Raman spectra of Si nanocrystals under high pressure: Metallization and solid state amorphization

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ABSTRACT

We have observed and identified two crystalline peaks at $\sim 270 \text{ cm}^{-1}$ and $\sim 400 \text{ cm}^{-1}$ in nanocrystalline silicon during both compression and decompression. We attribute the first peak to the orthorhombic *Imma* phase (Si-XI) and the second one to the *TO* mode of the silicon metallic β -Sn phase (Si-II). Also, in the process of decompression, we observed a first-order-like transition from a highly coordinated metallic crystalline β -Sn phase to the normal tetrahedral *LDA* phase of the amorphous semiconductor. When the pressure is completely relieved, the powder regains its initial crystalline structure, which suggests that the amorphous phase has retained some structural features of the parent crystalline phase.

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It is known that pressure-induced phase transitions in nanocrystals show a strong dependence not only on their size but also on their shape.¹ Most often, nanocrystals are smaller than fragment domains that result when a single crystal undergoes a solid-solid phase transition. In this case, phase transformations can exhibit an exotic behavior when new mechanisms of these transformations are revealed.² For example, the transition of nanocrystalline Si to the metal phase, measured by optical absorption, appears at approximately 22 GPa,¹ in sharp contrast to the bulk cubic Si to β -Sn transition that takes place around 11 GPa.^{3,4} The main measurements in Ref. 1 were carried out using x-ray diffraction, and the sizes of nanocrystals ranged from 10 to 50 nm in diameter. We believe that it is necessary to carry out similar measurements on Si nanocrystals having smaller sizes using Raman scattering, which is more sensitive than x-ray diffraction to remaining traces of crystallinity. The crystalline peak in Si disappears in the x-ray diffraction spectra at a pressure of 11 GPa and that in the Raman spectra completely disappears at 19 GPa during a normal compression cycle.

If we turn to modern publications in leading journals,^{6,7} we see that, using x-ray diffraction, the influence of various factors on the transitions of nanocrystalline Si to the metal phase is determined. Despite this, it turns out that, currently, there are no Raman spectra in nanocrystalline Si in the literature at high pressures when polymorphic transitions CD $\rightarrow \beta$ -tin $\rightarrow Imma \rightarrow sh$ are observed, which are predicted by the theory and x-ray diffraction experiments (here, CD is the structure of a semiconductor cubic diamond). Although, as we mentioned, Raman spectroscopy is more sensitive than x-ray diffraction to remaining traces of crystallinity, this method has substantive significance.

To date, the only direct observation of pressure-induced amorphization in nanocrystalline Si using Raman scattering was made in Ref. 5, where high-pressure experiments were carried out on porous silicon (π -Si). The analysis of the Raman band profile indicated two distributions of nanocrystallites with average diameters \sim 3 nm and \sim 7 nm. However, many experimental studies of π -Si have shown that it has a fractal microstructure below a certain length scale,^{8,9} and therefore, the representation of a real microstructure in the form of two distributions of nanocrystallites is, in our opinion, an impermissible simplification. We consider this remark to be important because the pressureinduced phase transitions (especially in small semiconductor crystals) show a strong dependence not only on their size but also on their shape.¹ As we mentioned above, in this case, the phase transformations can exhibit an exotic behavior when new mechanisms of these transformations can be discovered.² We therefore made similar measurements on silicon nanocrystals having a spherical shape with a narrow size distribution of about 3 nm and observed a number of significant differences from Ref. 5.

Since we are studying nanocrystalline silicon, the complexity associated with the nanoscale of the particles under study is added. The surface effects in these particles greatly influence the phase stability, resulting in new stabilized structures or metastable states. For example, in the case of TiO_2 , which is a poor glassformer, obtaining the initial amorphous state can be done only for nanometer sized particles. The combination of high pressure and nanometer particle size is an ideal way of obtaining metastable amorphous states.

This research is an extension of our earlier studies^{10,11} dealing with the amorphous-amorphous transitions in tetrahedral crystals. In this paper, Raman spectroscopy is used to study the pressure effect of up to 26 GPa on the crystalline silicon nanopowder structure with a particle size of about 3 nm obtained using an ELV-6 direct-action electron accelerator. The accelerator was equipped with a system for releasing an electron beam into the atmosphere. The energy of irradiating electrons is 1.4 MeV. The electron beam power was maintained as to be sufficient for the evaporation of a bulk silicon sample in the argon atmosphere with a pressure slightly above the ambient pressure. Silicon nanopowder was collected on a special filter and then stored in air so that it would be covered with a silicon oxide layer. The pressure was generated in a diamond anvil cell in the helium medium and was measured based on the shift of the R_1 -ruby band accurate to ± 0.03 GPa. Since the phase transitions in amorphous materials are reversible, they cannot be observed in samples when the strain is released, and thus, these transitions must be studied in situ.

The Raman spectra of silicon nanopowder were recorded *in situ* at high pressures for one compression/decompression cycle [Figs. 1(a) and 1(b)]. The lower spectrum in Fig. 1(a) and the upper spectrum in Fig. 1(b) are the asymmetric *TO* peaks of crystalline Si at \sim 520 cm⁻¹ at the center of the Brillouin zone. It is evident from Fig. 1(a) that with



FIG. 1. Raman spectra of silicon nanopowder with a particle size of about 3 nm, recorded *in situ* during one compression/decompression cycle.

the increasing pressure to 15.64 GPa, two crystalline peaks appear at \sim 270 cm⁻¹ and \sim 400 cm⁻¹ simultaneously with the remaining crystalline peak of cubic silicon. This fact suggests the possible coexistence of several phases in a certain pressure interval. The optical properties of the powder have drastically changed: it became completely black and weakly reflecting light. This is because the compression of the bulk silicon, which is tetrahedrally coordinated at the atmospheric pressure, brings about a transition to higher coordinated metal phases.¹² According to the shape of the peak and its energy position, we attribute the peak at $\sim 400 \text{ cm}^{-1}$ to the TO-mode of the metallic β -Sn phase of silicon (Si-II).¹³ We believe that these two peaks belong to the mixed β -Sn-Imma phase, which was recently detected in a certain pressure interval by x-ray diffraction,⁶ which means that the second peak at $\sim 270 \text{ cm}^{-1}$ belongs to the orthorhombic *Imma* phase (Si-XI). Then, at a higher pressure of 22.40 GPa, the β -Sn phase completely disappears, i.e., the β -tin \rightarrow *Imma* transition ends, and then, a simple hexagonal sh phase (Si-V) is added to the remaining Imma phase since at this pressure, the x-ray diffraction pattern shows a mixed Imma-sh phase.¹⁴ Therefore, the Raman spectrum retains only one weak peak of the *Imma* phase at \sim 270 cm⁻¹ at a higher pressure 25.96 GPa, and the peak belonging to the simple hexagonal shphase is not visible, since this phase is monatomic and has no optical phonons, and is not active in the Raman scattering.

The first difference between the spectra of Ref. 5 and our spectra is different Raman spectra at higher pressures. In Ref. 5, the spectrum consists of a weak, broad band between 200 and 400 cm⁻¹, which the authors ascribe to an evenly distributed spectrum of vibrational modes of silicon with the amorphous metallic β -Sn structure. Additionally, it should be noted that in two other papers,^{15,16} where the Raman spectra were recorded on the volume amorphous but not on nanocrystalline silicon at high pressures, completely similar spectra were obtained for the HDA phase. There is a certain contradiction with Ref. 17 where the pressure-induced phase transition in the amorphous *a*-Si and crystalline silicon c-Si was studied using ab initio constant pressure molecular-dynamic simulations. The research carried out in Ref. 17 has revealed that crystalline silicon shows a phase transition from a diamond to a simple hexagonal phase at 29.5 GPa, while a-Si presents an irreversible sharp transition to an amorphous metallic phase at 16.25 GPa.

The second difference from Ref. 5 is that we have found and identified two crystalline peaks at $\sim\!\!270\,\text{cm}^{-1}$ and $\sim\!\!400\,\text{cm}^{-1}.$ Judging from the fact that during decompression at 8.71 GPa, the peak at $\sim 270 \text{ cm}^{-1}$ disappears, and the peak β -Sn at $\sim 400 \text{ cm}^{-1}$ remains, so the peak at $\sim 270 \text{ cm}^{-1}$ corresponds to the phase that follows after the phase β -Sn with the increasing pressure. As we have mentioned above, after the β -Sn phase (Si-II) at ~12 GPa, with the increasing pressure, the orthorhombic Imma phase (Si-XI) at \sim 13 GPa follows and then follows a simple hexagonal phase sh (Si-V) at ~ 16 GPa,^{1,18} which is inactive in the Raman scattering because it is monoatomic and has no optical phonons. It should be noted that the Si-II \rightarrow Si-XI \rightarrow Si-V transitions are reversible upon decompression.¹⁸ Therefore, we once again have convinced that the peak at $\sim 270 \,\mathrm{cm}^{-1}$ corresponds to the orthorhombic Imma phase. The β -Sn peak at \sim 400 cm⁻¹ is more noticeable in the course of decompression [lower spectra in Fig. 1(b)] since the β -Sn phase is easily formed from a simple hexagonal Si-V structure than from the diamond-cubic structure [the weak peak at 15.64 GPa in Fig. 1(a)]. At a pressure of 8.71 GPa,

the peak at ~270 cm⁻¹ disappears and a band of Si–Si stretching vibrations characteristic of a tetrahedrally coordinated low-density *LDA* phase at ~500 cm⁻¹ appears at 6.68 GPa—this is the beginning of the β -Sn—*LDA* transition. At 1.67 GPa, the signal-to-noise ratio of the spectrum significantly improves, and the spectral features at ~270 cm⁻¹ and ~400 cm⁻¹ disappear, thus indicating the completion of the transition from the highly coordinated metallic crystalline β -Sn phase to the normal tetrahedral state of the *LDA* phase of the amorphous semiconductor. Upon depressurization, the powder regains its initial crystalline structure, which indicates that in our case, the amorphous phase, unlike Ref. 5, retains some structural features of the parent crystalline phase.

In conclusion, it should be noted that the representation of a real microstructure of π -silicon in the form of a distribution of nanocrystals with some average size has been reported in Ref. 5, which seems to be an unacceptable simplification leading to erroneous experimental results. Differences between nanocrystals and π -silicon are that below a certain scale of length, π -silicon has a fractal microstructure^{8,9} and its initial samples may contain a significant part of the amorphous phase,^{19,20} also there may be an inhomogeneous distribution of local stresses, aided by pores, different topologies of nanoparticles, the presence of intrinsic defects, etc. Therefore, we also have recorded the Raman spectra in situ at high pressures on silicon nanocrystals having a spherical shape with a narrow size distribution of about 3 nm and observed a number of significant differences from Ref. 5. Our study has shown that with the increasing pressure, crystalline silicon undergoes a phase transition from the diamond cubic structure (Si-I) to the metallic β -Sn phase (Si-II) and then to the orthorhombic *Imma* phase (Si-XI) [the upper spectrum in Fig. 1(a)]. On the contrary, in Ref. 5, π silicon is transformed into an amorphous metallic β -Sn structure, that is, it behaves like a-Si^{15,16} because a strong amorphous component is apparently present in it. Also, upon full release of pressure, instead of recovering the metastable BC8 phase²¹ observed in bulk crystalline silicon, our samples are transformed into a cubic diamond form of Si. Whereas π -silicon in Ref. 5 behaves like a-Si, it is transformed into the low-density LDA form of Si.

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