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SYNTHESIS OF CADMIUM SULFIDE NANOPARTICLES EMBEDDED IN POLYMER MATRIXES ANDFABRICATION OF ELECTRONIC DEVICES BASED ON THEM

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This work provides the method of obtaining CdS nanoparticles (NP) embedded in different host polymer matrixes and fabrication of the electronic devices based on them. From optical measurements the average size of the NP is estimated to be 5–8 nm. The pH of the solution has a direct influence on the size of the nanoparticles; the higher the pH, the larger the nanoparticle size. We produced device with ATO/ITO layers based on CdS nanoparticles in poly(sodium styrene sulfonate) (PSS_{Na}) matrix. Were fabricated n^{++}Si/CdS–PVP/Ag sandwich structures using CdS quantum dots. These devices show rectifying properties with on/off ratios. Furthermore, they also show electrical bistability and can be programmed in a high or in a low conductive state. They can be used as a non-volatile resistive memory. The films with a high concentration of nanoparticles in a polyvinylpyrrolidone (PVP) host matrix were prepared.In spite of a high concentration of nanoparticles, these thin films behave as insulating layers with a dielectric breakdown field higher than 10^8 V/m. This insulating behavior is tentatively explained by a charge coulomb effect.

Keywords: CdS nanoparticles; polymer matrix; poly(sodium styrene sulfonate) (PSS_{Na}); polyvinylpyrrolidone (PVP); electrical characterization.

Introduction

The unique properties of nanomaterial and its structures have received much attention in recent years due to their potential applications in many ыelds such as optoelectronics devices, catalysis, single-electron transistors, light emitters, electrically bistable devices, photoelectrochemical and nonlinear optical devices [1–6]. Semiconductor nanoparticles of II–VI compounds are an example of a low-dimensional structure with their unique electronic and optical properties that have been extensively investigated for a wide variety of applications. Cadmium sulыde (CdS) is a direct band gap material and it can be used in photoelectronic devices. The luminescent CdSnanocrystals have wide potential applications in optical switches, sensors, electroluminescent devices, lasers and biomedical tags [7].

In recent years, polymer–nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. These materials offer unique mechanical [8], electrical [9], optical and thermal properties [10]. Such enhancements are induced by the physical presence of the nanoparticle and by the interaction of the polymer with the particle and the state of dispersion. One advantage of nanoparticles, as polymer additives appear to have is that compared to traditional additives, loading requirements are quite low. Microsized particles used as reinforcing agents scatter light, thus reducing light transmittance and optical clarity [11].

There are different technics how to obtain CdS nanocrystals embedded in polymer matrixes. For example, NCs were synthesized in polymeric solution by heating method. The results showed evidence of chargetransfer and size variation depending on NCs and polymer concentration [12]. Nanocomposites of conducting polyaniline with CdS nanoparticles have been synthesized via in situ by oxidizing the complex of aniline with cadmium sulfate [13]. Conducting polymers like polyaniline have potential for wide variety of application in electronics, sensors, LED, etc owing to its easy polymerization and environmental stability [14–16]. By chemical precipitation method Cadmium sulfide nanoparticles can be synthesized with different sizes [17]. It is important to synthesize nanoparticle at the desired size within a narrow size distribution and in aneasy to handle conditions of precursor, solvent and temperature etc.

Some work have demonstrated that a thin-film planarstructure, using AgCl nanocrystals embedded in a polymer blendcan switch between different nonvolatile conductance states. Their findings support theview that resistive switching in AgCl-nanocrystal/polymer blendshas origin in a defect creation process (electroforming), followed bya charge carrier trapping mechanism responsible for the electricalbistability [18].

The purpose of this work is to obtain CdS nanocrystals in polymer matrixesand fabricate electronic devices based on them. The object of this research is to study nanocrystals of cadmium sulfide in the colloidal solution of different polymersand to investigate their electrical behavior.

Experimental

In this work were prepared and investigated few types of electronic devices based on CdS nanoparticles in the host matrixes ofdifferent polymers such as polyvinylpyrrolidone (PVP) and polystyrenesulfonate (PSS_{Na}). Below there are methods of the preparation of each device:

1) The object of research were nanocrystals of cadmium sulfide that were obtained from solutions of salts cadmium (cadmium nitrate) and sulfur (sulphide sulfur) in the colloidal solution of polymer PSS_{Na} – poly(sodium styrene sulfonate), 30 kD. The formation of CdS particles as a result of exchange reactions: $Cd(NO_3)_2+Na_2S=CdS+2NaNO_3$ [12]. Solution had yellow color. Average radius of cadmium sulfide nanocrystals was evaluated from the optical absorption spectra, R≈9 nm. After completion the synthesis process, the drop of solution which contained suspended in PSS nanoparticles of CdS, was sprayed on gold substrates with ATO/ITO layers and dried during 24 hours at room temperature.

Electrical measurements were carried out using a picoammeter/voltage source in the dark conditions with air at room temperature. Voltage on the gate was applied through wire connected to the glass with ATO and ITO layers. Source and drain voltage applied to the gold contacts. Fig. 1 shows the schematic diagram of the device structure.

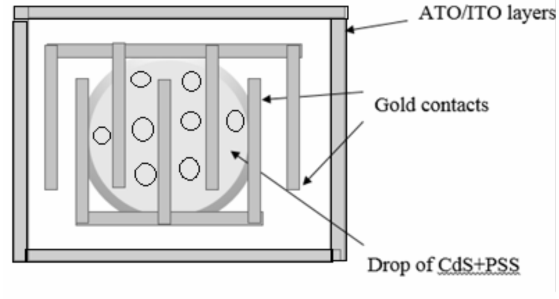

Fig. 1. Structure of device (top view)

2) Nanocrystals of cadmium sulfide that were obtained in the colloidal solution of polyvinylpyrrolidone (PVP) using method of colloidal chemistry [12]. PVP is a potentially useful material in which its dielectric strength is very high; furthermore, it has a good charge storage capacity and dopant-dependent optical properties [13]. The pH value of the solutions was in the range 4÷5. Average radius of cadmium sulfide nanocrystals R≈4.5 nm.

To increase the concentration, solution of CdS in PVP was centrifuged during 30 min. After that the precipitate of solution changed color from yellow to orange. Concentration of the final solution was 1:20. After completion the synthesis process, the drop of solution which contained suspended in PVP nanoparticles of CdS, was sprayed on silicon substrates and dried during 24 hours at room temperature. After 3 days in vacuum chamber the drop of CdS+PVP was cracked. Fig. 2 shows the schematic diagram of the device structure.

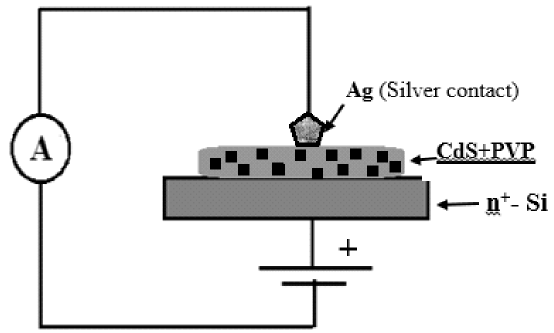

Fig. 2. Schematic diagram of the device structure. Positive polarities refer to the bottom n^{++} – Si

3) The preparation of NP CdS in PVP matrix uses the same exchange reactions: $Cd(NO_3)_2+Na_2S=$ $=CdS+2NaNO_3$. Changes on the pH of the solution from 4 to 8 allow to control the size of the nanoparticles from 5 to 8 nm. Solutions with high concentration of CdS nanoparticles were produced by centrifugation. Thin films were deposited on glass substrates by drop cast. When dried, these drop cast solutions naturally peel-off from the glass substrates leading to a free standing thin films with thickness in the range 2–5 μm. After that the precipitate of solution changed color from yellow to orange. Concentration of the final solution was 1:5, 1:10 and 1:20. Electrical measurements were carried on free standing films using a picoammeter/voltage source in the dark conditions under ambient atmosphere at room temperature. Electrical connections were made by gold wires connected using conductive silver paint to both surfaces of the free standing film as show in Fig. 3.

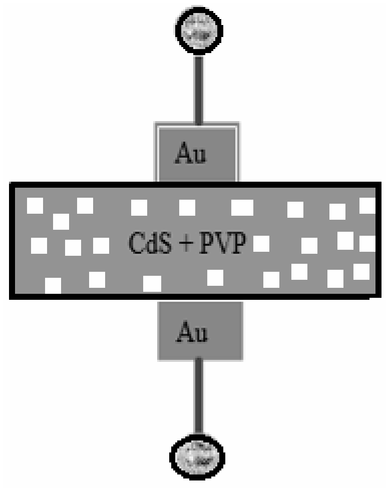

Fig. 3. Schematic diagram of a sandwich structure fabricated using free standing film of CdS in PVP

Optical Characterization

The UV-visible absorption spectra of the CdS nanoparticles were investigated. The weak broad absorption shoulders appeared in the range (380–450 nm) in all types of samples. As can be seen from fig. 4, absorption edge of nanocrystals is approaching to energy value of band gap from the bulk cadmium sulfide (2.42 eV) and in this case the quantum size effect is not observed and we can talk about the average radius of NC larger than 5 nm. This agrees with technological features obtaining nanoparticles, namely to obtain a higher concen-tration of nano-crystals, in the matrix were used high concentrations of the initial components.

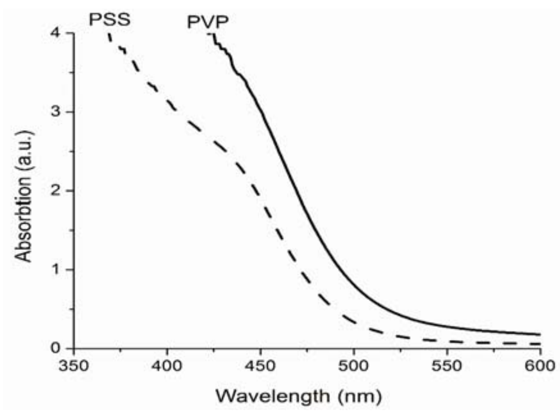

Fig. 4. UV-visible spectra of CdS nanoparticles with different polymers

Also was measured transmission spectra for CdS with different pH values (6, 8 and 10). From the optical measurements the size of the nanoparticles is estimated to be 3–8 nm. In all cases been a shift of the absorption edge towards higher energy than the band gap of bulk single crystal of cadmium sulfide. When changing the pH value from 10 to 6 average size of synthesized nanocrystals decreases from 8 to 3 nm. The observed behaviors of the absorption spectra NC CdS can be explained as follows. Used in the synthesis of aqueous solutions of the reactants of the reaction. This hydrolysis cadmium salts and sulfur, wherein the distribution of the products of hydrolysis depends on the pH [14]. Thus, at pH<6 present in the solution in a large amount of cadmium Cd^{2+} ions and small quantity of ions HS^{-}. The size of nanocrystals in this case, will limit the amount of hydrogen sulphide ions. In the pH range 7÷8 of cadmium ions and ions of hydrogen sulfide are equalized, thereby increasing the size of the nanocrystals. At pH>8 cadmium ions decreases, but increases the concentration of hydroxide cadmium ions $CdOH^{-}$ and ions HS^{-}, which leads to further growth of the nanocrystals.

Results and Discussion

1) In this work we produced devices based on CdS nanoparticles which may control the flow of electrons (or electron holes) from the source to drain by affecting the size and shape of a «conductive channel» created and influenced by voltage applied across the gate and source terminals. This conductive channel is the «stream» through which electrons flow from source to drain. Fig. 5 illustrates the I–V characteristics of the device based on the CdS:PSS thin ыlm with the applied voltage being scanned from –1 to 1 V. Measurements carried out in the air and dark conditions. Such behavior can be caused by trapping electrons and holes during measuring process. Fig. 6 shows fast increasing of current with changing voltage range from [–1; 1] V to [–5; 5] V. Measurements in the voltage range [–5; 5] V were repeating few times, curves were not changing. That means system is showing stability and does not depend upon the time of measurements. Further increasing voltage range from [–5; 5] V to [–10; 10] V illustrates that current value is becoming higher.

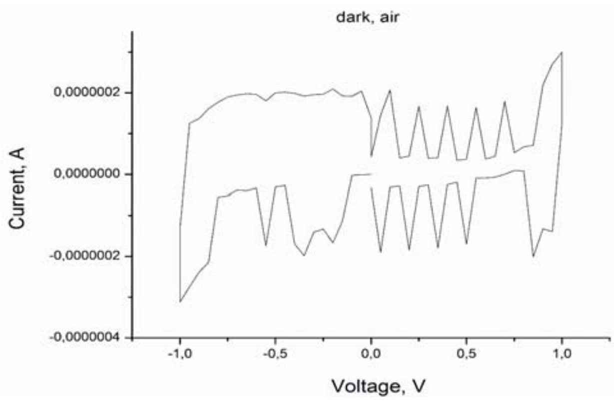

Fig. 5. I–V characteristics of the device in the voltage range [–1; 1] V

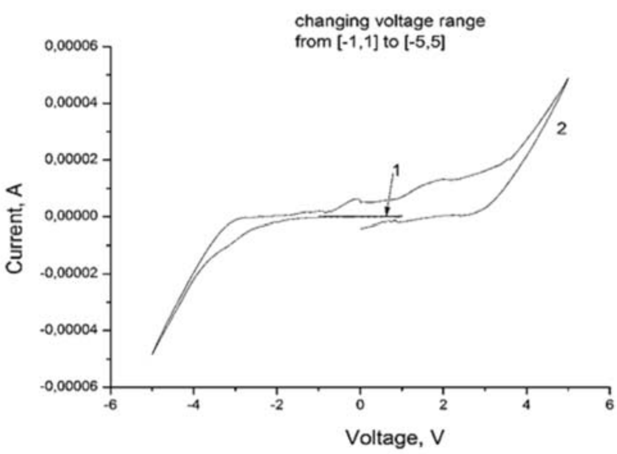

Fig. 6. Changing voltage range from [−1; 1] V (curve 1) to [−5; 5] V (curve 2)

2) Current-voltage (I−V) characteristics were employed to study the electrical bistability properties of the device, and the conduction mechanisms in both ON- and OFF-states were considered. Fig. 7 illustrates the I−V characteristics of the device based on the CdS:PVP thin film with the applied voltage being scanned from −2 to 2 V. Plots of the graphic are in the semilog scale (logarithmic vertical axis and linear horizontal axis). An electrical hysteresis is clearly observed, which displays current of a high-conducting (μA) state ON-state.

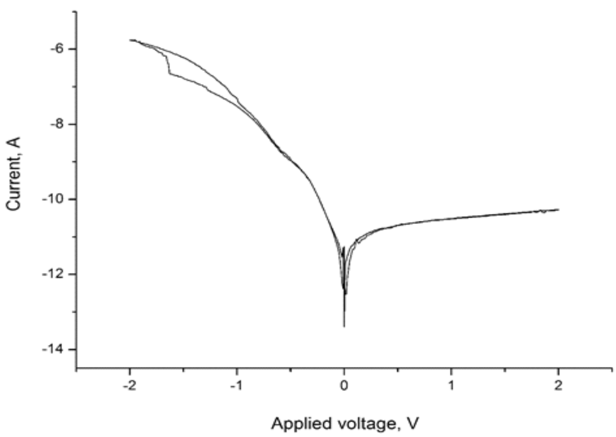

Fig. 7. IV characteristic of the ON-state of the system, measurements in the voltage range (−2; 2) V

Fig. 8 shows the behavior of the OFF-state of system: very low current, almost 0A (pA). After can be observeappearing of the ON-state: increasing current to nA with increasing voltage range (−4; 4) V. Further increasing voltage (−6; 6) V can help to stabilize ON-state and increase the current value to μA.

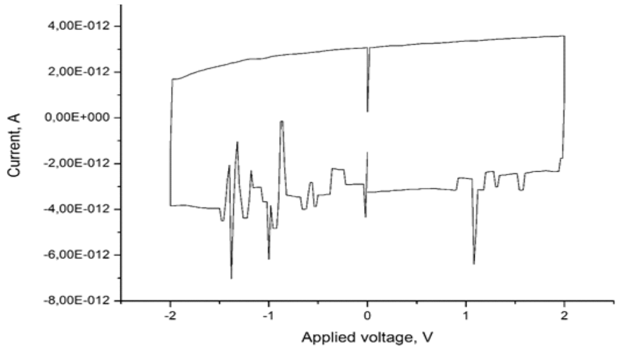

Fig. 8. IV curve of the OFF-state of the system after pulsing +3 V during 5 sec

Electrical measurement (I−V characteristics) of the system shows the behavior of diode with memory. It switches on by increasing voltage from [−2; 2] V (Fig. 6) till [−6; 6] V and turns off with pulsing +3 V (Fig. 8). Such an electrical hysteresis behavior is an essential feature for a bistable device. When the voltage with value 3 V is applied on the device, the current decreases. An increase in the current is observed when a forward bigger value of voltage is applied. As the applied voltage is scanned from −2 to 2 V, the current of the device changes from the ON-state to the OFF-state with pulsing 3 V. The OFF-state can be recovered to the ON-state when a bigger voltage is applied (from 2 to 6 V).

3) Electrical measurements were carried out in free stand thin-films with typical thickness around 2 μm. Symmetric sandwich junctions were prepared by painting two silver contacts in both faces of the films. Fig. 9 shows typical current-voltage characteristics. The junctions behave as a pure capacitor. The residual current measured (I) is essentially due to the displacement current (I=CdV/dt), where C is the device capacitance and dV/dt the voltage ramp speed. An electrical field $E \approx 10^8$ V/m can be applied across the junction without causing dielectric breakdown. It was not possible to test the electric field required to cause dielectric rupture because we were limited to a 300 V power supply. This field is close to the required field to cause dielectric breakdown in conventional oxide layers such as aluminum oxide ($E=10^9$ V/m). This high dielectric strength is surprising in view of the high density of nanoparticles present in the host polymer matrix.

As possible explanation we propose that the CdS nanoparticles have a cloud of charges in their surfaces. This charging compensated by trapped charges in the polymer, may create a Coulomb blockade effect that impedes the electrical conduction across the nanoparticles-polymer matrix. More measurements are required to elucidate the origin of this high dielectric strength.

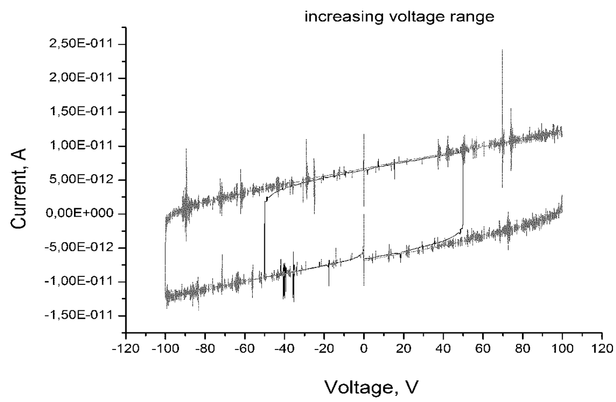

Fig. 9. Current-voltage characteristic of a 2 μm thick free standing film of CdS in PVP matrix

Conclusions

In this work were fabricated few types of electronic devices based on nanocrystals of cadmium sulfide and carried out electrical analysis of CdS nanoparticles embedded in different polymer matrixes. From optical measurements the average size of the NP is estimated to be 5–8 nm. The pH of the solution has a direct influence on the size of the nanoparticles, the higher the pH the larger the nanoparticle size.

For each type of electronic devices we concluded the following:

1) We produced device based on CdS nanoparticles which controls the flow of electrons (or electron holes) from the source to drain by affecting the size and shape of a «conductive channel» created and influenced by voltage applied across the gate and source terminals. This conductive channel works like a stream through which electrons flow from source to drain.

2) Were providing on electrical characterization of n^{++}Si/CdS–PVP/Ag sandwich structures. These devices show rectifying properties with on/off ratios reaching 10^6 at 4 V. Also they show electrical bistability and can be programmed in a high or in a low conductive state. Possible affiliation of such devices as a non-volatile resistive memory.

3) Free standing films of nanoparticles in a polyvinylpyrrolidone (PVP) matrix behave as insulating layers with a dielectric breakdown field higher than 10^8 V/m. This insulating behavior can be explained by a charge coulomb effect.

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