Sensitisation of Silicon: Distance dependence of energy transfer

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Light harvesting is used in photosynthesis to significantly enhance the absorption ability of the reaction centre in photosynthetic systems via a series of resonant energy transfer steps of the absorbed excitation energy. The transfer of excitation energy to the reaction centre is used for a subsequent transport of an electron across the cell membrane. The light harvesting energy transfer is very fast and results in efficient utilisation of the captured photon energy. Similarly, photovoltaic solar energy conversion consists of two steps; light absorption, followed by charge separation at a junction. Silicon, although an excellent charge separation material, is not an efficient light absorber due to an indirect energy gap. In application to crystalline silicon solar cells, light harvesting thus offers the promise of dramatic cost reduction by combining the advantages of high optical absorption of dye molecules with the efficient electronic properties of crystalline silicon [1].

Proposed originally by Dexter [2] a characteristic feature of this process is an enhancement of the photo-excitation rate in an indirect gap semiconductor by 1-2 orders of magnitude. Although a detailed theoretical understanding of this phenomenon is still lacking [3], the key reason for this enhancement is thought to be the absence of translational symmetry in the dye monolayer. Direct optical excitation of electron-hole pairs near the lowest silicon bandgap is symmetry forbidden, and can only occur with phonon participation. By contrast, a localised state at an individual molecule has an ill-defined value of k. The near-field dipole-dipole interaction with the semiconductor thus by-passes the constraints imposed by momentum conservation, and transforms in effect, silicon into a direct-gap material.

The key factor in designing successful light harvesting structures is the control of molecular organisation and inter-molecular distances to achieve high efficiency of excitation energy transfer while avoiding other non-radiative dissipation processes (i.e. quenching). This requirement is successfully addressed by using Langmuir-Blodgett films which are shown to be well suited for this purpose [4,5]. Previous fluorescence time resolved stu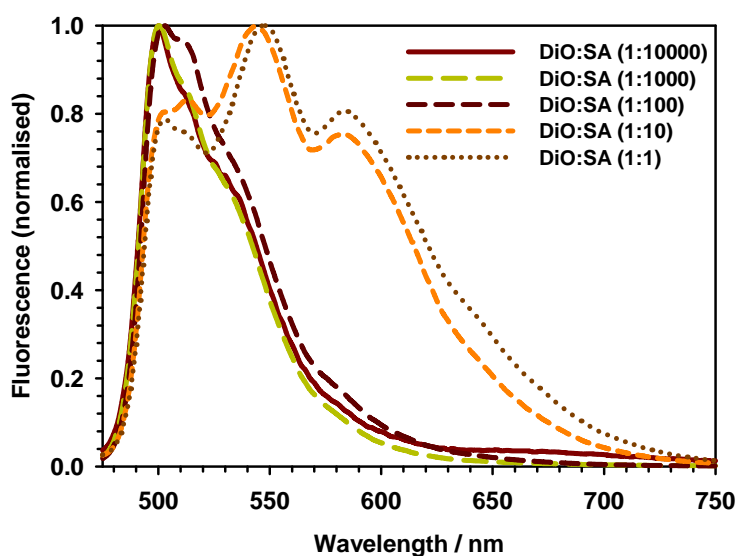dies have shown that the excitation relaxation energy in LB films depends on surface morphology; in particular on the dye concentration within the monolayer [6]. Excited dye molecules in LB monolayers may undergo various relaxation pathways and different relaxation processes can occur depending on the dye concentration. The fluorescence decay curves will therefore usually contain different fluorescence lifetimes which require multi-component exponential analysis. These extracted lifetimes will correspond to different relaxation processes in the monolayer. Figure 1 shows the fluorescence spectra recorded on DiO:SA monolayers deposited on glass for different mixing ratios with the Stearic Acid (SA). The emission spectra change with increasing

Figure 1. Fluorescence spectra of DiO:SA in LB monolayers on glass excited at 445 nm at different mixing ratios DiO:SA. DiO is a long chain carbocyanine dye, 3,3′ dioctadecyloxacarbocyanine perchlorate.

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dye concentration due to dimer and oligomer formation within the monolayer. These different relaxation pathways can be monitored in the fluorescence decay curves [6].

We have carried out fluorescence lifetime measurements using a time-correlated single-photon counting technique for cyanine LB dye monolayers near the silicon surface. The measurements have been carried out for both <100> and <111> crystal orientations of the silicon surface, showing the dependence of energy transfer rate as a fun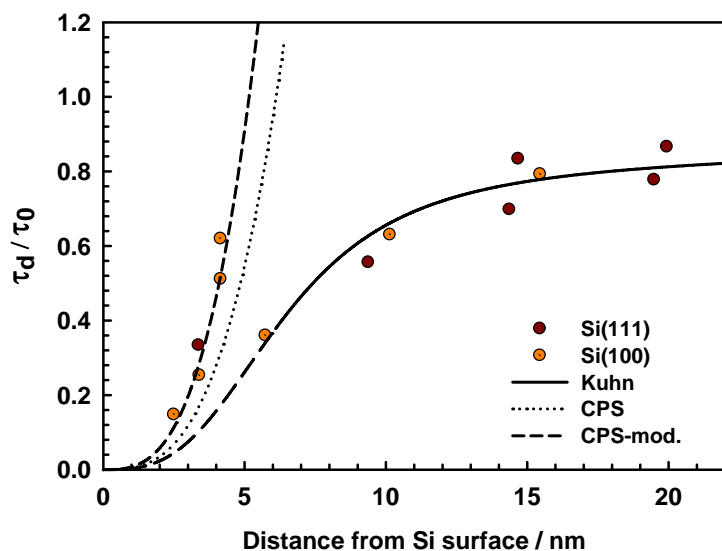ction of the separation between the dye layer and silicon. Langmuir Blodgett fatty acid layers were used to create a multistep structure and a monolayer of a cyanine dye was deposited on top of the stepped structure. Spectroscopic ellipsometry has been used to measure the thickness of the fatty acid steps and provide an accurate estimate of the distance of the dye monolayer to the silicon surface. We carried out a series of similar experiments with different silicon orientations. The results are shown in figure 2 which depicts the ratio of τ_d/τ_0, where τ_d is the measured fluorescence lifetime at specific distance d to the silicon surface as measured by ellipsometry and τ_0 is the measured fluorescence lifetime of the dye deposited on glass precoated with 4 stearic acid layers.

Figure 2. Experimental results of the fluorescence lifetime (τ_d/τ_0) of DIO:SA at different distances to the silicon surfaces and for different silicon crystal orientations. The solid curve is the model by Kuhn [7] and the dashed curve is the CPS model [8] assumed for an isotropic dipole orientation. The dotted curve is the modified CPS model, see text for details.

These data are compared with the Kuhn [7] model for large separations, and the Chance-Prock-Silbey (CPS) model [8] for distances < 5 nm to describe the energy transfer. It can be seen that at distances 5<d<20 nm the Kuhn model (which is an asymptotic limit of the CPS model at large distance) describes the data adequately. At a close distance from the silicon surface the CPS model gives the lifetime τ_d as proportional to d^3, with the constant of proportionality determined by the imaginary part of the dielectric constant. Both Kuhn and CPS models were developed for metals and, when applied with silicon parameters, some disagreement from observation in the current situation is expected. Notwithstanding, we find that quenching can be described well by a cubic dependence on the dye separation from silicon but with the proportionality constant used as a fitting parameter. We interpret this result as an indication that the imaginary part of the dielectric constant which determines the dye-silicon interaction in the near field, differs from its far-field counterpart as revealed by optical absorption.

References
1. T. Markvart, Progress in Quantum Electronics **24**, 107-86 (2000).
2. D.L. Dexter, J. Lumin. **18/19**, 779 (1979).
3. W.L. Barnes, J. Mod. Opt. **45** 661 (1998).
4. H. Kuhn, D. Mobius, H. Bucher, in: A. Weissberger, B.W. Rossiter (Eds.), Techniques of Chemistry, vol.1, John Wiley & Sons Ltd, New York, 1972, p. 594.
5. L. Danos, R. Greef and T. Markvart. Efficient fluorescence quenching near crystalline silicon from Langmuir–Blodgett dye films. *Thin Solid Films* 2008 (http://dx.doi.org/10.1016/j.tsf.2007.12.103).
6. N. Tamai, H. Matsuo, T. Yamazaki adn I. Yamazaki, J. Phys. Chem. **96,** 6550 (1992).
7. H. Kuhn, *J. Chem. Phys.* **53,** 101 (1970).
8. R.R. Chance, A. Prock, R. Silbey, in: I. Prigogine, S.A. Rice (Eds.), *Advances in Chemical Physics,* **vol. 37**, Wiley, New York, 1978 pp1.