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Formation of a heterojunction by electrophoretic deposition of CdTe/CdSe nanoparticles from an exhaustible source

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ABSTRACT

Fast and well controlled electrophoretic deposition of CdTe and CdSe nanoparticle (CdTe-np and CdSe-np) layers and nanoparticle layer systems from an exhaustible source has been demonstrated. Using a small volume of pyridine based nanoparticle suspensions with varying concentrations, these were completely drained of nanoparticles during deposition. Our proposed approach is well suited to a practical realization of engineering materials with different band gaps for various promising applications such as fabrication of nanodevices. The formation of a charge selective contact across the CdTe-np/CdSe-np heterojunction was investigated by surface photovoltage methods and evidence of the separation of charge carriers at a CdTe-/CdSe-np heterojunction in-between was demonstrated.

1. Introduction

Semiconductor nanoparticles (np) and quantum dots (QD) broaden opportunities for photovoltaic solar energy conversion, for example, by extending the strategic potential of highly absorbing semiconductors made from earth abundant elements [1], by engineering the absorption edge with respect to light absorption and charge separation at injecting contacts [2], or by implementing specific effects such as multi-exciton generation [3] for overcoming the Shockley–Queisser limit of photovoltaic solar energy conversion [4]. Separation of photo-generated charge carriers is crucial for high efficiency of solar cells besides light absorption and photo-generation. However, charge separation within QD layer systems is still challenging for the application in solar cells, for example, in solar cells with extremely thin absorber [5]. The possibility of charge separation across type II QD heterojunctions has been demonstrated by surface photovoltage (SPV) measurements for CdSe-QD/CdTe-QD layer systems [6]. The QD layers and layer systems were prepared by a very time consuming layer-by-layer technique in Ref. [6]. The fast and controlled deposition of QD layers and layer systems with thicknesses of the order of 100 nm is important for the development of solar cells based on QDs.

In this work we propose electrophoretic deposition (EPD) of CdTe-np and CdSe-np from an exhaustible source for fast and well controlled deposition of nanoparticle layers and layer systems. Similar to a previous work from the group of Salant et al. [7], organic based nps were deposited onto a substrate. In difference to their work, pyridine capped nps were used, which were not embedded into a mesoporous structure but formed layers on one of the electrodes. The key point of this work is the use of a small with respect to the treated surface area volume of a diluted nanoparticle solution from which all nanoparticles are deposited on a conductive substrate. By this way a wide technological window with a minimum of control parameters could be realized for absorber deposition. The thickness, morphology, structure and element distribution were analyzed for deposited nanoparticle layers and layer systems. The formation of a charge-selective CdTe-np/CdSe-np heterojunction was documented by SPV measurements in the fixed capacitor and Kelvin-probe arrangements.

2. Experimental details

2.1. Electrophoretic deposition

The electrophoretic deposition took place in a horizontal setup with two parallel electrodes (distance 6 mm). The upper electrode, a platinum electrode, served as the counter electrode whereas the lower working electrode, was an In_2O_3:Sn (ITO) or SnO_2:F (FTO) coated glass substrate (1 × 1 in.). To avoid voltage ramps at the beginning and end of the deposition a time-controlled relay was used. The deposition was performed in a glove box to prevent oxidation of the layers.

The volume between the electrodes was filled with 1 mL of pyridine capped nanoparticles suspended in pyridine (CdTe d = 8 nm; CdSe d = 5 nm from Bayer Technology Services) with a known concentration (0.075 to 0.175 mg/g). For better adhesion of nanoparticles the FTO and ITO substrates were pretreated with an argon plasma. A voltage of 500 V was applied for 8 min during the deposition. The suspension was clear after deposition and was depleted of all nanoparticles. The deposition of nanoparticles took place on the negatively charged electrode and resulted in a layer thickness of 100 to 300 nm.

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To see the effect of heat treatment on the performance of nanoparticle layers, some of the deposited layers were annealed at 200 °C under nitrogen atmosphere in the glove box. Transmission electron microscopy images show that the nanoparticles are not sintered at that temperature and keep their shape. Thus, the tempering serves to remove residual solvent in the layer, probably some surfactants and to stabilize surface states.

As the nanoparticles exhibit strong absorption in the visible spectra, UV/VIS spectroscopy (Lambda 950) was used for the documentation of depletion of nanoparticle suspensions. Therefore measurements of the suspension before and after deposition were recorded.

Nanoparticle thin films were analyzed by scanning and transmission electron microscopies. The scanning electron microscopy (SEM) image was recorded at an acceleration voltage of 18 kV (Zeiss, LEO 1530 GEMINI). The energy dispersive X-ray (EDX) measurement was performed in the SEM at an acceleration voltage of 7 kV by a Thermo Noran X-ray silicon drift detector (acquisition and evaluation software Noran System Seven).

Transmission electron microscopy (TEM) images were recorded at an accelerating voltage of 120 kV (Philips CM12/STEM, LaB6 cathode). Preparation of the samples was done by gluing two samples face to face and thinning the cross section to 50 nm thickness.

2.2. Surface photovoltage analysis

Surface photovoltage (SPV) is a well-established method to measure photo induced charge-separation in single and multiple layers [8]. To detect a change in the surface photovoltage two consecutive processes are required. First, additional free charge carriers are created by absorption of light, which are separated in space in the second step. The sign of the SPV signal displays the direction of charge separation. Electrons that separated towards the surface are detected as a negative signal, whereas electrons that separated towards the substrate are detected as a positive signal and for the holes vice versa. Basically the SPV signal can be measured either in the arrangement of a parallel-plate capacitor [9], or by a Kelvin-probe arrangement detecting the contact potential difference (ΔCBD).

The intensity dependent SPV measurements were performed with in a parallel-plate capacitor arrangement in the same glove box as used for the deposition. Thus, the samples could be measured immediately after deposition; oxidation of the layers was avoided. The capacitor was formed by a SnO_2:F coated quartz cylinder, a thin mica sheet (~30 μm) and the grounded conducting sample. The coated quartz cylinder was connected to a high impedance buffer (input resistance 150 G Ω). The sample was excited through the quartz cylinder by an ultrabright LED (CREE-XRE5) and focused on the electrode (diameter of the electrode 6 mm, maximum light intensity of about 800 mW/cm^2). The relative light intensities were calibrated with a pyro-electric detector. The whole arrangement was placed in a closed metal box. During measurements the light was switched on for ~2 s and the change in voltage at the buffer (the SPV signal) was measured with a voltmeter. After each measurement, the capacitor took ~1 min to discharge. All measurements were started at low intensities going to the higher intensities to minimize charging effects.

The spectral dependent measurements were done by contact potential difference (ΔCBD) measurements with a Kelvin probe (Besocke Delta Phi, Germany). The light-induced changes of the work-function difference between the sample and a vibrating gold grid were monitored. The work-function of the gold is assumed to be independent of illumination. Therefore the changes in the work-function difference correspond to the ΔCBD which is equal to the negative of the SPV signal of the sample. Thus SPV spectra shown in this publication were derived from ΔCBD spectra which were set to zero at ΔCBD in the dark and multiplied by −1.

A halogen lamp and a quartz prism monochromator (SPM2) were used for illumination. The spectra were not normalized by the light intensity, because of the nonlinear dependency of the SPV signal on light intensity. The resolution time of the measurement is in the order of 10 s. Note that for these measurements the samples were transported through air and thus changes in surface states due to oxidation may occur.

3. Results and discussion

Fig. 1 shows UV/VIS absorption spectra of pure pyridine and CdTe-np suspension before and after deposition of CdTe-np. Absorption due to CdTe-np took place at wavelengths below 760 nm. After deposition of nanoparticles no absorption was present in this range, indicating a practically complete electrophoretic deposition of nanoparticles from the suspension onto the substrate.

A scanning electron microscope (SEM) image of a broken cross section of a deposited CdTe nanoparticle layer on ITO is shown in Fig. 2(a). The layer was deposited from a solution with a concentration of 0.175 mg/g. The layer thickness measured with the SEM is 290 ± 20 nm. Fig. 2(b) shows a TEM image of CdTe-np on ITO annealed at 200 °C. The TEM image shows that the particles were not sintered due to annealing at 200 °C, or due to reaction between the nanoparticles at the voltage of 500 V. The nanoparticles still have a size of around 7 nm.

Fig. 3 shows an energy-dispersive X-ray spectroscopy (EDX) mapping and an EDX line scan of a CdTe/CdSe-np layer system, which was deposited via multiple EPD on a FTO substrate. The first EPD was performed with a solution of CdTe-np, the second with CdSe-np. For the EDX mapping the energy of the electron beam was 10 keV. The line scan over the cross section showed a continuous signal of cadmium over the CdTe/CdSe-np layers. The Se and Te signals show a slight mixing of CdSe-np and CdTe-np at the interface as well as some penetration of CdSe-np in the CdTe-np layer. The reason for the mixing was solving of particles at the surface when the solution of CdSe particles for the second EPD is filled in the EPD cell. At the CdSe- and CdTe-np layers, a carbon signal could be observed. The origin of this signal was the organic capping of the nanoparticles.

Fig. 4 shows intensity dependent SPV signals of electrophoretically deposited nanoparticle layers measured in the glove box. In the single, pristine CdTe-np and CdSe-np layers (Fig. 4a), a positive SPV signal was observed. The non-monotonous dependence observed for the CdSe-np layer points towards slow charging and discharging of surface states. Annealing of the layers stabilized the occupation of surface states. This led to a monotonous increase of the SPV signal with increasing light intensity. The SPV signal of the annealed CdTe-np layer was

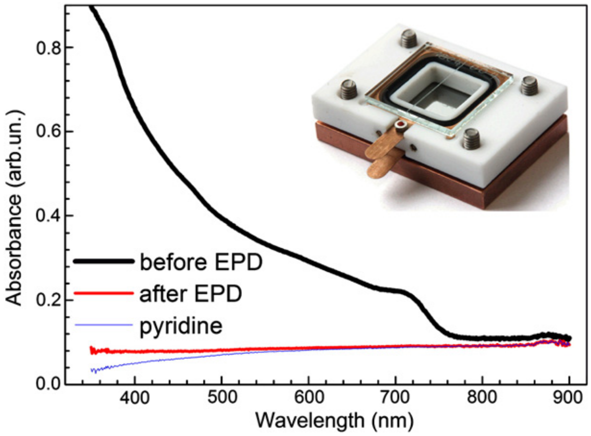

Fig. 1. Absorbance spectra of a pyridine solution with CdTe nanoparticles before (thick black line) and after (medium red line) electrodeposition. The thin blue line gives the spectrum of the pure pyridine solution. The insert shows the opened electrochemical cell with the substrate.