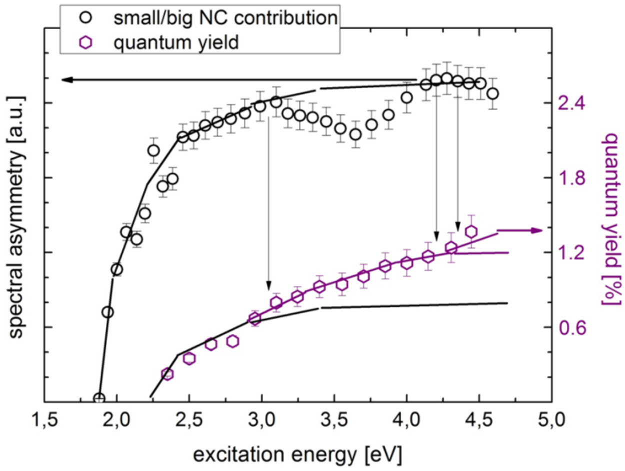
Carrier multiplication and energy dissipation in Si and Ge nanocrystals

Tom Gregorkiewicz

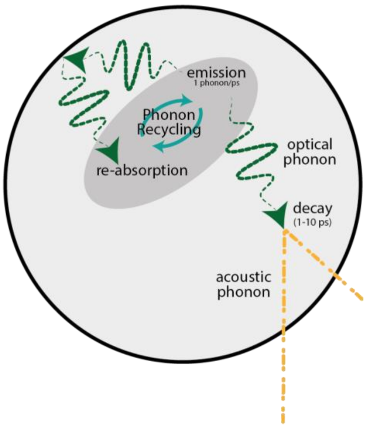
Van der Waals – Zeeman Institute, University of Amsterdam
Science Park 904, 1098 XH Amsterdam, The Netherlands

Carrier-carrier and carrier-phonon scattering in semiconductors involve multiple physical processes which become seriously modified in nanostructures. In particular, quantum confinement strongly affects properties of hot carriers, enhancing their effective lifetime – by reduction of phonon emission, and promoting impact excitation rates and enabling multiple exciton generation. At the same time, energy transfers to the outside of the nanostructure may be suppressed. In my presentation, I will discuss some results of investigations of these effects in Si and Ge nanocrystals embedded in large bandgap solid state matrices. The motivation for these investigations is provided by possible application of Si and Ge nanocrystals for modification of solar spectrum for the use in future, highly efficient photovoltaics. In particular, I will review the most recent progress in following specific subjects:

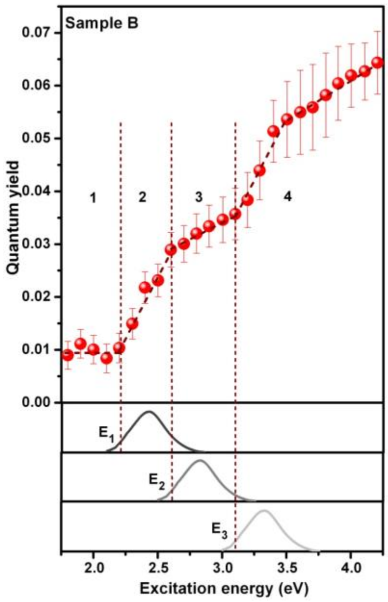
1. Carrier multiplication in Si and Ge nanocrystals.
   Here I will present results as obtained by calibrated ultrafast transient absorption and advanced photoluminescence quantum yield spectroscopies. These will be supported by theoretical modeling of the relevant energy transfer processes. For Ge nanocrystals prepared by a variety of techniques, I will discuss different emission bands and their possible microscopic origin. I will then present results of very recent investigations where which identified efficient multiple exciton generation for Ge nanocrystals in SiO_2 matrix prepared by co-sputtering. For Si nanocrystals, I will discuss the effect of doping on the process of multiple exciton generation. Finally I will also review the on-going investigations towards identification of a spectral finger fingerprint of the carrier multiplication process. In this case, the unique properties of Si nanocrystals in SiO_2 are explored in order to provide a novel and purely spectroscopic method for investigation of the carrier multiplication process.



2. Energy recycling process in Si nanocrystals.
   Building on the recently proposed theoretical treatment, I will discuss how the simultaneous occurrence of impact excitation and Auger recombination of multiple excitons co-localized within the same nanostructure facilitates energy "recycling" between excitons and hot carriers. In that way, the effective lifetime and concentration of hot carriers are increased and new recombination channels are being promoted. I will then present very recent investigations of emission under conditions of high-flux pumping: I will show that saturation of photoluminescence intensity is not always obtained. I will propose a model to describe the case of intense pumping and will argue that under such conditions equilibrium between hot carriers and phonon bath is reached, leading to suppression of nonradiative recombination of (multiple) excitons.



3. Energy exchange between neighboring Si nanocrystals.
   I will review results of our recent study of energy migration in ensembles of Si nanocrystals. By carefully following photoluminescence intensity, decay time and quantum yield as function of pump fluence at different energies, we identified certain peculiarities in the exciton lifetime. These arise due to energy exchange between neighboring nanocrystals and offer potential for realization of long-range energy diffusion. In the past similar effects have been observed for nanocrystals of direct bandgap materials. I will discuss potential of these findings for possible development of excitonic solar cell based on Si nanocrystal layers.



4. Excitation of Er emitters by hot carriers generated in Si nanocrystals.
   I will present our recent work concerning quantum yield of infrared (1.5 μm) emission from Er^{3+} ions upon indirect excitation via Si nanocrystals. I will demonstrate strong enhancement of the quantum yield at high excitation energies, and will argue that it appears due to transfer of excess energy of hot carriers generated in Si nanocrystals by absorption of highly energetic photons. This process is sufficiently efficient to overcome hot carrier cooling by phonon emission. I will comment on possible application of this phenomenon in future photovoltaics, where it could mitigate heat losses by hot carrier generation.

[1] M.T. Trinh *et al*., Nature Photonics 6, 316-321 (2012).
[2] S. Saeed *et al*., Nature Communications 5:4665 (2014)
[3] F. Priolo, T. Gregorkiewicz, M. Galli, and T. Krauss, Nature Nanotechnology **9**, 19 (2014)
[4] S. Saeed *et al*., NPG Light: Science and Applications, 2015