CdS nanoparticles surfactant removal transport study by transient charge measurements

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Abstract: The electronic transport of CdS nanoparticles (nano-CdS) covered by hydrophilic alkanolamine molecules as surfactants was studied. The nanomaterial was prepared by low-temperature decomposition of cadmium ethylxanthate in hydrophilic solvents like mono-, di- or triethanolamine. The nanoparticles were isolated by precipitation procedures in solid state and they are easy to re-disperse in water systems. Films with nanoparticles were exposed to UV radiation, with the exposure varying in time interval 10 – 60 min.

The goal of the work was to study the electronic transport in the array of nanoparticles. The experimental techniques used was the Isothermal charge transient spectroscopy (IQTS) working with the a unique charge transient processor in the sampling range 2 μs – 900 ms with resolving power of about several hundreds of electrons. The second method was the surface photovoltaic method (SPV). Two basic novel phenomena were observed on the film formed by nano-CdS provided with tu surfactant, in *I-V* characteristics the increase of current was observed with a strong nonlinearity, marking the increased transport via nanoparticles, and the occurrence of charging–discharging phenomena with strong maximum described by the distribution of relaxation times and/or trapping states occurrence. The photoconductivity action spectra agree with the absorption edge of size distributed nanoparticles.

Keywords: CdS nanoparticles, Alkanolamine surfactants, Isothermal charge transient spectrum, Hybrid solar cells.

1. Introduction

The organic/inorganic hybrid solar cells work on the concept of bulk heterojunction, where excitons created upon photoexcitation are separated into free charge carriers at interfaces between two semiconductors-inorganic nanoparticle and bulk organic polymer forming a composite thin film[1][2][3]. Electrons will be then accepted by the inorganic nanomaterial with the higher electron affinity (electron acceptor, here the inorganic nanoparticle) and the hole by the polymer with the lower ionization potential (electron donor, here the polymer matrix). Both types of carriers are then transported by independent mechanisms to corresponding electrodes. The contemporary problems with the hybrid solar cells are the choice of suitable components for hybrid solar cells to match the solar spectrum, the solubility of both components and the transport of holes on the array of nanoparticles[4][5].

The aim of the paper is to elucidate the influence of the surfactant in the core – shell model on the transport of carriers (holes) by the process of diffusion on the array of nanoparticles. The main idea is to change the medium distance of nanoparticles by the surfactant length and thus changing the hopping probability of charge carriers resulting in the change of the average mobility and diffusion coefficient. For this purpose a new, extremely sensitive method for the study of transport and traps distribution, isothermal charge transient spectroscopy (IQTS) and surface photovoltaic method (SPV) for the diffusion study was used. For this purpose we examine one component of the hybrid organic/inorganic system MEH – PPV/nano-CdS nanoparticles covered by alkanolamine molecules as surfactant produced by a new technique.

2. Methodology

2.1. Sample preparation

The preparation of nano-CdS was described in detail elsewhere [6] so we will mention only few facts here. A new nano-CdS covered by hydrophilic alkanolamine molecules was prepared by low-temperature decomposition of cadmium ethylxanthate in hydrophilic solvents of mono-, di- or triethanolamine. By appropriate choice of reaction time, temperature and xanthate concentration, it was possible to tune the size and physical properties of resulting nanoparticles. The samples were deposited from ethanolamine solution by spincoating or drop casting on Au film evaporated on p-Si substrate or on borosilicate glass provided with ITO film and dried under the vacuum (rotary pump 10 Pa annealed at 80 ^{o}C and turbomolecular 10^{-4} Pa annealed at 100°C) to remove the solvent. For the characterization of nanoparticles the UV-VIS absorption, photoluminescence and Raman spectroscopy was used [6].

2.2. Isothermal charge transient spectroscopy (IQTS)and Surface photovoltaic method (SPV)

Electronic transport measurements were performed with charge transient processor (CTP) in local mode [7], when the usual evaporated top electrode is replaced by the tip of the scanning probe in form of a sharpened 80-μm-tungsten wire oriented perpendicularly to the surface. The charge to voltage converter has the resolution of hundreds of electrons and time resolved transients from 2 μs to hundreds of ms can be recorded. The input converter integrates the current transients following the voltage pulses periodically applied to the sample. The duration of excitation pulses was set from 1 to 100 ms, their amplitude from 0.5 to 5 V, and the period from 147 to 547 ms. The isothermal charge transient spectrum (IQTS) is created by combining samples from charge transients at particular times using the formula $\Delta Q(t_1) = Q(t_1) - 1.5Q(2t_1) - 0.5Q(4t_1)$ [8] with t_1 swept with 2 μs step starting at the trailing edge of the pulse up to the maximal point for which $4t_1$ fits before start of the next pulse. This way of transient processing acts as a filter of measured relaxation times, i.e., IQTS signal is detected when the time constant of the relaxation process is comparable to t_1. In addition, this formula eliminates the linear component of the response, which is caused by the integration of dc current. The peak maximum corresponds to 0.174 of the total charge Q_0 responsible for the peak. To reduce the noise usually 50 transients were summed. The charge transient processor allows to evaluate in one special mode also the dc current by measurements of charge without application of excitation pulses using the formula: $I_{DC} = \Delta Q(t_2) - Q(t_1)) / (t_2 - t_1)$, and to obtain the current voltage characteristic by sweeping the bias voltage.

2.2.1. Surface photovoltaic method (SPV) [9] [10]

Electrical field of space charge region (SCR) of the thickness d (Fig.1). drives the photogenerated charge carriers leading to the photovoltage. The photovoltage was measured in a sandwich structure between the substrate silicon and the top glass / ITO with a Mylar sheet serving as a separating dielectric layer The scanning microscope view of the film is in Fig.1. A capacitive couple is formed in this way. Illumination was performed through the top electrode into the bulk. The samples were irradiated by low-intensity monochromatic light chopped with a low frequency of 11 Hz generating an alternating voltage which was measured by lock-in amplifier Stanford SR 830. In our experiment the chopper frequency was sufficiently low to obtain saturated pulses not influenced by relaxations. The spectra were taken at room temperature and in air.
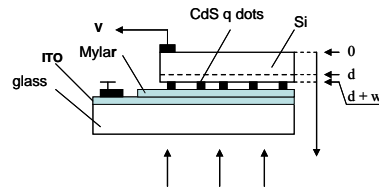
Fig.1. Arrangement of the SPV experiment. The polymer is illuminated with a chopped monochromatic light through transparent conductive electrode. As the second electrode serves the Si substrate.

3. Results

The SEM picture of the nano-CdS is in Fig.2 with the nanoparticles in the range of 20-30 nm. The representative I –V characteristics of Au / ano-CdS nanoparticles film / W probe (prepared in the standard way, i.e. annealed at 80 ^{o}C in the rotary pump 10 Pa vacuum) taken by IQTS for as deposited and UV irradiated sample (for 20, 40 and 60min are in Fig.3). We adjusted the filling and waiting time to ensure near to the steady-state characteristics. Corresponding IQTS signals are in Fig.4. The enormous increase of the *I-V* characteristics for positive applied voltage on ITO is recorded for degradation time 20 min, which gradually disappears with progressive degradation (40, 60 min). IQTS signals show for both polarities of the applied excitation pulses and do not depend on injection as the ability of both contacts (ITO and W) contacts are quite different as obvious from I–V transient characteristics. If we take into consideration the fact that the IQTS is stripped of the dc current, we then may conclude the observation is a bulk (contrary to contact) effect and most probably enhanced due to the decreased average distance among particles in the nano-CdS array.
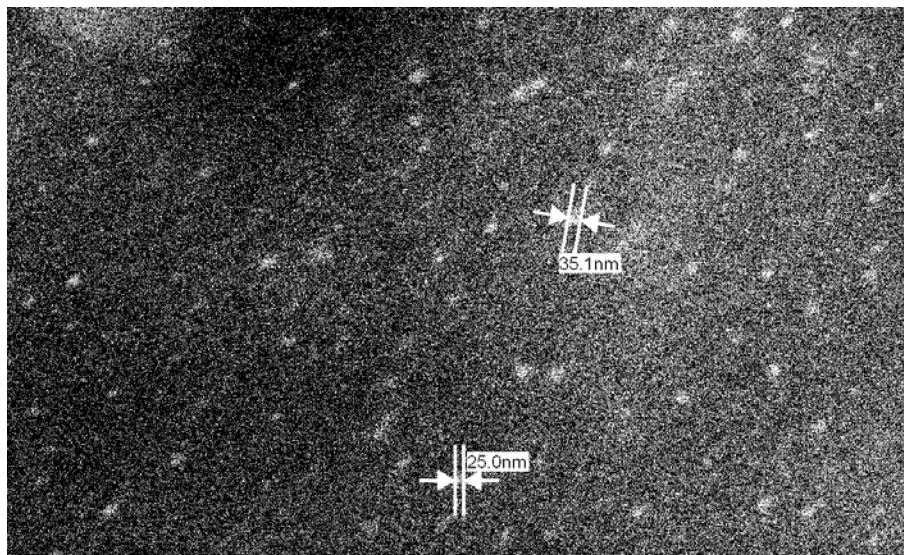

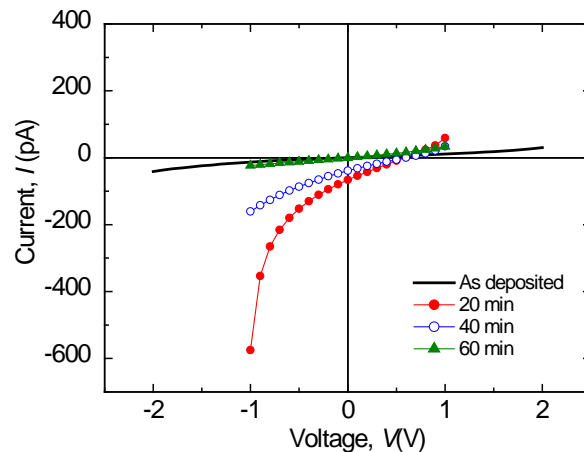*Fig.2. SEM photograph of nano-CdS on silicon substrate.*

Fig. 3. Evolution of I-V characteristics (voltage is taken with respect to W probe) of the structure Au / nano-CdS nanoparticles film / W probe with exposure time to UV irradiation.
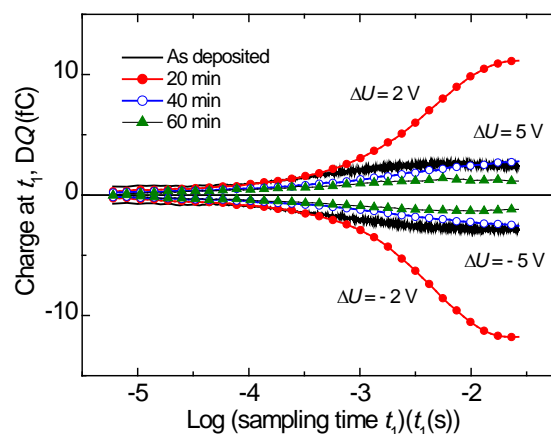

Fig. 4. Evolution of IQTS spectra of Au/nano-CdS /W.The parameter was the UV irradiation time and the polarity with respect to W tip. Bias voltage, U_b = 0, U_{ex}= 5 V for as deposited and 60 min exposed states, 2 V for 20 and 40 min exposed states. The period and duration of excitation pulses were set to 147 ms and 10 ms, respectively.

As the next step we measured we took the measurements on the identical sample degraded by 60 min UV (see Fig. 3 and Fig. 4) and carried out the anneal in vacuum 10^{-4} Pa at 100^oC for 10 min. The I –V characteristics taken by CTP for annealed at 100^oC and corresponding IQTS signals nearly returned to their original shapes (in Fig.3 and Fig.4). UV irradiation (for 20, 40 min) caused the same changes in I – V characteristics (Fig. 5) and corresponding IQTS signals in Fig. 6. The surprising recovery tendency and susceptibility to UV degradation changes are evident both in I - V and IQTS signals. The degradation for 20 min creates the bulk relaxation, similar to that in Fig.3 and Fig. 4.This observation may be due to the metastable degradation – recovery steps.
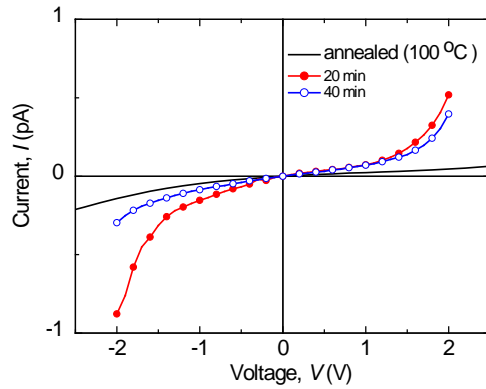
Fig. 5. Influence of annealing (100 ^{o}C for 10 min) on I-V characteristics (voltage is taken with respect to W probe) of the structure Au / nano-CdS nanoparticle film / W probe.
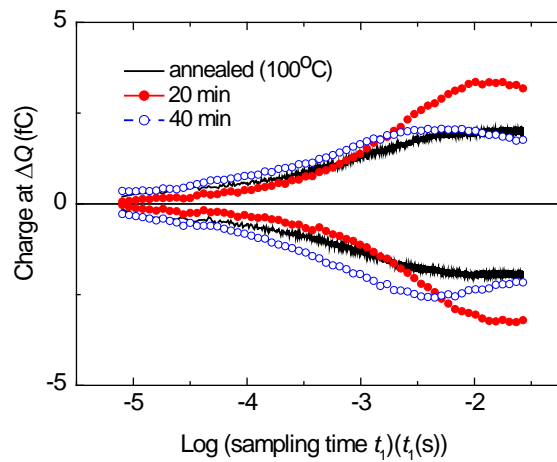

Fig.6. Influence of annealing (100 ^{o}C for 10 min on IQTS, all parameters identical to those in Fig.4.
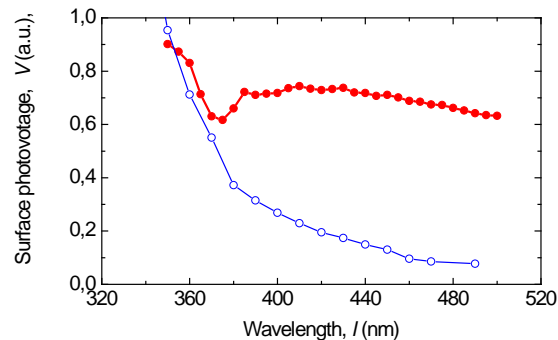
Fig.7. SPV spectrum of p-type silicon with nano-CdS (solid circles). The quantum size effect in the nanoparticles influences the spectrum from the 375 nm to 500 nm. SPV spectrum of the wafer is shown for comparison (open circles).

The SPV signals of nano-CdS on p-Si substrate isvisible in Fig. 7. The composed signal results both from photoconductivity of nano-CdS and from the Si substrate, as it is obvious from the signal on the bare Si substrate. The measurements of the diffusion coefficient in CdS due to the hopping transport diffusion is under way.

4. Discussion and Conclusions

The idea behind this experimental activity presented here was the obvious knowledge about the limiting ill influence of the hole transport in hybrid solar cells by hopping transport, where the average distance and coupling among particles was given by the shell (surfactant in this case) [4][5]. With this on mind and realizing our recent results on UV degradation of σ conjugated polymers resulting in weak bonds concept and metastability of PMPSi that may be recovered by alloying[11] we attempted to modify the interaction of nano-CdS provided with alkanolamine molecules as surfactant by UV radiation.

The results are encouraging. On the UV degradation considerable changes in relaxation processes of the fresh prepared sample (dried under vacuum 10 Pa and annealed at 80 ^{o}C) to irradiated (for 20 min), where relaxation process is emerging – subsequently disappearing (for 40 and 60 min) (Fig. 3 and Fig. 4). The same ordering of observations is visible when the same sample of nano-CdS is subjected to anneal at the turbomolecular vycuum 10^{-4} Pa and annealed at 100°C (Fig. 5 and Fig. 6). No traps connected with the nano-CdS were visible on these experiments .

The detailed explanation is not obvious at the moment, there are following possibilities for explaining the observed phenomea. One is the decrease of the average distance among nanoparticles due to the decreased lengths of alkanolamine molecules due to their scissoring, or the stripping of the part of the alkanolamine molecules from CdS surface. Both these phenomena should posses the metastability in reconstruction of the original state by anneal.
The conclusions drawn from the presented results may be formulated:
- both applied highly sensitive methods of isothermal charge transient spectroscopy and surface photovoltaic method turned out to be very sutable methods for characterizing the transport processes in nanomaterials due to their sensitivity and spectroscopical character,

- the changes in surfactant on U V radiation cause the changes in collective relaxation processes and may positively influence the transport of hole charge carriers after their injection or charge-transfer processes. This may positively influence the efficiency of conversion of hybrid solar cells.

Acknowledgements

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