Investigation of quantum dot contact systems by pulsed surface photovoltage

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Colloidal semiconductor nanoparticles do not form intimate charge-selective, passivating or Ohmic contacts due to the surfactant layers at the surface of nanoparticles. This makes the realization of highly efficient and stable electronic and photo-electric devices such as solar cells based on semiconductor quantum dots rather complicated. Charge separation by injection from quantum dots (QDs) into TiO_2 [1] or CdS [2] layers, for example, or by disruption of excitons at CdTe-QD / CdSe-QD interfaces [3] has been shown in the past. In this work we investigate charge separation in CdSe-QD contact systems by pulsed surface photovoltage (SPV). It is shown that asymmetric trapping and relaxation of SPV signals in CdSe-QD contact systems depend strongly on surface treatment, substrate and temperature. Multiple trapping in an isolated QD is proposed as an approach for a model system.

(a) Experimental

CdSe-QDs (diameter 5 nm) with pyridine surfactants were deposited by dipping in CdSe-QD solution and controlled pulling speed to realize layer thicknesses of about 1 monolayer and 5 monolayers of CdSe-QDs. Substrates of ITO, steel and Au coated glass were used. Post-treatments were performed in benzene-dithiol in acetonitrile or in 0.1 M NaOH in methanol solutions. Samples were prepared under nitrogen atmosphere in a glove box; SPV measurements were performed in vacuum (10^{-5} mbar) in the fixed capacitor arrangement.
SPV transients were excited with laser pulses (NT343/1/UVE EKSPLA, duration time of a pulse: 5 ns) while 8 transients have been averaged (repetition rate 1 Hz).
The influence of substrate, surface conditioning and annealing (heating up to 220°C and cooling) on charge separation in CdSe-QD layers with fixed diameter of 5 nm was studied by time dependent SPV measurements while wavelength and intensity were fixed at 590 nm and at about 3 mJ/cm², respectively.

(b) Dependencies on substrate and treatments

Sign and relaxation of SPV transients depended strongly on the substrate and on the surface treatments (see, for example, figure 1).
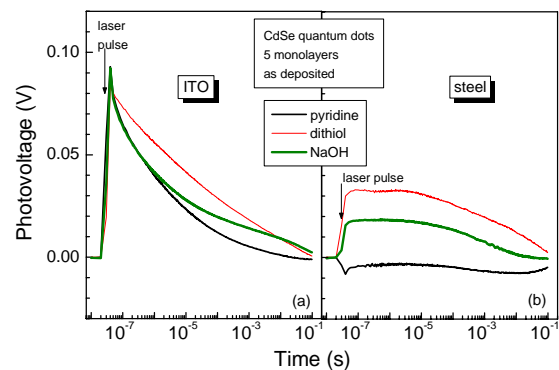

Fig. 1: SPV transients of as deposited 5 ML thick CdSe-QDs layers on ITO (a) and steel (b) substrates for different surface treatments.

The SPV signals and times at which the transients decayed to ½ are summarized in figure 2. Largest SPV signals were observed for ITO substrates while the differences were low for the different treatments. The longest SPV transients were observed for steel substrates. After annealing in vacuum the differences between pyridine, dithiol and NaOH treatments decreased, i.e. a homogenizing process lead to a decrease of bonding specific differences. The process is, in our opinion, related to the generation of deep defect states due to partial evaporation of surfactants and / or selenium atoms from the surface of CdSe-QDs.

(c) Temperature dependent SPV transients

Figure 3 shows typical SPV transients of CdSe-QD layers (1 ML and 5 ML) deposited on ITO. One stretched exponential was sufficient to fit the transient for 1 ML whereas two stretched exponentials with op-

posite sign were needed for fitting the transient for 5 ML. Therefore, an additional transport process with opposite direction of charge separation appeared for the thicker layer.
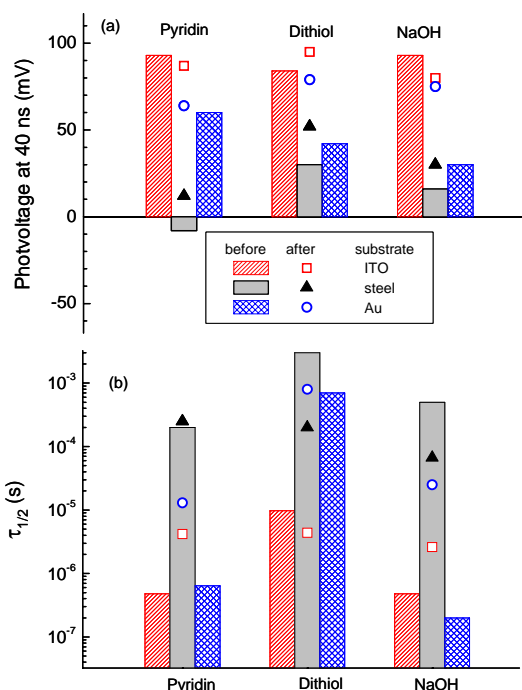

Figure 2: Summary of the SPV signal at 40 ns (a) and of the times at which SPV transients decayed to half maximum (b) for pyridine dithiol and NaOH treated CdSe-QDs deposited at ITO, steel and Au surfaces before and after annealing at 220°C in vacuum.

The thermal activation energy of the average decay times was obtained from SPV transients measured during cooling from the highest temperature and amounted to about 0.95 eV for both processes with positive and negative signs.
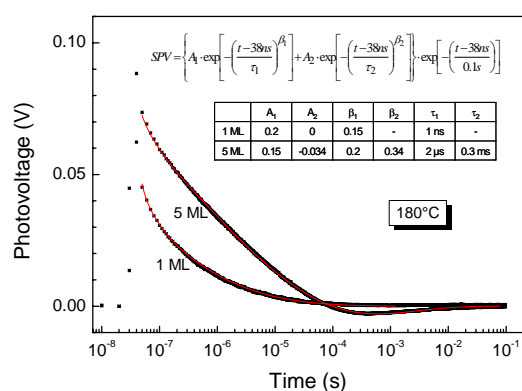

Figure 3: SPV transients measured at 180°C of 1 and 5 ML thick CdSe-QDs layers deposited at ITO and treated with dithiol.

(d) The isolated quantum dot approximation

An exciton photo-generated in a QD is destroyed by trapping of one of the charge carriers at a surface state acting as a strong electron acceptor or donor. The remaining second charge carrier is still delocalized, in contrast to the trapped carrier. Initial charge separation at short times, i.e. below the resolution time of the measurement system, is driven by asymmetric trapping within the ML of QDs closest to the contact layer in the case of CdSe-QD adsorbed at ITO [4]. The asymmetric trapping can be observed by SPV. The driving force of initial charge separation is the different occupancy of states at the QD due to interaction with the substrate, depending on the distance to the substrate surface and / or different workfunctions. The relaxation of the asymmetrically trapped charge carriers can be described, for example, by Miller-Abrahams hopping. [5]. In the simplest cases, electron transfer from an isolated QD into a surface state at the substrate / QD interface or into a neighbored QD should be considered (figure 4). It should be remarked that the distance between separated charge carriers can further increase in time if the carriers are trapped in neighbored QDs. SPV transients of CdSe-QD layers were simulated by averaging the distances between separated charge carriers perpendicular to the electrode over a large number of samples within the single QD approximation for different trap concentrations and energy distributions.
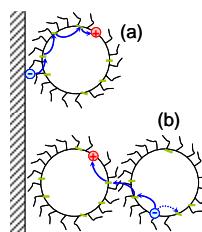

Figure 4: Schematic of the isolated QD approximation model with relaxation of a mobile electron from an interface state at the ITO surface (a) or from a neighbored QD (b).

References

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