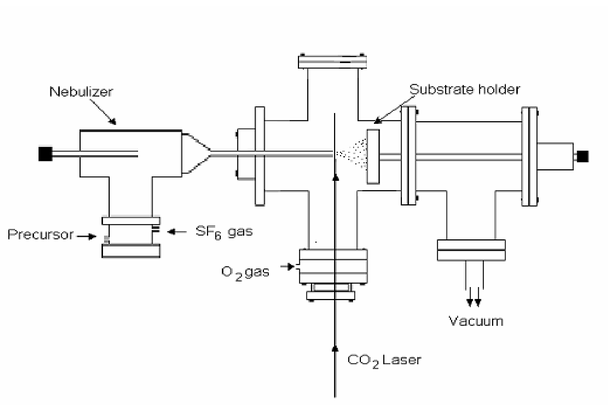
A New Method for Forming Surfactant-Free PbSe Quantum Dot Films and QD-Polymer Composites for Excitonic Solar Cells

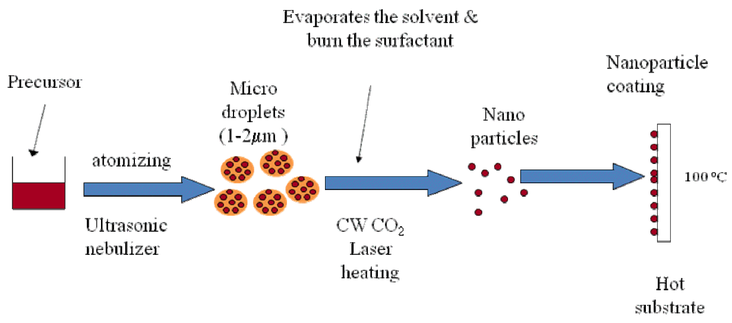
Gayan Dedigamuwa, Xiaomei Jiang, Jian Zhang, Pritish Mukherjee, and Sarath Witanachchi [a]
Department of Physics, University of South Florida, Tampa, FL 33620 (a) E-mail: switanac@cas.usf.edu

Abstract

Multiple exciton generation in semiconductor quantum dots (QD) promises a new generation of solar devices that include flexible inorganic-organic hybrid structures. In these devices incorporation of PbSe or PbS quantum dots in a polymer matrix without a surfactant barrier at the QD-polymer interface is important for the dissociation of excitons and subsequent collection of carriers. We have developed a laser-assisted spray process to deposit surfactant-free crystalline PbSe nanoparticles on substrates. In the first step of the process, nanoparticles of PbSe were formed by reaction between tributyl-phosphine selenium and lead oxide in the presence of Oleic acid and 1-octadecene. Solutions of narrow particle distributions were obtained by centrifugation. In the second step, LASP techniques was used to deposit PbSe nanocrystals directly on the substrate while burning the surfactant during the CO_2 laser interaction. Nanoparticles within the film grown by this method are uniformly distributed and are in intimate contact with each other. TEM studies confirmed the single crystal nature of each QD and absence of surfactants. A second nebulizer was used to inject aerosols of P3HT polymer that was dissolved in toluene onto the substrate. SEM and TEM analysis of the co-deposited films showed a uniform distribution of PbSe particles within the polymer matrix. Conductivity of PbSe QD films and QD-polymer composite films have been measured in several electrode configurations. Comparison of these results with films formed with surfactant coated QD will be presented.



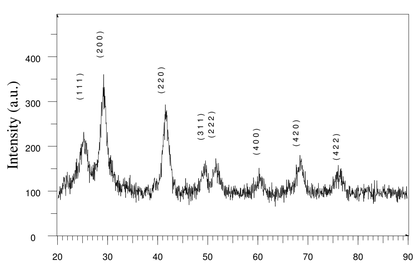
This laser-assisted spray (LAS) process for the growth of nanoparticle films offers two main advantages over the more conventional spin-coating and drop-casting methods: (1) the surfactants are burnt-out prior to deposition and thus QDs form intimate contacts between QDs and QDs and the host materials, (2) nanoparticles are sprayed uniformly over the substrate preventing local segregation of QDs.



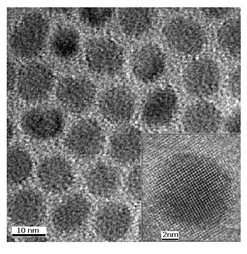
An ultrasonic nebulizer that operated at a frequency of 2.4 MHz. is used to atomize the hexane-PbSe nanoparticle precursor to produce an aerosol with droplet sizes of about 1.5 μm. Each droplet contains thousands of PbSe nanoparticles. The aerosol is carried by the SF_6 gas into the growth chamber through a nozzle. The SF_6 gas has a high absorption coefficient at the 10.9mm wavelength of a CO_2 laser. By focusing a Continuous Wave (CW) 14W CO_2 laser beam at the nozzle increases the temperature of the aerosol-gas mixture to a temperature of about 300°C. The high temperature causes the solvent and the surfactants to evaporate while PbSe nanoparticles are deposited on a substrate.

Results

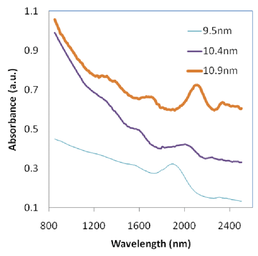
Characterization of PbSe QDs prior to LASP deposition



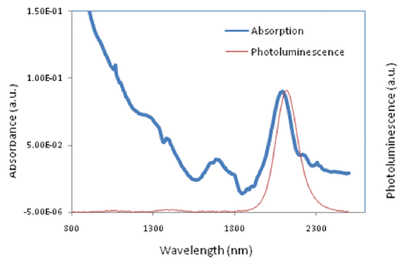
(1)



(2)



(3)

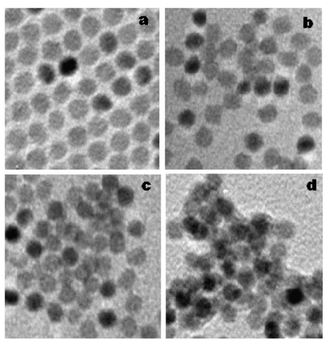


(4)

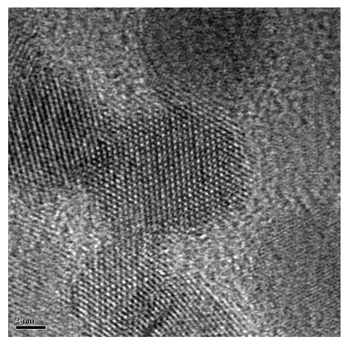
X-ray diffraction pattern of sample made by dropcasting is shown in Fig. 1. A self-assembled monolayer of surfactant coated PbSe QDs produced in the first step of the growth process on a TEM grid is shown in Fig. 2. This images confirm that the QDs grown by the solution technique are single crystals. In addition, the surfactants cause the particles to be separated by about 1-2 nm.

The UV- absorption spectrum of PbSe QDs in PCE exhibits a blue shift with decreasing size. Fig. 3 illustrates the size dependent spectra of various-size PbSe semiconductor nanocrystals. Well defined peaks reflect the narrow size distribution and corresponding bandgap edges to each particle size distribution. Also it confirms the quantum confinement of these PbSe semiconductor nanocrystals and tunablity of the badgap. The perfect Gaussian shape in Photoluminescence graph in Fig. 4 clearly shows the strong near-infrared emission of as-synthesized PbSe semiconductor nanocrystals. There is a 25nm Stokes shift between the absorption and emission spectrum due to energy difference between absorbed photon and emitted photon.

Characterization of PbSe coatings deposited by LASP

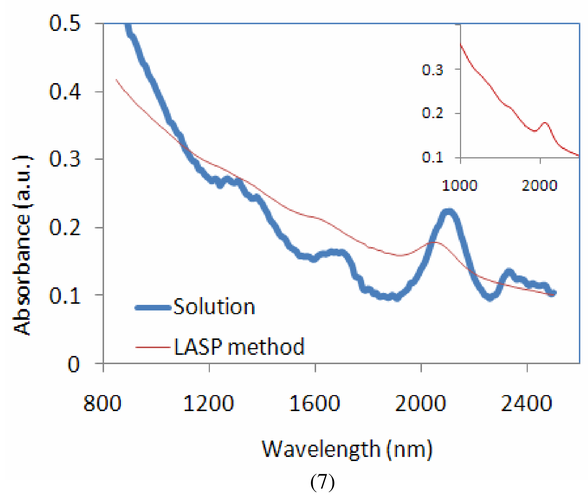


(5)



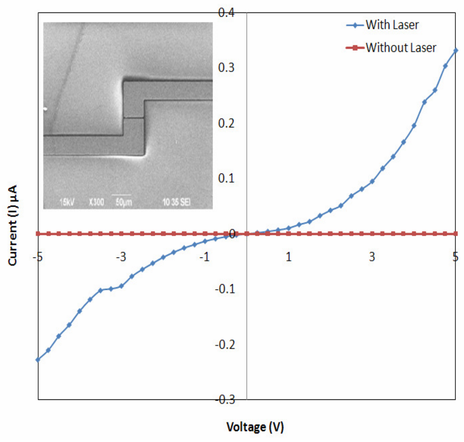
(6)

The temperature of the LAS process is controlled by the gas flow rate. Increasing the flow rate decreases the temperature due to reduced interaction time. Fig. 5 shows TEM images of PbSe QDs collected on TEM grids for gas temperatures in the ranges of 80-100°C, 150-200°C, and 200-250°C. Particles appear to agglomerate above a temperature of 200°C while temperature in the range of 150-200°C provided the best condition for producing an interconnected network of particles. High resolution TEM images of a PbSe QD film grown by the LAS process in the temperature range of 150-200°C are shown in Fig. 6. The QDs appear to make intimate contacts with each other while the integrity of the crystal structure of individual QDs are preserved.



(7)

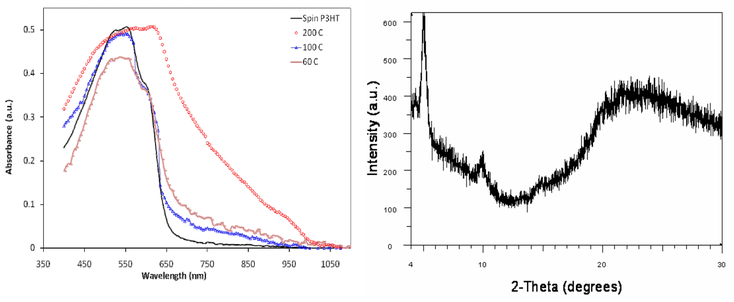
The UV- absorption spectra of the 200 nm thick film and colloidal solution of PbSe QDs with average particle sizes of 9.5 nm is shown in Fig. 7 The first, second and the third quantum levels were observed in both samples. In addition, the blue shift in the absorption peaks corresponding to decrease in particle size is also noticeable. Lower intensities are observed due to the small absorption length in the film in comparison to the solution.



(8)

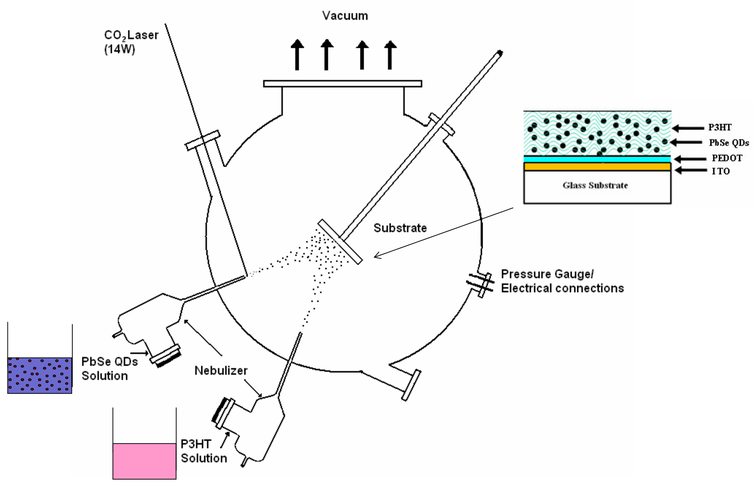
Fig.8 shows the measured current for an applied voltage across the 2 mm gap. The current produced by the LAS deposited film is more than three orders of magnitude larger than that measured for the drop-casted film, which indicates a low resistant carrier percolation path across the electrodes.

Characterization of P3HT coatings deposited by LASP

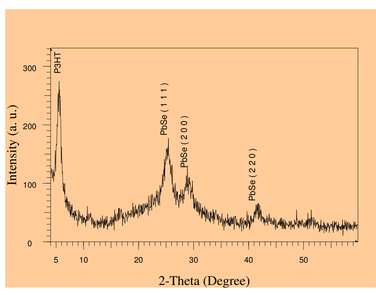


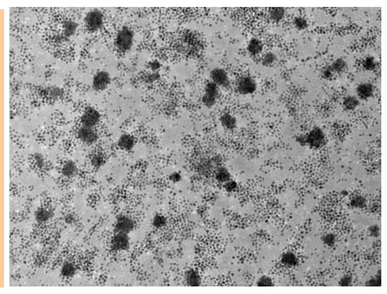
XRD pattern clearly shows the crystalline peaks corresponding to P3HT polymer. This is very similar to XRD patterns observed in Spin coating technique . The samples deposited at 100 °C show identical absorption spectrum compared to Spin-coated absorption spectrum. Therefore, it confirms that P3HT polymer can be deposited by LASP technique

Laser Assisted Co-deposition



This method allows depositing two materials at the same time, which required in hybrid quantum dot/polymer structure deposition. In case of PbSe QDs/Polymer deposition, one nozzle carries aerosol of PbSe quantum dots/hexane precursor while other nozzle carries aerosol of P3HT polymer precursor. The CW CO_2 laser is focused on to the PbSe quantum dot carrying nozzle to burn the surfactant during the deposition. The P3HT polymer droplets will deposit on the substrate with out any laser interaction. During the deposition the both P3HT polymer and surfactant free quantum dots will mixed on the flight and deposit on the substrate to form a hybrid structure. Gas flow rate through the nebulizer will control the growth rate of each species at the substrate.





Peaks of XRD pattern confirms the formation of P3HT polymer and the PbSe NC in the film.TEM imaged shows the initial formation of P3HT polymer and the PbSe NC on the film. It provids a good evidence of uniformity of PdSe Qds in the hybrid structure.

CONCLUSIONS:

This work demonstrated the growth of surfactant-free PbSe QD films by using a laser assisted spray process. Laser heating during film growth evaporated the organic surfactants and formed a uniform coating of the QDs on the substrate. TEM images of LAS deposited QDs were seen to retain their single crystal nature while forming intimate contacts between adjacent PbSe nanoparticles. Absence of surfactant in LAS deposited films improved the conductivity by more than three orders of magnitude. Finally, laser assisted co-deposition is very successful in depositing PbSe/P3HT hybrid structures.

.

UNIVERSITY OF SOUTH FLORIDA
COLLEGE OF ARTS & SCIENCES

This project was supported by the Department of Defense (DOD)-USAMRMC
Grant Number W81XWH-07-1-0708

LAMSAT Laboratory for Advanced Material Science and Technology
Department of Physics – University of South Florida