Supporting Information

The supporting information contains 6 pages and includes 6 Figures and 1Table.

Photophysical Properties of Ball Milled Silicon Nanostructures

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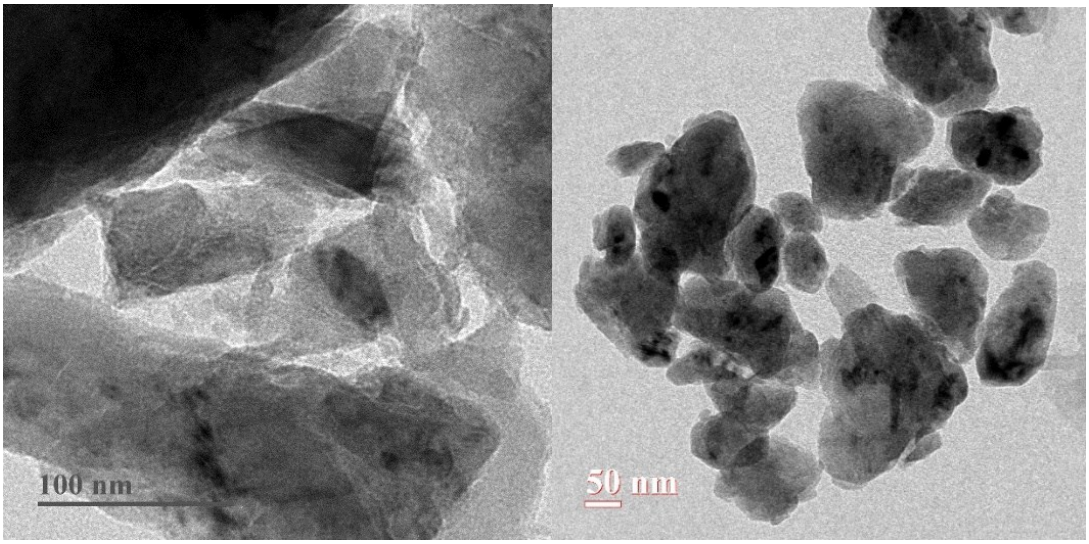
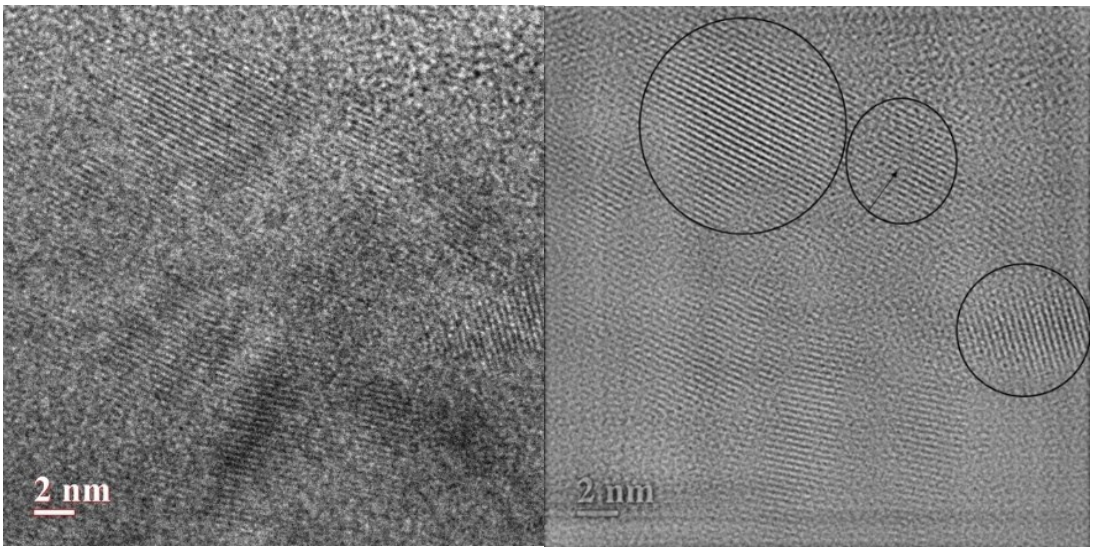
1. Transmission electron microscopy



(a) (b)



(c) (d)

Figure S1: Transmission electron microscope images of un-milled (a) and milled (b) Si powders. 20 hours of milling has reduced the size of powder particles to the nanometer range (<100 nm). TEM imaging was performed on the ensemble particles thus showing only bigger particles which could be agglomerates of smaller particles or itself a bigger particle. (c) HRTEM image of the milled Si powders shows nano-crystallites with presence of amorphous region which could be SiO_2. (d) FFT of the image in (c); black arrows are showing missing planes in crystallites which is related to dislocations caused by high energy ball milling.

2. X-ray Diffraction of Si (Un-milled and milled) powders:

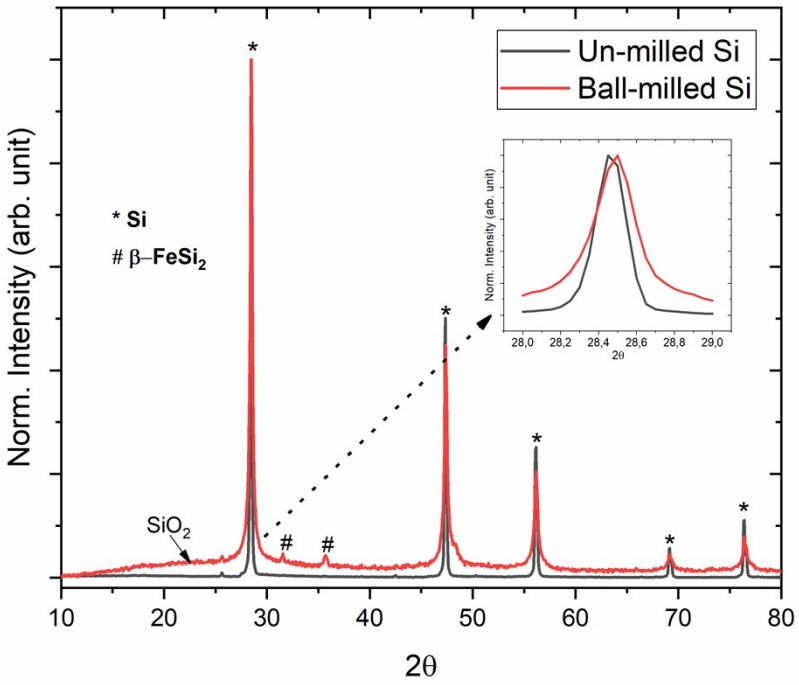


Figure S2: X-ray diffraction patterns of un-milled (black line) and milled (red line) Si powders. Presence of amorphous oxide phase (SiO_2), β-$FeSi_2$ phase at 32º and 35.5º 2θ can be seen. Milled and un-milled Si powder both has the diamond cubic structure with <hkl> indices of <111>, <220>, <311>, <400>, <331> corresponding to the peak positions (2θ) at 28.57, 47.42, 56.25, 69.37 and 76.52, matched with a JCPDE standard database (ref 00-027-1402). Inset of the XRD figure shows zoom in plot of <111> plane, showing peak broadening after 20 h of milling. FWHM of milled powder was increased to 0.27 from 0.20 in the un-milled powder.

Structural parameters extraction from XRD:

Table ST1: Strain%, dislocation density and crystallite size of milled and un-milled Si powders

Si Powder	Lattice Strain	Dislocation density (cm^{-3})	Crystallite size (nm)	Stress (from Raman spectroscopy)
Un-milled	0.25	2.0×10^{11}	45.5	125
Milled	0.63	8.5×10^{11}	25.2	4250

Strain and crystallite sizes are approximated considering broadening in XRD (after reducing instrumental broadening) peak due to reduction in crystallite size and induction of strain. Lattice strain, ε, was determined by the Eq. (1), where β_{hkl} is the full-width half maximum (FWHM) of the spectra peaks [1].

$$\varepsilon = \beta_{hkl} / 4 \tan \theta \ \% \qquad (1)$$

The dislocation density, $\rho_{d,}$ was approximated by eq. (2) [2], where Ɛ is lattice strain, D is crystallite size and, b is burgers vector for dislocations.

$$\rho_d = 2\sqrt{3}\,\text{Ɛ} / D \,.\, b \qquad (2)$$

Crystallite size (D) was calculated using Scherrer equation [3], where β_{hkl} is the full-width half maximum (FWHM) of the spectra peaks, k is constant and λ is wavelength of the X-ray used in the measurements.

$$k\lambda = D.\,\beta_{hkl}\cos\theta \qquad (3)$$

Mechanical stress, δ, was calculated using an empirical formula, shown in eq. (4), where Δω is the change in the frequency of Raman peak [4].

$$\delta\,(\text{MPa}) = -\,250\,\Delta\omega\,(\text{cm}^{-1}) \qquad (4)$$

3. Energy Dispersive X-ray Spectroscopy (EDX)

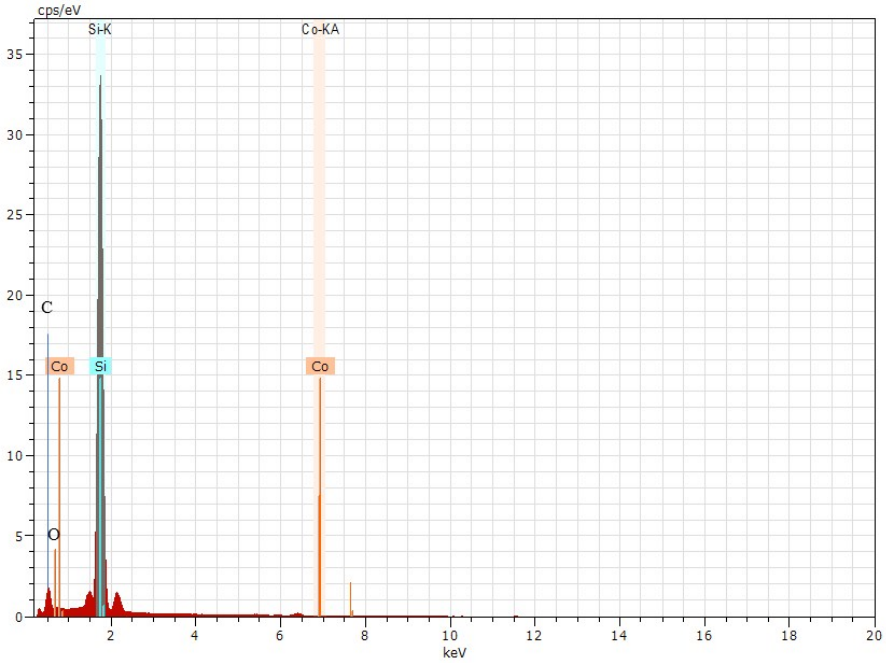


Figure S3**:** EDX (as an attachment to SEM) spectrum recorded for the milled Si powder. No traces of Fe could be seen. Trace amounts of O and Co were detected. Carbon is also present, but it is difficult to say whether it came from the sample or the carbon tape used for to hold sample while measuring. EDX is unable to trace elements in trace amount and thus should be considered only for a broader estimation.

3. Raman spectroscopy

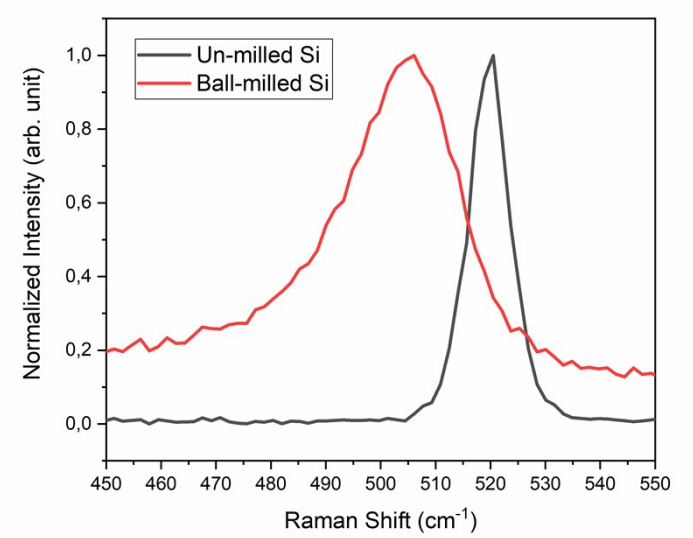


Figure S4: Raman spectra recorded for un-milled and milled Si powders using 0.3 mW energy of laser (532 nm). Un-milled Si powder shows characteristic sharp crystalline peak at 520 cm^{-1}, which is broadened and shifted to 505 cm^{-1} in the milled Si powder. The peak position of milled Si powder suggest nanocrystalline Si and broadening suggests presence of heavy stresses.

5. Photoluminescence excitation contour plot spectra of un-milled Si Powder

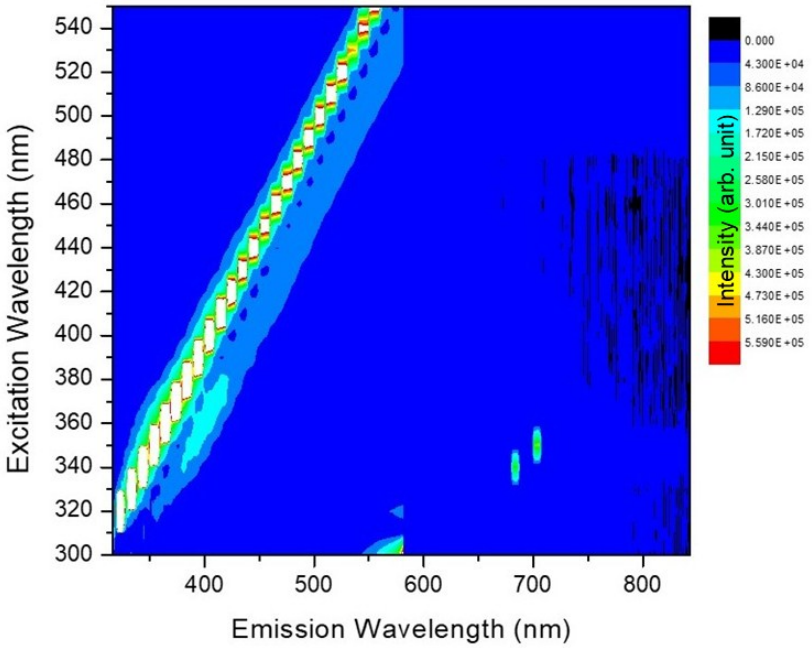


Figure S5: PLE contour plot of un-milled Si powder recorded on Fluorolog setup with integration time of 60 second for each data points.

6. PL Decay

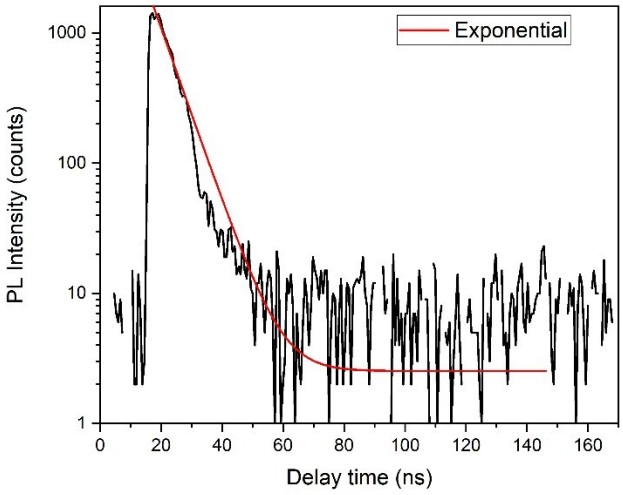


Figure S6: PL lifetime measured using 60 ps pulsed laser excitation at 405 nm (pulse width at maximum power is ~300 ps, 20 MHz repetition rate). Signal was detected in our PL microscopy setup using TCSPC detection setup from Becker & Hickl (DCP-230 card and single photon detectors ID Quantic 100).

References:

1. O. Maulik, D. Kumar, S. Kumar, D. M. Fabijanic, V. Kumar, Intermetallics, 2016, 77, 46-56.
2. G. K. Williamson and R. E. Smallman, Philosophical Magazine, 1956, 1 (1) :34–46.
3. P. Scherrer, Göttinger Nachrichten Gesell. 1918, 2, 98-100.
4. I. D. Wolf, Semiconductor Science and Technology, 1996, 11, 139-154.