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# Spectroscopic evidence of resonance energy transfer mechanism from PbS QDs to bulk silicon

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**Summary.** — In this work, we study the efficiency of the resonance energy transfer from PbS quantum dots to bulk silicon. We present spectroscopic evidence that resonance energy transfer from PbS quantum dots to bulk silicon can be an efficient process for separation distances below 12 nm. Temperature measurements are also presented for PbS quantum dots deposited on glass and silicon with 5 nm and 20 nm spacer thicknesses substrates. Our findings show that the resonance energy transfer efficiency remains constant over the 50 K to 300 K temperature range.

## 1. – Introduction

Semiconductor Quantum Dots (QDs) are promising materials for photovoltaic applications, as they can be engineered to absorb light ranging from the visible to the near infrared and single absorbed photon can generate multiple excitons [1-5]. However, these materials suffer from low carrier mobility, which severely limits the prospects of efficient charge extraction and carrier transport [6]. For this reason, photovoltaic devices based on semiconductor nanocrystals have efficiency not higher than 6% [6].

Silicon photovoltaic devices can efficiently extract carriers created in  $p$ - $n$  junction. Nevertheless, crystalline silicon solar cells suffer from low light absorbance and require a thickness between 180 to 300  $\mu\text{m}$  [7]. Therefore, in order to improve the absorption efficiency of silicon solar cells and minimize their thickness, the combination of different materials is required [6, 8].

The combination of different materials for efficient photovoltaic devices was first considered by Dexter in 1979 [9]. He proposed a structure combining an organic material and a semiconductor. The organic material could work as an efficient solar absorber and excitons could be created in the semiconductor by means of fluorescent Resonance Energy Transfer (RET). RET is an electrodynamic phenomenon that occurs between a donor in the excited state and an acceptor in the ground state [10]. The “donor” fluorophore absorbs a photon and transfers its energy to the “acceptor” molecule. The RET rate scales with the separation distance between donor and acceptor, the spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, the quantum yield and decay rate of the donor and the relative orientation in space of the transition dipoles of the donor and the acceptor.

Experimental spectroscopic evidence for RET from lead sulfide (PbS) QDs to epitaxially grown quantum well was demonstrated by S. Lu *et al.* in 2007 [11]. The quantum well was a  $\text{GaAs}/[(\text{InAs})_1(\text{GaAs})_2] \times 8/\text{GaAs}$  short period superlattice buried below a sulfur-passivated GaAs surface. Two years later, S. Chanyawadee *et al.* [12] presented a hybrid photovoltaic device taking advantage of the RET mechanism. This device was a patterned  $p$ - $i$ - $n$  structure consisting of multiple GaAs quantum wells with AlGaAs barriers in which channels were fabricated and filled with cadmium selenide/cadmium sulfide (CdSe/CdS) QDs. The authors combined spectroscopic evidence of RET and photocurrent measurements that showed a sixfold enhancement of the photocurrent in the patterned hybrid devices in comparison with the bare  $p$ - $i$ - $n$  structure.

Further evidence supporting the potential feasibility of the solar cell paradigm based on the RET mechanism from deposited PbS QDs on the top of silicon nanowires, was reported the same year by S. Lu *et al.* [13]. Photocurrent time resolved measurements were performed and showed a clear increase in the photocurrent at delay times of ten to hundreds nanosecond in the case of the hybrid structure in comparison with the bare silicon nanowire structure.

Experimental demonstrations of RET into silicon substrate are of particular interest due to the potential development of efficient thinner silicon-based photovoltaic devices. Hybrid structures of silicon substrates and semiconductor QDs have the potential to improve the low absorption of silicon and to lead to thinner efficient silicon photovoltaic devices.

In this paper, we investigate the transfer of excitons from PbS QDs to a silicon  $p$ - $n$  junction by performing time-resolved measurements. PbS QDs are placed onto silicon samples of variable silica spacer thicknesses and the efficiency of RET from PbS QDs to bulk silicon is studied. The efficiency of the RET mechanism is then modulated by varying the separation distance between PbS QDs and silicon. These results identify that RET from colloidal QDs to bulk silicon can occur for spacer thicknesses below 12 nm.

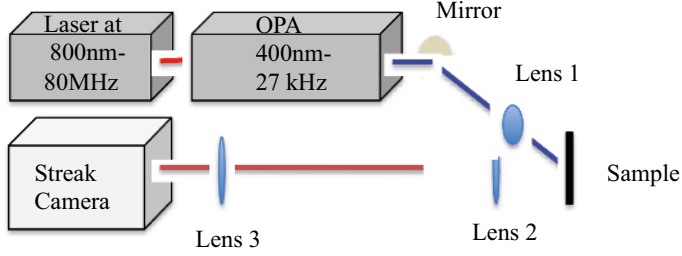


Fig. 1. – Time-resolved experimental setup. The focal distance of lens 1 and 2 was 5 cm, while the focal distance of lens 3 was 15 cm.

Temperature measurements are also presented and show that the RET efficiency remains constant across the 45 K to 300 K temperature range. The demonstrated findings are encouraging for further investigations and open the way for the development of hybrid QDs silicon photovoltaic devices.

## 2. – Experimental setup

The devices studied in this work consisted of PbS QDs deposited on silicon substrates with different thicknesses of silica ( $\text{SiO}_2$ ). To produce the silica spacers on the silicon sample, a 100 nm thick silica film was thermally grown on a silicon wafer in a furnace. This wafer was then diced into  $20 \times 20 \text{ mm}^2$  samples. Each sample was finally etched down by using reactive ion etching to obtain the required spacer thickness. The thickness was measured using ellipsometry. The QDs were deposited using drop-casting.

Time-resolved measurements were performed using a streak camera system with a temporal resolution of 30 ns. All QDs were excited non-resonantly at 400 nm with 150 fs pulses at a 71 kHz repetition rate. Glass substrates with PbS QDs were mounted on a cold finger helium flow cryostat and excited at oblique angle as illustrated in fig. 1. The fluorescence was collected at normal incidence to the sample surface.

The PL decay kinetics of PbS QDs were found to exhibit a non-single exponential behaviour that was satisfactorily described by the bi-exponential equation

$$(2.1) \quad I_{PL}(t) = A_1 * e^{-k_1 * t} + A_2 * e^{-k_2 * t} + C,$$

or with a stretched exponential function, an equation widely used for the analysis of energy transfer:

$$(2.2) \quad I_{PL} = C + A \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right).$$

The average decay rate is given by

$$(2.3) \quad \langle k_{aver} \rangle = \frac{A_1 * \tau_1 + A_2 * \tau_2}{A_1 * \tau_1^2 + A_2 * \tau_2^2}$$

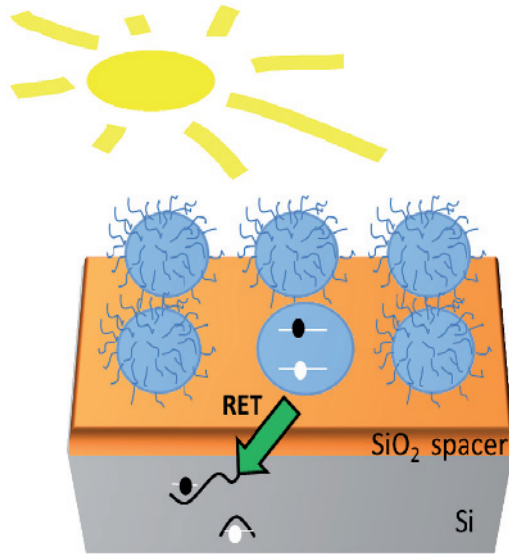


Fig. 2. – Schematic description of the RET mechanism from oleic-acid-capped PbS QDs to a bulk silicon substrate, through a SiO<sub>2</sub> spacing layer [14].

in the case of a bi-exponential fitting or

$$(2.4) \quad \langle k_{aver} \rangle = \left( \frac{\tau_1}{\beta} \Gamma \left( \frac{1}{\beta} \right) \right)^{-1}$$

in the case of stretched exponential fitting. In the above equations  $\Gamma$  represents the gamma function and  $\tau_1 = \frac{1}{k_1}$  and  $\tau_2 = \frac{1}{k_2}$  are used to monitor the overall trend of the decay dynamic.

### 3. – Results and discussion

Hybrid structures of oleic-acid-capped PbS QDs deposited on substrates consisting of SiO<sub>2</sub> thin films of various thicknesses on silicon were used for the study of RET from PbS QDs to bulk silicon, as illustrated in fig. 2. The absorption and emission spectra of the PbS QDs used in this experiment are shown in fig. 3a, showing a 1s emission peak at 1.35 eV and a 1s absorption peak at 1.5 eV. As illustrated in fig. 3b, these particles are excellent solar absorbers due to the good match of their absorption spectrum with the solar radiation.

Resonance Energy Transfer mechanism can be detected through an acceleration in the PL dynamics of the donor or a slight temporal shift in the PL decay of the acceptor. Silicon being an indirect band gap semiconductor, its emission at room temperature is negligible and consequently the PL decay of PbS QDs measured here for the study of

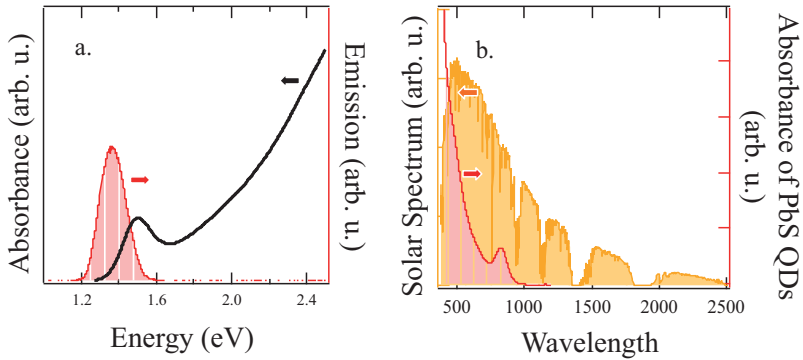


Fig. 3. – (a) PL and absorption spectra of oleic-acid-capped PbS QDs, (b) solar spectrum (orange colour) plotted with the absorption spectrum of PbS QDs (red colour).

RET from the PbS QDs to silicon. The PL lifetimes of the oleic-acid-capped PbS QDs, with an excitonic peak at  $\sim 800$  nm, were measured for different QDs/SiO<sub>2</sub>/Si samples where the thickness of the SiO<sub>2</sub> spacer was varied from 5 to 56 nm. Time-resolved measurements were performed using the setup described in sect. 1. The PbS QDs were excited at 400 nm, with a 81 kHz repetition rate. The PL decay of the PbS QDs was observed to be significantly shorter for thinner SiO<sub>2</sub> layers as shown in fig. 4.

The full dependence of the PL decay rate on SiO<sub>2</sub> spacing thickness is shown in fig. 4. The PL decay rate increases significantly for SiO<sub>2</sub> spacer thicknesses below 12 nm [14]. It remains almost constant for SiO<sub>2</sub> spacer thicknesses greater than 12 nm, with values comparable to the decay rate of PbS QDs deposited on a glass substrate. The observed

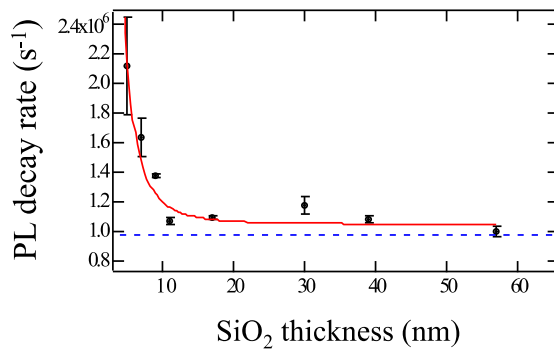


Fig. 4. – PL decay rate of oleic-acid-capped PbS QDs plotted as a function of spacer thickness. The blue dashed line shows the PL decay rate of PbS nanoparticles deposited on glass. The red line illustrates the fitting with an  $R^{-3}$  function [14].

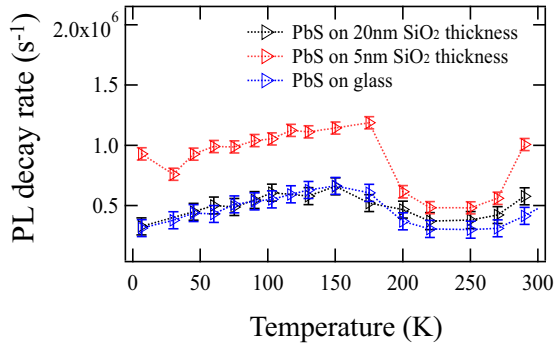


Fig. 5. – Average PL decay rate of oleic-acid-capped PbS QDs deposited on a glass substrate (blue markers) and on a 5 nm (red markers), and 20 nm SiO<sub>2</sub>/Si substrates (black markers) as a function of temperature.

acceleration in the lifetimes of PbS QDs for short separation distances is a strong evidence of RET from the QDs to the bulk silicon [14].

For spacer thickness greater than 12 nm, there is no net absorption of energy by the silicon and the decay rate of the PbS QDs is found to be almost equal to the value on glass [14]. For separation distances below 12 nm, the lifetime is sharply reduced due to the gradual opening of the transfer channel to silicon. In this case, the near field of the PbS QDs can directly excite a vertical transition in the semiconductor band structure of the silicon. In this regime, the dependence of the lifetime of the PbS QDs on the separation distance is found to fit well with an inverse-third-power function. This is in good agreement with previous studies that recorded RET from a dye molecule to bulk silicon [15] and also as expected theoretically for RET from a point dipole to a continuum of absorbing exciton states [16].

Temperature-dependent measurements were also performed on three different samples: PbS QDs deposited on a 5 nm SiO<sub>2</sub> spacer-silicon substrate, a 20 nm SiO<sub>2</sub> spacer-silicon substrate and on a glass substrate. The behavior of the average decay rate for these three different samples is illustrated in fig. 5.

The average decay rate of the PbS QDs exhibits a similar trend for the different samples, which is attributed to the electronic structure of PbS QDs. The observed trend has been extensively explained in ref. [17], where it was shown that the radiative decay rate of bright excitons is around two orders of magnitude larger than the rate of dark excitons. It is therefore understood that in the framework of RET the bright excitons dominate the dynamics. To derive the energy transfer dynamics from PbS QDs to crystalline silicon as a function of temperature we decouple the contribution of bright and dark exciton from the observed PL by fitting the decay dynamics using a bi-exponential function. The fast and slow components correspond to bright and dark exciton dynamics respectively as shown in fig. 6a for 5 nm and fig. 6b for 20 nm SiO<sub>2</sub> separation layer. The



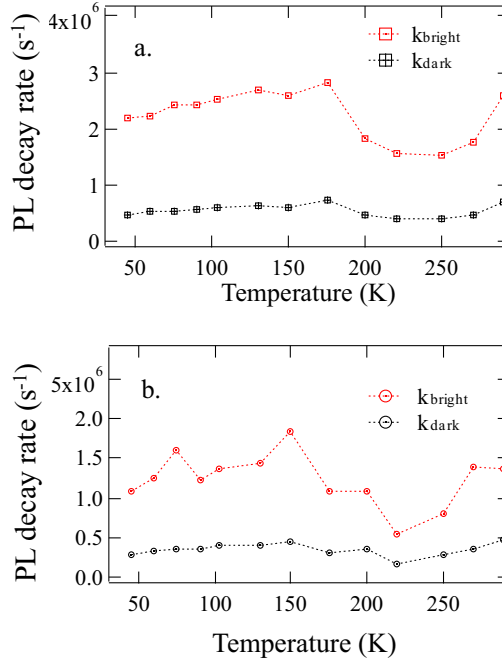


Fig. 6. – Bright (red) and dark (black) rates of oleic-acid-capped PbS QDs deposited on (a) 5 nm and (b) 20 nm SiO<sub>2</sub>/Si substrates as a function of temperature.

RET rate and the efficiency of the process as function of temperature is shown in fig. 7. The RET rate at the different temperatures is extracted from the relation

$$(3.1) \quad k_H = k_{\text{PbS}} + k_{\text{RET}}$$

and the RET efficiency is calculated according to the equation  $\eta = \frac{k_{\text{RET}}}{k_H}$ , where  $k_H$  is the rate of PbS QDs deposited on the 5 nm SiO<sub>2</sub> spacer/Si sample,  $k_{\text{PbS}}$  is the rate of PbS QDs deposited on the 20 nm SiO<sub>2</sub> spacer/Si sample and  $k_{\text{RET}}$  the RET rate. As expected we observe that the RET rate and the efficiency of the process depends only weakly on temperature due to the temperature-independent nature of the radiative rates.

#### 4. – Conclusions

In conclusion, RET can occur from PbS QDs to bulk silicon for spacer thicknesses below 12 nm. RET is found to scale with the inverse cube power of the separation distance between the PbS QDs and bulk silicon. In addition, the efficiency of the RET mechanism from PbS QDs to bulk silicon remains constant between 45 K and 300 K, with a value of 46% for a 5 nm spacer thickness. As was mentioned previously, the absorption spectrum



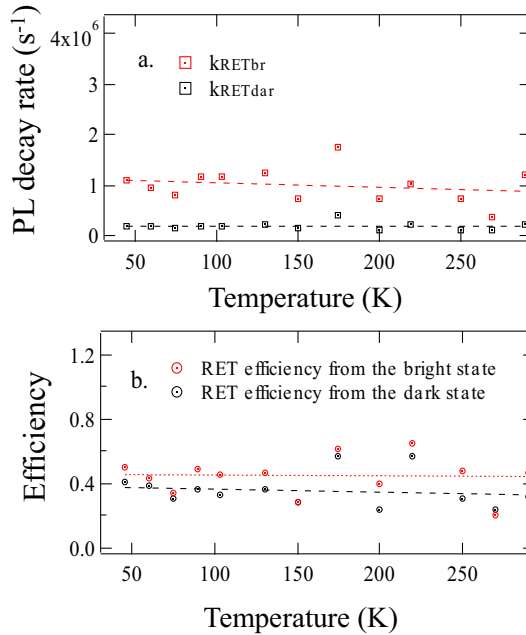


Fig. 7. – (a) Calculated RET rate from the radiative rates of the dark (black) and bright (red) state as function of the temperature; (b) efficiency of the RET process attributed to the dark (black) and bright (red) states as a function of temperature.

of PbS QDs matches the solar radiation and is an efficient light absorber. Therefore hybrid photovoltaic devices potentially could have larger absorption cross-sections than bare silicon devices, while retaining high carrier efficiencies, thus enhancing the overall quantum efficiency.

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