

## ULTRATHIN ORGANIC DYE LAYERS FOR SENSITISATION OF SILICON

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### ABSTRACT

*Combination of affordable organic dyes of high quantum yield with silicon can be an interesting way for development of highly efficient thin film photovoltaic cells utilizing silicon sensitisation.*

*This work is focused on investigating the energy transfer processes including photon tunnelling from photosensitive molecules of BASF R305 high quantum yield dye to silicon substrate. Energy transfer from dye molecules to silicon substrate is evaluated by measuring the quenching of molecular photoluminescence lifetime using time-correlated single photon counting (TCSPC) technique. Energy transfer is further studied in dependence on dye layer thickness. The results can be useful for further studies leading to design of ultrathin silicon solar cells.*

***Keywords:** energy transfer, silicon sensitisation, TCSPC, photoluminescence quenching.*

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### INTRODUCTION

Crystalline silicon photovoltaic (PV) is dominating the PV market with more than 95 % of global share [1, 2]. The cost of silicon wafer as base material dropped over last years but still plays a significant part in PV module cost [3]. Due to silicon being an indirect bandgap semiconductor, thick wafers are necessary to ensure good sunlight absorption.

Photosensitisation of silicon is a new way how to avoid the need for thick wafers. Electron-hole pairs are generated via non-radiative energy transfer from dye molecules close (less than 2 nm) to the silicon surface. This process was proposed by Dexter and is described as dipole - dipole interaction in the near field similar to the Förster resonance energy transfer (FRET) [4]. By this, momentum conservation law is not limiting factor, because molecular excited states are localised

and turn silicon into direct band gap semiconductor [5]. The lifetime of an excited molecule based on force damped oscillator and the complex dielectric constant of the media was modelled by Chance, Prock, Silbey (CPS) in their original paper [6]. Multiple studies have experimentally verified FRET from quantum dots [7, 8] or Langmuir-Blodgett (LB) monolayers [9, 10] to silicon surface. For distances between 10 - 50 nm the photon tunnelling process dominates the energy transfer [11]. Energy transfer was also described for covalently attached molecules on silicon surfaces [12]. In this work we propose simple and precise thin layer deposition method using spin coating of affordable dye. We vary the thickness of the deposited dye layer in nanometre scale, and we observe the photoluminescence (PL) quenching indicating energy transfer or photon tunnelling from thin dye layer to silicon.

## EXPERIMENTAL

The silicon substrate used in this work was p-type, orientation <100>, resistivity 0.001 - 0.005 Ohm cm, 500  $\mu\text{m}$  thick. The wafer with diameter of 100 mm, was cut into smaller pieces. These were cleaned in mixture 95 %  $\text{H}_2\text{SO}_4$ , 30 %  $\text{H}_2\text{O}_2$  (3:1 ratio "piranha solution") to remove all organic residues and hydroxylate the surface. Then the samples were rinsed with ultrapure water obtained from Puranitu TU (VWR) with stated resistivity 18,2 M $\Omega$  cm and dried by nitrogen. One sample was etched using HF by submerging the Si wafer in 2 % HF for 60 s, leading to silicon dioxide layer removal.

Fluorescent dye Lumogen F Red 305 by BASF was chosen for depositing on Si surface, as it is commercially available dye with high fluorescence yield (98 %) and good photostability [13]. The molecular formula is  $\text{C}_{72}\text{H}_{58}\text{N}_2\text{O}_8$  and the molecular mass 1079.561 g mol $^{-1}$ . The dye in powder form was diluted in toluene to achieve desired concentrations  $1 \cdot 10^{-2}$  -  $1 \cdot 10^{-6}$  mol dm $^{-3}$ .

Fig. 1 shows the absorption and PL emission spectra of the chosen dye in solution.

The chosen deposition method was spin-coating (spin coater Laurell WS-650). Samples of different dye concentrations ( $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$  mol dm $^{-3}$ ) were prepared.

The variable angle spectroscopic ellipsometry (VASE) method with modulated ellipsometer (M-2000 V Automated Angle, J. A. Woollam Co., Inc., USA) was used to measure thickness of deposited layers and their uniformity.

The luminescence time decays of BASF R305 dye layers on Si were measured by time-resolved PL spectroscopy using PicoQuant FluoTime 200 setup (with TCSPC module TimeHarp 300, and photomultiplier PMA-185). Excitation of samples provided 440 nm picosecond pulse diode laser (LDH 440, PicoQuant with PDL 800-D driver). The signal was detected at 600 nm which corresponds to BASF R305 dye PL peak maximum. Time resolution is given by laser pulse duration which is 250 ps.

## RESULTS AND DISCUSSION

We prepared a testing set of samples of BASF R305 layers using different concentrations of the dye, keeping the spin coating deposition parameters constant. To avoid

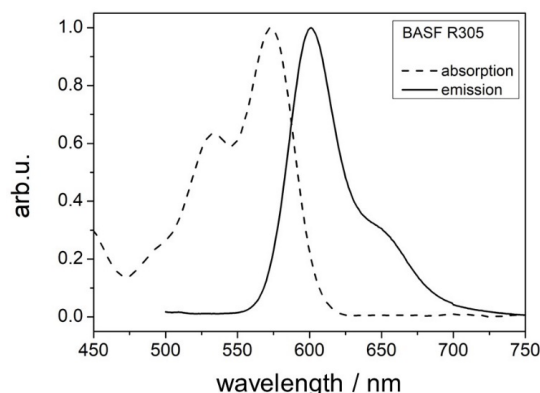


Fig. 1. Absorption and PL emission spectra BASF R305 dye solution (concentration  $10^{-5}$  mol dm $^{-3}$ ).

aggregation as well as optical reabsorption processes, we chose relatively low concentration of dye solutions ( $10^{-5}$  mol dm $^{-3}$ ) for further preparation of samples with variable dye layer thickness. The PL spectra of deposited layers were compared to liquid solution spectrum to confirm that degradation or presence of impurities is not observed. Keeping the concentration of dye solution constant ( $10^{-5}$  mol dm $^{-3}$ ), we prepared several samples with different thicknesses of BASF R305 dye layer as well as one sample of BASF R305 dye layer deposited on bare Si substrate with etched  $\text{SiO}_2$ . Thickness of BASF R305 layers were evaluated as the average thickness from ellipsometry surface scan measurement. Fig. 2 shows the result of ellipsometry measurements on the set of samples. The results show that deposition of BASF R305 by spin coating led to formation of highly regular layers over large area of silicon substrates.

The PL decays were measured on all prepared samples as well as on reference liquid solution of BASF R305. With decreasing thickness of deposited BASF R305 layers, quenching of PL signal was observed (see Fig. 3(a)). PL signal decays can be fitted by single exponential except the thinnest dye layers (2.03 nm BASF R305 on etched Si, 3.07 nm BASF R305 on Si and 5.61 nm BASF R305 on Si) where double exponential decay is observed. Therefore, the total lifetime was calculated using expression [5]:

$$\tau_{AV} = \frac{\sum_i A_i \cdot \tau_i}{\sum_i A_i} \quad (1)$$

Example of fitting is shown in Fig. 3(b).

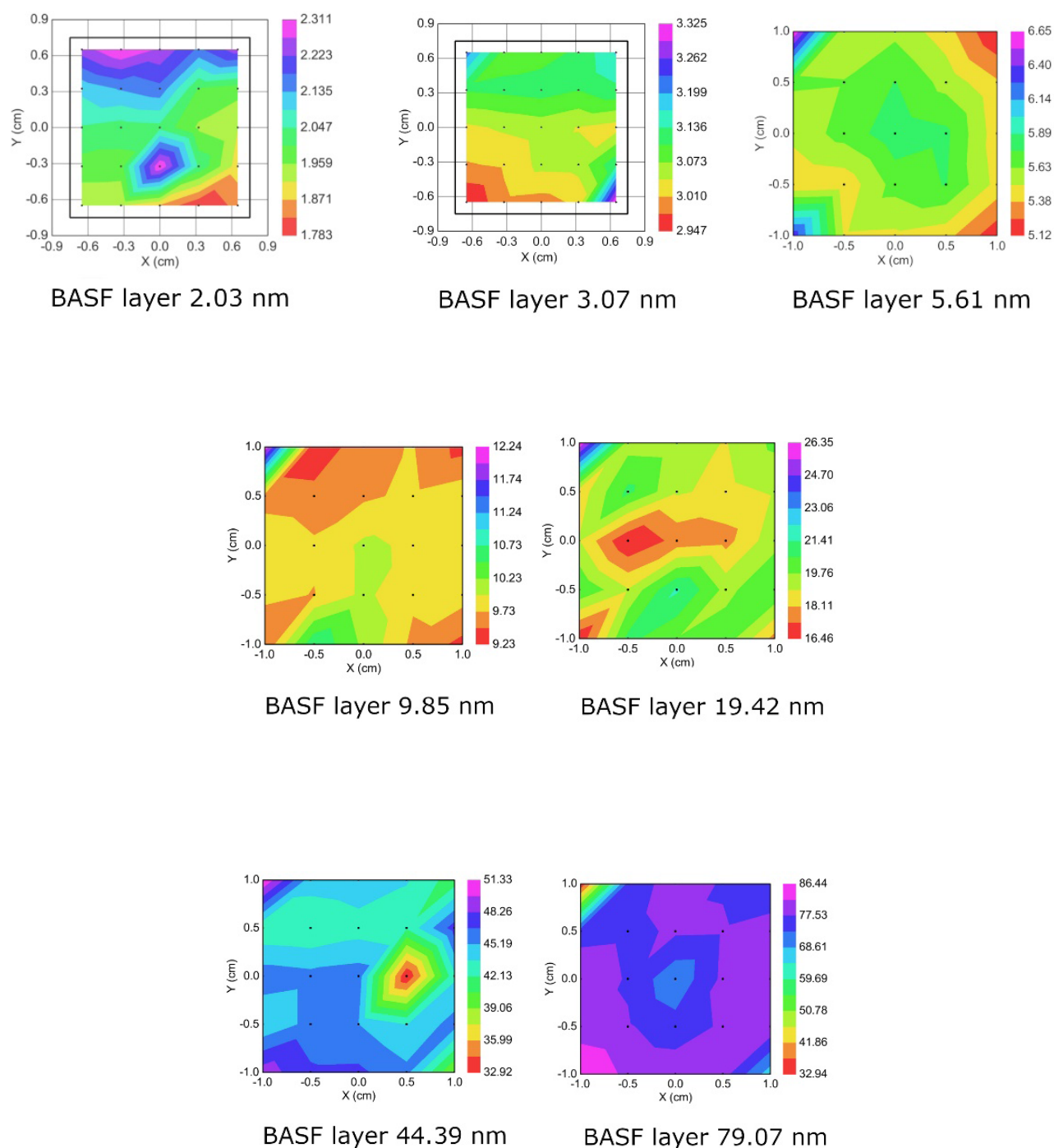


Fig. 2. Thickness profiles of BASF R305 layers deposited on silicon substrates. BASF layer 2.03 nm corresponds to the sample with BASF R305 deposited on bare Si surface with etched  $\text{SiO}_2$ .

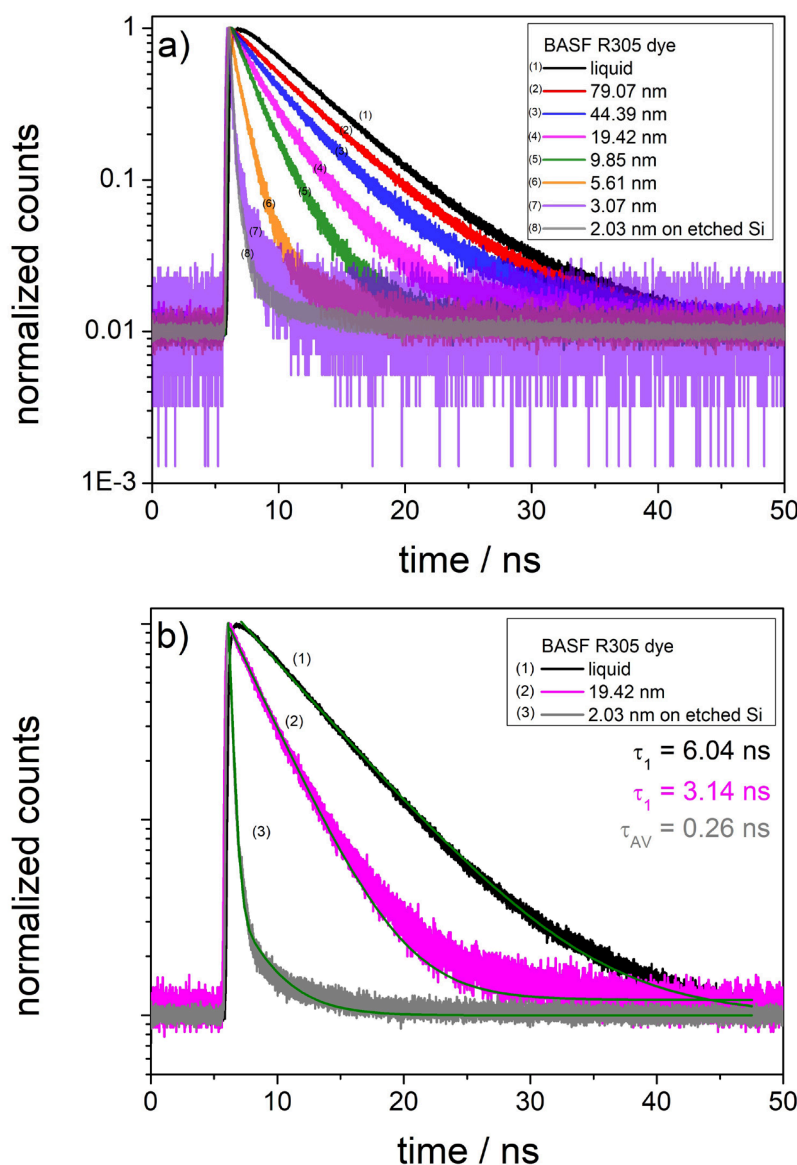


Fig. 3. a) Measured PL decay at 600 nm for reference liquid BASF R305 and deposited BASF R305 on Si; b) Fitted measured PL decays for liquid BASF R305 sample (single exponential fitting), 19.42 nm thick layer on Si (single exponential fitting) and 2.03 nm thick layer on etched Si (double exponential fitting).

Dependence of PL lifetimes on dye layer thickness is shown in Fig. 4. Decreasing the thickness of deposited BASF R305 dye layer leads to faster decay of PL indicating observation of photon tunnelling or energy transfer from dye molecules to silicon.

Observation of PL quenching from the thinnest dye layer on etched Si substrate is limited by the time resolution of the setup (given by the excitation laser pulse duration). For more precise data acquisition and

evaluation new experimental setup is needed with higher time resolution. Further work with a higher time resolving system will also contribute to clarification of the observation of two exponential decays in thinner layers. It will also be beneficial to employ detection of infrared PL signal from Si substrates which could confirm the energy transfer by detecting recombination of excited carriers in Si. In particular, novel dyes and deposition methods are required to ensure preparation of

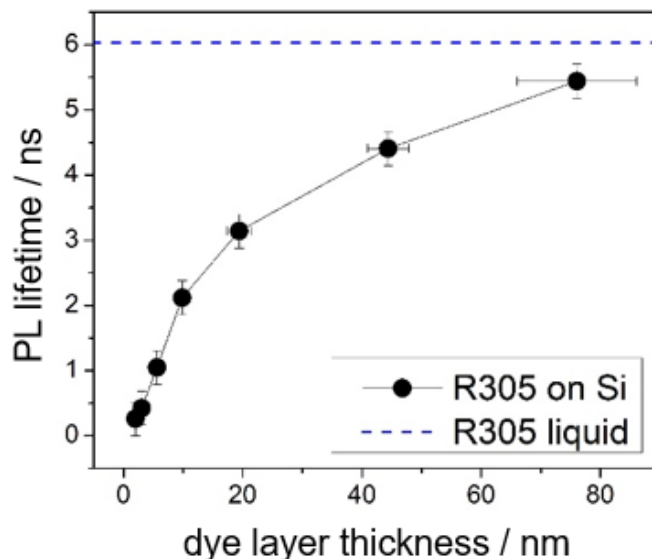


Fig. 4. Measured PL lifetimes at 600 nm for samples of various BASF R305 dye thicknesses. Black circles - measured samples lifetimes, blue line - measured lifetime of reference dye liquid solution.

samples containing constant thickness of the dye layer while only the spacer layer thickness is modified. This will lead to more precise interpretation of observed PL changes.

## CONCLUSIONS

Photosensitisation of silicon via energy transfer from organic dye layers is a promising area of research for development of efficient and thin silicon solar cells. In this work we prepared various samples of different dye layer thicknesses, with decreasing dye thickness we observed significant quenching of dye PL indicating efficient energy transfer and photon tunnelling from dye molecules to Si. Results suggest that our further research should focus on preparation of new organic layer materials, possibly emitting in distinct spectral ranges and developing deposition methods to achieve variable thickness of transparent spacer layer with ultrathin dye layer attached on the top.

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