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Structural changes of silicon upon high-energy milling investigated by Raman spectroscopy

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Abstract
This study showed pronounced changes in the Raman scattering of silicon powder during
high-energy ball milling. The powders were milled for 1–18 h in a steel ball mill in argon. The
approximate pressure imposed on particles was 2 GPa. The spectra of the as-milled powders
were compared with the initial silicon. It was found from the Raman peak position shifts that
milling generated strains in the silicon lattice, bringing about a transformation of cubic silicon
to tetragonal silicon and amorphization. The relative amount of new phases was determined
from the area under the measured Raman peaks.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physical properties of materials are strongly determined by
their crystal structure and the presence of defects. Therefore, it
is important that the changes of the crystal structure induced
by various processing routes are carefully tailored to the
needs of various applications. This in particular refers to
silicon, the most technologically important semiconductor
material.

High-energy milling is now one of the materials
processing methods that is widely used in powder technology.
The advantage of high-energy milling is its simplicity and
effectiveness. In addition, it can greatly alter both the surface
and the bulk of a milled material. Particle and grain refinement,
lattice transformation and amorphization are likely to occur.
Also, the generation of dislocations and stacking faults takes
place [1], as well as mechanical alloying [2]. Structural
changes in various materials, including silicon, during their
milling have been a subject of many investigations [1, 3, 4].

The products of milling are usually characterized using
x-ray diffraction (XRD). Raman studies of silicon after high-
energy milling have not been carried out so far to the

best knowledge of the authors. The advantage of Raman
spectroscopy over XRD analysis is that the spectra can be
collected from a very small volume, even below 1 μm in
diameter, which is simultaneously observed using a light
microscope. Also, the amorphous phase does not contribute to
a background of the spectrum, thus reducing the information
noise.

Raman spectroscopic studies presented in [5] showed a
transformation of silicon from cubic to tetragonal, due to
high loads applied during indentation tests. High-energy
milling, like other non-equilibrium methods, has a potential
to distort the lattice and produce amorphous silicon. In
the latter, so-called coordination defects are generated which
affect the electron density of states [6]. This in turn changes
the dielectric and thermal properties of silicon. Amorphous
silicon is nowadays a popular semiconductor, for example in
photovoltaic solar cells and thin-film resistors [7].

Raman spectroscopy can be used to examine crystal
structures [8] and stresses [9] and to indicate temperature
changes in the investigated materials [10]. It was used here
to investigate the evolution of the structure of silicon during
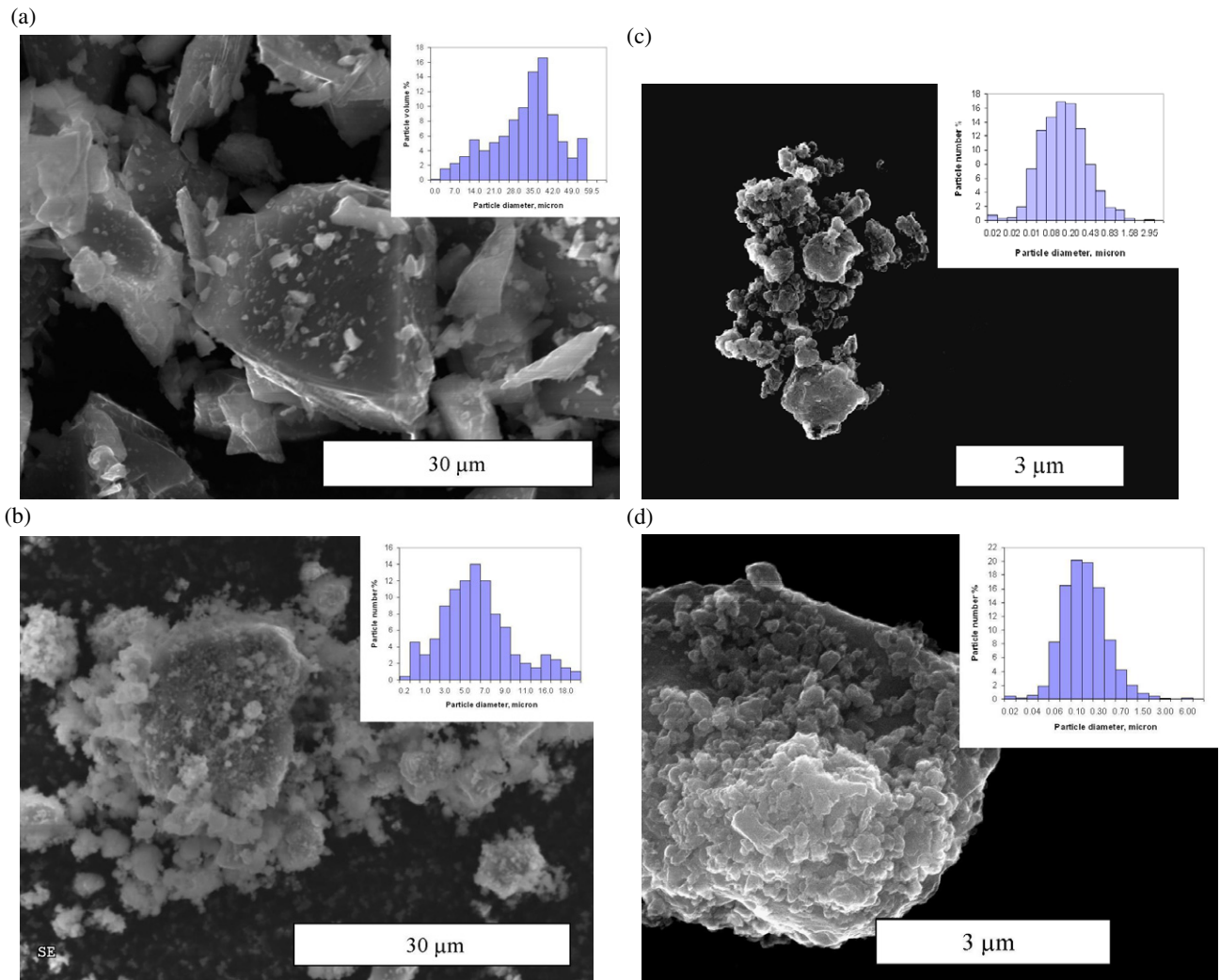high-energy ball milling.

(a)

(c)

(b)

(d)

Figure 1. SEM micrographs of the investigated Si powders: (a) initial, (b) after 1 h, (c) after 6 h and (d) after 18 h ball milling with the histograms of particle diameter (μm).

2. Experimental details

The investigated silicon powder containing 2.3×10^{17} cm^{-3} antimony and less than 0.005 wt% of iron had a mean particle diameter of 2.2 μm. The Si powder was produced by crushing and ball milling a monocrystal obtained using the Czochralski method and then sieving the powder. The weight ratio of balls to powder upon high-energy milling was 14.5. The pressure imposed by the balls on 1 g of powder during milling was approximately 2 GPa.

The particle diameter (d_{10}, d_{50}, d_{90}) of the milled and the initial silicon was measured on the basis of the scanning electron microscope (SEM) micrographs, figure 1. The obtained values are summarized in table 1.

The Raman spectra were measured using a Renishaw Raman spectrometer of inVia type, integrated with a light microscope. The laser wavelength was 0.633 μm. The spectra were collected in the Raman shift range 200–600 cm^{-1} at a resolution of 1.64 cm^{-1}. Calibration of the spectrometer was performed using a monocrystalline silicon wafer, setting the peak at 520 cm^{-1}. The magnification of the microscope

Table 1. Distribution of particle diameter for the initial Si and the milled Si powders.

Si powder	Grain size (μm)				
	d_{10} vol	d_{50} vol	d_{90} vol	Average vol	Average no.
Initial	15	47	62	29	2.2
1 h-milled	2.0	6.2	16.7	6.6	1.5
6 h-milled	0.33	0.89	2.6	1.1	0.24
18 h-milled	0.93	5.1	5.3	4.7	0.27

objective was 50 and the time of exposure was 10 s. The intensity of the laser beam varied between 0.18 ± 0.01 and 1 ± 0.1 mW, respectively. In order to increase the signal-to-noise ratio, a higher laser power was preferable. However, due to the low thermal conductivity of the powder beds, the Raman shifts become a function of laser power. Immersion of the powders in water prevents this thermal drift, so that reproducible Raman shifts can be collected independently of the laser power.
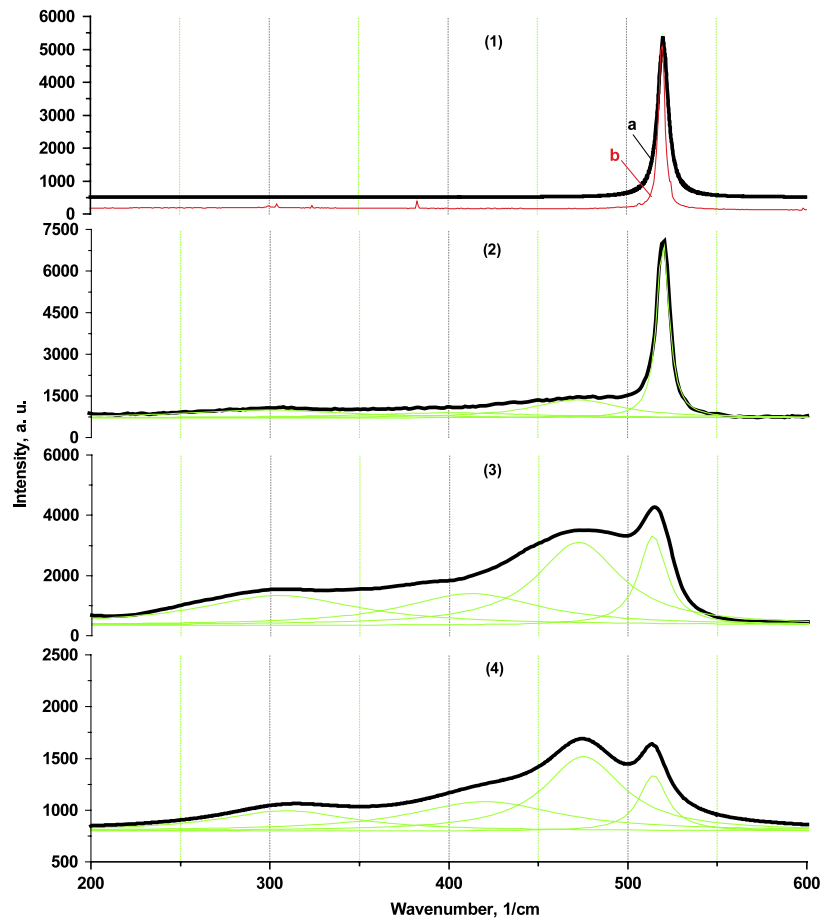
Figure 2. Raman spectra of (1a) initial Si, (1b) Si nanopowder after evaporation and condensation, (2) Si milled for 1 h, (3) 6 h, (4) 18 h with Lorentz function fitted to the peaks.

3. Results and discussion

3.1. Influence of high-energy milling on the Raman spectra of silicon

Raman spectra collected for the as-received silicon powder and the powders milled for different periods of time are shown in figure 2. After deconvolution of the curves, Lorentz functions were fitted in order to obtain the individual peaks. The measured parameters (centre of the peak X_c, full width at half-height, W, and the area under the peak, A) are plotted as a function of milling time in figures 3(a)–(c).

The following Raman peaks characteristic for phonon vibrational modes of silicon were identified, according to reported data:

- crystalline silicon, c-Si, having face-centred cubic (fcc) diamond structure type, at about 300 cm^{-1} [11] and 520 cm^{-1} [8, 9];
- crystalline silicon, t-Si, having body-centred tetragonal structure, bc8 type, at 420–430 cm^{-1} [9];
- amorphous silicon, a-Si, at 470–480 cm^{-1} [11].

The evolution of the peak parameters with milling time, figure 3, shows that the characteristic peak of cubic silicon, c-Si, was found at 520 ± 2 cm^{-1} for all investigated samples. This represents the longitudinal optic phonon mode in silicon

of cubic diamond structure [8]. Besides the c-Si, peaks of two additional phases appeared in the milled powders, i.e. tetragonal and amorphous silicon. The presence of a-Si and t-Si peaks proved the lattice transformation of c-Si, which was expected due to the high loads imposed on the material [5]. The peak at 300 cm^{-1} was ascribed to transverse acoustic phonon vibrations of the defected cubic silicon, c-Si, lattice.

It was observed that the c-Si peak centre shifted toward lower wavenumbers by 6 cm^{-1}, while the peak width increased by around 10 cm^{-1} for 6 h milled silicon; figures 3(a) and (b). The first effect indicates that the lattice has been strained, resulting in a change in the Si–Si bond length. On the other hand, the effect of peak broadening was due to a higher discrepancy in the distribution of the bond lengths in the as-milled powder.

The shift of the c-Si peak with milling time was combined with changes of other peak positions. After 1 h of milling, the t-Si peak and the defect-induced c-Si peak shifted toward higher wavenumbers. This was attributed to a deformation of the crystal lattice by high compressive stresses and to an increase in the density of lattice defects rather than to the refinement of the particles. It was stated in [8] that the peak found between 510 and 514 cm^{-1} is typical of microcrystalline silicon. However, the Raman spectrum of a nanocrystalline Si powder with a non-defected lattice, investigated by Vaucher [10], did
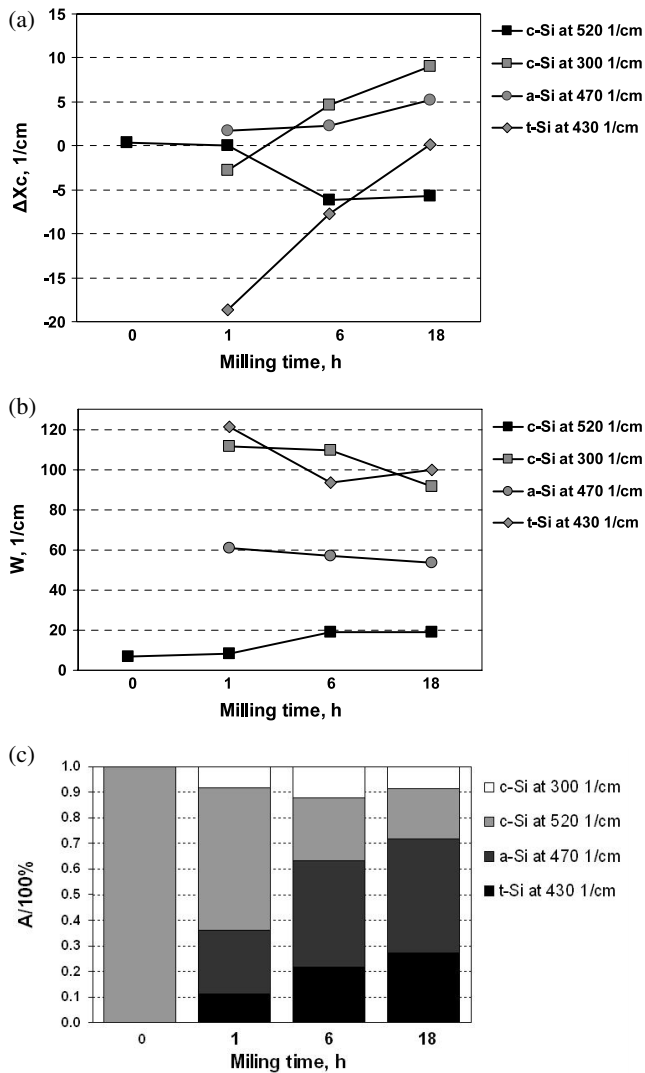
Figure 3. Raman peak parameters versus milling time for Si:
(a) centre positions, (b) full width at half-height and (c) relative peak
area.

not differ from the spectrum of the coarse-grained initial Si
powder; figure 2, spectrum 1(a, b). Therefore, the particle
size seems to have no influence on the Raman spectrum. The
amorphous Si peak shifted slightly toward lower vibrational
frequencies, which could be explained in terms of changes in
the range of order in the amorphous structure.

Assuming that the total number of Raman scattering
events gives rise to the area under the peak, the relative amount
of a particular phase can be estimated. Accordingly, the peak
intensity of c-Si in the milled powders decreased compared
with the initial intensity, figure 3(c), due to a decrease in the
relative amount of c-Si. In contrast, for t-Si after 6 h of
milling there was a decrease in the peak width and a rise in
the intensity. An 18 h milling did not significantly change the
peak width. Only a small increase in the intensity, by about
7%, was observed. Similarly, for the a-Si and defected c-Si,
the peak widths became smaller and the peak areas rose with
milling time. This is likely to be related to an increase in the
relative amount of the respective phases.

The relative area under the peak, A, is expressed as:

$$A = \frac{A_n}{\sum_n A_n},$$

where A_n is the absolute peak area and n is the peak number.

Among the powders milled for different times, one can see
that the relative area of c-Si peak decreased from 100% for the
initial silicon to 40, 15 and 13% for 1, 6 and 18 h milled silicon,
respectively. This indicates that the amount of cubic silicon
decreases with milling time, especially in the early stage, after
1 h of milling. On the other hand, the area under the tetragonal
and amorphous peaks grew with milling time, while the biggest
increase was observed at 6 h. The area of the defect-induced c-
Si peak rose after 6 h of milling, which was most likely related
to the increase in the number of lattice defects. However, at 18
h of milling, this peak was reduced by about 4%, which could
be due to annihilation of the defects, with regard to an elevated
temperature of the powder upon milling.

3.2. Influence of cooling on the measured Raman spectra of the Si powders

During Raman measurement, the powder is usually heated by
the laser beam focused on the surface of the material under
investigation, which affects the Raman shift. The intensity of
this heating depends on the thermo-physical properties, size
and shape of the particles, and also on the laser power. It was
observed that the lower the power that was used, the bigger the
noise was that interfered in the spectra; this rationalizes the use
of a high-power laser. However, high power causes heating
of the powder, which affects the results of measurements.
Pure water was used in the current experiments to avoid the
undesirable effect of heating.

Water is an efficient heat-removing medium which is not
Raman-active, thus it was used for cooling the powders during
the measurements. The Raman spectrum of the as-obtained
silicon powder was compared with the same powder in a drop
of distilled water; figure 4.

In the case of the uncooled powder, the position of the c-
Si peak shifted by about 2 cm^{-1} toward lower wavenumber,
to 517.5 cm^{-1} when the laser power was increased from
0.2 mW (10%) to 1 mW (50%); figure 4(a). Peak shifts
towards lower wavenumber with an increase in temperature
were also observed in [12]. According to the results of Raman
measurements for silicon powder given in [10], the Raman
peak at 517.5 cm^{-1} for cubic Si corresponded to a temperature
of approximately 400 K, which seems to have a significant
influence on the Raman measurements. In the case of the
cooled silicon powder, figure 4(b), the peak centre position
shifted only slightly, by less than 0.1 cm^{-1}. In comparison
to the uncooled powder, the powder placed in water showed
smaller peak intensities.

4. Conclusions

It was found that Raman spectra followed the changes in
the silicon structure subjected to high-energy ball milling,
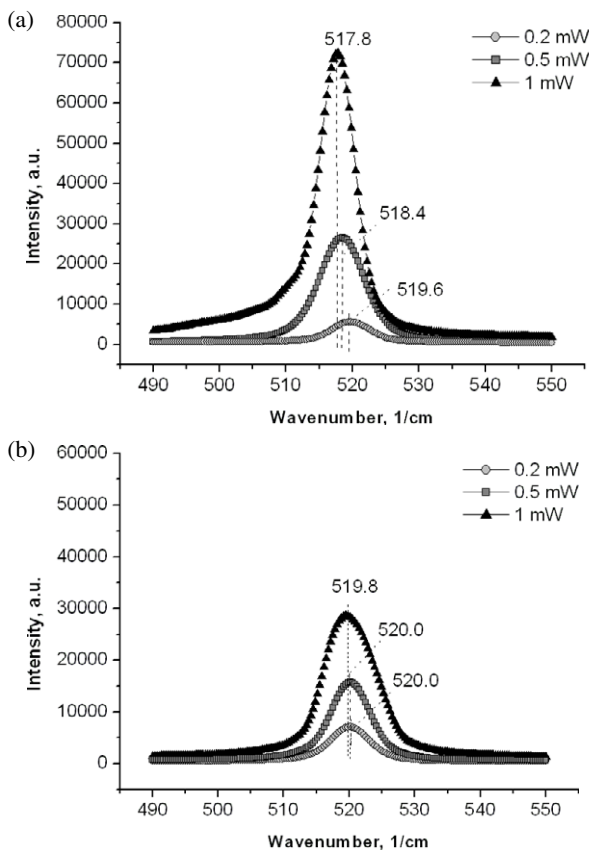causing amorphization and transformation of a cubic lattice

Figure 4. The influence of laser power, *P*, on the Raman shifts of initial Si powder: (a) without and (b) with cooling.

into a tetragonal lattice and the generation of lattice defects. These effects were already observed after 1 h of milling, while after 18 h the amount of a-Si and t-Si was the highest. The shifts of the c-Si peak position to lower wavenumbers indicated the change in bond vibration frequency with milling time. This was attributed to deformation of the silicon lattice, in particular to its straining and an increase in the density of defects. Water cooling during Raman measurement prevented heating of the powder by the laser beam, helping to overcome misinterpretation of the results. This resolution can be particularly advantageous in the Raman measurement of nanopowders.

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