Materials Science-Poland, Vol. 26, No. 2, 2008

Properties of films fabricated from ZnS/Mn^{2+} nanoparticles

A. ZDYB*, K. CIEŚLAK, J. M. OLCHOWIK

Institute of Physics, Technical University of Lublin, ul. Nadbystrzycka 38D, 20-618 Lublin, Poland

Nanoparticles of manganese doped zinc sulfide (ZnS/Mn^{2+}) were obtained by wet chemical method. AFM images of the nanoparticles were analysed and their size distribution was estimated. The layer of ZnS/Mn^{2+} nanoparticles reveals a semiconducting character. Conductivity increases with temperature and its value is of the order of 10^{-9} $\Omega\cdot cm^{-1}$.

Key words: *nanoparticles; ZnS*

1. Introduction

II–VI semiconductor nanoparticles attract much attention because of their size-dependent properties and promising applications in optoelectronics. ZnS is a II–VI material that can find future applications such as window layers of solar cells, data storage, data transfer and coatings sensitive to UV light. ZnS has also the advantage of being safer than commonly used CdS, considered to be very harmful. In a bulk state, ZnS has a direct large bandgap of 3.66 eV at 300 K. It exists both as cubic zinc blende and hexagonal wurtzite structures. ZnS and ZnS/Mn^{2+} nanoparticles can be obtained in many ways, e.g., by a spray-based method [1], mechanochemical route [2], ultrasonic radiation method [3], synthesis by γ-irradiation of solution [4], and in chemical reactions [5–10]. ZnS nanoparticle films are very promising for large scale solar cell production with low material consumption. The bandgaps of sulfide nanoparticles can be adjusted by a change in their sizes. This allows use them as sensitizers in quantum dot sensitized solid-state solar cells [11–13].

In this work, a chemical technique is applied [14] to obtain ZnS/Mn^{2+} nanoparticles. The AFM studies of nanoparticles size distribution have been performed, supplemented with temperature dependent conductivity measurements.

*Corresponding author, e-mail: a.zdyb@pollub.pl

2. Experimental

To obtain ZnS/Mn^{2+} nanoparticles the wet chemical synthesis method was used. Nanoparticles were fabricated by a co-precipitation reaction from homogenous solutions of zinc acetate and manganese acetate. Sodium sulfide was added resulting in formation of white precipitate of ZnS/Mn^{2+} nanoparticles that were stabilized with equal amounts of sodium tripolyphosphate and sodium hexametaphosphate. All syntheses were carried out under ambient conditions. All chemicals used were of high purity purchased from Sigma-Aldrich.

Nanoparticles were washed several times with distilled water and their existence in the colloid suspension was proved by the atomic force microscopy (AFM) study. The samples for AFM analyses were fabricated at room temperature. Water suspension of nanoparticles was dropped on a clean GaAs substrate and allowed to dry in air. The samples were examined with a Nanosurf easyScan 2 AFM. In *I–V* measurements, two Au stripes, 15 mm distant, deposited on glass using a Cressington sputter coater played the role of electrodes. Ag colloidal paste was used to make electric contacts to the Au stripes. ZnS/Mn^{2+} nanoparticle suspension was deposited onto the area between the electrodes and allowed to dry at room temperature. For heating the samples, ITO glass was used. The electric contacts were made of Ag colloidal paste at two ends of the ITO glass and applied voltage was tuned in order to obtain a proper temperature. A thermocouple was used to measure the temperature of ZnS/Mn^{2+} sample placed on the ITO glass.

3. Results

AFM images of ZnS/Mn^{2+} nanoparticles are shown in Fig. 1. The mean particle size is 19.4 nm and ranges from 11 nm to 34 nm as revealed from the AFM images. They are well immobilized on the GaAs substrate. Figure 2 presents the particle size distribution as determined from the AFM images.

Figure 3 presents the temperature dependence of current for voltages in the range from 20 V to 50 V applied to the sample. The current increases during heating and it has higher values for higher voltages. The curves shown in Fig. 3 reveal semiconductor like behaviour of ZnS/Mn^{2+} nanoparticle films.

The temperature dependence of ZnS/Mn^{2+} nanoparticle film conductivities is shown in Fig. 4. In order to determine the specific conductivities of a ZnS/Mn^{2+} layer, its dimensions should be estimated. The ZnS/Mn^{2+} film thickness was estimated by measuring the mass of the film and its surface area. First a glass slide with Au contacts was weighted without and with ZnS/Mn^{2+} film deposited on it. Using macroscopic ZnS/Mn^{2+} density of 4.06 g/cm^3, the thickness value was calculated according to the formula:

$$d = \frac{m}{\rho A} \tag{1}$$

where m is mass, ρ – density, A – surface area. The calculated thickness equals to 14.3 μm.

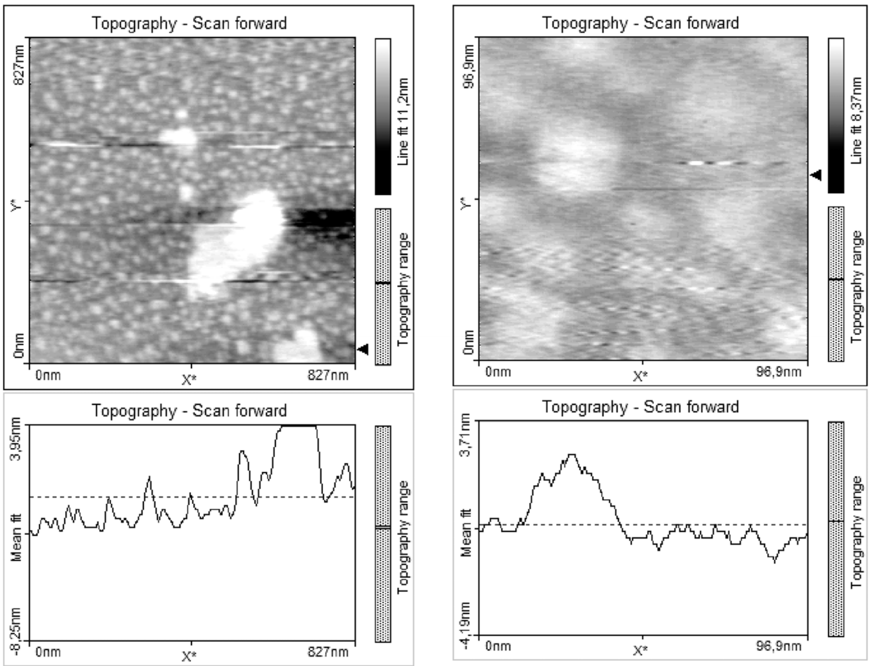

Fig. 1. AFM images of ZnS nanoparticles

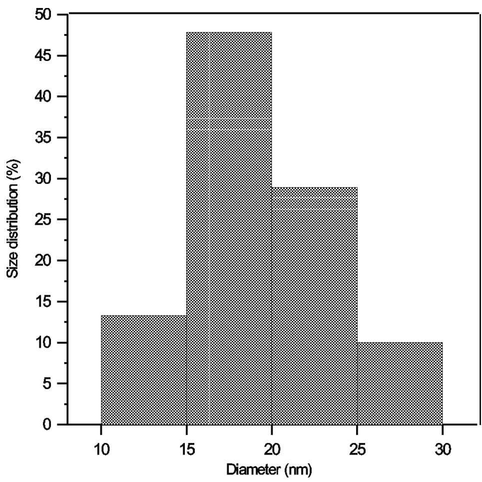

Fig. 2. Size distribution of ZnS nanoparticles.
The average particle diameter is 19.4 nm

The film conductivity was calculated from the formula:

$$\sigma = \frac{Il}{SU} \tag{2}$$

where I is the current, l – the sample length, S – area of cross section, U – voltage.

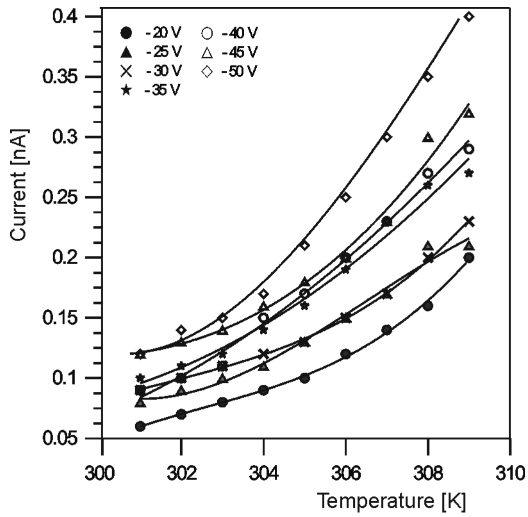

Fig. 3. Temperature dependence of current for the voltage 20–50 V applied to the sample

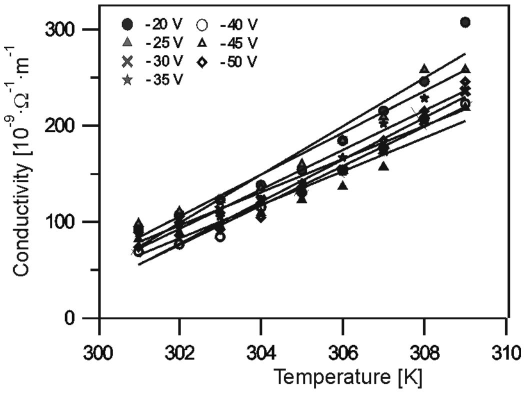

Fig. 4. Temperature dependence of ZnS nanoparticle film conductivity for voltage 20–50 V applied to the sample

The obtained values of conductivity are of the order of 10^{-9} $(\Omega\cdot\text{cm})^{-1}$ locating the investigated ZnS/Mn^{2+} nanoparticle films in semiconductor materials. They are lower than the reported conductivity of ZnS film [15] which is 10^{-4}–10^{-5} $(\Omega\cdot\text{cm})^{-1}$. In the paper of Fathy and Ichimura [15], ZnS film is prepared by electrochemical deposition from aqueous solutions and therefore it is certainly more homogenous than our nanoparticle layers. Low conductivity of our samples is caused by highly defected structure of the film which in turn comes from grains walls.

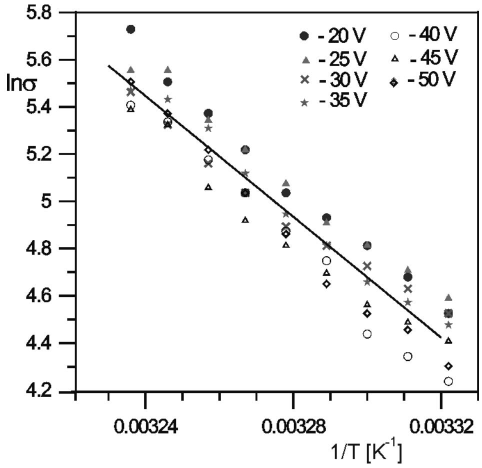

Fig. 5. Temperature dependence of conductivity;
points – experimental data, line – a least square fit

Figure 5 shows the plots $\ln\sigma f(1/T)$. The particular sets of data measured at various voltages and marked by different symbols follow straight lines. The plotted line is a least square fit made using all experimental points. From the line slope, the energy of 2.22 eV was determined, corresponding to 559.6 nm. This value is close to the value of 590 nm reported in the luminescence experiment [16] for energy transfer between $^4T_1$–$^6A_1$ Mn^{2+} states. This suggests that manganese levels act as intermediate levels for electrons to be excited to the conductivity band.

4. Summary

We have obtained ZnS/Mn^{2+} nanoparticles by a co-precipitation reaction. Their size distribution was determined by the AFM with the mean size of 19.4 nm in diameter. Conductivity measurements were performed and from the temperature dependence the wavelength of 559.6 nm was calculated which might be associated with energy transfer between $^4T_1$–$^6A_1$ Mn^{2+} dopant states.

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Received 28 April 2007
Revised 16 February 2008