Enhanced charge-transport in surfactant-free PbSe quantum dot films grown by a laser-assisted spray process

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A laser-assisted spray process was developed to deposit surfactant-free PbSe quantum dot (QD) films directly on a substrate. These QDs are in close contacts with each other, forming a percolation path for charge transport. Absorption spectroscopy confirmed the quantum confinement of the deposited particles. Room temperature current-voltage measurements across a 2 μm tunnel junction formed by the QDs produced a power-law dependence of the form $I \propto V^{2.25}$, which describes a percolation path of dimensionality slightly above two dimensions. Temperature dependent conductance studies showed thermally activated transport at high temperatures and temperature independent tunneling, followed by previously unobserved metallic conduction at low temperatures. © *2009 American Institute of Physics*. [doi:10.1063/1.3233926]

Absorption of a UV photon with energy much higher than the band gap energy by an electron in the valance band excites it to a higher energy level in the conduction band, followed by thermal relaxation to the conduction band edge.[1,2] This one *e-h* pair per photon limitation is one of the major factors incorporated into determining the Shockley–Queisser theoretical efficiency limit in *p-n* junction solar cells.[3] The possibility of suppressing the thermal relaxation in quantum confined systems such as quantum dots (QD) and imparting the excess energy of UV photons via an impact ionization process to generate additional *e-h* pairs (excitons) has been demonstrated in recent years.[4–6] However, as a result of the discrete energy levels in a quantum structure, the formed *e-h* pairs are bound excitons and thus require dissociation for transport.

Dissociation of excitons requires them to overcome the binding energy between the *e-h* pairs, which is of the order of 0.01 eV.[7,8] However, when embedded in a host material, dissociation via transfer of one or both charge types into the host material is possible based on the band alignment at the host/QD interfaces if QDs make a close contact with the host material.[7,9] Typically, PbSe QDs are fabricated by solvothermal methods where surfactants are used to control the particle size and to prevent agglomeration.[10] These organic ligands on QDs form resistive barriers to charge transfer. Removal of surfactants by chemical means after forming QD/host composite structures is not possible.[11] In this paper, we report the transport properties of surfactant-free PbSe QD films deposited directly on a substrate by a laser-assisted spray (LAS) process, which was described in detail in a previous publication.[12] The main advantage offered by this method is that the surfactants are burnt-out prior to deposition and thus the QDs are in close contact with each other.

The growth process consists of two steps. In the first step, a colloidal solution containing 9–10 nm PbSe nanoparticles was formed by a solvothermal technique.[10] This method offers the added advantage of using noncoordinating solvents.[13,14] As-grown particles are coated with oleic acid that prevents agglomeration. The precipitated PbSe nanocrystals were redispersed in hexane. A self-assembled monolayer of surfactant coated single-crystal PbSe QDs produced in the first step on a transmission electron microscope (TEM) grid is shown in Fig. 1. The surfactants cause the particles to be separated by about 2–3 nm.

In the second step, the hexane solution containing the PbSe nanoparticles was used as a precursor in the LAS process. The aerosol produced by a nebulizer was carried by the SF_6 gas into the growth chamber through a nozzle that contained an inert gas at an ambient pressure of 200 Torr. The SF_6 gas has a high absorption coefficient at the 10.9 μm wavelength of a CO_2 laser. A continuous wave 14 W CO_2 laser beam focused at the nozzle exit increases the temperature of the aerosol-gas mixture. The optimum gas temperature was determined to be in the range of 150–200 °C. Below this range the surfactants were not completely burnt-out, while above this range particles began to coalesce. The high

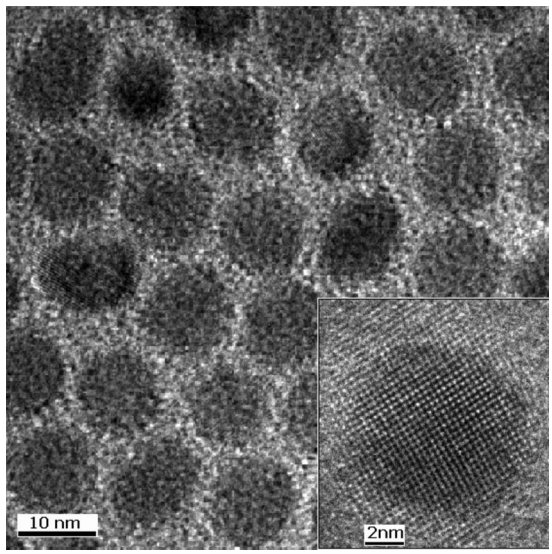

FIG. 1. TEM image of a monolayer of PbSe QDs with surfactant coating. Inset is a high-resolution TEM image of individual PbSe QD. The single-crystal structure is clearly apparent.

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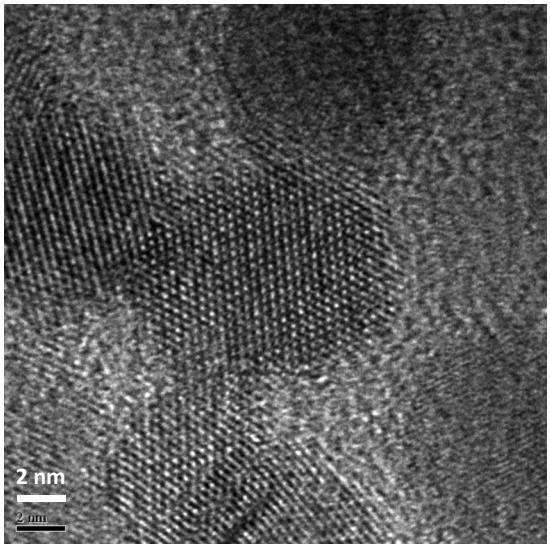

FIG. 2. TEM image of QDs deposited by the LAS process showing single crystalline particles in contact.

temperature causes the solvent and the surfactants to evaporate, while surfactant-free PbSe nanoparticles are deposited on a substrate. Figure 2 is a TEM image of a PbSe QD film grown by the LAS process. QDs in these films are uniformly distributed and in contact with each other, while the integrity of the crystal structure of individual QDs are preserved.

The absorption spectra of a 200 nm thick film deposited by the LAS process and that for QDs dispersed in hexane are shown in Fig. 3. The first, second, and third quantum levels of the PbSe QDs in the colloidal solution are observable. The quantum confinement of the QDs in the film is evident even though the intensities are much lower due to the small absorption length in the film in comparison to the solution.

The current-voltage (*I-V*) characteristics of LAS deposited films were compared with those grown without laser heating. Films were deposited within a 2 μm gap that was patterned on Ti/Au alloy electrodes deposited on a glass substrate.[15] Figure 4 shows the measured current for an applied voltage across the 2 μm gap. The current produced by the LAS deposited film is more than three orders of magnitude larger than that measured for films deposited without laser heating. Several previous experiments on mono- and

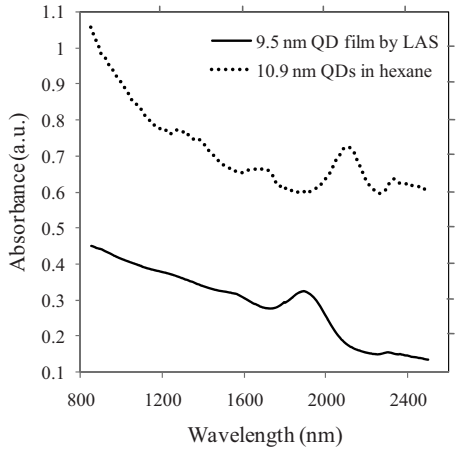

FIG. 3. UV absorption spectra of 10.9 nm QDs in solution and 9.5 nm QD film formed by LAS deposition. There is a 29.1 nm blueshift between them due to the reduce QD sizes after burning the surfactant.

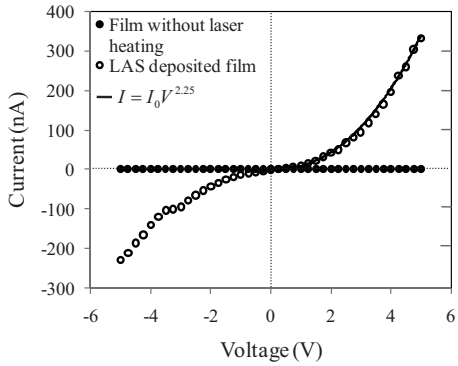

FIG. 4. Comparison of the conductivity of caped PbSe QD films formed by the spray process without laser heating and surfactant-free PbSe QD films by LAS process across a 2 μm gap between Ti/Au electrodes. The solid line is a functional fit of the form $I \propto V^{2.25}$.

multilayered nanoparticle arrays have shown the *I-V* characteristics to follow a functional dependence of the form $I \propto V^{\xi}$, where ξ is a scaling exponent.[15–18] The value of the exponent is related to the number of percolation paths available for current flow, and thus depends on the dimensionality of the junction.[19] For arrays of one-dimensional and two-dimensional percolation paths, the observed dependences are $\xi \approx 1$ and $1.6 < \xi < 2.1$, respectively. For a junction of dimensionality slightly higher than two dimensions, the observed dependence is $2.1 < \xi < 2.7$. This mode of transport is in agreement with the 2.25 exponent we observed for the films grown by the LAS process (Fig. 4).

The temperature dependent conductivity of QD films studied by a four-point technique indicated three different transport regimes (Fig. 5). From room temperature down to about 200 K, a thermally activated hopping of electrons between QDs described the transport process (inset in Fig. 5). From 200 to about 110 K, the conductance became less dependent on temperature, indicative of a tunneling mechanism. However, below 110 K conductance turned to metallic behavior that has not been observed for caped QD assemblies. This phenomenon can be explained by using theoretical models that have been developed based on the quantum mechanical coupling of energy levels of adjacent QDs, facilitated by negligible interparticle separations.[15,20,21] The coupling energy between two neighboring QDs is given by $h\Gamma$, where h is the plank constant and Γ is the tunneling rate between two ground state orbitals. In the weak coupling regime where $h\Gamma \ll k_B T$, the tunneling is restricted to adjacent

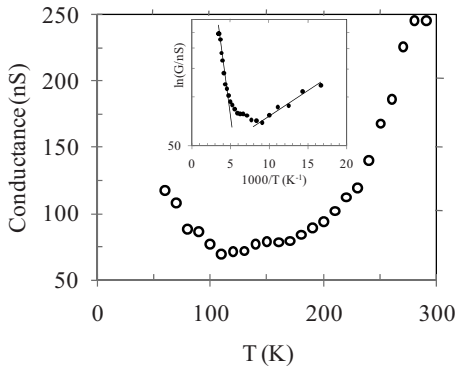

FIG. 5. Temperature dependence of conductance (*G*) in LAS deposited PbSe QD films determined by a four-point probe technique. The inset shows *G* in log scale vs the inverse of *T*.

QDs. However, in the strong coupling regime ($h\Gamma > k_B T$) orbitals may extend over many QDs forming a continuous band that enhances carrier transport. This condition may be satisfied for our films at low temperatures since the interparticle spacing is negligible.

In conclusion, the current transport at room temperature in QD films formed by LAS process was enhance by more than three orders of magnitude and the power-law description of the *I-V* characteristics points to a percolation path with dimensionality slightly higher than two dimensions. At high temperature, the carrier transport is thermally activated, while at low temperature strong coupling between neighboring QDs form a continuous band that produced metal-like conductivity.

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