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Optical properties of quantum dots layers: Application to photovoltaic solar cells

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ABSTRACT

Hybrid optical layers of PMMA containing different concentrations of CdSe/ZnS core/shell semiconductor quantum dots were fabricated. Their absorption and luminescence showing quantum confinement effects are given. A frequency down-conversion is then obtained. The external quantum efficiency measurement performed on silicon solar cell with and without the down-conversion layers shows that the luminescence induces new charge generation. In addition, Finite Difference Time Domain (FDTD) simulation of organic solar cell shows that, added to the frequency conversion effect, one can expect to have an increase in light confinement when quantum dots are embedded in the active layer.

1. Introduction

The response of photovoltaic solar cells depends on the part of the solar spectrum efficiently collected. Generally a large part of the solar spectrum is lost both in the infrared and in the UV. It is estimated [1] that the efficiency of bulk silicon solar cells could be increased of 32% if the UV spectrum was used to create carriers. In the solar cell materials, UV photons generate hot electrons which are thermalized by phonon coupling and most of them do not give current. More than that, they induce a temperature increase that will again decrease the global solar cell efficiency. In the case of organic materials, the UV can also break the molecular bonds and can reduce the solar cell lifetime.

A lot of studies have been performed on up-conversion and down-conversion processes to change IR and UV photons in photons having energy in the useful spectrum range [2]. A particular attention has been held on lanthanides materials [3] and, more recently, on quantum dots (QDs).

In our study, we focus on the possibility of converting UV photons in visible photons by using PMMA layers including CdSe/ZnS QDs and we performed calculation of the electromagnetic field in organic solar cells including QDs.

It is well known that electron confinement occurs in semiconductor nanocrystals of a few nanometer sizes, i.e. sizes smaller than the de Broglie wavelength. The possible discrete energy levels of the electrons in such QDs depend on their size and so do their bandgap [4]. The optical properties of the quantum dots naturally depend on their electronical properties. So their absorption spectrum is modulated by confinement effects and, generally, they exhibit luminescence which can be excited with a wide range of wavelengths in their absorption spectrum. Therefore, the UV range of solar spectrum from wavelength of around 300 nm is generally an efficient excitation source as shown in Fig. 1. In [1] it is estimated that additional 1/3 of the conventionally used solar energy spectrum may be collected if the UV fraction is utilized with a frequency down-conversion process.

2. Realization of PMMA thin films containing semiconductor quantum dots

Poly(Methyl MethAcrylate) (PMMA) is known to be highly transparent in UV and in the visible spectrum. So it is an interesting material to host QDs having an absorption and a luminescent spectra in these wavelength ranges.

In this study, we utilized core shell type CdSe/ZnS QDs which have a diameter around 3 nm. They have been bought from the company PlasmaChem GmbH. The advantage of the core/shell structure is that the shell prevents electron recombination and then helps to have a greater luminescence efficiency.

In order to obtain a homogeneous layer, the spin coating method [5] is applied for fabricating different PMMA layers containing different weight ratio percentage of QDs. The rotation speed we used was in the range of 1000–2000 rpm to have film thicknesses larger

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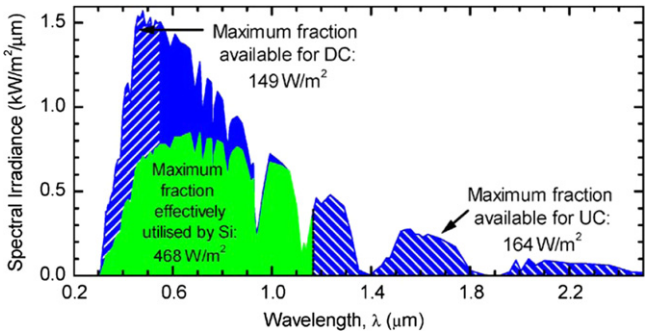

Fig. 1. AM1.5G spectrum showing the fraction that is currently absorbed by a thick silicon device and the additional regions of the spectrum that can contribute toward up- and down-conversion [1].

than 1 μm. A heat treatment at 80 °C is required to evaporate the rest of chloroform solvent after the spinning process. The heat treatment has been performed at a temperature not too high to preserve the layers from being damaged.

Before depositing the layer, we used chloroform as a solvent for both PMMA and QDs. CdSe/ZnS QDs can be well dispersed in the chloroform solvent due to their hydrophobic properties. Magnet stirring and ultrasonic vibration are also used during the homogenizing procedures. The solution of QDs is then mixed with the PMMA solution. For our study we used 4.2%, 8.3%, and 16.6% weight ratio percentages of QDs in PMMA. A few drops of the mixed solutions are then sent on rotating silica substrates to make PMMA thin films including QDs.

3. Experimental results and discussions

3.1. Size distribution of the CdSe/ZnS QDs

We used transmission electron microscopy (TEM) measurement to observe the exact particle size and spatial distribution of CdSe/ZnS quantum dots. Before making the TEM measurement, the QDs were first homogeneously dispersed in $CHCl_3$ solution and a drop of the solution was deposited on a carbon coated grid for the TEM observation. As can be observed in Fig. 2, the CdSe/ZnS QDs exhibit an average core diameter of around 3 nm. The ZnS is an epitaxial layer of a few molecules thick. It is known that this size is small enough to have strong quantum confinement effects. It can also be seen that the QDs size distribution is homogeneous. In addition, the TEM image also reveals an electron diffraction pattern corresponding to the QDs crystalline phase.

In the PMMA layers, for the considered concentrations, as the QDs are well dispersed, the distances between the QDs should be large enough not to have QD coupling phenomena. Indeed the absorption spectra have the same shape for different concentrations (Fig. 3).

3.2. Absorption and luminescence of PMMA layers containing CdSe/ZnS QDs

Reflectance (R) and transmittance (T) spectra of the layers with the different weight ratios have been measured. The losses $A=1-R-T$ are shown in Fig. 3 for the three considered concentrations. The thicknesses of the three QDs layers with different weight ratio are of 1.96 μm, 1.85 μm and 1.25 μm for 4.2%, 8.3% and 16.6% QDs concentrations, respectively.

In these three spectra, the position of the first main absorption peak, corresponding to the first excited energy level of the electrons, is located at around 545 nm for the three different

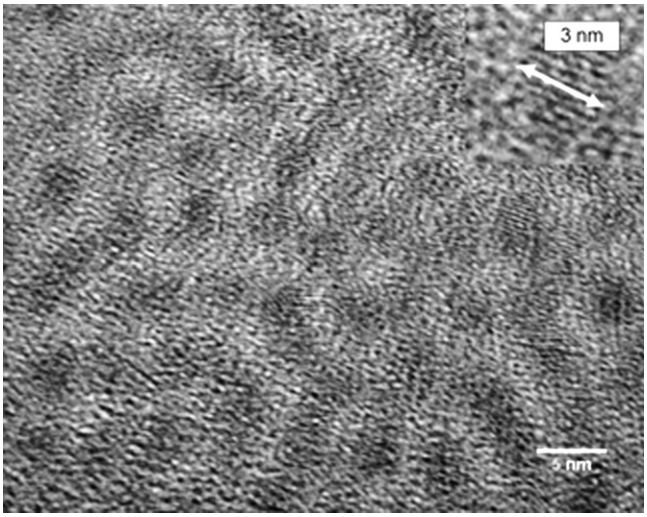

Fig. 2. Transmission electron microscopy image of CdSe/ZnS quantum dots showing a size around 3 nm.

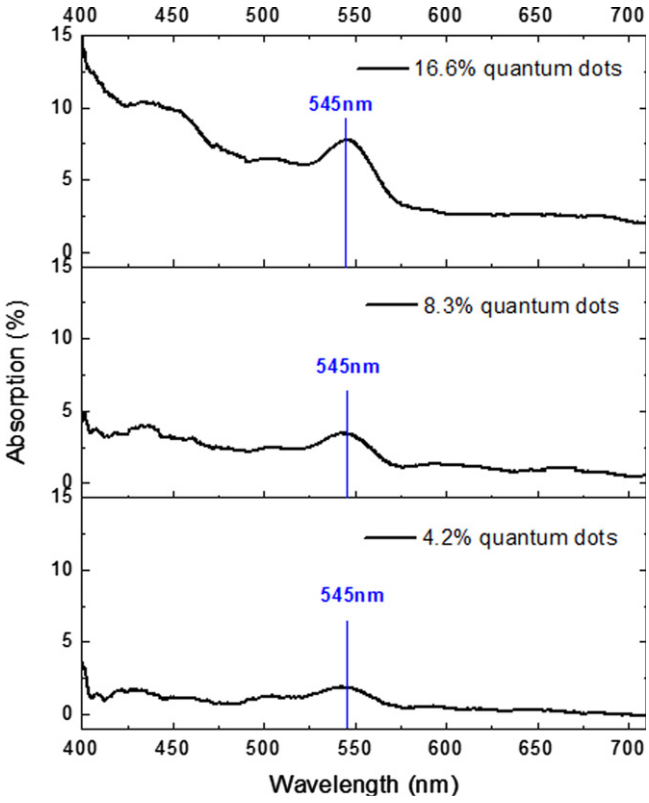

Fig. 3. Absorption spectra of PMMA layers containing CdSe/ZnS QDs with weight ratio percentage of 4.2%, 8.3% and 16.6%.

weight ratios. A bandgap shift phenomenon confirms the effect of quantum confinement. It can also be noticed that, as expected, the absorption increases with the concentration. In addition, other absorption peaks are also revealed not only at 545 nm but also at around 500 nm and 450 nm. This shows that several different excitonic effects occur in the QDs embedded in the layers as predicted by quantum theory.

We also measured the photoluminescence of the layers with the different weight ratio percentages. The excitation source used for these measurements is an Ar^+ laser emitting at 514.53 nm. A strong luminescence around 560 nm in good agreement with the specifications from PlasmaChem GmbH was obtained for all

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