

Carrier Dynamics in Coupled Silicon Nanocrystal Systems

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# Summary

## Carrier Dynamics in Coupled Silicon Nanocrystal Solids

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### Motivation of research

The transition from conventional (fossil fuel based) energy generation methods to renewable energy variants is set in motion but can certainly use an additional impulse. A good example is the solar energy market which is successfully fighting the traditional household power prices and has become a cost-effective source of electricity for private citizens. Still, for the industry, the prices of electricity generated in the conventional way ("gray current") are low enough to prevent a smooth and effective transition to a photovoltaic-dominated electricity market. One way of breaking the established equilibrium is to increase the conversion efficiencies of solar panels without inducing skyrocketing prices.

Typically, high-energy (ultra-violet) solar photons are inefficiently converted into electricity due to thermalization and front surface recombination. A possible route towards the efficiency increase is to make use of spectral shaper layers, which are add-on devices that can be combined with solar cells in order to transform the solar spectrum into a range optimal for efficient conversion by the cell. This dissertation focuses on the investigation of Si nanocrystals for the purpose of being used in these spectral shapers. The nano-scale dimensions of the Si particles increase their interaction potential with light due to quantum confinement. As a result, changes are induced in (among others) the bandstructure, transition strength and the electron-phonon coupling. By making use of the bandgap tunability of Si nanocrystals that arises from quantum confinement, the problem of front surface recombination can be completely surmounted; a results that can in principle also be obtained without the use of nano-materials. In contrast, Si nanocrystals might be able to circumvent the thermalization losses as well, by efficient dipole-dipole interactions between proximal nanocrystals.

## Results

### Part I

In the first part of this dissertation I focused on the fundamental question whether the excess energy, that is present after absorption of high-energy photons, can be utilized before efficient thermalization takes place. My approach is based on two different experimental techniques. In *Chapter 4* I used induced absorption measurements that allow probing the carrier densities with a sub-ps resolution. The relative carrier generation efficiency is retrieved, by applying a rigorous absorption calibration procedure, as a function of the excitation energy. From this data I conclude that excess energy can be efficiently utilized by means of the "space-separated quantum cutting" process. In *Chapter 5* I used a different approach that is free from almost any experimental error, which allows me to zoom in at the spectral changes that occur as a result of the size dependence of the space-separated quantum cutting process. Also here, a confirmation of the presence of the space-separated quantum cutting process is presented. Hence, via these two chapters I conclusively show that close-packed solid state dispersions of Si nanocrystals can transfer excess energy (in integer amounts of bandgap energies) to neighboring nanocrystals. This occurs on a sub-ps time-scale and is therefore efficient enough to successfully compete with thermalization. Essentially, this finding is the backbone of the shaping potential of close-packed ensembles of Si nanocrystals.

### Part II

Although the investigated form of Si nanocrystal ensembles possesses all the necessary properties to develop a winning spectral shaper layer, the successful implementation is only conceivable once the shaping efficiency (photon in – photon out efficiency) is high enough. To be exact, at least 60 % of all the absorbed photons need to be emitted in the desired range of the solar cell to enhance the conversion efficiency of the complete photovoltaic system (compared to a standalone solar cell) – this limit is obtained in the last chapter of the thesis. In this second part I (firstly) aim to understand and (secondly) try to increase the emission efficiency of ensembles of Si nanocrystals.

In *Chapter 6* I show, by correlating external and internal quantum efficiencies, that the vast majority of nanocrystals act as direct quenchers of the excitation energy. They behave as so-called "dark" nanocrystals. Furthermore, by exploring the carrier lifetime dependence on the excitation power – in *Chapter 7* – I show that resonant energy transfer between neighboring nanocrystals (1) is present and (2) irreversibly quenches excitation energy by transferring it to these dark nanocrystals. Note that resonant energy transfer is not to be confused with space-separated quantum cutting since it involves a totally relaxed initial state. A combination of a high defect probability (not to be confused with defect density) and a decreasing bandgap for larger nanocrystals leads to an indirect and efficient drain of the absorbed energy. The result is that typical solid state dispersions of Si nanocrystals do not exceed emission efficiencies of 20 %, being far too low for the implementation in practical solar shapers.

In the last chapter of this second part (*Chapter 8*) I demonstrate Si nanocrystal ensembles with world record emission efficiencies, for solid state dispersions, of 35 %. This optical quality is reached by applying a hydrogen surface passivation technique in combination with the exploration of a large set of Si nanocrystal ensembles with varied properties, such as the nanocrystal size, density and initial surface quality. The different nanocrystal systems are produced by altering the Si content in the sputtered layers and their

annealing temperature. While the emission efficiency is still being almost a factor 2 too low for development of a practical spectral shaper, it is encouraging to see that the deeper fundamental understanding of the quenching processes of emission can result in nearly a doubling of the PL efficiency.

### Part III

Part three of this dissertation consists of two chapters that are both taking the research towards a higher level of application. Having determined the maximal PL efficiency of 35 % for conventional Si nanocrystals ensembles I change gears in *Chapter 9*. By making use of multilayered structures, consisting of sequential passive and active layers, I explored a possibility to increase the control over the nanocrystal size and density – material parameters that are inherently linked to each other as a result of the self-organizing nature of the nanocrystal formation process. When successful, this would potentially enable the production of highly emissive nanocrystals and furthermore it would give an enormous freedom in material design of nanocrystal shaper layers. I show that, while the multilayer structures do increase the level of control, the nanocrystal size and density cannot be uncoupled from each other, in contrast to some previous claims. Nevertheless, due to their smaller nanocrystal size-dispersion, multilayer structures might be the elected choice for achieving ensembles of highly emissive Si nanocrystals.

In *Chapter 10* I use the results obtained in my studies, to prepare an actual Si nanocrystal-based spectral shaping layer. In collaboration with ECN Solar Energy, I applied state-of-the-art Si nanocrystal layers on top of a p-type crystalline Si solar cell. By making use of ray-trace simulations in combination with modeling of the photonic mode density modification, we were able to account for all the physical processes occurring in such a hybrid system. As a result, we have determined the minimal PL efficiency of Si nanocrystals needed for a practical shaper to lead to an actual increase of the solar cell conversion efficiency to be 60 % (for excitation energies below the carrier multiplication threshold).

## Outlook

Although – at the moment – solid state dispersions of Si nanocrystals cannot be manufactured with high enough emission efficiencies for development of spectral shaper layers, this dissertation reveals their enormous potential for that purpose. Different routes can be followed for the necessary factor 2 increase of the emission efficiency. One way would be to utilize the full potential of multilayer structures with their narrow size distributions. The dominating presence of dark nanocrystals could be significantly decreased and both direct and indirect excitation quenching would be reduced. Furthermore, the hydrogen passivation that is explored in this thesis is not optimized for the passivation of the curved interfaces. Evidently, it would be desired to focus on this specific step, testing different annealing techniques, ambients and time-scales. Both proposed directions are examples of pure Si-oriented research routes. In addition, one should definitely consider alternatives that deal with non-pure Si materials, such as P- and B- doped Si nanocrystals, Si nanocrystal- sensitized rare earth atoms and/or graphene/2D material – Si nanocrystal hybrids.