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THE INFLUENCE OF TEMPERATURE AND CONCENTRATION OF SOLUTIONS TO PHYSICAL PROPERTIES OF Cu_xS NANOPARTICLES

L. GAHRAMANLI[a*], M. MURADOV[a,*], O. BALAYEVA[b], G. EYVAZOVA[a], N. DADASHOVA[a]
[a]*Chemistry Department,Baku State University, Z. Khalilov str., 23, AZ-1148, Azerbaijan*
[b]*Physics Department,Baku State University, Z. Khalilov str., 23, AZ-1148, Azerbaijan*

Copper sulfide -Cu_xS nanoparticles has been synthesized in thin films of polyvinyl alcohol polymer (PVA) matrix by successive ion layer adsorption and reaction (SILAR) method. The effect of the concentration of solution (0.1M and 0.25M) and the ambient temperature (25°C and 50°C) on formation process of nanoparticles was studied. For studing of the thermal annealing effect on nanocomposites which samples had been prepared at 25°C temperature (70 °C and 100° C) for 4 hours were annealed in the vacuum oven. The structure, morphology, elemental analysis and optical properties of the samples were investigated by X-ray diffraction (XRD), UV-Vis spectrophotometer and Scanning Electron Microscope (SEM).The band gap value has decrease as a result of the growth of particle size due to the increasing of the concentration and number of growth cycle of the sample.

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1. Introduction

One of the main members of semiconductor family is copper sulfide (Cu_xS)thin films have p-type semiconductivity [1-3]. Copper sulphide compounds are used in the preparation of solar cell elements [4-6], energy-converter devices [7], fluorescent devices [8], microwave protective coatings and lithium ion batteries [9,10]. Copper sulfide is used as photovoltaic converter of solar energy, electroconductive electrodes [6,11], electro-conductive coatings, catalysts, optical filters [8,12], as well. As Cu_xS is highly effective and economically advantageous and it is estimated to be one of the materials that can be replace Cu (In, Ga) Se_2 thin films, recently used in solar cell elements. It has been possible to achieve up to 10% efficiency of CuS based solar cells. But on the other hand, resistance has emerged as an important issue [13]. Changing of x index ($1 \leq x \leq 2$) of the Cu_xS combination causes the formation of different stoichiometry compounds [7]. At room temperature, Cu_xS has covellit (CuS) [14], anilith ($Cu_{1.75}S$) [15], digenite ($Cu_{1.8}S$)[16], djurleit ($Cu_{1.95}S$) [16], chalcocite (Cu_2S) [15], and yarrowite ($Cu_{1.12}S$) [17] compounds. The direct band gap of chalcocite phases varies between 1.3-1.5 eV [18]. The anilite($Cu_{1.75}S$) combination of copper sulfide has high stability and band gap value is E_g=1,4eV [3].

In formation of CuS nanoparticles are used different method such as microwave irradiation method [19] , molecular template method [20], spray pyrolysis [4,21], photochemical precipitations [22], solvothermal [9], hydrothermal [12], vacuum evaporation [23], chemical bath deposition [24,25], successive ion adsorption and reaction methods [1,6,7,26,27], sonochemical [28] and etc.The SILAR method is one of the methods of chemical deposition, which was first introduced in 1985 [2]. The SILAR method is more convenient than other methods with simplicity, process speediness, economic efficiency and can be applied at room temperature, as well as requiring no special devices and tools.

* Corresponding author: qahramanli.lala@mail.ru

It is important to study of the dependence on temperature and concentration in the particles formation as well the affect on changing of the temperature and concentration at the sorbtion and particle's growth process (speed of growth, crystal structure, etc.).The main purpose of the present work is to investigation of the effects of parameters of crystallization environment (temperature, concentration) on formation of copper sulfide nanoparticles in PVA matrix,as well the effects of thermal annealing on the physical properties of nanocomposites.

2. Experimental

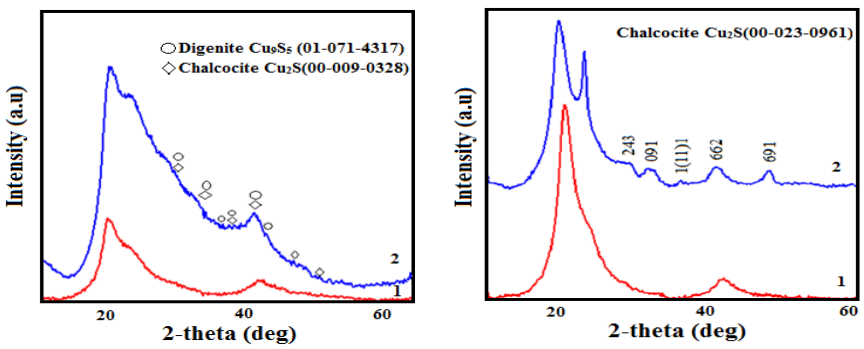
Copper sulfide nanoparticles have been formed in the polymer matrix using by SILAR method. PVA was used as polymer matrix. PVA film is easily dissolved in the water. At the experiment, the solution of copper sulfate ($CuSO_4 \cdot 5H_2O$) as cation source, the solution of sodium sulfide ($Na_2S \cdot 9H_2O$) as anion source and ethylene glycol were used as solvent and washing agent.

Two concentrations of $CuSO_4 \cdot 5H_2O$ solution (0.1M and 0.25M) were used to investigate the effect of the concentration of reaction on the formation of nanoparticles. Adsorption duration was chosen for 30 min. After the polymer film was removed from the solution, it was washed twice with ethylene glycol for cleaning electrolyte residues on the surface of samples. PVA has a porous structure, therefore CuS nanoparticles are formed in these pores beside the functional groups and this reduces the likelihood of spontaneous growth of nanoparticles. In order to increase the density of adsorbed copper sulfide nanoparticles within the PVA matrix , the process should be repeated for several periods: 3; 7 and 11 cycle. Samples were obtained at room temperature and at 50°C temperatures for study the effects of ambient temperature on the formation of nanoparticles. The termal annealing of the samples were carried out in the vaccum oven at 70°C and then again at 100°C for 4 hours. Properties of samples were investigated before and after thermal annealing.

XRD measurements were performed using a monochromatic CuKα radiation (λ = 1.540600 Å) in a Rigaku Mini Flex 600 X-ray diffractometer.The optical properties were investigated with Ultraviolet-visible (Specord 250) spectrophotometer. For to determine morpology and element analysis-energy-dispersive X-ray analysis (EDAX) were studied by SEM (JEOL JSM-7600F).

3. Results and discussion

XRD pattern of CuS / PVA thin films obtained at room temperature (25^0C) and 50^0C using 0.1M of Cu^{2+} ions after 3 and 7 cycles have been shown in Fig.1. The XRD result of same cycled, but two different concentrated of CuS/PVA samples and annealed at 100^oC have been shown in Fig. 2.



a) *b)*

Fig.1.The XRD results of 0.1M of CuS/PVA thin films.

a) 3 cycle - at room temperature (1) and 50^0C (2); b) 7 cycle - at room temperature (1) and 50^0C (2)

The XRD results show that, structure and stoichiometric composition of the Cu_xS nanoparticles changes depending on parameters of crystalization medium (concentration, reaction temprature, number of growth cycles and temperature of thermic annealing). In the low concentrations of solutions (0.1M), there are no observed crystal structures in the samples of Cu_xS, which had been formed at the room temperature (25^0C) (Fig.1.a (1), b(1); Fig.2.a(1), b (1)).Copper sulfide nanoparticles were started to form crystalline structure with increasing of reaction temperature from 25^0C to 50^0C. The XRD results show that, in 3 growth cycled 0.1M concentrated sample at 50^0C temperature were formed mixture of digenit $Cu_{1.8}S$ (01-071-4317) and chalcocite Cu_2S (01-072-0617) structures of copper sulfide (Fig 1.a(2)) in polymer matrix. In 7 growth cycled 0.1M concentrated sample at 50^0C is formed chalcocyte (Cu_2S) structure of copper sulfide in polymer matrix. The five peaks with 2Θ values of 29.2^0, 30.3^0, 37.5^0 47.6^0, 51.06^0 correspond to (243), (091), (1(11)1),(662), (691) planes of chalcocite Cu_2S(00-023-0961) have been observed (Fig 1.b (2)).

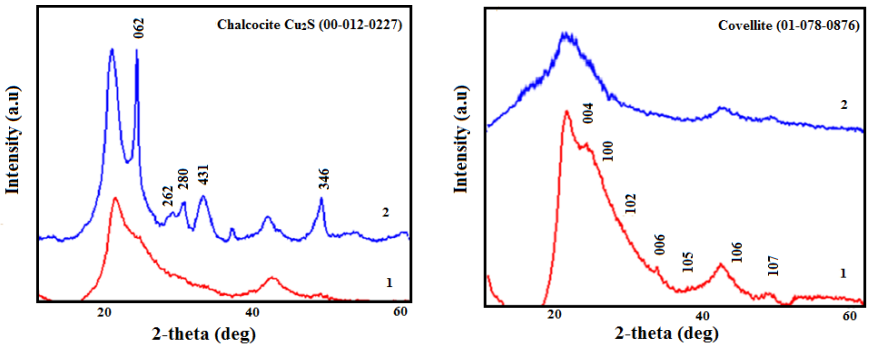


Fig.2. The XRD result of same cycled two different concentrated CuS/PVA samples (11 cycle a) 0.1M- at room temperature (1), and 50^0C (2); b) 0.25M – at room temperature (1) and thermal annealed at 100^0C (2)

The peaks which belong to Cu_xS nanoparticles appear due to increases of number of cycle (11 cycles). From results appears that, in 50^0C temperature 11 cycled 0.1M concentrated sample compatible with to chalcocite (Cu_2S) structure of copper sulfide in polymer. The XRD pattern exhibit slightly deviation prominent peaks at 2Θ values of 23.6^0, 28.11^0, 29.8^0, 32.5^0,48.45^0. These results are in agreement with corresponding to the (062),(262),(280),(431), (346) plans which are compatible with (00-012-0227) standards (Fig 2.a(2)). In 0.25M concentrated sample with 11 cycles is observed the simple covellite phase of copper sulphide nanoparticles. The spectra is observed that the major diffraction peaks with 2Θ values of 20.9^0,27.1^0, 29.5^0, 32.9^0, 37.3^0, 41.8^0correspond to respectively, (004),(100), (102),(006),(105),(106),(107), planes which are compatible with (01-078-0876) standards (Fig.2.b(1)). It can be considered that, as a result of the increased concentration of the sample occurs different modifications (covellit, digenit, chalcocyte) of copper sulfide. The factors which have a positive effect on the crystallization process and growth of nanoparticles size can be considered as an increase in the amount of anion and cation ions that are sorbitated, as well as increased temperature and concentration. Besides, it should be noted that change in concentration and temperature of solutions influence to the chemical potential of solution and the anions and cations in the particle which has been formed [29].This causes the formation of different modification of Cu_xS nanoparticles.

In XRD results of the thermal annealed (100^0C) of 0.1M concentrated sample (11 cycle) was observed peaks which belong to copper sulfid and copper sulfate (Fig.3.2). We can explain formation of copper sulphate at thermal annealing that, the functional groups in the polymer bonds hold oxygen, under the influence of the temperature oxygen atoms have entered crystals and as chemical composition have been formed oxygenated compounds.

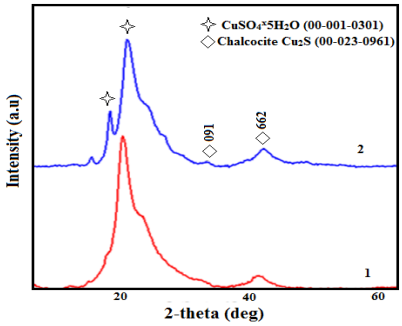


Fig. 3. The XRD result of thermal annealed (100^{0}C) of 0.1M of CuS/PVA samples 1)3 cycle; 2)11 cycle.

Particles average size were calculated by Debay Sherrer equation (1) from XRD [13].

$$D=0.9\lambda/\beta\cos\alpha \quad (1)$$

D-is average particles size, β-is full at half maximum value, λ-wavelength of X-ray and α-the angle of Bregg.

Table 1.Average size of nanoparticles.

Number of cycles and Cu^{2+} ions concentration	Cu_xS / PVS, XRD $D_{(nm)}$		
	Medium temperature		Thermal annealing
	25°C	50°C	100°C
3 cycle 0.1M	5.62	10.53	-
7 cycle 0.1M	16.85	16.88	12.05
11 cycle 0.1M	9.37	16.88	19.38
11 cycle 0.25M	7.02	-	3.67

As the reaction temperature increases, cause of formation of large particles is explained by the increasing of movement speed of ions which involved in the reaction. In this case, the crystallization speed increases and growth of particles accelerates.When the concentration of ions is 0.25 M, the initial sorbum is weak and the active centers of the polymer are not completely caught.When the concentration of metal ions is 0.1M, the diffusion rate of ions in the solution increases, the active centers of the polymer have been used more in the nucleation process. At 0.25 M of solution, are observed the process of growth at the next cycles and re-nucleation process in the active centers. Therefore, the average size of the particles has been reduced by the increase in the concentration of ions in the solution. On the contrary, it has gone in 0.1M solution. In the first cycle, the nucleus is full, and in the next cycles only the growth has occurred. At the same concentration, as the number of periods increases particle size has been increase at room temperature. But since the system was unstable at the next cycle growth process has not continue. On the contrary, it has fragmented and become stable. This situation also occurred when the sample was thermal annealed at 100°C. At same concentration, as the number of periods increases (at 50°C) temperature, particle size increases. At the same concentration (thermal annealing), the smaller particle grew and larger particles reduced. The increasing of size of small particles after thermal annealing can be explained by their large surface energy. Because of the collapse of the polymer by the influence of the temperature, the small particles are passes through easily to free case and aggregated by joining each other. After thermal annealing in the 7 cycle , decrease of the

large particles size are related to destruction of the polymer by the effect of the temperature, the reduction of large particles to the certain size and become energetically stable.

The value of band gap were calculated by following equation (2). The particle size of samples were given in Table 1.

Table 2.Band gap values of CuS/PVA thin films.

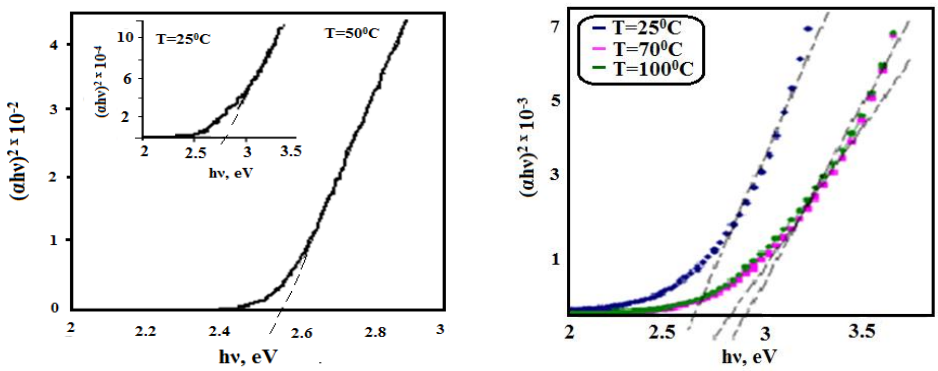
Number of cycles	E_g of CuS/PVA		
	Medium temperature	Thermal annealed	
	(25°C)	70°C	100°C
3 cycle 0.1M	2.8	-	-
7 cycle 0.1M	2.75	2.82	2.90
11 cycle 0.1M	2.42	2.64	2.52
11 cycle 0.25M	2.38	2.33	2.27

Optical absorption spectrum of samples were measured in the 300-800 nm wavelength range. The values of band gap were calculated as follows (2).

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

Where,
A- is a constant, dependent on optical transitions; E_g - is optical band gap of the sample;
h - is Planck constant; ν - is the frequency of falling rays; α- is absorption coefficient;
n- is characterized by type of optical transition [7].

The band gap value of samples are shown in Fig.4 and Fig.5.



a) *b)*

Fig.4. The band gap energy of 0.1M of CuS /PVA thin films
a) 3 cycles at different growth temperature (25^0C,50^0C);
b) 7cycles at 25^0C and thermal annealing (70^0C, 100^0C).

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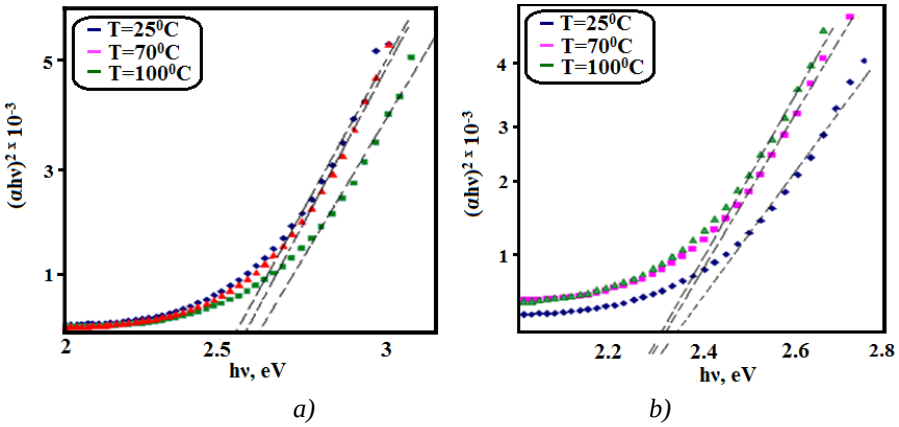

Fig. 5.The band gap energy of 11 cycled CuS /PVA thin films at 25^{0}C and thermal annealing (70^{0}C, 100^{0}C) a) 0.1M; b) 0.25M.

The band gap value of samples and particles size calculated according to band gap values are shown in the Table 2 and Table 3. As seen from Fig.4, the band gap value has decrease as a result of the growth of particle size due to the increasing of the concentration and cycle number of the sample. The band gap value of 0.1M of CuS / PVA (7 cycles) was increased when, thermal annealing were carried out at 70^{0}C and 100^{0}C. In the 11 cycles this value increased at 70^{0}C, then reduced at 100^{0}C. 0.1M of CuS / PVA (7 cycle) was decreased at 70^{0}C and 100^{0}C. Initially band gap value of samples which prepared at 25^{0}C temperature (11 cycles) was increased (at), then after thermal annealing at100^{0}C reduced. That can be explained that at 70^{0}C temperature, occurs the oxidation of the surface of the particles and the reduction of the particle size.When the temperature is 100^{0}C the polymer softens, then particles in the pores are merged, and consequently the size of the particles grows. In 0.1M concentration, as increasing of period number as 3-11 cycle, the band gap value are declined.This is due to an increasing of particles size.

In subsequent thermal annealing , the increasing of band gap value can be explained by increasing of free movement of electrons due to the influence of temperature and the increasing of distance between the valence zone and the conductive zone.when the number of cycles is eleven in 0.25M concentration, as a result of thermal annealing, decreasing of band gap value can be explain by the increasing of the particles size.

Table 3. Average sizes of particles in CuS / PVAthin films from band gap value.

Number of cycles	Nanoparticles size of PVA / R_{nm}		
	Medium temperature	Thermal annealed	
	(25°C)	70°C	100°C
3 cycle 0.1M	7.55	-	-
7 cycle 0.1M	6.6	6.36	6.28
11 cycle 0.1M	9.9	9.45	9.75
11 cycle 0.25M	11.1	11.5	11.75

As seen from Table 1 and Table 3, the particles size calculated by XRD results are less than the particles size calculated from band gap value. This is due to the following facts: XRD shows crystallites size, however the measured according to the band gap values is the size of the electrons localization.When calculating the particles size by the change of band gap values are used the effective mass of carries of bulk crystals.However in nanoparticles this value is different from bulk crystals [30].

EDAX analysis was applied to determine the chemical composition of synthesized copper sulfide nanoparticles. SEM analysis was investigated in order to determine morphology of samples. In Fig.6 results of SEM analysis shows that, average size of nanocomposites are approximately 101 nm, 113 nm, 153 nm, respectively. These values are very large than the values obtained from XRD results. In the SEM image are observed as larger particles as a result of coagulation of smaller copper sulfide nanoparticles.

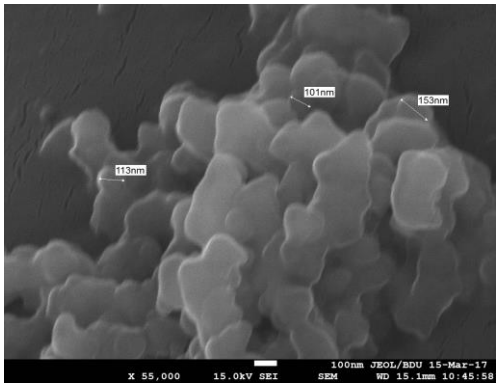

Fig. 6. SEM analysis of 11 cycles 0.25M of CuS/ PVA.

As can be seen in Fig. 7, atomic percentages of Cu and S ionsare 12.3% and 10.3%, respectively. The ratio of obtained copper sulfide is Cu / S=1.19 , because it has been formed in different composition. This value show that, by the quantity of CuS is dominated in composition.

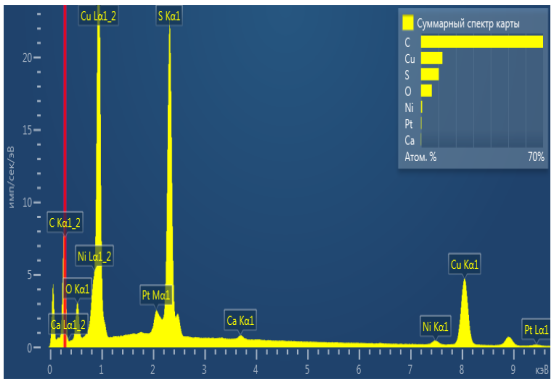

Fig 7. EDAX result of 11 cycles 0.25M of CuS/ PVA.

4. Conclusions

Cu_xS nanoparticles were formed on PVS polymer matrix using successive ionic layer adsorption and reaction method.The influence to sample concentration and ambient temperature on the formation of nanoparticles has been studied.The average size of the particles has been reduced by the increase in the concentration of ions in the solution.The band gap value has decrease as a result of the growth of particle size due to the increasing of the concentration and cycle number of the sample.Finally, average size of copper sulfide nanoparticles from SEMresults are determined approximately 113 nm. From EDAX results have been determined,the ratio of obtained copper sulfide is Cu : S=1.19.

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