Luminescence of silicon and quartz crystals at mechanical destruction

V I Vettegren\textsuperscript{1,2}, A V Ponomarev\textsuperscript{2}, R I Mamalimov\textsuperscript{1,2}, I P Scherbakov\textsuperscript{1} and V B Kulik\textsuperscript{1}

\textsuperscript{1}Ioffe Institute, 26 Politekhnicheskaya, St Petersburg, 194021, Russian Federation
\textsuperscript{2}Schmidt Institute of Physics of the Earth of the Russian Academy of Sciences, 10–1 Bol’shaya Gruzinskaya, Moscow, 123242, Russian Federation

E-mail: Victor.Vettegren@mail.ioffe.ru

Abstract. Spectra and time dependencies of fractoluminescence (FL) signals of silicon (Si) and quartz (SiO\textsubscript{2}) crystals are obtained when diamond crystals are scratched on their surfaces. Signals are generated when barriers preventing dislocation movement along sliding planes are broken. Simultaneously, the Si and SiO\textsubscript{2} crystals break down into nanocrystals (nc). The band 1.62 eV and 2.14 eV corresponds in FL spectra of Si and SiO\textsubscript{2} nc accordingly. After the crystals are broken, powders are formed. The size of Si and SiO\textsubscript{2} nc in powders was determined by photoluminescence (PL) and Raman spectroscopy.

1. Introduction
Currently, a popular method for producing nanocrystalline silicon (nc-Si) is electrochemical etching followed by milling of the porous silicon obtained [1]. Recently, silicon has been milled in ball mills. In this method, the crystals are subjected to impact and friction, resulting in their milling to nanosize. The structure of nc-Si formatted by this method was investigated by methods of PL, infrared and Raman spectroscopy, electron microscopy, X-ray diffraction, etc. [1-3]. Mechanism and the dynamics of the fracture process had not been studied until recently. In this work, the nc-Si obtained by scratching the Si crystal surface by diamond micro crystals. For comparison, nanocrystalline quartz (SiO\textsubscript{2}) was obtained in the same manner. The mechanism and dynamics of the process of grinding Si and SiO\textsubscript{2} crystals was studied.

2. Experimental
Samples from Si crystal were cylinders with diameter of 20, height of 30 mm, and SiO\textsubscript{2} were cylinders with diameter of 15, height of 5 mm.

The samples studied were pressed against a disk with diamond microcrystals attached to an electric motor (figure 1). After switching on the motor, fractoluminescence (FL) appeared. The FL spectrum is registered by the AvaSpec-ULSi2048L-USB2 OE fiber-optic spectrometer. Simultaneously, the powder flew out of the fractured zone. The PL spectra of the powder excite by UVTOP280TO39HS light diode and registered by the spectrometer. Raman powder spectra were excited by Ar\textsuperscript{2+} 16508 laser, 488.0 nm line, and recorded by the Ramalog 5 spectrometer. The scattering angle is 180°. To study a time dependency of the radiation generated at fracture it was focused by quartz lens on the surface of the photomultiplier tube PEM-136. Electric voltage at its output was supplied to the input of...
the analog-digital converter ADS-3106 of ACTACOM. Voltage at ADS output every 2 ns was recorded in computer memory.

**Figure 1.** Destruction unit: 1 - sample holder; 2 - studied crystal; 3 - steel disk with diamond microcrystals.

### 3. Results and discussion

#### 3.1. Spectra of FL Si crystal at destruction and PL of the powder from Si.

The FL spectrum at fracture of Si crystal and PL spectrum of powder from Si are shown in figure 2.

**Figure 2.** The FL spectrum at fracture of Si crystal (a) and PL spectrum of powder from its (b).

In FL spectrum (figure 2a) the band ≈ 1.62 eV is observed. Appearance of this band caused a confinement [2, 3], i.e. increase of the band gap and violation of the momentum conservation. The maximum ≈ 1.62 eV corresponds to nc-Si with a grain size of ≈ 4 nm [2, 3]. The intensive band 2.25 eV (figure 2a) and 1.62 eV which intensity in ≈ 10^3 times less than that one for crystal can be seen in PL spectra of Si powder obtained after a few hours after destruction (figure 2b). The intensive band of 2.25 eV corresponds to nc-Si with a grain size of ≈ 2.3 nm. Existence of a weak band shows that the powder consist a small amount of nc-Si with a grain size of ≈ 4 nm.

Figure 3 shows the 520.8 cm⁻¹ band in the Raman spectra of the Si crystal [4] and in the 512.1 cm⁻¹ in spectrum of the powder from Si. The maximum of the band is displaced towards low frequencies on ≈ 8.7 cm⁻¹, at the same time a band is non-uniform widened from the same party in a powder
spectrum. This effect is caused by phonon confinement [4], i.e. violation of the momentum conservation low, due to scattering of phonon at boundaries of nc.

![Raman spectrum](image)

**Figure 3.** Raman spectrum of Si crystal (1) and powder from it (2).

The analysis of a form of the band and shift of its maximum showed that the Si nc sizes in powder is ≈ 2.2 nm, which coincides with the nc sizes, found from the analysis of a PL spectrum. Possibly, the internal tension formed at destruction in powder particles led to their cracking and reduction of the sizes in time after fractured and recording Raman and PL spectra (several hours): the sizes more than 99% of Si nc decreased in ≈ 2 times.

3.2. The FL spectrum of the SiO2 crystal and PL spectrum of powder from it.

The FL spectrum of the quartz crystal is shown in figure 4a. The band ≈ 2.14 eV is observed. According to [5] it corresponds to negatively charged =Si-O ions formed after a rupture of Si-O-Si of bonds.

![FL and PL spectra](image)

**Figure 4.** Spectrum of FL of quartz single crystal (a) and PL spectrum of powder from it crystal (b).

The band of 2.4 eV is observed in spectrum of PL received in several hours after destruction.
(Figure 4b). The band corresponds to the $≡\text{Si}−\text{O}^-$ ions their negative charge of oxygen is compensated by positive charged ions of $\text{Li}^+$, $\text{Na}^+$ or $\text{H}^+$ [6]. These ions get into particles of powder of quartz and compensate a negative charge of $≡\text{Si}−\text{O}^-$ ions during several hours after fracture.

Figure 5 shows the band 206 cm$^{-1}$ in the Raman spectrum of quartz crystal. It corresponds to vibrations the crystal of quartz [7].

![Raman spectrum of quartz crystal](image)

**Figure 5.** The 206 cm$^{-1}$ band in Raman spectra of quartz crystal (1) and the powder (2) from one.

Maximum of this band is displaced towards high frequencies on $\approx 2$ cm$^{-1}$, and the band is widened non-uniform to the same party in spectrum of powder. This effect is also caused by phonon confinement. The analysis of a form and shift of a maximum of this band showed that the size of quartz nc in powder is $\approx 10$ nm.

3.3. Time dependence of FL signal intensity

The time dependencies of the intensity of the FL signals at the friction of the Si and SiO$_2$ crystals consisted from several hundred of signals. They are shown in figure 6.

![FL signals at friction](image)

**Figure 6.** FL signals at friction of silicon (a) and quartz (b).

Signal duration is $\approx 42 - 48$ ns. They contained 4 maxima arising one after another through $\approx 10 - 15$ ns. How do they form? The mechanical stresses cause dislocations to move along the sliding planes. When planes are crossed, there are created the barriers preventing dislocation movement.
When barriers break cracks are formed [8] and FL signals appear. Si crystal has a cubic lattice and quartz has trigonal one. They have 4 systems of dislocation sliding planes and 4 cracks formed when barriers break. Because the FL signals contain 4 maximums.

We measured the temperature $T_f$ in the fracture zone. The measurement method is described in [9]. It turned out that for quartz $T_f \approx 120 \, ^\circ C$, and for silicon $T_f \approx 80 \, ^\circ C$. An increase in temperature could affect the measurement results. To reduce the temperature, the friction area was blown with a jet of dry nitrogen, cooled to $-50 \, ^\circ C$. At the same time, the temperature in the friction zone decreased to 50 $^\circ C$ for quartz and 40 $^\circ C$ for silicon. It turned out that the decrease in temperature did not lead to a noticeable change in the intensity of the maximum position in the FL spectra of silicon and quartz. Note that in the FL and PL spectra of silicon, a band is observed at the same energy value - 1.62 eV. This shows that the temperature change did not affect the maximum energy of this band.

4. Conclusion

The dislocations begin to move along sliding planes when crystals of silicon and quartz are broken. At the intersection of the planes, barriers are formed to prevent their movement. At break of barriers the crystal lattice of Si and SiO$_2$ the Si nc with sizes $\approx 4$ nm and SiO$_2$ with ones 10 nm are formatted. Results the bands 1.62 eV and 2.14 eV appear in luminescence spectra Si and SiO$_2$. At the same time powder is released from friction zone. The sizes of Si nc decrease to $\approx 2.2$ nm after 2 hours after destruction in powder.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant No. 20-05-00155a).

References

[1] Gauthier M, Mazouzi D, Reyter D, Lestriez B, Moreau P, Guyomard D and Roué L 2013 Energy Environ. Sci. 6 2145-55
[2] Rumman Md R, Song J-W, Lee I, Hong S-J and Koo J M 2014 Curr. Nanosci. 10 441-44
[3] Diaz-Guerra C, Montone A, Piqueras J and Cardellini F 2002 Semicond. Sci. Technol. 17 77-82
[4] Russell J P 1965 Appl. Phys. Lett. 6 223-24
[5] Kawaguchi Y 1998 Jpn. J. Appl. Phys. 37 1892-96
[6] Götzte J 2012 Microsc. Microanal. 18 1270-84
[7] De Boer K, Jansen A P J, van Santen R A, Watson G W and Parker S C 1996 Phys. Rev. B 54 826-35
[8] Cottrell A H 1964 Theory of Crystal Dislocations (New York: Gordon and Breach) p 91
[9] Vettegren V I, Ponomarev A V, Shcherbakov I P and Mamalimov R I 2017 Phys. Solid State 59 2286-89