NANOPARTICLE SIZE EFFECT ON WATER VAPOUR ADSORPTION BY SS-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0.1)

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Based on the results, we can confidently state that SS-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0.1) with nanosize reacts to both light and moisture. Because of these properties, chalcopyrite crystals can be used to create light-emitting diodes, photo detectors, solar cells, and humidity sensors. Humidity sensors utilize changes in the physical and electrical properties of a sensitive material (SS) when exposed to the atmospheric humidity conditions of a surrounding area.

Keywords: nanoparticle, vapor adsorption, humidity sensors, Schottky barrier.

INTRODUCTION

At present, researchers are showing particular interest in semiconductors that can compete with conventional photo converters based on silicon and gallium arsenide. At the moment, the $CuInSe_2$ ternary compound is the most promising among these semiconductors [1–12]; it can be used for solar cells and compete with silicon and gallium arsenide. $CuInSe_2$ is a semiconductor with a band gap of 0.96*eV*; it falls into A^IB^{III} diamond like semiconductors that are characterized by the presence of a chalcopyrite structure. Intense interest in $CuInSe_2$ and solid solutions on its basis has been aroused owing to the fact that the complex electron energy spectrum and the anisotropy of the optical properties give the possibility to use chalcopyrite crystals for designing light emitting diodes, photo detectors, solar cells, and coherent and incoherent sources of polarized radiation [1].

Note that the possibility of varying the structure and chemical composition of $CuInSe_2$ and the synthesis and doping conditions provides for the controlled preparation of materials with a wide range of physical characteristics, such as their band gap, the energy position of the emission bands, the conductivity type, and the electric conductivity. This fact can be of interest, because chalcopyrite is a fairly cheap and available material [13].

In recent years, has become more urgent question of creating materials that would simultaneously possess magnetic, optical and semiconductor properties [1-5]. In our previous articles was shown that, the introduction of atoms of transition elements with unfilled 3*d*-shell in ternary semiconductor type $A^1B^{III}C_2^{VI}$ results in new materials, saving the presence of a chalcopyrite structure that combine both semiconducting and magnetic properties [14]. In the literature is known that introduction of the manganese atoms in the compound $A^1B^{III}C_2^{VI}$ made it possible to obtain materials with Curie temperature of 350*K* [1-4]. Intensively also conducted research on the effect of manganese and iron atoms on the properties of ternary compounds $A^1B^{III}C_2^{VI}$ for creating high-performance solar energy converters. However, despite high values of efficiency ~20.3% of solar cells-based film Cu (In, Ga) Se_2 as compared with other semiconductor materials, this value does not match the theoretically expected ~30% for this class of materials. Reasons for this are multi-component chemical composition, the lack of accurate data on many important fundamental parameters of materials, limited and contradictory information about the nature of their own growth defects in these semiconductors and their energy levels in the forbidden zone, determining the recombination processes. Of course, the further development of the physics of semiconductors with the chalcopyrite structure can be an important step in improving technology and efficiency values approaching ~ to the theoretical 30%.

It has high absorption coefficient combined with excellent thermal stability in air [l]. Due to this fact, 90% of the photons are absorbed in a thickness of 1 μm, which makes a CIS film thickness of l-3 μm good enough for thin-film solar cell applications.

Moreover, electrostatic charging is familiar to most persons, but knowledge on this topic is still rather empiric, 1-3 mainly because fundamental ideas on the structure of matter are not well connected to the phenomenology of insulator charging. [4-12]. Some work shows that water adsorption and desorption modify charge status of solids. The insufficiency of current knowledge on electrostatic charge mechanisms is not restricted only to the materials area: current geophysical research has not yet disclosed effective models for atmospheric cloud electrification, [15] but there is growing evidence on the ability of water to accumulate excess charge [16]. Thus, the rates of charge dissipation and accumulation are dependent on adsorption-desorption rates that in turn depend on the nature of the surface, on the atmospheric relative humidity, and temperature.

Creation of novel alternative energy generation processes is of major importance in nowadays conditions of extreme electricity consumption [1]. Water is the one of the main conventional sources of alternative energy used by mankind. Its liquid phase is traditionally used for the kinetic into electric energy conversion by so-called hydropower plants [17].

With the development of nanotechnology, the implementation of these ideas becomes potentially possible. Nowadays it is known that gas adsorption (including water vapor) can generate electric charges on metal surfaces [17]. Due to the interaction of gas molecule with a metal film of nanometer thickness <10*nm* the so-called "hot" electrons can occur and ballistically *i.e.*, without the loss of energy reach a Schottky barrier, cross it through kinetic energy, and by entering into the semiconductor material create an electric current in the external chain. However, efficiency of the conversion method is limited by a low number of "hot" electrons (10^{-3}–10^{-5}) generated per an interaction act.

Moreover, a small cross-section of free charge carriers in semiconductor crystals leads to a decrease of the conversion efficiency. Thus, the electric field (of heterojunction) decays drastically with an increase of the distance from the surface even for a few interatomic distances, therefore, only a small fraction of gas can act effectively at the heterophase process on the front surface of a semiconductor crystal. From this aspect it is of high interest to use dielectric materials with a developed surface area. We expect the electrostatic field of dielectric materials to exceed significantly the electric field of heterojunction and consequently leads to an increase of conversion efficiency.

EXPERIMENTAL DETAILS

Mikro-nano powder of SS-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ (*x*=0.1) were mixed in magnetic stirrer during 20 min with dissolved in water PVC (polyvinyl chloride), 1/20 ratio in order to obtain homogenous suspension. We take dielectric substrate with Pd-Cu electrodes. The distance between electrodes was 1and 2mm (fig.2). Before dropping on it the suspension the substrates were cleaned in the ultrasonic bath machine during 10min in propyl alcohol solution. Synthesis of SS is the same as an article [14]. The reaction for humidity and light were verified using Digital-to-analog convertor. Electric properties of obtained humidity sensors were investigated using *VICTOR-VC9808* multimiter on a direct current in the dynamic mode. Each measurement has been repeated three times. Related humidity was varied 20 ÷ 95%. For humidity measurement the *CENTER 311 RS*232 Meter was used. Mass fractions of humidity in samples under various conditions of saturation were measured useing *CPA225D* (Sartorius) gravimetric balances on powder hinge plates of 1g.

RESULTS AND DISCUSSION

According to *TEM* microscopy the size of *SS* particles were around 50*nm*-1000*nm* (Fig.1) and from the *X*-Ray analysis [14] *SS* remain chalcopyrite structure of $CuInSe_2$ with different band gap energy~1.04*eV*.

The difference in the size of the particles can be explained by the fact that after the solid solutions were synthesized, they were grounded in a planetary mill, which caused agglomeration.

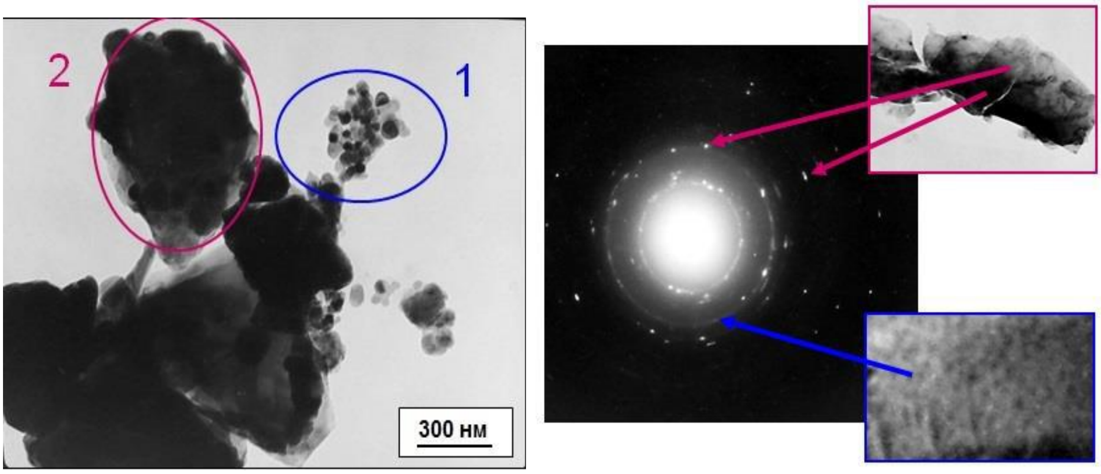

*Fig.1.*TEM image of *SS*
1-50*nm*; 2-1000*nm*

Fig.2. Investigated samples
a-Pd-Cu 1mm   b-Pd-Cu 2mm

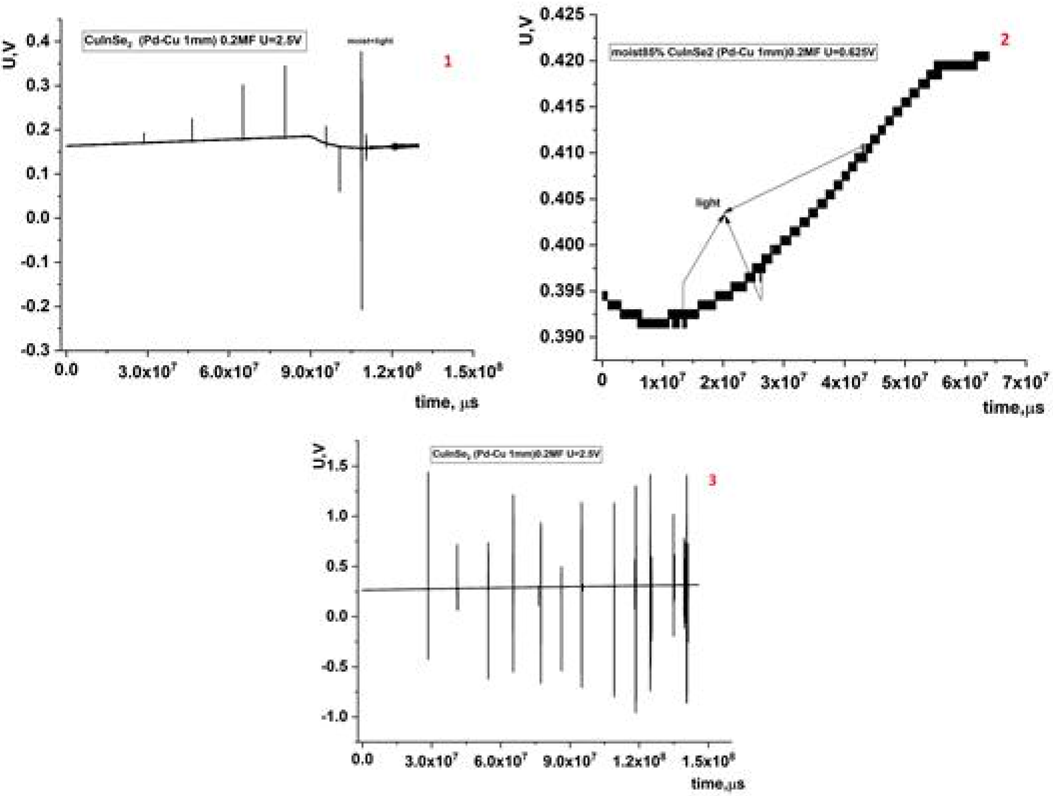

Fig.3. Reaction on light and moisture $CuInSe_2$
1-$CuInSe_2$ (U=2.5V) with instant moisture and light; 2- $CuInSe_2$ (U=0.625V) 85% moisture and light;
3- $CuInSe_2$ (U=2V) with instant moisture and light

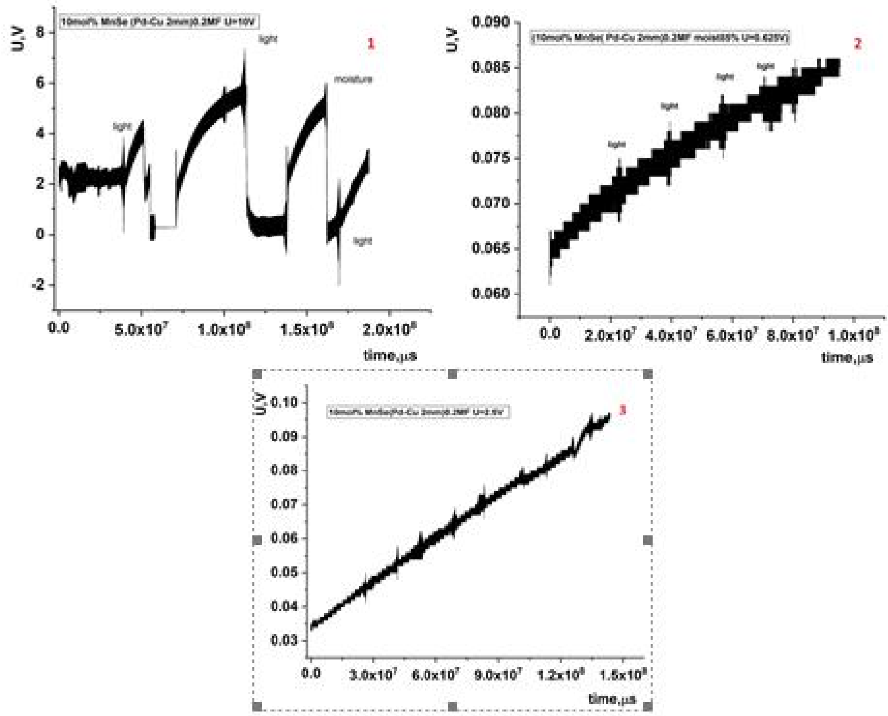

Fig.4. Reaction on light and moisture *SS*
1-*SS*-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ ($x=0.1$) (U=10V) with instant moisture and light; 2- *SS*-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ ($x=0.1$) (U=0.625V) 85% moisture and light;
3- SS-$(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0.1) (U=2.5V) with instant moisture and light

From the analysis of the figure 3 and 4 it is clear to say that both $CuInSe_2$ and solid solutions based on MnSe show reaction on light and moisture. Adding the 3d transition element Mn to $CuInSe_2$ chalcopyrite system does not change its characteristics due to the substitution process.

Generally, in the literature, there is no clear explanation for the observed phenomenon. According some authors gas adsorption (including water vapour) can generate electric charges on metal surfaces [8].

Due to the interaction of gas molecule with a metal film of nanometer thickness < 10 nm the so-called "hot" electrons can occur and ballistically *i.e.*, without the loss of energy reach a Schottky barrier, cross it through kinetic energy, and by entering into the semiconductor material create an electric current in the external chain. However, efficiency of the such conversion method is limited by a low number of "hot" electrons (10^{-3}–10^{-5}) generated per an interaction act. Moreover, a small cross-section of free charge carriers in semiconductor crystals leads to a decrease of the conversion efficiency. Thus, the electric field (of heterojunction) decays drastically with an increase of the distance from the surface even for a few interatomic distances, therefore, only a small fraction of gas can act effectively at the heterophase process on the front surface of a semiconductor crystal. From this aspect it is of high interest to use dielectric materials with a developed surface area.

Obtained results can be explain with the fact that when materials consist of nano particles these particles show reaction to the humidity. In the [17] work it is shown handling and properties of nanoparticles strongly depend on processes that take place on their surface. Specific surface area and adsorption capacity strongly increase as the nanoparticle size decreases. A crucial factor is adsorption of water from ambient atmosphere.

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NANOÖLÇÜ EFFEKTİNİN $(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0,1) BƏRK MƏHLULUNDA SU BUXARININ ADSORBSİYASINA TƏSİRİ

Nəticələrə əsasən əminliklə deyə bilərik ki, nanoölçülü $(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0.1) bərk məhlulu (BM) həm işığa, həm də nəmə reaksiya verir. Bu xüsusiyyətlərinə görə xalkopirit kristallarından işıq yayan diodlar, foto detektorlar, günəş batareyaları və rütubət sensorları almaq üçün istifadə edilə bilər. Rütubət sensorları ətraf mühitin atmosfer rütubəti şəraitinə məruz qaldıqda həssas materialın (BM) fiziki və elektrik xassələrindəki dəyişikliklərdən istifadə edərək işləyir.

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ВЛИЯНИЕ РАЗМЕРА НАНОЧАСТИЦ НА АДСОРБЦИЮ ПАРОВ ВОДЫ В ТВЕРДОМ РАСТВОРЕ $(CuInSe_2)_{1-x}$ $(MnSe)_x$ (x=0,1)

На основании полученных результатов можно с уверенностью утверждать, что твердый раствор (ТР) $(CuInSe_2)_{1-x}(MnSe)_x$ (x=0,1) с наноразмерами реагирует как на свет, так и на влагу. Благодаря этим свойствам кристаллы халькопирита можно использовать для создания свето- излучающие диоды, фотодетекторы, солнечные элементы и датчики влажности. Датчики влажности используют изменения физических и электрических свойств чувствительного материала (ТР) при воздействии условий атмосферной влажности окружающей среды.