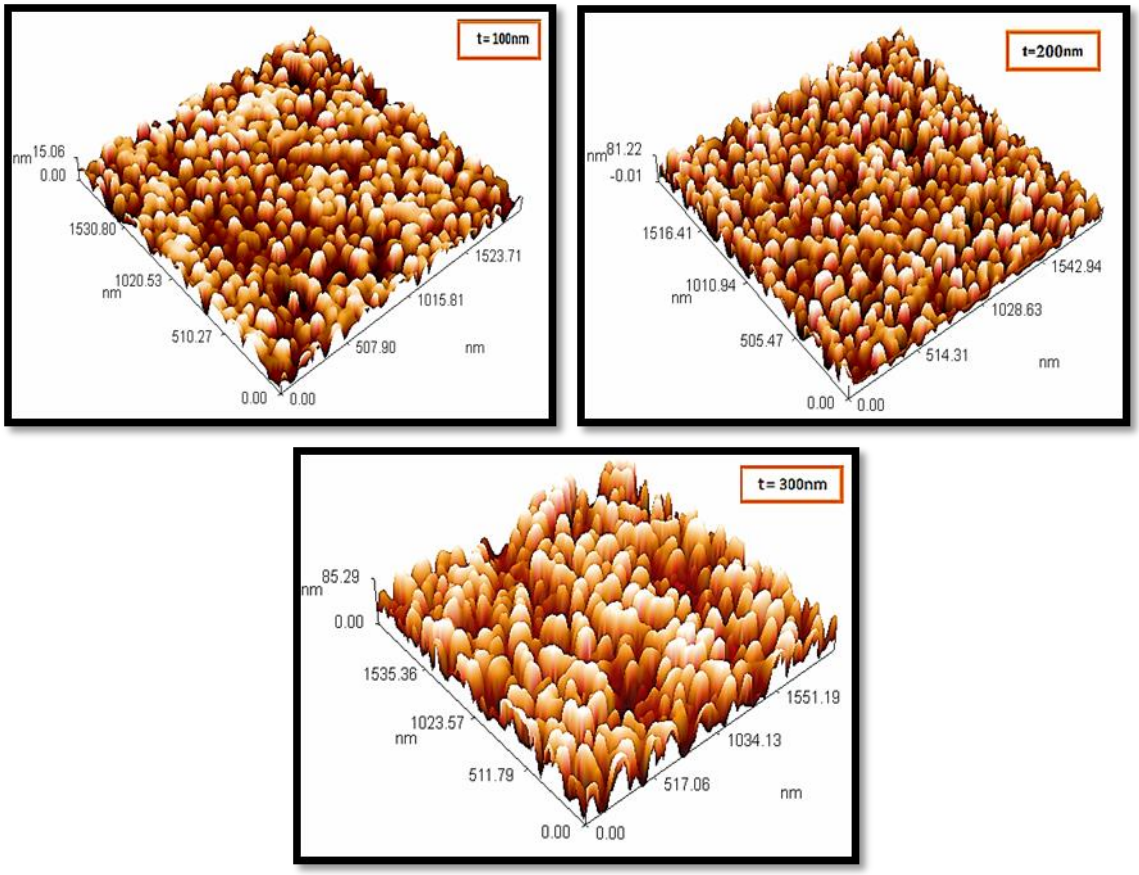

Figure (2) AFM images for CuS films at different thickness

Table (4-14) AFM parameter of CuS different thickness.

Thickness nm	Roughness nm	RMS nm	Grain size nm
100	3 .31	3.89	78.65
200	20.3	23.4	76.91
300	21.2	24.4	101.32

Optical properties:

The optical properties of all thin films at different thicknesses (100, 200 and 300 nm) can be determined by transmittance (T) and absorbance (A) spectrum with in (370-900 nm). Figure (3) and figure (4) shown that the transmittance decreases and absorbance increases as the thickness increase may due to thickness or to absorption coefficient . The absorption coefficient (α) which is a function of the photon energy ($h\nu$) is calculated from the optical transmittance spectra results using following [7]:

$$\alpha = \ln (1/T)/t \quad \ldots\ldots\ldots \quad 4$$

All films as shown in Figure (5) give high absorption coefficient, ($\alpha > 10^5$ cm^{-1}) above the fundamental absorption edge, indicates existence allowed transitions, and the absorption coefficient increase as the thickness increase.
The optical band gap was calculated using following [8]:

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \quad \ldots\ldots\ldots \quad 5$$

Where his the photon energy, E_g energy gap between direct transition , B is a constant depend on type of material and r exponential constant, its value depended on type of transition, r =1/2 for the allowed direct transition, r= 3/2 for the forbidden direct transition. A satisfactory linear fit is obtained for $(\alpha he)^2$ vs. he, indicating the presence of direct allowed transition for thin films. The intercept on the energy axis, as shown in Figures (6), gives the band gap E_g of the material and listed in table (3).

The results showed that the optical band gap increased at increase thickness in CuS thin films [9, 10, 11].

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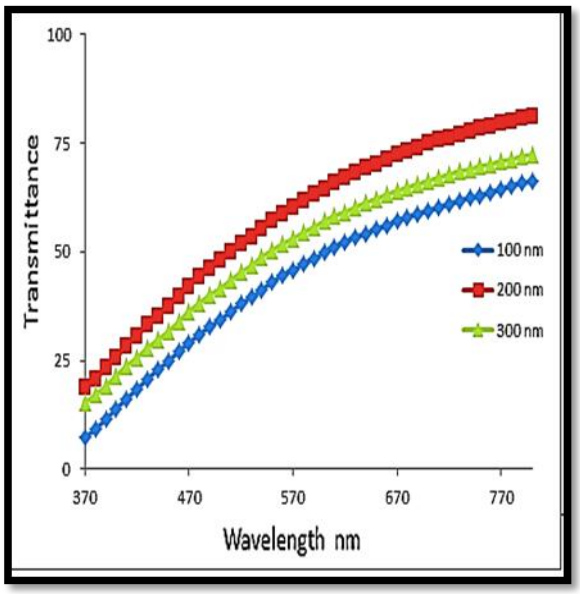

Figure (3) Transmittance as a function of wavelength at different thickness

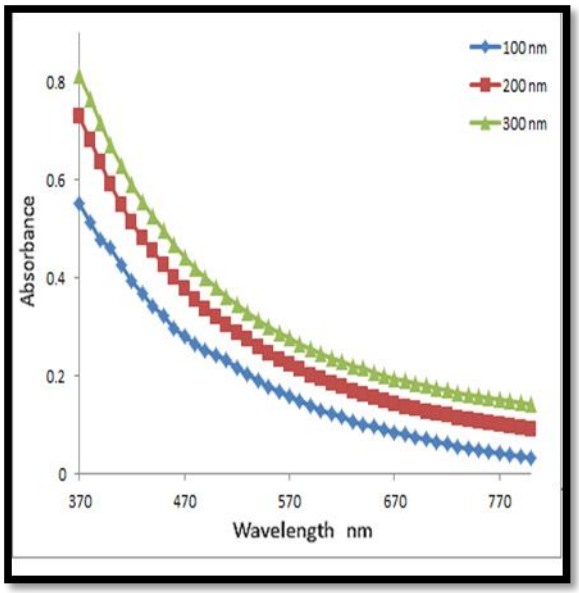

Figure (4) Absorbance as a function of wavelength at different thickness

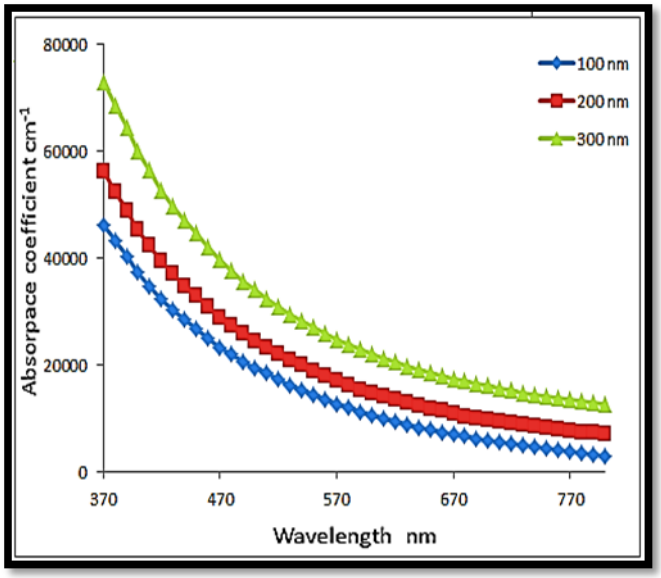

Figure (5): Absorption coefficient as a function of wavelength at different thickness

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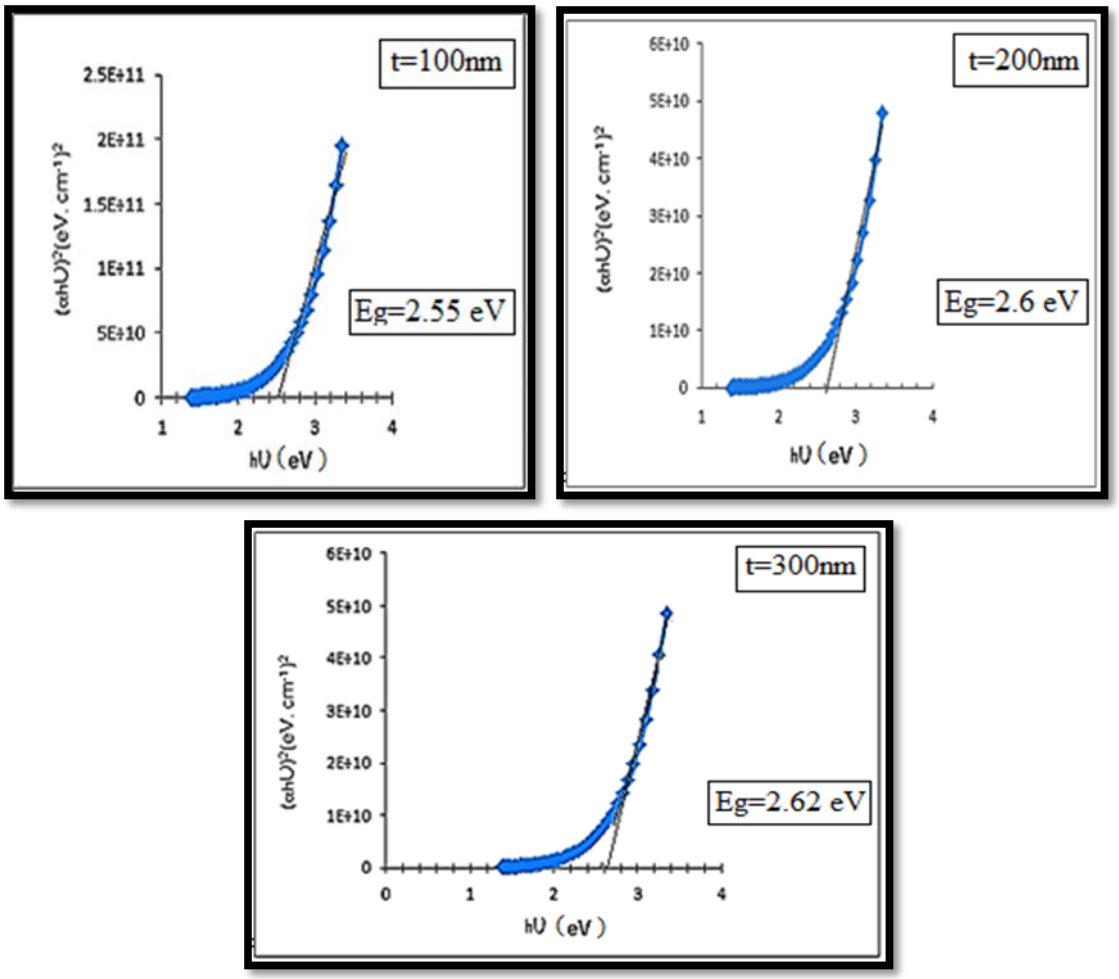

Figure (6) $(\alpha h\nu)^2$ versus photon energy for CuS films with different thickness.

Table (3) Optical band gap for CuS films with different thickness.

Thickness	100nm	200nm	300nm
E_g (eV)	2.55	2.6	2.63

3 Hall Effect Measurement

The type of the charge carrier of the CuS thin films, their carrier concentrations, carrier mobility, Hall coefficient and resistivity has been calculated from Hall measurements.

The results showed that all the films are p-type, and the carrier concentration and carrier mobility decrease, while the Hall coefficient increase as thickness increased, as shown in table (4). The results refer to decreasing mobility that influence with increasing thickness by reason of increasing crystallite film and this leads to increasing resistivity. The hall effect increases as thickness increase this due to inversely depend RH on carrier concentration [12].

Table (4) Hall parameter of CuS thin films

Sample Thickness nm	Carrier Concentration cm^{-3} $x10^{11}$	Carrier Mobility $cm^2/V.\ s$	Resistivity Ohm cm X 10^3	Hall coefficient cm^3/C $x10^6$
100	852	1.398	0.549	0.071
200	27.1	0.78	2.96	2.30
300	12.3	0.48	10.6	5.07

Conclusion

CuS thin films were successfully deposited by Ultrasonic Nebulizer Deposition (UND) onto glass substrates at temperature (330^{o}C). The XRD spectrum shows that all films are polycrystalline. Pure CuS can prepare by Ultrasonic Nebulizer Deposition (UND) with thinner thickness. According to AFM results the Grain size range values between (76.91-101.32 nm), the direct energy band gaps of the films were determined as (2.55 -2.65 eV).

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تحضير ودراسة اغشية CuS الرقيقة بطريقة الترذيذ بالموجات فوق السمعية

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الخلاصة

تم ترسب اغشية رقيقة من كبريتيد النحاس وبسمك مختلفة (100، 200 و 300) نانومتر على قواعد زجاجية مسخنة الى درجة (330^oC) عن طريق الترذيذ بالموجات فوق السمعية. تأثير السمك على الخواص التركيبية ,البصرية والكهربائية. اشارت أنماط حيود الأشعة السينية إلى أن اغشية CuS لها تركيب سداسي متعددة البلورات وباتجاهية (103). واظهرت نتائج مجهر القوة الذرية زيادة الحجم الحبيبي مع زيادة السمك ضمن المدى nm(76.91-101.32). درست الخصائص البصرية للأطوال الموجية nm(370-1100) , حساب فجوة الطاقة وقيمها بين (2.55-2.62eV)، تعتمد على سمك الغشاء وطور البلورة. تأثير السمك على الخصائص الكهربائية للأغشية تمتلك حاملات شحنة (p-type)، وان تأثير معامل هول يزداد بزيادة السمك بسبب الاعتماد العكسي R_H على حاملات الشحنة.

المصطلحات الرئيسة: CuS, الأغشية الرقيقة, الترذيذ بالموجات فوق السمعية UND.