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# Thickness dependent structural, optical and electrical properties of chemical bath deposited $Cu_2SnS_3$ thin films

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**Abstract:** $Cu_2SnS_3$ thin films of different thicknesses were prepared onto the glass substrate by chemical bath deposition technique at the deposition temperature of 323 K. X-ray diffraction pattern reveals that all the thin films prepared are polycrystalline in nature and crystallized in cubic structure with preferential orientation along (111) direction. The crystallite size increases from 17 nm to 22 nm with increase of film thickness. Morphology of the films as observed from the SEM indicates the presence of spherical particles. EDAX analysis shows that the films prepared are nearly stoichiometric without much deviation. From the optical spectra the nature of transition were found to be allowed and direct. The transmission of the film was found to decrease with increase of film thickness. The band gap energy decreased from 1.45 to 1.36 eV on increasing the film thickness. Electrical conductivity increased with increase of deposition time and the sheet resistances of the films are in the order of megaohms.
**Keywords**: $Cu_2SnS_3$, thin film, UV-vis, Electrical properties.

## Introduction

$Cu_2SnS_3$, a I-IV-VI group compound is one of the most attractive ternary absorber material for thin film solar cells due to its direct band gap (0.93-1.51 eV) and high absorption coefficient ($10^4$ $cm^{-1}$). $Cu_2SnS_3$ elements are found to be nontoxic and abundant in the crust of the earth. It is a p-type semiconductor with band gap and optical absorption coefficient similar to that of CZTS ($Cu_2ZnSnS_4$) material which is currently being comprehensively studied in the photoelectronic field. The control of composition and phase structure in $Cu_2SnS_3$ compound is more convenient due to its fewer elements compared with CZTS[1]. Owing to these properties, $Cu_2SnS_3$ is considered to be a suitable material for application in low cost and environmentally friendly thin film solar cells. Many experimental techniques have been employed for preparing Cu–Sn–S compound thin films: sequential chemical deposition, solvothermal processing, solid-state reaction, spray pyrolysis, sputtering, chemical bath deposition and electrodeposition[2-10]. Among them, the chemical bath deposition method is highly attractive since the technique possesses a number of advantages over conventional thin film deposition methods. The main advantages of this method are low cost, low deposition temperature and easy coating on large surfaces. The method is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. Therefore, attempts were made to prepare $Cu_2SnS_3$ thin films by chemical bath deposition method and to investigate its optical and electrical properties by varying the deposition time.

## Experimental

All the reagents obtained from Merck were of analytical grade and are used without any further purification. Chemical bath deposition method was used to deposit $Cu_2SnS_3$ thin films onto amorphous glass substrates at 50°C. Thin films of copper tin sulfide were prepared from a base bath (pH=10.0) using copper sulphate ($CuSO_4$) as a copper ion source, sodium thiosulphate ($Na_2S_2O_3$) as a sulfide ion source, tin chloride ($SnCl_2 2H_2O$) as a tin ion source and ethylene diamine tetra acetic acid (EDTA) used as a complexing agent. The stock solution of 0.2 M copper sulphate was added to the 20 ml of deionized water and stirred until the clear solution is obtained. Then the stock solution of 0.2 M of ethylene diamine tetra acetic acid was dissolved in 10 ml of deionized water and 0.2 M of sodium thiosulphate was dissolved in 20 ml of deionized water and were added to the as prepared copper sulphate solution. Again the 20 ml of 0.2 M tin chloride was added to the above solution. The pH of the solution was adjusted to10 by adding few drops of ammonia. The mixed solution was kept at a temperature of 323 K. Substrates were then immersed vertically in the solution. Thin films of different thicknesses are prepared by varying the deposition time (30, 45 and 60 minutes). Influences of thickness on the properties of films are carried out in our work. After completion of film deposition, the deposited films were rinsed with deionized water and dried in air for further characterization. The thickness of the deposited film was determined by a weight difference method.

The structural studies of the chemical bath deposited $Cu_2SnS_3$ thin film samples were done by using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation (λ=1.5406A°). The morphological and compositional analysis of the film were carried out using JEOL mode JSM 6390 SEM with EDAX and optical studies of the samples were done using spectrophotometer Jasco corp. V-570 which allows measurement in the spectral range 200-2500 nm with 1 nm resolution. Electrical resistivity was measured by the four-point probe method.

## Result and discussion

### X-ray diffraction pattern

XRD pattern of $Cu_2SnS_3$ thin films prepared at different thicknesses are shown in Fig. 1 (a-c). It is clear that the thickness plays an important role in determining the structure of the films. The XRD peaks appear super imposed on the XRD profile of the glass substrate, which is indicated by broad signal in the range $20^o$ to $35^o$. The XRD pattern also reveals that the intensity of the peak is increased with the increase of thickness. The film (Fig.1a) prepared at 30 minutes appear to be microcrystalline in nature with smaller peaks at 2θ equal to 28.53°, 47.42°, 56.19° corresponding to the planes (111), (220) and (311). The XRD pattern of the film (Fig.1b) prepared at 45 minutes shows improvement in peaks. On further increase of deposition time to 60 minutes, large improvement in peaks is observed from the Fig. 1(c). It is observed that the intensity of the peaks increase with increase of deposition time/thickness. The crystallite size is calculated using Scherrer's formula for the most preferred orientation along (111) direction. The crystallite size of the films increased from 17 nm to 22 nm with increasing deposition time from 30 minutes to 60 minutes. The intensity of the peaks increases with increase of film thickness and full width half maximum (β) decreases, thereby leading to an increase in crystallite size.

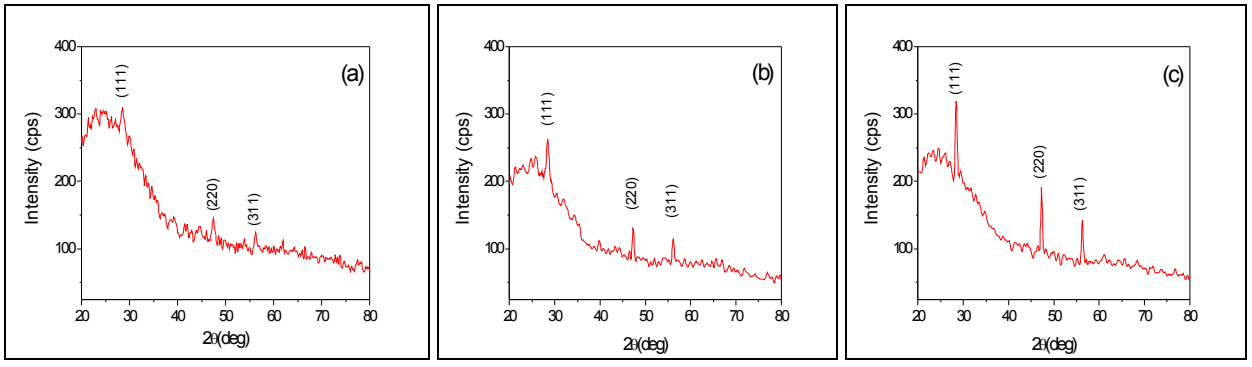


**Fig. 1. XRD spectra of $Cu_2SnS_3$ thin films of thickness a) 247 nm b) 451 nm c) 623 nm**

Structural parameters of $Cu_2SnS_3$ thin films were tabulated in Table 1. The result shows dislocation density and strain of the film decreases with increasing film thickness. The lattice parameter value 'a' was found to be a=5.55 nm for 247 nm, a=5.53 nm for 451 nm and a=5.57 nm for 623 nm. The observed results are in good agreement with the standard JCPDS data (Card No. 89-2877) thus confirming the presence of cubic structure. In literature, various crystal structures have been reported such as monoclinic by Onoda et al. [2], triclinic by Li et al. [3], hexagonal by Wu et al. [9], cubic by Fernandes et al. [10] and tetragonal by Chen et al. [11].

**Table 1. Structural parameters of $Cu_2SnS_3$ thin films**

| Deposition time (min) | Film thickness (nm) | 2θ (Deg) | Crystallite size D (nm) | Dislocation density δ ($10^{15}$ lines/$m^2$) | Strain ε ($10^{-3}$ m) | Lattice parameter (Å) | |
|---|---|---|---|---|---|---|---|
| | | | | | | JCPDS | Observed |
| 30 | 247 | 28.53 | 17 | 3.4602 | 2.1081 | a = 5.53 | a = 5.55 |
| 45 | 451 | 28.51 | 20 | 2.5000 | 1.5710 | | a = 5.53 |
| 60 | 623 | 28.54 | 22 | 2.0661 | 1.2401 | | a = 5.57 |

**SEM analysis**

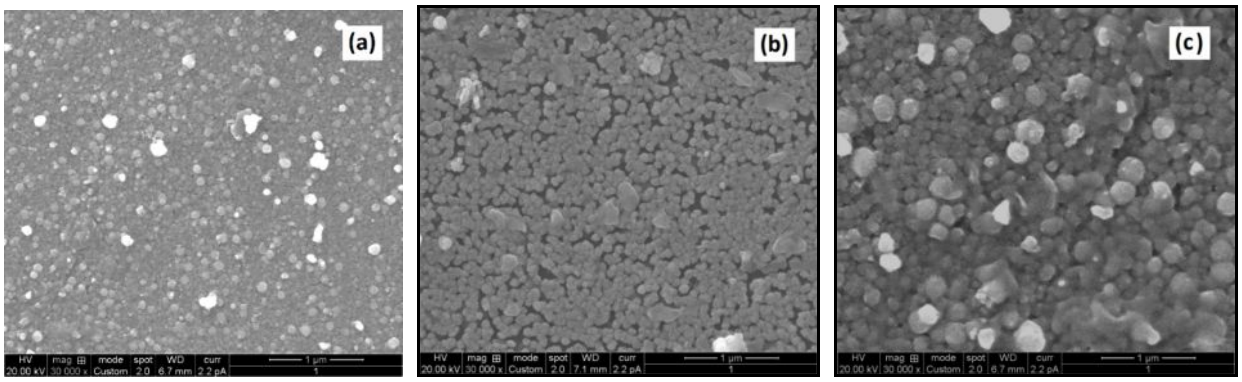


**Fig. 2. SEM Micrographs of $Cu_2SnS_3$ thin films of thickness a) 247 nm b) 451 nm c) 623 nm**

In order to study the surface morphology, the films are examined by the SEM technique. The scanning electron micrographs of the $Cu_2SnS_3$ thin films of different thicknesses on glass substrate at various deposition times are shown in Fig. 2 (a-c). It is observed that all the films are homogeneous and have dense microstructures. The film surface looks smooth and uniform. It is well clear from the micrographs that the particles are spherical and adherent. It can be seen that these spherical grains are uniformly distributed to cover the surface of the substrate completely. From the micrographs it is observed that the size of the grain increased with increase in deposition time as evinced by the XRD spectra.

**Compositional analysis**

The elemental analysis of the $Cu_2SnS_3$ thin films deposited at different deposition time on glass substrate is carried out by energy dispersive X-ray analysis (EDAX) technique. The respective EDAX spectra are shown in Fig. 3 (a-c). EDAX analysis indicates the presence of copper, tin and sulfur for all the deposited films. The stoichiometric ratio of Cu, Sn and S were computed by integrating the area under each Cu, Sn and S peak.

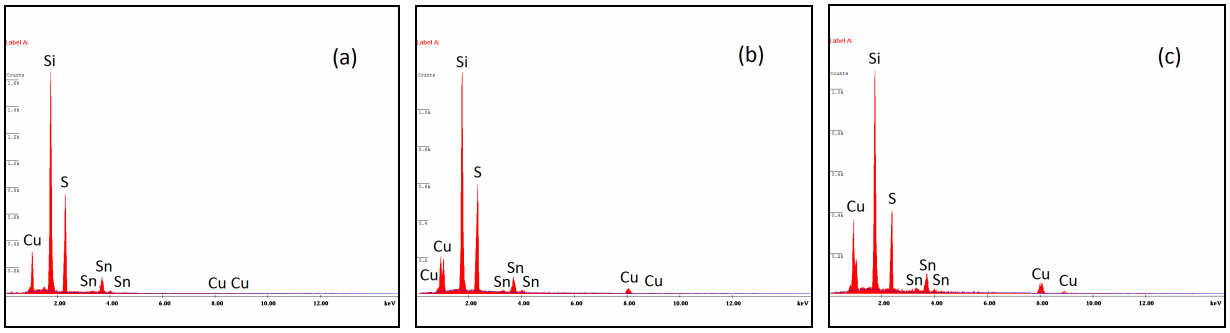


**Fig. 3. EDAX spectra of $Cu_2SnS_3$ thin films of thickness a) 247 nm b) 451 nm c) 623 nm**

Atomic percentage of Cu, Sn and S in $Cu_2SnS_3$ thin films for different thickness and the corresponding standard values are shown in Table 2. The film prepared at 45 minutes is found to be nearly same as that of standard value. It is also worth mentioning that the stoichiometric composition of the three film samples did not change significantly. EDAX spectrum also shows that prepared films are free from impurities. The presence of silicon is due to the glass substrates.

**Table 2. Atomic percentage of Cu, Sn and S in $Cu_2SnS_3$ thin films**

| Deposition time (min) | Standard | | | Calculated | | |
|---|---|---|---|---|---|---|
| | Cu | Sn | S | Cu | Sn | S |
| 30 | 33.33 | 16.67 | 50.00 | 32.18 | 18.78 | 49.04 |
| 45 | | | | 33.72 | 16.95 | 49.33 |
| 60 | | | | 34.054 | 17.01 | 48.94 |

**Optical analysis**

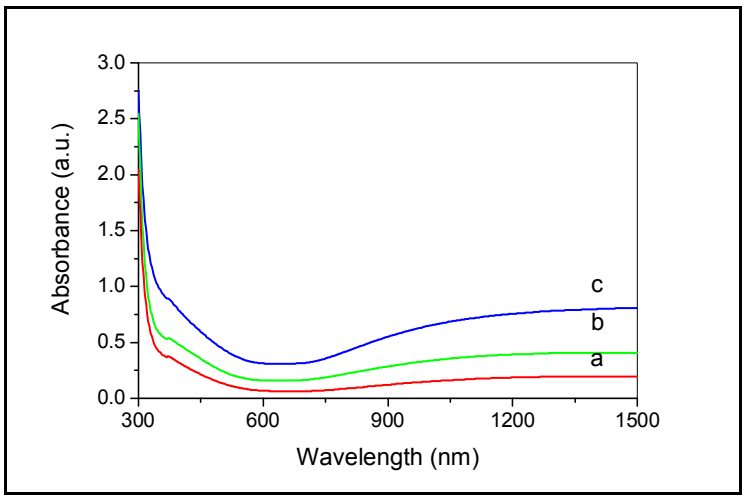


**Fig. 4. Wavelength Vs Absorbance of $Cu_2SnS_3$ thin films of thickness** a) **247 nm b) 451 nm c) 623 nm**

The optical properties of the films deposited on glass substrates for different deposition time are determined from the absorbance and transmittance measurements in the range 300-1500 nm. Fig. 4 shows the absorbance spectra for $Cu_2SnS_3$ thin films of varying film thicknesses deposited at different deposition time. $Cu_2SnS_3$ film of 623 nm thickness has high absorbance (Fig. 4 a) when compared to lower thickness films, i.e. absorbance increases with film thickness.

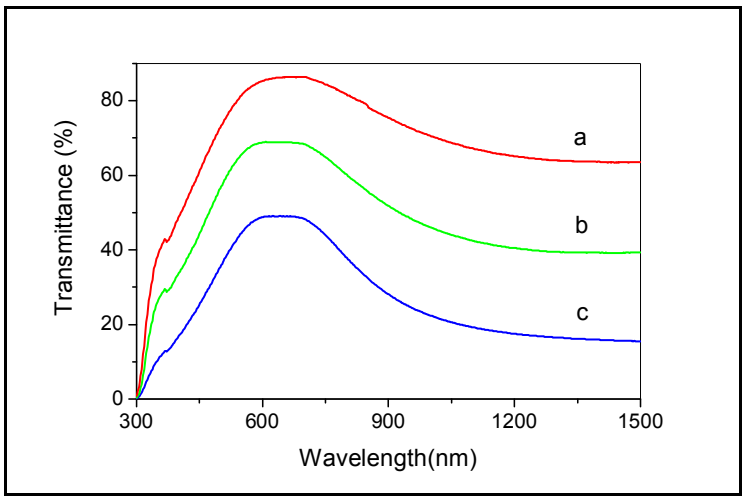


**Fig. 5. Wavelength Vs Transmittance of $Cu_2SnS_3$ thin films of thickness** a) **247 nm b) 451 nm c) 623 nm**

The optical transmittance spectra of $Cu_2SnS_3$ thin films of different thicknesses measured as a function of wavelength of incident photons is shown in Fig. 5. The transmission spectrum (Fig 4 b) demonstrates that the films are highly transparent in the visible region. The transmission curves shift toward lower values of wavelength by decreasing the film thickness, indicating that the reduction of thin film thickness leads to an increase of the optical band gap. The band gaps have been determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ graph and is shown in Fig. 6 (a-c) for different film thickness of $Cu_2SnS_3$ thin films. Extrapolating the straight line portion of the plot of $(\alpha h\upsilon)^2$ against $(h\upsilon)$ to energy axis for zero absorption coefficient ($\alpha = 0$) gives optical band gap energy. The linear nature of the plots indicate the existence of the direct transitions. It is found that the band gaps of the 247, 451 and 623 nm thickness $Cu_2SnS_3$ samples are 1.45, 1.41 and 1.36 eV, respectively. Film thickness together with the energy band gap shows that these films can be used as potential absorbers in solid state solar cells.

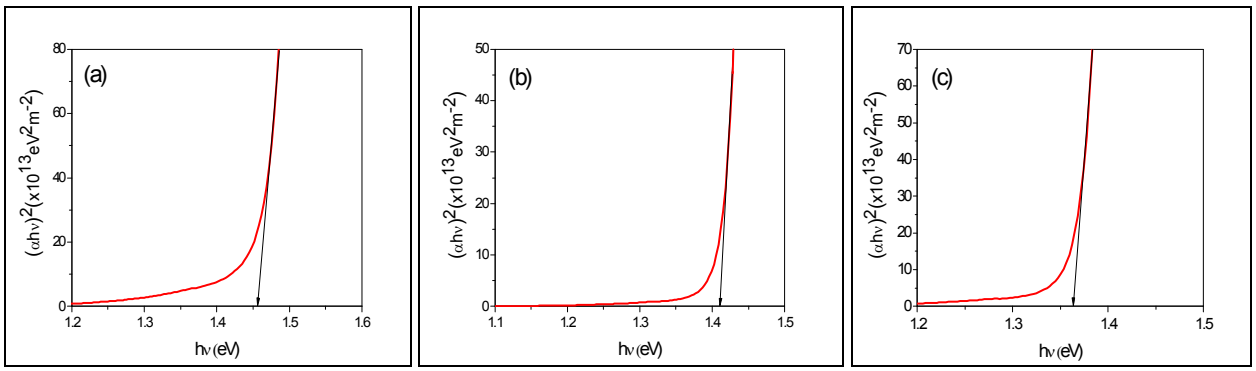


**Fig. 6. Plot of $(\alpha h\upsilon)^2$ Vs $(h\upsilon)$ of $Cu_2SnS_3$ thin films of thickness** a) **247 nm b) 451 nm c) 623 nm**

## Resistivity studies

The electrical measurements on $Cu_2SnS_3$ thin films for different thicknesses are made using four point probe technique and the resistance-temperature measurements show that the films behave as a typical semiconductor. Variation of sheet resistance and resistivity with different film thicknesses at room temperature are shown in Fig. 7 and 8. The decrease of sheet resistance and resistivity with increase of film thickness are found to be in agreement with the literature datas [12] and the reason may be that the electrical resistivity of nanocrystalline thin film decreases with increase in film thickness because for very thin films, there are islands of aggregated particles with lot of insulating gaps [12]. As thickness increases the islands of aggregated particles transform into continuous bands. So the insulating gaps are minimized with increase in film thickness.

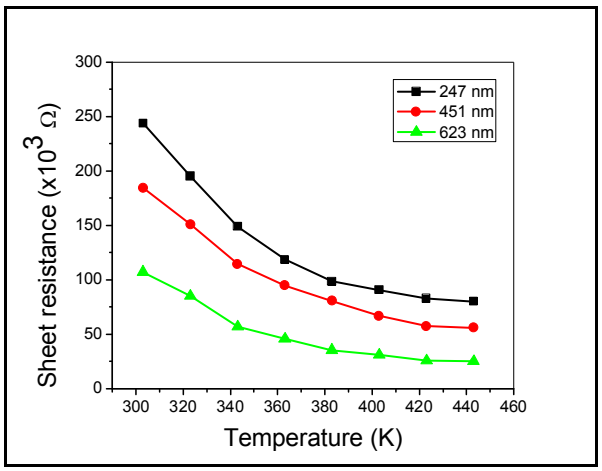


**Fig. 7. Sheet Resistance Vs Temperature of $Cu_2SnS_3$ thin films of different thicknesses**

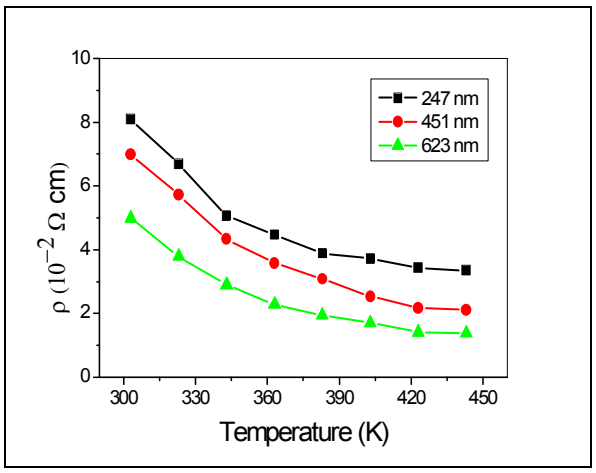


**Fig. 8. Resistivity Vs Temperature of $Cu_2SnS_3$ thin films of different thicknesses**

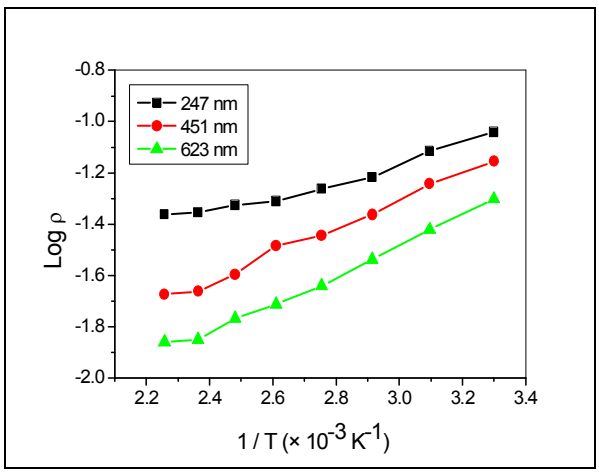


**Fig. 9. Logρ Vs 1000/T of $Cu_2SnS_3$ thin films of different thicknesses**

The decrease in sheet resistance and resistivity linearly with increase in temperature indicates the semiconducting behavior of the material. The high resistivity for the thinner films could also be attributed to the lattice defects and dislocations in the thin films and can be explained on the basis of Sondheimer's theory [13] that the scattering of carriers at the surface of the film effectively reduces the mean free path of the carriers, so that the resistivity decreases with increase in film thickness. From the plot of logρ against 1000/T (Fig. 9), the activation energy of the film could be determined. The activation energies calculated for different thicknesses are 0.54, 0.42 and 0.35 eV. The decrease of activation energy with increase of film thickness may be due to the

increase in grain size of $Cu_2SnS_3$ thin films and may also be due to the change in barrier height caused by the grain size variation with increase of film thickness as suggested by Slater's model [14]. An alternate explanation for higher value of activation energy for thinner films may be given qualitatively on the basis of island structure theory suggested by Neugebaur [15].

## Conclusion

Cubic structured $Cu_2SnS_3$ thin films of different thicknesses were prepared onto the glass substrate by chemical bath deposition technique at the deposition temperature of 323 K. XRD studies revealed that the crystalline size of the films increases with increase of thickness. Morphological analysis shows that the films are homogeneous and well covered to the substrate. Composition of the films as observed from the EDAX spectra are found to be nearly stochiometric without much deviation. From the optical measurements, the band gap of the films decreases with increasing deposition time. Decrease of activation energy with increase of film thickness is observed from resistance-temperature measurements.

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