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Efficient photoluminescence upconversion in porous Si

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Abstract. We report on a new phenomenon specific for a system of spatially interconnected nanocrystal assemblies: efficient low temperature photoluminescence (PL) upconversion at resonant optical excitation of porous Si. The upconverted photoluminescence (anti-Stokes PL) is observed at intensities as low as 0.1 W/cm^2 and its intensity is as large as that of the Stokes PL band. The confirmation of the essence of connectivity between nanocrystals comes from the same type of studies performed on systems containing Si nanocrystals surrounded by a thick SiO$_2$ shell where the anti-Stokes PL is completely absent for any excitation energy and intensity used while the properties of the Stokes PL are very similar to those of porous Si.

The nonlinear optical response of nanocrystal assemblies has been clearly observed in single CdSe and InAs nanocrystals [1, 2]. The occupation of one nanocrystal with two electron-hole (e-h) pairs leads to Auger photo-luminescence damping, Auger autoionization and Auger quenching of the PL in the ionized crystal. In porous silicon, an assembly of silicon nanocrystals, the lifetime of e-h pairs is on the order of microseconds to milliseconds and therefore a double occupation of one nanocrystal with e-h pairs leading to strong nonlinear effects can be achieved at very low excitation intensity [3].

We observed efficient low temperature anti-Stokes PL at resonant excitation of a broad porous Si PL band. Figure 1 shows typical low temperature resonant PL spectra for a naturally oxidized and a hydrogen passivated porous Si sample, excited on the low energy side of the nonresonant emission band.

The samples were prepared from (100)-oriented p-type c-Si with resistivities 4–6 Ωcm by anodic etching in a HF solution in the dark. The strongly oxidized Si nanocrystals were prepared either by oxidation of macroporous Si at 1000 °C or by Si ion implantation in a SiO$_2$ layer and subsequent annealing. For the excitation of the resonant and nonresonant PL a He-Cd and Ti:Sapphire laser were used. The PL was detected with a Si charge-coupled device or a fast photomultiplier. In order to suppress stray light from the exciting chopped CW laser the entrance slit of the monochromator was blocked by a mechanical shutter when the laser beam illuminated the sample. The Stokes PL consists of a set of peaks assigned to transisions involving no phonon, 1TA-, 2TA-, 1TO-, TO+TA- and 2TO-momentum-conserving phonons in the absorption-emission cycle [4]. The intense upconverted emission grows progressively relative to the Stokes PL with decreasing excitation energy and the efficiency of the anti-Stokes PL reaches that of the Stokes PL at the lowest excitation energy used. Different mechanisms are possible to provide the additional energy for the anti-Stokes PL. The energy gain from a phonon bath can be excluded since in this case the intensity of the anti-Stokes PL grows with increasing temperature in contrast to the observed temperature dependence. Also the thermal energy available from the phonon

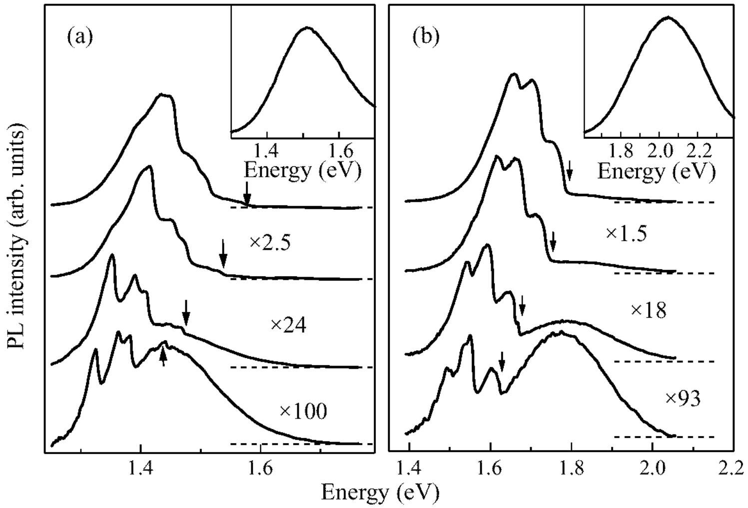

Fig. 1. Resonantly excited PL spectra of two porous silicon samples having different average nanocrystal sizes. (a) Naturally oxidized. (b) Hydrogen passivated. Excitation energies are indicated by arrows, $T = 4.2$ K, $I_{\text{exc}} = 1$ W/cm^2.

bath at experimental temperatures ~4 K is much too small to explain the spectral extension of the anti-Stokes spectra of up to a few hundreds of meV (see Fig. 1). Therefore the additional energy can only come from the absorption of a second photon or from the nonradiative Auger recombination of a second e-h pair. A simultaneous absorption of two exciting photons involving extremely short-lived virtual states is impossible because it would require much higher excitation intensities on the order of MW/cm^2–GW/cm^2 than those used in the experiments (down to 0.1 W/cm^2).

The source of the anti-Stokes PL can be identified by comparing the lifetimes of the Stokes and anti-Stokes PL. The conventional Stokes PL lifetime of porous Si in thermal equilibrium depends on the temperature and is determined by the short-lived spin-singlet and the long-lived spin-triplet luminescing exciton state [5]. The lifetime of the anti-Stokes luminescence exactly follows the behavior of the Stokes PL lifetimes (Fig. 2) suggesting

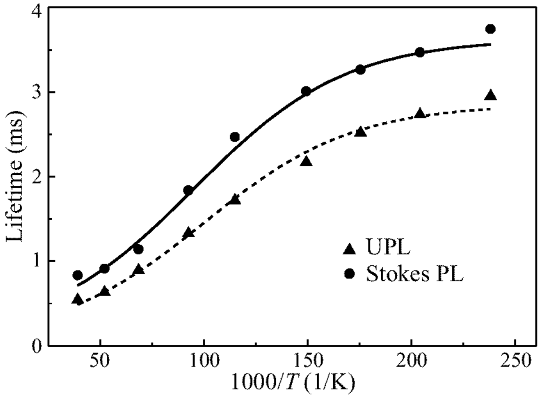

Fig. 2. The temperature dependence of the Stokes PL (circles) and anti-Stokes PL (triangles) lifetime.

that the excitons confined in Si nanocrystals are the source of both Stokes and anti-Stokes PL.

As can be seen in Fig. 3 the experiments show a linear dependence of the anti-Stokes PL on the excitation intensity (below the Auger PL quenching limit) and can be explained by a two-step absorption process with a saturation of a long-lived intermediate state giving rise to the anti-Stokes PL. The long decay time of these states allows them to be occupied even at very low excitation intensities. This long-lived state behaves like a spatially separated e-h pair state with the electron and the hole existing in neighboring nanocrystals. The overlap of wavefunctions of electron and hole localised in neighboring nanocrystals is weak and thus results in an enhanced decay time for the spatially separated state. The optical excitation of a second e-h pair in the larger of these nanocrystals occupied by an electron or hole, having the smaller bandgap leads to a nonradiative Auger process followed by the injection of a carrier into the smaller nanocrystal having larger bandgap with subsequent emission of anti-Stokes PL. The role of the charge separation can be studied by using nanocrystals

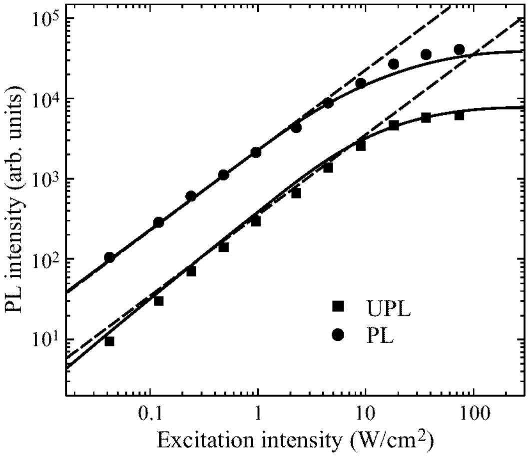

Fig. 3. Excitation intensity dependence of the PL measured at the 2TO peak energy position (circles) and anti-Stokes PL ($E_{\text{det}} = 1.5$ eV, squares). $T = 4.2$ K, $E_{\text{exc}} = 1.483$ eV.

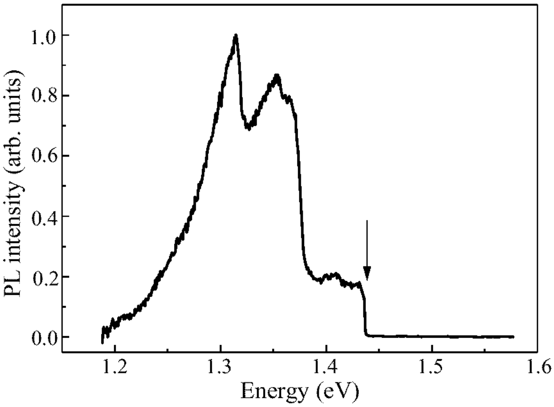

Fig. 4. Resonantly excited PL from Si nanocrystals having a thick oxide shell, $T = 4.2$ K, $I_{\text{exc}} = 1$ W/cm^2. The excitation energy is shown by the arrow.

isolated by high potential barriers. For Si nanocrystals surrounded by a thick SiO_2 shell which prevents any carrier transfer between the crystallites the anti-Stokes PL is completely absent for all excitation energies used (Fig. 4).

This implies that the carrier transfer between nanocrystals plays an important role for the anti-Stokes PL. The existence of long-lived spatially separated charges is crucial for the model of the anti-Stokes PL. One has to assume lifetimes of the intermediate long-lived state to be on the order of seconds. Experimental evidence for such states comes from the observation of an extremely long-lived component of the PL after CW illumination of a porous Si sample immersed in superfluid He by a high energy Ar^+ laser beam. This illumination creates spatially separated e-h pairs which recombine slowly after switching off the excitation source (in a seconds time domain).

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