Formation and study of PbS quantum dot films with different ligands

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Abstract. We study the influence of various organic molecules of ligands on the optical properties of the condensates of lead sulfide quantum dots (QD) and photoconductivity of diode structures made on their basis. It is shown that the decrease of the molecule length of surface ligands by a factor of 4 leads to the significant increase in the conductivity, and the emergence of photocurrent. We also demonstrate that the thickness of the photoactive QD layer plays an important role in the performances of photovoltaic cells.

1. Introduction
Due to the dependence of the absorption and luminescence spectra on the size of quantum dots (QDs), their high photostability and wide absorption spectrum, QDs are considered to be a promising material for use in optoelectronic devices. QDs based on lead chalcogenide, which are capable of absorbing light in the infrared spectrum region, are of great interest [1-3]. Photovoltaic cells, up-conversion devices and IR photodetectors can be created on their basis. However, without achieving a low defect concentration and good charge carrier transport in QD layers, it is difficult to obtain high-efficiency values of such devices. The important factor determining the effectiveness of QDs application is a presence of the layer of organic molecules (ligands) on the nanocrystal surface. The selected molecules should not form high barriers for the charge carriers tunneling, but at the same time, they should spatially separate the nanocrystals in order to avoid their aggregation. Since charge transfer between quantum dots occurs via "hopping" mechanism [4], the important factor affecting the electrophysical properties of thin QD films is the ligand molecule length which determines the distance between QDs. Ligands should also provide passivation of uncompensated bonds on the nanocrystal surface since they can form traps for charge carriers. At the same time, it is promising to use ligands, which are able to chemically bind QDs together, forming a uniform covalent nanostructure.

In this paper, we studied the effect of various organic ligands on the electrophysical properties of QD layers.

2. Sample fabrication
The used PbS quantum dots were synthesized by the colloid chemistry method. To produce a QD film, 50 μl of QD solution in toluene with concentration of 10 mg /ml was applied by automatic pipette onto
a pre-cleaned glass substrate and then the substrate was rotating for 30 seconds at an angular rate of 1500 rpm with spin-coating method. After that 50 μl of ligand molecules solution (1 mol/l of hydrazine in methanol; 0.1 mol/l of HDT (1,6-hexanediithiol) in acetonitrile) was applied onto the film and after 30-second exposure the film was rotating for 30 seconds at angular rate of 1500 rpm. To remove the excess of ligand molecules from the film surface, a suitable for each ligand solvent was applied on it, and then the film was rotating for 30 seconds at angular rate of 1500 rpm. The described procedure was repeated 5 times [5, 6].

Initially, as a result of the synthesis, the QDs surface has been covered with a layer of oleic acid molecules (OA), which length is approximately 1.5 nm. After ligand replacement, the QDs surface was covered with a layer of hydrazine and 1.6-hexanediithiol (HDT), the molecules length of which are approximately 0.5 nm and 1 nm, respectively. Such choice of ligands is caused by small length of their molecules and the high affinity of thiol groups to sulfur molecules.

Also, on the base of QD films photovoltaic elements were produced (ITO/PEDOT: PSS/PbS/ZnO/Al). Polymer PEDOT: PSS was deposited by the spin-coating method on a transparent glass substrate, covered with an ITO layer. The substrate angular rate was 2000 rpm and the layer thickness was 30 nm. After that, the sample was dried at the temperature of 60°C for several hours. Then a layer of QDs was deposited, and the ligands were replaced according to the procedure described above. The number of QDs layers in the structures was varied. The subsequent buffer layer of ZnO QDs was deposited by the spin-coating method at an angular rate of 2000 rpm, the layer thickness was 30 nm. Due to the quantum-size effect, the ZnO QDs were chosen so that the energy levels of the buffer layer do not create a barrier and do not prevent the diffusion of charge carriers to the contacts. After applying all the layers aluminum contacts were sprayed on each structure through the mask.

3. Results and discussion
Figure 1 shows the IR spectra of films with different ligands obtained with the IR spectrometer SHIMADZU IRaffinity-1S. The vibrational peaks characteristic only for a specific molecule are indicated for each ligand. In this case, the distinguishable peak for oleic acid (C_{18}H_{34}O_{2}) is one at 3080 cm\(^{-1}\), corresponding to stretching vibrations of the bond =C-H; for 1.6-hexanediithiol (C_{6}H_{14}S_{2}) molecule – the peaks corresponding to stretching vibrations of the bond S-H (2620 cm\(^{-1}\)) and C-S (670 cm\(^{-1}\)); for hydrazine (N_{2}H_{4}) – the peak of stretching vibrations (3280 cm\(^{-1}\)) and deformation vibrations (1590 cm\(^{-1}\)) of the N-H bond. Thus, the presence of the above peaks confirms the replacement of the original ligands with the new ones.

![Figure 1. IR spectrum of QD films with oleic acid (OA), 1,6-hexanediithiol (HDT) and hydrazine as surface ligands.](image-url)
For all film samples, conductivity was measured in the dark and under irradiation by a wide-range halogen lamp Ocean Optics LS-1. For this purpose, thin aluminum contacts were sprayed onto the surface of the films through a mask. On the basis of the I-V characteristics measurements, the relative conductivity has been calculated for each sample. Figure 2 shows that the conductivity increases exponentially with decreasing of ligand molecule length. This result is in good agreement with the theory of the hopping mechanism of charge transfer between QDs in a film, within which the mobility contains the exponential factor \( \exp(-2\gamma l) \), where \( \gamma \) - is the inverse radius of wave functions localization, \( l \) - is the tunnel jump length (ligand molecule length).

![Figure 2. The relative change of QD film conduction with the decrease of ligand length.](image)

Thus, the replacement of relatively long molecules of the initial OA ligands by shorter ones that are capable of chemically bonding QDs to each other leads to an efficient charge transfer between the QDs. In this case, conductivity is largely determined by the ligand molecule length, rather than its chemical nature.

Using the proven technique of manufacturing QD films, photovoltaic elements on the basis of QDs with substituted ligands layers (ITO/PEDOT:PSS/PbS/ZnO/Al) were made and the dependence of the I-V characteristics on the nanocrystals layer thickness was studied. The thickness was varied by changing the number of QD layers. Structures with 3, 5, 6 and 10 QD layers were made. All the samples demonstrated pronounced diode characteristics (figure 3). The measured representative I-V characteristics of the samples under irradiation are shown at figure 4. Samples with six QD layers showed higher values of efficiency compared to the others. Thereby, the optimal thickness of the photovoltaic structure is about 70-90 nm (6 layers of QDs).
4. Conclusion
Thus, the choice of surface ligands plays an important role in the efficiency of charge transfer between QDs in the film. We have shown that the decrease in the ligand length by a factor of 4 leads to a significant exponential increase in conductivity of the QD film, which is in a good agreement with the theory of the hopping mechanism of charge transfer in QD solids [JPCLett]. We propose that for the electrical conductivity of QD solids, the length of the ligand molecule is the crucial factor rather than its chemical structure. For PbS QD solid used as a photoactive layer in photovoltaic cells ITO/PEDOT: PSS/PbS/ZnO/Al, we found the optimal QD layer thickness of 70-90 nm which provides the enhanced performance.

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References
[1] Dayneko S, Linkov P, Martynov I et al 2016 Physica-E: Low-dimensional Systems and Nanostructures 79 206
[2] Dayneko S, Tameev A, Tedoradze M et al 2013 Appl. Phys. Lett. 103 063302
[3] Dayneko S, Tameev A, Tedoradze M et al 2014 Proc. SPIE 8981 898113-1
[4] Fischer S A, Crotty A M, Kilina S V, Ivanov S A and Tretiak S 2012 Nanoscale 4 904–914
[5] Kurian P A, Vijayan C, Suchand Sandeep C S, Philip R and Sathiymoorathy K 2007 Nanotechnology 18 75708
[6] Xu F, Gerlein L, Ma X, Haughn C, Doty M and Cloutier S 2015 Materials 8 1858–1870