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Synthesis of Novel Nanoparticles by Using «Europium Instead of Indium in the Conventional CIS Composition for Photovoltaic Application»

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Eu has been placed instead of In in Cu-In-S2 which is used for CIS solar cells and effect of different capping agents on composition, size, distribution and morphology of the nanoparticles was investigated by scanning electron microscopy equipped with energy dispersive X-ray and transmission electron microscopy with the corresponding selected area electron diffraction pattern.

Keywords: Cu-Eu-S_2, Nanoparticles, SEM, TEM, CIS solar cells, capping agent, Table of samples.

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1. INTRODUCTION

Low cost production of solar cells on flexible substrates using printing or other technologies is promising highly cost efficient alternative to traditional Si-based solar cells. Recently, solution based solar cells fabricated from copper, Indium and sulfur have been developed [1].

One of the most conventional researched materials for thin film solar cells is CuInS2 (CIS) [2, 3].

For CIGS solar cells we have to put some layers on a substrate such as sodalime glass or flexible materials. In our case the first layer is Mo and the second layer is CIS nanoparticles and the latter is ZnS window and the next layer is ZnO window and the next one is an anti reflex coating such as MgF_2 and for electric connection we should have a Al/Ni layer as the last layer.[4]

A nanoparticle based CIGS ink has great utility for low cost web coating of ink based photovoltaic cells.

The ideal band gap of a solar cell is known to be 1.4 eV, and the band gap of $CuInS_2$ (E_g = 1.5 eV) is well-matched to the AM0 solar spectrum for photovoltaic performance [1, 5].

This paper concentrates on a new nanoparticle, which obtains with addition of the element Europium to the common ternary composition of CIS used as absorber material in solar cells.

In this study, the new Cu-Eu-S nanoparticles were synthesized by very fast and easy way of co-precipitation at room temperature. This new composition have been selected because of the photoluminescence properties of Europium.

Size, distribution and morphology of nanoparticles depend to type and amount of capping agent or surfactant in the solution.

2. DESCRIPTION OF APPROACH AND TECHNIQUES

2.1 Procedure of nanoparticles preparation

Conventional ternary CIS nanoparticles ($CuInS_2$) may be fabricated according to a chemical reaction of the form:

$(CuCl + InCl_3 + Na_2S + Pyridine \rightarrow CuInS_2)$

The same reaction in which the formation of the Eu-containing nanoparticles occured would have the form of:

$CuCl + EuCl_2 + Na_2S + Pyridine \rightarrow CuEuS_2$

Copper chloride and Europium chloride have been dissolved in ethanol with 0.8 to 1 molar ratio. The concentration of In and Cu in solution can be between 5 to 10 milimolar , here this quantity is 5 milimolar. Sodium sulfide salt have been dissolved in ethane, separately. Since the molar ratio of Sulfur atoms should be two times the amount for Copper and Europium atoms, therefore the concentration of sulfur should be 10 milimolar for equal amount of solutions. In following the surfactant would be added to the first solution and then it would be placed on a stirring device and addition of second solution would perform while stirring. The mentioned reaction occurred as the second solution added and it was obviously observable because of the color changing of solution. Different samples had different colors. Details of the solutions has been reported in Table 1.

After production of nanoparticles, each solution was centrifuged to gathering and separating the sediments and then the nanoparticles were washed with toluene to dissolve the additional material accompanied with the nano particles and to increase the purity of the final powder.

Table 1 – **S**amples details

Sample	Partial concentration of In in Cu-In solution (mM)	Partial concentration of S in Sulfur solution (mM)	Partial concentration of Cu in Cu-In solution (mM)	Amount of capping agent (gram)	Capping agent	Solution color
A	5	10	5	0.1	pyridine	brown
B	5	10	5	0.05	pyridine	brown
C	5	10	5	0.2	pyridine	Opaque blue
D	5	10	5	0.01	PEG	Opaque blue
E	5	10	5	0.01	CTAB	Clear brown

Finally the powder would be dissolved in pyridine because it is a volletile material and in the sintering process of coating would leave the surface so there won't remain any pollution of undesired materials.

3. CHARACTERIZATION TECHNIQUES

The influence of three different capping agents (according to Table 1) on the composition, size, distribution and morphology of the nanoparticles was investigated by scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) with The corresponding selected area electron diffraction pattern.

4. RESULTS AND DISCUSSION

The distribution of copper, Europium and sulfur elements in all samples using EDAX analyzer were shown in Fig. 1. The images illustrates that there is no uniform distribution for sample A, but however the density of sulfur atoms is two times the amount for Europium and Copper atoms. For B sample there is obviously a more uniform distribution of the mentioned atoms but not better than sample E. The distribution of samples D and C is uniform and better than other samples.

The SEM results of samples were shown in Fig. 2. The bright areas refer to the nanoparticles sediments and the dark areas refer to the sub layer of specimens. SEM image of sample A in resolution × 500 illustrates that the nanoparticles have been agglomerated and it is impossible to determine single particles but bright points are distributed all over the samples that their size is too much smaller than 1 µm. In SEM image of sample B in resolution × 1000 the bright points are more visible and also there is some cracks in the pictures

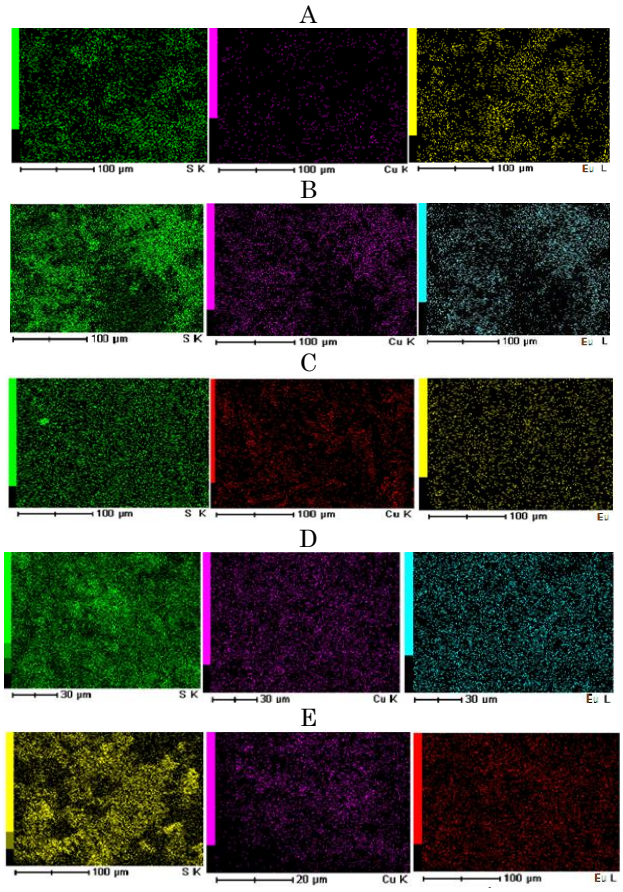

Fig. 1 – EDX analysis of nanoparticles with different a) Sample A, b) Sample B, c) Sample C, d) Sample D, e) Sample E

that been formed while drying of specimen. From the SEM image of sample C in resolution × 2500 illustrated that the growth mechanism of particles haven't become arrested and the particles size is yonder nanomaterials borders. The average size of these particles is about 5 µm. A lateral rose shape has been formed in sample D and the particle size is more than nano domain and therefore the particles are not in the category of nanoparticles. The resolution of this image was ×

2000. In SEM image of sample C in resolution ×1000, bars with average length of 30 µm and average diameter of 10 µm can be observed.

Electron diffraction pattern of samples A and B by transmission electron microscope in Fig 4-4 shows the o-ring pattern which is characteristic of nanostructure particles and pattern feature affirms the formation of $CuEuS_2$ phase in particles.

Fig. 3 illustrates images of nanoparticles of sample A and B have been prepared with a transmission electron microscope. These pictures indicate that the average size of nanoparticles are almost 20 nanometer for both samples A and B. the nanoparticles in sample B have been agglomerated.

Electron diffraction pattern of samples A and B by transmission electron microscope in Fig. 4 shows the o-ring pattern which is characteristic of nanostructure particles and pattern feature affirms the formation of $CuEuS_2$ phase in particles.

5. CONCLUSION

The Results shows the variation of morphology and composition by different capping agent. Using EDX analysis the existed elements in the resulting powder and their distribution, were obtained. The results have shown that the nanoparticle phase is the exact expected composition of sulphide. Homogenous distribution of Eu in sample C is shown in Fig. 1.

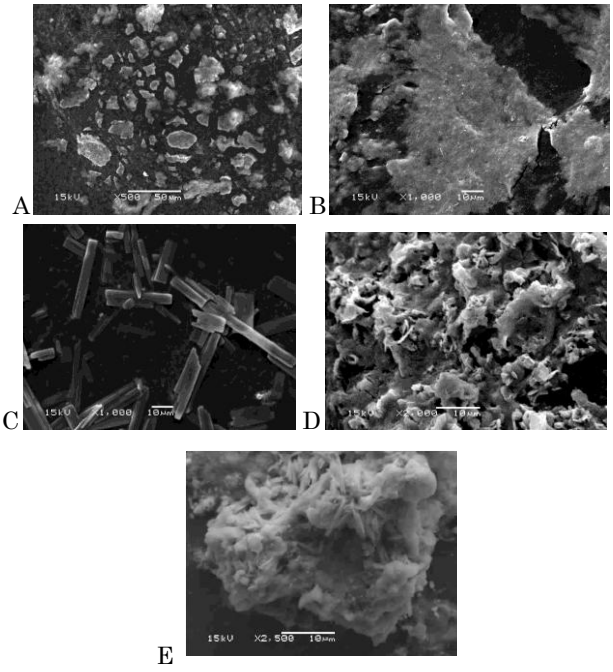

Fig. 2 – SEM images of a) Sample A, b) Sample B, c) Sample C, d) Sample D, e) Sample E

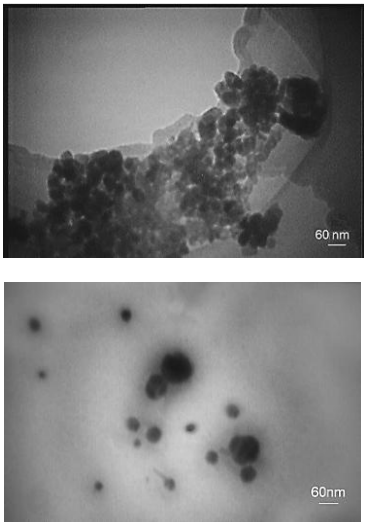

Fig. 3 – Images of samples A and be obtained from TEM

SEM analysis have been done for investigation of the particles size and morphology the results in Fig.4-2 indicate the formation of course rod in sample C and irregular shape in sample D but agglomerations of tiny spherical particles in other samples. A transition in morphology from speherical particles to rod shape

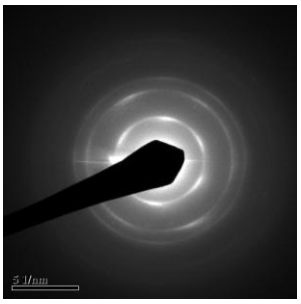

Fig. 4 – Diffraction pattern of sample A by transmission electron microscope

occurred by addition of CTAB instead of pyridine. Addition of PEG leads to formation of Irregular morphologies like rose-like morphology. Increasing in pyridine amount leads to reduction in size of nanoparticles

Electron diffraction pattern of sample C by transmission electron microscope in Fig. 3 shows the o-ring pattern which is characteristic of nanostructure particles and pattern feature affirms the formation of $CuEuS_2$ phase in particles.

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