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REPORT on Experiment MA2459 performed at ID10-ESRF, 1-7 Oct. 2014

Title: Photoluminescence emission in Si nanocrystals

Our group has investigated optical and microscopic properties of Si nano-particles (NPs) obtaining the following results: PL emission was observed from Si nanocluster in various environments, with time spectra revealing radiative vs. non-radiative photon emission in a range of wavelength 650-900 nm (Faraci et al. Phys. Rev. B **78**, 245425, 2008.); a more recent study by our group on the photoluminescence (PL) produced by faceted grains of silicon (fg-Si) 100 nm in size has obtained a **giant PL yield** with an amplification gain as high as 0.14 cm/Watt. This result published on a prestigious journal of the Nature group (Faraci et al. Scientific Reports 3, 2674, 2013), required further investigations, in order to determine how the PL emission was dependent on the high local temperature induced by the laser beam. It was hypothesized that the high temperature reached by the sample spot at the highest values of the laser power, could be dependent on the Si NPs agglomeration during deposition. In fact, the porous deposition layers of octahedral shape could be responsible of the local heating due to the poor thermal contact preventing phonon exchange and propagation.

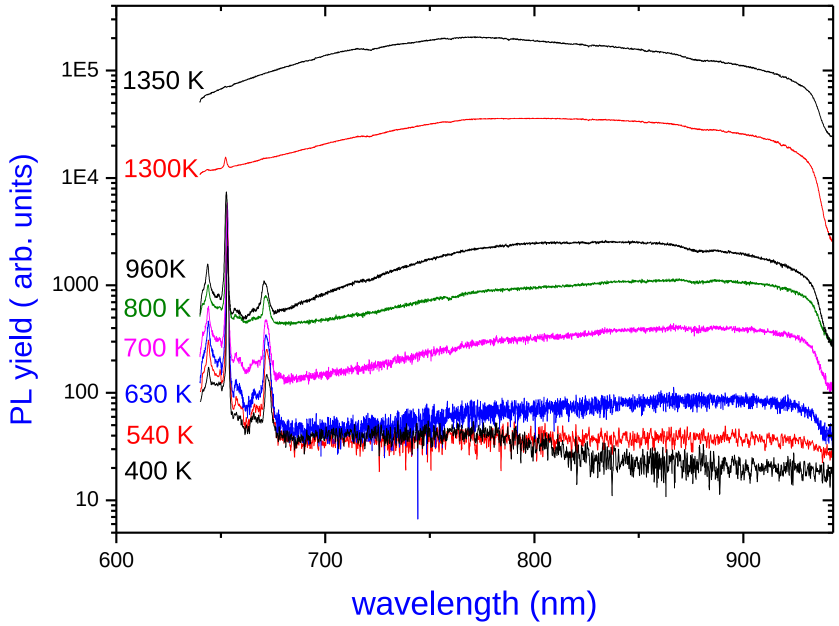

Fig. 1 Photoluminscence emission spectra from fg-Si layer. The PL yield dramatically increases as a function of the temperature, with a broad peak centred at about 770 nm. Afterwards a rapid decrease is observed with a minimum around 940 nm. Being the laser energy at E_0*=1.963 eV (633 nm) and the TO phonon energy* E_p*=63meV the main peak visible in the PL spectrum corresponds to the Raman Stokes peak at* $E_S=E_0-E_p$*=1.9 eV (i.e. 654 nm).*

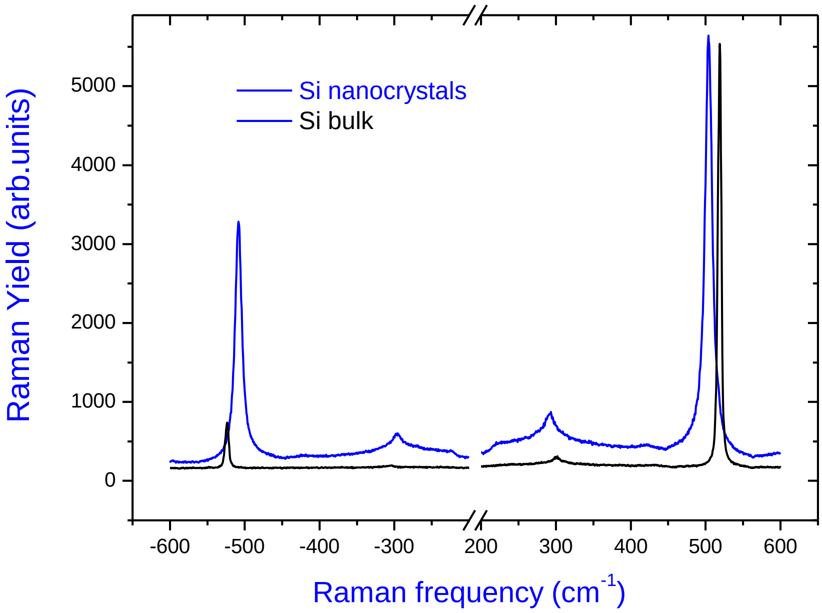

Fig. 2 Typical Raman spectra obtained in bulk-Si and fg-Si layer. Clearly visible the relative shift and broadening corresponding to a temperature of 1000 K. The modification of the relative yield provides the local temperature measurement.

In order to individuate the spatial configuration of each kind of NPs, tri-dimensional tomography was performed at the European Synchrotron Radiation Facility (ESRF) using Coherent X-ray Diffractive Imaging (CXDI), a novel scattering technique that exploits the high degree of coherence of modern synchrotron sources (see Experimental details). The high quality of the reconstructed images reveals individual Si nano-crystals with unprecedented detail. (Fig. 3)

As clearly visible in Fig. 3, the deposition of the Si-NPs results in a superposition quite porous of grains more or less compact according to the shape and size. From the CXDI data the “porosity” parameter p ($0 < p < 1$) of the specific deposition can be extracted simply as the deposition average density, referred to the bulk silicon density. The p parameter, as discussed in the following, determines the local temperature in the sample spot illuminated by the laser.

The previous effects of high PL suggest an evident resonance of the Raman scattering with electron transitions in the nanocrystal ensemble, stimulated by the high phonon production due to the high temperature of the sample.

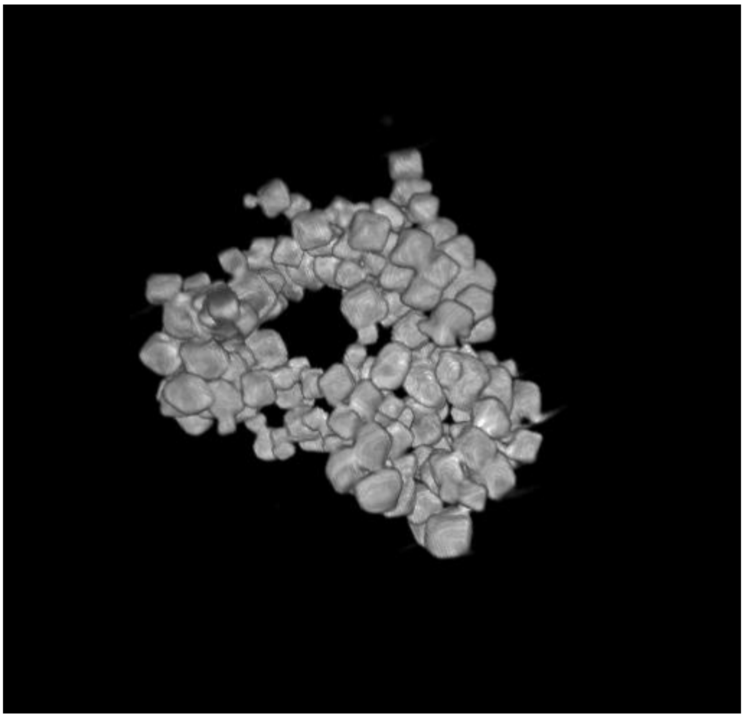

Fig. 3 CXDI for typical deposition of octahedral Si-NPs

We sketch a simple model indicating the competition processes and the amplification reasons:

Step 1: Absorption with two possible paths. The laser beam in the nanocrystals can be absorbed via Raman scattering or via electron excitation. The Raman first order process can produce or absorb TO phonons (about 63meV); the electron excitation is possible since the laser photon energy (1.96 eV) is larger than the bulk silicon gap. Therefore electron excitations are particularly enhanced since the phonons can stimulate indirect interband electron transitions.

Step 2: Electron excitations produce excitons. These can decay via non-radiative and/or radiative processes giving PL. These two decay paths are of course in competition to each other. They generate the following step 3 and step 4.

Step 3: Whenever the nonradiative process is dominant a phonon production enhances the Raman yield.

Step 4: Whenever the radiative process is dominant a PL production is of course magnified.

We have confirmed that an intense PL spectrum is obtained when silicon is deposited as layer formed by isolated nanoparticles, scarcely in contact with each other. A huge amplification is detected not only in the visible range but also in the NIR side of the Si gap (0.8 eV at 1200 K). Furthermore, PL signal is independent from the Si nanoparticle specific size but depends solely from the capability of the nanoparticles to exchange heat induced by the laser source with neighborhood particles. This result is simply explained by the amount of energy transferred by the laser to the sample spot and not transmitted outside as a consequence of the voids surrounding each Si-NP. We suggest that the main parameter playing a role is the porosity. This result is of particular importance for the applicative point of view, since it widens the possibility to obtain photoluminescence from any ensemble of grains of arbitrary shape. A joint paper in collaboration is in progress for publication.

Experimental details:

We intended to investigate the formation and determine the 3D configuration of micrometric clusters of Si nano-particles of well defined shape (spheres or octahedra) and size (from 20 to 150 nm) synthesized by using an Inductively Coupled Chemical Vapour Deposition System. Several samples were prepared as a function of the particle size, shape and density. Also the overall layer thickness was varied with the scope of enhancing the signal. Samples produced on several substrates (silicon, glass, polymer) were extracted and deposited as single particles on Si_3N_4 membranes. We selected the cluster size by measuring the shift of the Raman line typical for bulk Si (521 cm^{-1}) toward smaller wave numbers, which is determined by the strength of the quantum confinement, and of local temperature. Typical samples were produced by piling up several layers in order to obtain a porous sample about 2 μm thick.

Coherent X-ray Diffractive Imaging (CXDI) is a recent scattering technique using the high degree of coherence of modern synchrotron sources. (Y. Chushkin and F. Zontone, J. Appl. Cryst. 46, 319, 2013). Very high resolution imaging of isolated microscopic objects represents an interesting tool to bridge the gap between high resolution electron and visible light microscopy. The image in the real space is obtained by applying phase retrieval algorithm to the diffraction pattern measured with sufficient oversampling. Because of the high penetration power of the X-rays, with a typical energy of 7 keV, at the European Synchrotron Radiation Facility, (beamline ID10, with a coherent flux 1.8 1010 ph/s/100mA), we have been able to obtain 3D reconstruction of porous Si clusters. CXDI is a lens-less imaging technique based on the inversion of the (over-sampled) speckle pattern in the far-field diffraction pattern produced by an isolated object. "Speckle" refers to the grainy structure observed when a coherent beam (as a laser or a coherent X ray source) is reflected from a diffusing surface. This phenomenon results from interference effects in a coherent beam with random spatial phase fluctuations. The speckle grains can be identified with the coherence domains of the Bose-Einstein statistics. CXDI is a very powerful technique for 3D imaging objects as low as 1 μm at 10nm resolution. The diffraction pattern must be oversampled by a factor of two or more. Since the resolution in real space depends on the maximum wave vector where the intensity is detected, i.e. on the detector field of view, there is a practical limitation on oversampling in reciprocal space and resolution in real space that is ultimately determined by the number of pixels. The lost phase is retrieved by an iterative algorithm applied to the oversampled speckle pattern. Oversampling σ is defined as: $\sigma = \lambda D/p S$, where λ is the wavelength, D the sample-detector distance, p the pixel size, S the sample size. Practically, $\sigma > 3$. The real space image is obtained simply by inverse Fourier transform.

The samples were also investigated by micro Raman spectroscopy for detecting the transversal optical (TO) vibrational peak situated for bulk Si at 521 cm^{-1}, at room temperature (300 K). Raman spectra are collected in backscattering geometry with a HORIBA Jobin-Yvon system, equipped with Olympus BX41 microscope. He-Ne laser radiation at a wavelength of 632.8 nm is focused to a spot size of the order of 1 μm by a 100x objective. The laser power on the sample is 6 mW, and a 550 mm focal length spectrometer with 1800 lines/mm grating is used for collecting Raman spectra.

PL spectra were collected with the same apparatus for the visible range (2.3 – 1.5 eV).