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S.L. Prokopenko, G.M. Gunya, S.M. Makhno, P.P. Gorbyk

ROOM-TEMPERATURE GAS SENSOR BASED ON SEMICONDUCTOR NANOSCALE HETEROSTRUCTURES ZnS/CdS

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: sprokopwork@gmail.com

Nanoscale heterostructures ZnS/CdS have been synthesized in order to put into effect those gas sensors, which work at room temperature. Synthesis was carried out in two stages. The first stage is the formation of CdS nanorods. The second stage is solvothermal approach, it leads to deposition and growth of a ZnS particles on CdS nanoparticles. A number of samples with different molar ratio Zn/Cd were synthesized.

The XRD method shows appearance of the cubic phase of ZnS on hexagonal CdS. The size of the synthesized ZnS/CdS nanorods is an average length of 150–200 nm and a thickness approximately of 20 nm. Optical spectra for all the synthesized samples were recorded in the wavelength ranging of 350–800 nm at room temperature. The band gap of the synthesized CdS nanorods is 2.40 eV, those of the heterostructures 0.75 ZnS/CdS and 1.0 ZnS/CdS are 2.38 and 2.35 eV respectively.

The dynamic response characteristics of sensors was measured in air and in the presence of acetone or ammonia gas. The measurement was performed at room temperature. Each exposure/recovery cycle was carried out for an exposure interval of 200–250 s followed by a recovery interval of 200 s in air. With an increase of amount of the ZnS on the CdS surface, the response of the sensor increases respectively. All the investigated sensors based on ZnS/CdS heterostructures have better sensitivity for NH_3 *atmosphere (for 0.75 ZnS/CdS about 1.4 times higher) in comparison with acetone atmosphere.*

Keywords: *sensor, ZnS/CdS heterostructures,* NH_3*, acetone, nanorods*

INTRODUCTION

Semiconductor nanoparticles have attracted much attention because of their peculiar optical and electronic properties, quantum size effect, and other important physical and chemical properties [1, 2], which have great potential for many applications. Both CdS and ZnS belong to II-VI group semiconductors, and they have similar crystalline structures. Wurtzite CdS and ZnS are direct band gap semiconductors with energy gap of 2.42 and 3.70 eV at 300 K (being measured in bulk) respectively. Due to higher band gap energy, ZnS has been used as surface passivation material of CdS. These heterostructures can be used in design of sensors for detection of harmful gases under ambient conditions. Meanwhile, semiconductor sensors are small and cheap.

In detection of gases such as acetone, ammonia gives significant advantage in various applications, such as industrial manufacturing, environmental monitoring, and finding out of toxic gas or volatility poisonous chemical leakage [3].

By now, great efforts have been directed to developing acetone gas sensors using various sensing materials such as polymers [4], ceramics [5], metal oxide semiconductors (MOS) [6], carbon nanotube-based composites [7].

Various sensing materials such as transition metal compounds, various metal oxide semiconductors and conducting polymers were extensively studied for NH_3 gas sensor applications, but still most of the works on NH_3 sensors [8–10] were focused on high temperature applications (up to 300 °C).

This study shows how semiconductor heterostructures ZnS/CdS were applied successfully in toxic gas detection under ambient conditions.

EXPERIMENTAL SECTION

Heterostructures ZnS/CdS were synthesized using a two-step solvothermal approach. The first step is the formation of CdS nanorods.

Nanorods CdS were synthesized by crystallization of 0.004 M $Cd(NO_3)_2\cdot 4H_2O$ (analytical grade) and 0.008 M thiourea (analytical grade) from ethylenediamine (analytical grade; 30 ml) at 393K.

Second step leads to the formation of ZnS and further coalescence-exchange, which consequently lead to deposition and growth of ZnS particles on CdS ones. A number of samples with different molar ratio Zn/Cd, such as 0.25, 0.5, 0.75, 1.0, 2.0 were synthesized. A mixed aqueous solution of zincacetate and thiourea was prepared by stirring for 1 h. The solution was then added dropwise to the CdS nanorods in water. Final solution was deposited into a Teflon-lined autoclave and treated at 433 K for 4 h. CdS nanorods being coated with ZnS were centrifuged in water continuously for many times, later dried to obtain final powdery product.

Crystalline structures of obtained samples were determined using X-ray analysis (DRON-4-07, Lomo, USSR) in the emission of copper cathode with nickel filter in Bragg–Brentano geometry. UV-Vis spectra were recorded using a Lambda-35 spectrophotometer (Perkin-Elmer). Electrical properties were measured on a Solartron SI 1271 potentiostat (Solartron analytical, UK) at the 500 mV.

For gas sensing purposes, the ZnS/CdS nanopowder obtained as described above was mixed with a suitable amount of adhesive and then grounded into a paste. In order to compose the experimental sensor, a fiberglass plate was coated with the fresh semiconductor paste using a small brush aiming to form thick film between two parallel gold electrodes. Sensing measurements were carried out in saturated vapours of acetone or ammonia.

RESULTS AND DISCUSSION

Identification of structure characteristics was performed by using diffraction patterns. X-ray diffraction (XRD) graphs show diffraction peaks which indicate the formation of ZnS/CdS heterostructures.

The peaks were identified by comparing the *d*-values obtained from the XRD patterns with the standard JCPDS data-cards *d*-values. XRD spectra of the obtained ZnS/CdS heterostructure is in good correspondence with CdS (JCPDS 75-1545) and ZnS (JCPDS 05-0566) in a hexagonal phase (Fig. 1). XRD pattern exhibits three preferential peaks assigned to (002), (110), and (112), orientations of hexagonal phase of CdS material. From JCPDS data for CdS, the intensitive diffraction peak can be indexed as (111) cubic and (002) hexagonal. It has been also reported that the cubic and hexagonal phases of CdS overlap [11, 12]. However, the XRD patterns show additional peaks corresponding to distinctly plane (102) for hexagonal phase CdS. The XRD pattern of ZnS can be identified as the cubic zinc blend structure. The observed three main diffraction peaks of ZnS at $2\theta = 28.9$, 48.1 and 57.1° correspond to (111), (220) and (311) planes.

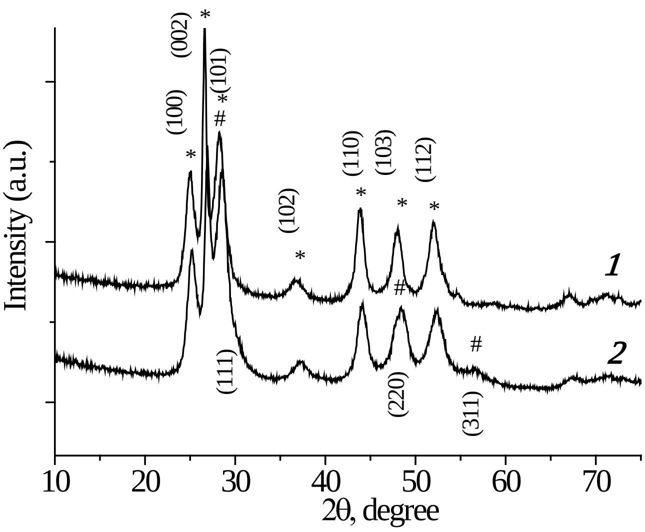

Fig. 1. X-ray diffraction patterns of nanorods CdS (*1*) and heterostructure 0.5ZnS/CdS (*2*); CdS (*), ZnS(#)

The size of the synthesized ZnS/CdS nanorods is an average length of 150–200 nm and a thickness approximately of 20 nm [13].

Optical spectra for all samples were recorded in the wavelength ranging of 350–800 nm at room temperature (Fig. 2). Fig. 2 (curve 1) shows the absorption spectrum of CdS nanoparticles. From the figure one can see that broad absorption peak is observed at 465 nm in visible region. Fig. 2 (curves 2–6) shows the optical absorption of ZnS/CdS nanoparticles. The absorption edge of ZnS/CdS nanoparticles exhibited blue shift compared to those of CdS nanorods. This blue shift could be attributed by an increase in the amount of a wide-gap semiconductor ZnS in the heterostructure ZnS/CdS.

CdS nanorods can provide the lowest energy states for electrons and holes, and the electron–hole pairs tend to localization in semiconductor with lower band gap energy. The CdS/ZnS nanoparticles show the blue-shift of the absorption spectrum and can lead to an increase in the transition energies with respect to CdS nanorods. Furthermore, due to the lattice mismatch of ZnS and CdS nanoparticles (the unit cell parameter *a* of the hexagonal crystal system of ZnS and CdS respectively equals to 0.382 and 0.413 nm), the stress is induced and asymmetric internal electric field is developed across the interface. This can lead to changing the electronic states and absorption properties of heterostructures [14].

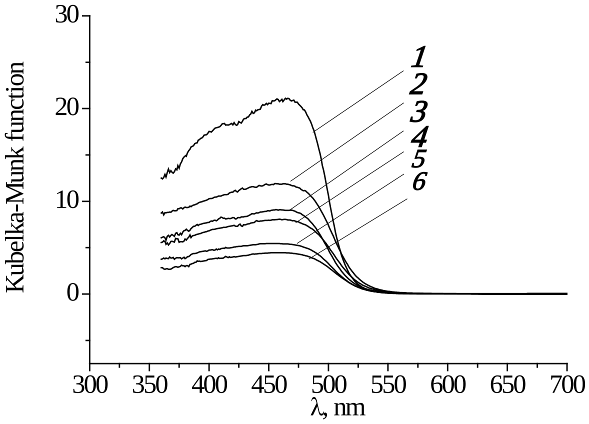

Fig. 2. UV-Vis spectra (plotted as the Kubelka-Munk function) of nanorods CdS and heterostructures ZnS/CdS: *1* – CdS, *2* – 0.25 ZnS/CdS, *3* – 0.5 ZnS/CdS, *4* – 0.75 ZnS/CdS, *5* – 1.0 ZnS/CdS, *6* – 2.0 ZnS/CdS

The optical band gap energies are evaluated by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs $h\nu$ graph to hν axis at $a = 0$. The obtained band gap values of CdS, 0.75 ZnS/CdS and 1.0 ZnS/CdS nanoparticles are 2.40, 2.38, and 2.35 eV, respectively.

To calculate the sensitivity (S) of the sensor, current measurement was used at a constant voltage. The sensitivity is usually defined as the current variation ratio of the measured gas concentration. If the background gas is air, the gas sensitivity is defined as follows:

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100,$$

where R_a and R_g are sensor resistances in normal air and under gas [15, 16].

The high performance of the sensor was confirmed through the repetition and reproducibility experiments. Three or more cycles of gas-sensing characteristics were performed on each material for repetition. Gas-sensing characteristics of three or more samples of each type were tested for reproducibility.

Sensor's resistance was measured in air and in the presence of acetone or ammonia gas. The measurement was performed at room temperature. Each exposure/recovery cycle was carried out for an exposure interval of 200–250 s followed by a recovery interval of 200 s in air.

The transient response characteristics of all the samples in acetone gas are shown in Fig. 3.

Chemisorbed oxygen molecules tend to capture electrons from the material, which leads to increase in hole concentration and decrease in electron concentration (1)–(2). Therefore, the sensor is in high resistance state in atmosphere air as experimentally observed. When the sensor is exposed to reducing gas such as acetone, the gas molecules react with the oxygen ions on the surface of sensor (3)–(5). Such reactions result in retrieving the trapped electrons back to the conduction band of the sensor and lead to decrease of resistance for the gas sensor [17].

$$O_{2\,(gas)} \rightarrow O_{2\,(ads)} \quad (1)$$

$$O_{2\,(ads)} + e^- \rightarrow O_2^- \quad (2)$$

$$CH_3COCH_3 + O_2^- \rightarrow CH_3C^+O + CH_3O^- + e^- \quad (3)$$

$$CH_3C^+O \rightarrow CH_3^+ + CO \quad (4)$$

$$CO + O_2^- \rightarrow CO_2 + e^- \quad (5)$$

The gas-sensing mechanism is generally ascribed to *p*-type semiconducting behaviour and is dominated by positive charge carriers (holes), whereas the adsorbed acetone gas on the sensor surface serves as electron donor. The absorbed acetone gas molecules cause a change of holes concentration in semiconductor heterostructures ZnS/CdS, resulting in increase in the surface conductivity.

The values of electrical resistance of the sensor decrease quickly as soon as the NH_3 gas reacts with sensor material and then quickly returns to its initial values being refreshed with air, indicating a good repeatability and reversibility of the NH_3 sensor (Fig. 4).

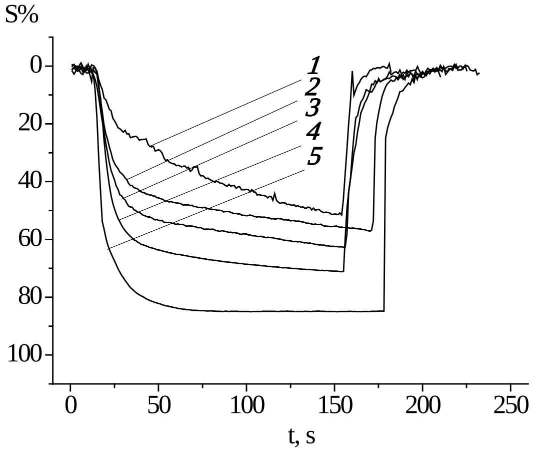

Fig. 3. Plot of dynamic response and recovery curves to acetone gas of the heterostructures ZnS/CdS: *1* – 0.25 ZnS/CdS, *2* – 0.5 ZnS/CdS, *3* – 0.75 ZnS/CdS, *4* – 1.0 ZnS/CdS, *5* – 2.0 ZnS/CdS

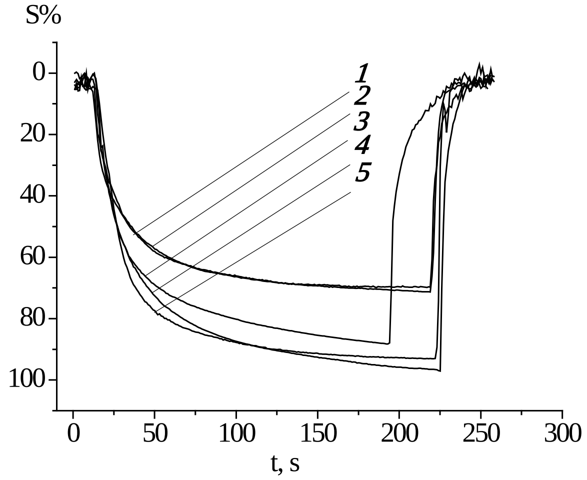

Fig. 4. Plot of dynamic response and recovery curves to NH_3 gas of the heterostructures ZnS/CdS: *1* – 0.25 ZnS/CdS, *2* – 0.5 ZnS/CdS, *3* – 0.75 ZnS/CdS, *4* – 1.0 ZnS/CdS, *5* – 2.0 ZnS/CdS

It is known from the literature that ZnS acts as a *n*-type semiconductor, which at room temperature tends to adsorb ions of oxygen (O_2^-) from the atmosphere by reacting with reducing gases, such as NH_3. Reactions of NH_3 molecules with the oxygen species cause more electrons to return to the conduction band because ammonia acts as a donor of electrons. The surface reactions between the NH_3 and the sensor material can be described as shown in (6)–(8) [18–20]:

$$NH_{3(gas)} = NH_{3(ads)} \tag{6}$$

$$2NH_{3(ads)} + 3O^- \rightarrow N_2 + 3H_2O + 3e^- \tag{7}$$

$$2NH_{3(ads)} + (7O_{(ads)})^{2-} \rightarrow 2NO_{2(gas)} + 3H_2O_{(gas)} + 14e^-. \tag{8}$$

When the sensor is exposed to NH_3 containing gas, the electrons being trapped by the adsorptive states will be released, so leading to decrease in sensor resistance, as experimentally observed. All sensors, based on heterostructures ZnS/CdS, have better results for NH_3 atmosphere in comparison with acetone atmosphere.

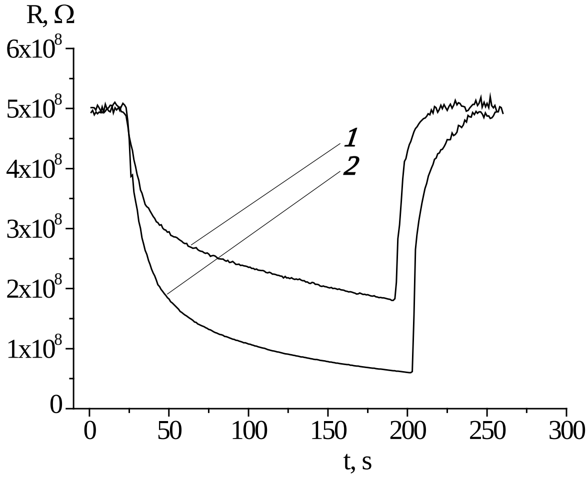

Fig. 5. Comparison of electrical responses of 0.75 ZnS/CdS: *1* –in acetone atmosphere, *2* – in NH_3 atmosphere

Fig. 5 shows that in ammonia atmosphere the responses of 0.75 ZnS/CdS-based sensors are about 1.4 times higher than those in acetone atmosphere.

CONCLUSION

Semiconductor heterostructures ZnS/CdS were successfully synthesized using two-step solvothermal method. From the result of XRD, hexagonal phases of CdS and cubic phases of ZnS are confirmed. The as-prepared samples are used to study the structural, optical, and sensor properties. All investigated samples of heterostructures ZnS/CdS have shown decrease in electrical resistance at room temperature in ammonia and acetone atmosphere.

With an increase of amount of the ZnS on the CdS surface (a change in the molar ratio of Zn/Cd from 0.25 to 2.0), the response of the sensor increases respectively. All the investigated sensors based on ZnS/CdS heterostructures have better sensitivity for NH_3 atmosphere (for 0.75 ZnS/CdS about 1.4 times higher) in comparison with that of acetone atmosphere.

Газовий датчик на основі нанорозмірних напівпровідникових гетероструктур ZnS/CdS, що працює при кімнатній температурі

С.Л. Прокопенко, Г.М. Гуня, С.М. Махно, П.П. Горбик

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, sprokopwork@gmail.com

Синтезовано нанорозмірні дисперсні гетероструктури ZnS/CdS для створення газових датчиків, які ефективно працюють при кімнатній температурі. Методом РФА показано виникнення кубічної фази ZnS на гексагональному CdS. Показано зменшення ширини забороненої зони зразків з 2.40 еВ для CdS до 2.35 еВ для 1.0 ZnS/CdS. Висока селективність, відтворюваність і невеликий, до 100 с, час зміни опору дозволяють використовувати синтезовані зразки як економічні газові датчики на амоніак і ацетон.

Ключові слова: *датчик, ZnS/CdS гетероструктури,* NH_3*, ацетон, нанострижні*

Газовый датчик на основе наноразмерных полупроводниковых гетероструктур ZnS/CdS, работающий при комнатной температуре

С.Л. Прокопенко, Г.М. Гуня, С.Н. Махно, П.П. Горбик

Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина, sprokopwork@gmail.com

Синтезированы наноразмерные дисперсные гетероструктуры ZnS/CdS для создания газовых датчиков, эффективно работающих при комнатной температуре. Методом РФА показано образование кубической фазы ZnS на гексагональном CdS. Показано уменьшение ширины запрещенной зоны образцов с 2.40 эВ для CdS до 2.35 эВ для 1.0 ZnS/CdS. Высокая селективность, повторяемость и небольшое, до 100 с, время изменения сопротивления позволяют использовать синтезированные образцы в качестве экономичных газовых датчиков на аммиак и ацетон.

Ключевые слова: *датчик, ZnS/CdS гетероструктуры,* NH_3*, ацетон, наностержни*

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