Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2023, **33**, 209–211

Mendeleev Communications

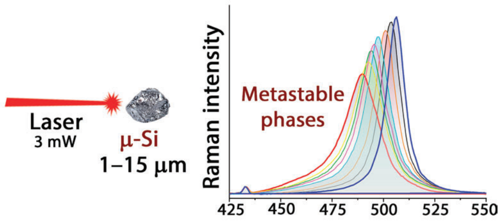
Laser induced metastable phases in microcrystalline silicon

Sergey S. Bukalov and Rinat R. Aysin*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: aysin@ineos.ac.ru

DOI: 10.1016/j.mencom.2023.02.019

It has been found using Raman spectroscopy that metastable Si phases reversibly appear in silicon microparticles (μ-Si) due to local heating on increasing the power of a He–Ne excitation laser from 0.03 to 3 mW. Prolonged annealing of these phases by laser radiation makes it possible to estimate that local heating occurs to a temperature of ~250 °C rather than 1000 °C as it was believed previously.



Keywords: silicon, Raman spectroscopy, line broadening and shifting, local heating, metastable phase.

Within the framework of the modern ‘green chemistry’ concept,[1] the ever-increasing production of silicones requires not only minimization of the cost of processes and energy consumption but also reduction of harmful emissions since silicones are traditionally synthesized from dichlorosilanes with release of HCl.[2] The most promising approach involves the alternative chlorine-free synthesis of silicones from alkoxysiloxanes[3,4] that are formed in reactions of silicon with simple alcohols and ethers. Since the reagents are rather inert, this process called direct synthesis employs elevated temperatures and metal catalysts, particularly, copper.[5–7]

In view of this, the Raman scattering (RS) method is now becoming particularly efficient for studying the structure of possible silicon modifications,[8,9] such as doped, nanosized, porous or nanofibrous silicon.[10–13] At the first step of direct synthesis, silicon is ground down to a few μm in size,[5] therefore the Raman spectra of metallic Si particles 1–35 μm in size (μ-Si) under conditions close to those used in this reaction were studied systematically in this work. The microphotographs of samples (Figure S1) and a description of the experiment are provided in Online Supplementary Materials.

The Raman spectra of monocrystalline silicon ($\mathrm{Si_{Met}}$) comprise a series of single- and double-phonon transition bands,[12] among which three lines are most intense [Figure 1(*a*)]. The narrowest and most intense line at 520.5 cm^{-1} that has a full width at half maximum (FWHM) of 3.5–4 cm^{-1} corresponds to the full-symmetric TO mode in the center of the Brillouin zone (the Γ point). The weaker line at 300 cm^{-1} refers to the 2TA mode at the X point of the zone. Its unusual steep outlines at ~250 and ~400 cm^{-1} are caused by the shape of the density of state spectrum. The 2TO line of the most intense two-phonon transition lies in the 900–1050 cm^{-1} range, and its asymmetric contour is related to the overtones in the W and L points of the zone. Moreover, the vibrational spectrum also contains other weak lines.[12]

A large number (a few dozens) of μ-Si particles with various sizes obtained upon milling of single-crystal silicon were examined in this work. It was found that the position, FWHM values and intensity distribution of lines in room temperature Raman spectra of μ-Si particles strongly depend on the power of the excitation He–Ne laser (Figure 1). At low power (0.03 mW or less), the Raman spectrum [Figure 1(*a*)] of particles of any size does not differ from that of a monocrystalline sample. Increasing the laser power in the range of 0.03–3 mW leads to a downward shift of the frequency and broadening of the lines (Figure 1, Table S1). The most significant dramatic changes occur at powers greater than 1 mW [Figure 1(*d*)]. At 3 mW [Figure 1(*g*)], the TO line shifts to 491 cm^{-1} (by ~30 cm^{-1}), the 2TA line shifts to 283 cm^{-1} (by ~15 cm^{-1}), and the 2TO line shifts to 914 cm^{-1} (by ~35 cm^{-1}).

It is known that the position of Raman lines in the silicon spectrum significantly depends on the sample temperature[14] due to the anharmonicity of the vibrations.[15] The Raman spectral parameters obtained at high power are similar to those of the spectra obtained at high temperature in the point where Si plates are irradiated with high power laser pulses.[14–16] The correlation between the TO line position and half-width (Figure S2) with changes in the excitation laser power is well approximated by a linear relationship. This allows us to make the primary conclusion that the detected effect for μ-Si is caused by local heating under the impact of a focused laser beam. A shift of the TO line with an

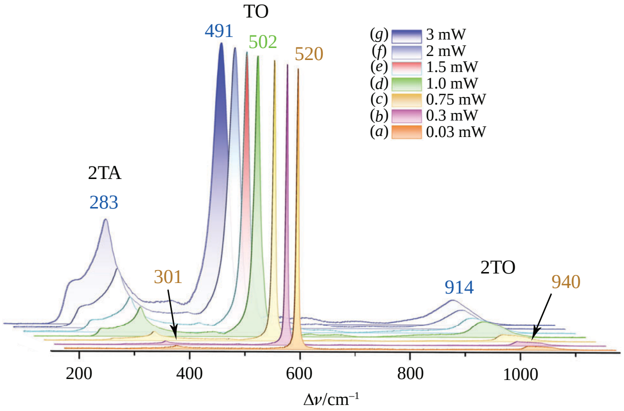


Figure 1 Typical Raman shift (cm^{-1}) of the TO, 2TA, and 2TO modes at a laser excitation power of 0.03–3 mW (λ_{exc} = 632.8 nm) recorded for a ~5 μm Si particle. The spectra are normalized to the TO line for better presentation.

increase in laser power was previously reported for silicon nanowalls (SiNW),[17–19] the reversibility of the process was reported by Eklund,[17] and local heating as the cause of this effect was reported by Ferrari.[18] The effect of local heating is confirmed by the fact that as the power is increased, the intensity of the 2TA and 2TO modes outside the Brillouin zone grows, which should occur on approaching the Debye temperature (T = ~370 °C).[20]

If the observed effect results from local heating, it is of interest to find out which band shift corresponds to which temperature. To estimate the local temperature (T_{loc}) in Raman spectroscopy, one can use the Stokes/Antistokes intensity ratio like it was done elsewhere,[14,17,18] but a large error (±300 K) is inherent in such an estimate for a ~500 cm^{-1} line.[14,15] To determine the real response of the Raman lines to temperature effects, milled µ-Si particles were heated in a Linkam cell from 25 to 300 °C. In this case, the Raman spectra were recorded at the minimum excitation laser power, namely, 0.01 mW. The resulting dependence of TO line position on temperature (Figure S3) is well described by a linear law, while formal approximation of the line to $\Delta\nu$ = 500 cm^{-1} corresponds to a temperature of 1000 °C, which is in good agreement with the data[14,17] considering the errors. It should be noted however that if the sample temperature would reach 1000 °C, the silicon should have oxidized, which did not in fact occur.[14–17]

Since ball grinder produces particles that have a size distribution, the Raman spectra of particles from 1 to 15 µm in size were recorded at 3 mW power. The TO line position was found to vary from 485 to 517 cm^{-1} (Figure S4). For relatively large particles with sizes of 30–35 µm, the TO shift from the normal position is small ($\Delta\nu \approx$ 512 cm^{-1}), while for 1–5 µm particles the TO line can broaden strongly and shift to ~485 cm^{-1}. A decrease in the laser power results in instantaneous return to the spectrum of non-excited Si. The process can be repeated many times, *i.e.* it is completely reversible and reproducible and there is no hysteresis between the gradual increase and decrease in laser power (Figure S5). Therefore, the assumption[12,19,21] that there is an amorphous state of silicon with a characteristic TO line below 500 cm^{-1} seems to be incorrect.

A broadband background regularly appears in the Raman spectra of the µ-Si particles studied, which is a line with a half-width of several thousand cm^{-1} with a maximum at ~2600–2900 cm^{-1} (Figure 2). It appears at a laser power above 2 mW, while the frequency of the TO line is below 500 cm^{-1}. It was noted that at a power of 2.3–2.5 mW the broadband background shows beats in intensity. On laser irradiation for ~5 h the background tends to be reduced significantly but does not disappear completely. As soon as the laser power is reduced to 2 mW or less, the background disappears. The background phenomenon is not usually given much attention in the literature since it is believed to be caused by fluorescent impurities. It has been shown[22] that the appearance of a background in Raman spectra is related to a non-equilibrium of the observed state and/or process.

A splitting of the TO line (Figures S6 and S7) is observed quite regularly. To understand the nature of the low-frequency TO line (<500 cm^{-1}), laser annealing at a power of 3 mW was performed. It was observed that different silicon µ-Si particles require different annealing times for the transition to the equilibrium state (Figures 3, S7 and S8), which is difficult to predict. Figure 3 shows the transformation of the TO line over 4 days; as a result, µ-Si passed to a near equilibrium state. Its Raman spectrum shows the absence of the background and one narrow line of 515 cm^{-1} (FWHM is 9 cm^{-1}) that corresponds to a local temperature of 250 °C. After annealing of the metastable phase, a series of laser power increase/decrease cycles does not cause its appearance. The observed behavior is typical of metastable states near a bifurcation point.[22,23] Based on the published data,[13,24] one can assume that the nature of metastability is also related to the appearance of strong local stress during local laser heating. It should be reminded that the term ‘metastable state’ is commonly understood as a thermodynamically unstable state in which the system can remain for a long time.

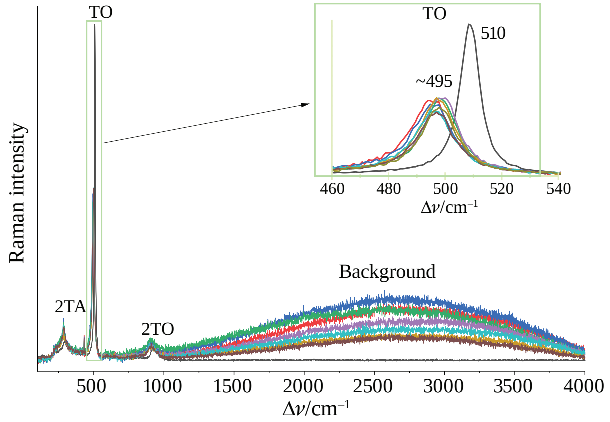


Figure 2 The background in Raman spectra recorded using 3 mW laser power. The black line corresponds to the unperturbed Si spectrum at 0.01 mW.

A study of the Raman spectra of milled monocrystalline silicon (µ-Si) particles shows that an increase in the excitation power of a He–Ne laser in the range of 0.03–3 mW results in a strong shift and broadening of the Raman lines. The frequency of the TO line shifts from 520.5 to ~485 cm^{-1}, while the FWHM value rises to 40 cm^{-1}. Previously, such dramatic changes in the parameters of lines in the Raman spectra of silicon were explained by strong local heating to 1000 °C.[14–19] An increase in the laser irradiation power above 2 mW also causes an appearance of broadband background with a maximum around 2600–2900 cm^{-1} in the Raman spectrum. Prolonged annealing of µ-Si under permanent laser exposure at 2–3 mW from a few hours to a few days brings it to a near equilibrium state. The position of the TO line reaches 515 cm^{-1}, which corresponds to a local heating to T_{loc} ~250 °C.

The broad TO line at 460–490 cm^{-1} at the power of the excitation line above 2 mW cannot be attributed to amorphous silicon, since as the power is reduced to 0.03 mW, this line acquires parameters characteristic of a crystalline silicon. The observed set of TO lines in the Raman spectra of µ-Si on varying the laser power corresponds to a set of metastable phases. Based on the Raman data observed, the important conclusion can be made that exposure of microcrystalline silicon to laser radiation causes the formation of metastable phases in Si but does not cause its oxidation in air. The phases formed under laser beam

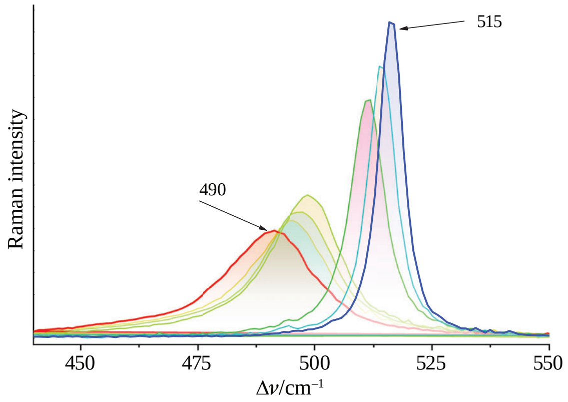


Figure 3 A series of Raman spectra recorded during annealing the µ-Si metastable phase over 24 h. The red line denotes the initial spectrum, while the blue one indicates the final one. Full range spectra are shown in Figure S9.

are probably more reactive, hence exposure to laser radiation and elevated temperature can be used for the chemical activation of Si in the direct synthesis. The position of the TO line in the Raman spectrum of silicon can be used to estimate the temperature during a chemical reaction.

This work was supported by the Russian Science Foundation (grant no. 22-13-00279). The Raman spectra were recorded using the equipment of the Center for molecular composition studies of INEOS RAS with support from the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00697-22-00).

This article is dedicated to the 90th anniversary of L. A. Leites.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.02.019.

References

1 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
2 D. Seyferth, *Organometallics*, 2001, **20**, 4978.
3 G. A. Abakumov, A. V. Piskunov, V. K. Cherkasov, I. L. Fedushkin, V. P. Ananikov, D. B. Eremin, E. G. Gordeev, I. P. Beletskaya, A. D. Averin, M. N. Bochkarev, A. A. Trifonov, U. M. Dzhemilev, V. A. D’yakonov, M. P. Egorov, A. N. Vereshchagin, M. A. Syroeshkin, V. V. Jouikov, A. M. Muzafarov, A. A. Anisimov, A. V. Arzumanyan, Yu. N. Kononevich, M. N. Temnikov, O. G. Sinyashin, Yu. H. Budnikova, A. R. Burilov, A. A. Karasik, V. F. Mironov, P. A. Storozhenko, G. I. Shcherbakova, B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapov, V. B. Shur, V. V. Burlakov, V. S. Bogdanov and M. V. Andreev, *Russ. Chem. Rev.*, 2018, **87**, 393.
4 J. M. Roberts, V. V. Pushkarev, J. J. Sturm and D. E. Katsoulis, *Ind. Eng. Chem. Res.*, 2020, **59**, 7457.
5 I. N. Krizhanovskiy, M. N. Temnikov, A. A. Anisimov, A. K. Ratnikov, I. S. Levin, A. V. Naumkin, S. M. Chistovalov and A. M. Muzafarov, *React. Chem. Eng.*, 2022, **7**, 769.
6 A. Boudin, G. Cerveau, C. Chuit, R. J. P. Corriu and C. Reye, *Organometallics*, 1988, **7**, 1165.
7 W. S. Putro, V. Ya. Lee, K. Sato, J.-C. Choi and N. Fukaya, *ACS Omega*, 2021, **6**, 35186.
8 V. Domnich and Y. Gogotsi, *Rev. Adv. Mater. Sci.*, 2002, **3**, 1.
9 L. Fan, D. Yang and D. Li, *Materials*, 2021, **14**, 3964.
10 S. Perkowitz, *Optical Characterization of Semiconductors: Infrared, Raman, and Photoluminescence Spectroscopy*, Academic Press, London, 1993, ch. 6.
11 R. S. Das and Y. K. Agrawal, *Vib. Spectrosc.*, 2011, **57**, 163.
12 R. Kumar and M. Tanwar, *J. Raman Spectrosc.*, 2021, **52**, 2100.
13 Z. Xu, Z. He, Y. Song, X. Fu, M. Rommel, X. Luo, A. Hartmaier, J. Zhang and F. Fang, *Micromachines*, 2018, **9**, 361.
14 A. Compaan, M. C. Lee and G. J. Trott, *Phys. Rev. B*, 1985, **32**, 6731.
15 M. Balkanski, R. F. Wallis and E. Haro, *Phys. Rev. B*, 1983, **28**, 1928.
16 D. H. Lowndes and G. E. Jellison, Jr., *Semicond. Semimetals*, 1984, **23**, 313.
17 R. Gupta, Q. Xiong, C. K. Adu, U. J. Kim and P. C. Eklund, *Nano Lett.*, 2003, **3**, 627.
18 S. Piscanec, M. Cantoro, A. C. Ferrari, J. A. Zapien, Y. Lifshitz, S. T. Lee, S. Hofmann and J. Robertson, *Phys. Rev. B*, 2003, **68**, 241312.
19 D. Volpati, N. Mårtensson, N. Anttu, P. Viklund, C. Sundvall, I. Åberg, J. Bäckström, H. Olin, M. T. Björk and J. Castillo-Leon, *Mater. Res. Express*, 2016, **3**, 125021.
20 *Silicon (Si), Debye temperature, heat capacity, density, hardness, melting point. Landolt–Börnstein – Group III Condensed Matter 41A1β (Group IV Elements, IV–IV and III–V Compounds. Part b – Electronic, Transport, Optical and Other Properties)*, eds. O. Madelung, U. Rössler and M. Schulz, Springer-Verlag, Berlin, Heidelberg, 2002.
21 V. Domnich, Y. Aratyn, W. M. Kriven and Y. Gogotsi, *Rev. Adv. Mater. Sci.*, 2008, **17**, 33.
22 S. S. Bukalov and L. A. Leites, *J. Raman Spectrosc.*, 1985, **16**, 326.
23 G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems. From Dissipative Structures to Order through Fluctuations*, Wiley, New York, 1977.
24 B. C. Larson, C. W. White, T. S. Noggle and J. F. Barhorst, *Appl. Phys. Lett.*, 1983, **42**, 282.

Received: 25th October 2022; Com. 22/7030