n- and p-type impurity co-doped and compensated silicon nanocrystals in silicate and in solution

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Nanometer-size silicon (Si) crystal (Si nanocrystal) is believed to be a new building block for future Si-based electronic and optoelectronic devices. In order to realize Si nanocrystal-based devices, precise control of shallow impurities and understanding of the energy state structure of doped Si nanocrystals are crucial. It has been demonstrated that optical properties of Si nanocrystals are strongly modified by doping very small number of impurities [1-5]. Doping of either n- or p-type of impurities results in the quenching of the photoluminescence (PL) because of Auger interaction between photoexcited excitons and carriers supplied by doping [1-3]. On the other hand, doping of n- and p-type impurities simultaneously modifies the PL property, especially PL energy, significantly without losing the intensity so much [4,5]. This suggests that impurity doping can be an additional parameter, following the size, shape, surface termination, etc., to control the optical properties of Si nanocrystals.

In this paper, we report growth and optical properties of phosphorus (P) and boron (B) co-doped Si nanocrystals embedded in silicate thin film matrices. We also prepare co-doped colloidal Si nanocrystals from co-doped Si nanocrystals in silicate matrices. We show that co-doped Si nanocrystals can be dispersed in polar liquids without functionalization by organic molecules and exhibit efficient PL in the visible to near infrared regions.

Doped Si nanocrystals were prepared by simultaneously sputter-depositing Si, SiO_2, B_2O_3 and P_2O_5 and annealing the deposited films in a N_2 atmosphere. Samples with different forms, i.e., silicate films in which co-doped Si nanocrystals are randomly dispersed [4], multilayer films consisting of co-doped Si nanocrystal layers and spacer layers [5], and isolated co-doped Si nanocrystals dispersed in solution [6,7], were prepared and the optical properties were studied.

Figure 1 shows a cross-sectional transmission electron microscope (TEM) image of a film consisting of thin layers of P and B co-doped Si nanocrystals and silicate. Co-doped Si nanocrystals with relatively narrow size distribution can be seen. The average diameter estimated from the TEM image is 5.2 nm with the standard deviation of 0.98 nm.

Fig.1 Cross sectional TEM image of a film consisting of thin layers of P and B co-doped Si nanocrystals and silicate [5].

By dissolving silicate films containing P and B co-doped Si nanocrystals in hydrofluoric acid solution, we produce isolated co-doped Si nanocrystals [6,7]. Figure 2(a) shows a photo of the Si nanocrystal colloid (methanol solution). The liquid is very clear and no agglomerations are found even after several months. Figure 2(b) shows a TEM image of the colloid, which evidences that Si nanocrystals are isolated. The average diameter is 3.0 nm with the standard deviation of 0.9 nm. Lattice fringes in the high-resolution TEM image in Fig. 2(c) correspond to {111} planes of Si. It should be stressed here that no surface functionalization process is added in the preparation procedure and thus there is no organic molecules on the surface. Another important fact is that the high-dispersibility in polar liquids can be obtained only when P and B are simultaneously doped. This suggests that doped impurities play a crucial role for the high solution dispersibility [7].

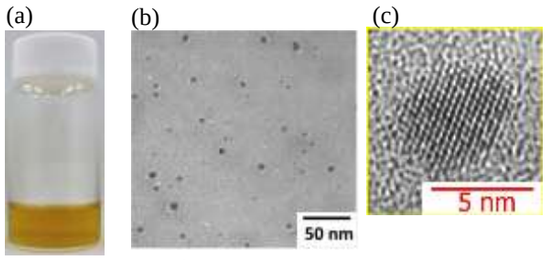

Fig. 2 (a) Photo of Si nanocrystal colloid. The liquid (ethanol) is very clear and the light scattering is very small. The optical transmittance in the near-infrared region is almost 100%. (b) TEM image of colloidal Si nanocrystals. Si nanocrystals are well-dispersed and no agglomerations are found. (c) High-resolution TEM image of one of the particles in (b). Lattice fringes correspond to {111} planes of Si. [6,7]

Figure 3 shows PL spectra of co-doped Si nanocrystals in silicate matrices. The PL peak energy is very low and, in some spectra, it is below the band gap energy of bulk Si crystal. These spectra are apparently different from those of intrinsic Si nanocrystals and are considered to arise from the transition between donor to acceptor states in the band gap of co-doped Si nanocrystals. Co-doped colloidal Si nanocrystals show similar spectra.

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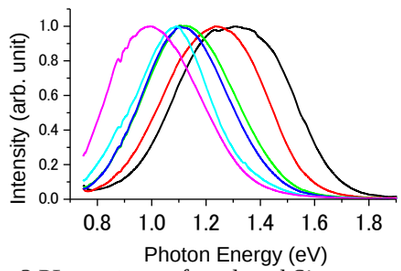

Fig. 3 PL spectrum of co-doped Si nanocrystals in silicate matrices. PL appears at much lower energy than that of intrinsic Si nanocrystals.

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