In situ x-ray diffraction study of silicon at pressures up to 15.5 GPa and temperatures up to 1073 K

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In situ x-ray diffraction measurements of silicon were conducted in the pressure range 6–15.5 GPa and at temperatures up to 1073 K. The results were used to improve the phase diagram for silicon. The pressure range where the Si_{II} phase is stable in the temperature interval 293–973 K was found. The positions of the $Si_I - Si_{II}$, $Si_{II} - Si_{XI}$, $Si_{XI} - Si_V$ equilibrium lines and the $Si_I - Si_{II} - Si_L$, $Si_{II} - Si_{XI} - Si_L$, $Si_{XI} - Si_V - Si_L$ triple points were determined.

I. INTRODUCTION

Rich high-pressure polymorphism of silicon was intensively studied over the last four decades. Most of these studies were conducted at room temperature. It was found[1-3] that the semiconducting phase Si_I with the cubic diamond type structure transforms at pressures 11–12 GPa into a metallic phase Si_{II} which has a tetragonal β-tin structure. This transition is very sluggish. Its onset pressure decreases significantly at nonhydrostatic conditions.[2,4-7] Upon relatively slow decompression Si_{II} transforms at pressures 8–10 GPa into a semiconducting Si_{XII} phase with the rhombohedral R8 structure,[8] which in turn transforms during subsequent decompression into the Si_{III} phase with the cubic body centered BC8 unit cell.[2] The latter is metastable at ambient pressure and transforms into the Si_{IV} phase (hexagonal wurtzite type structure) upon heating above 473–480 K.[2,9] Two tetragonal phases (Si_{VIII} and Si_{IX}) were found after the rapid decompression of Si_{II} to atmospheric pressure.[10] The Si_V phase was found at pressures above 16 GPa.[5,7] Its lattice is simple hexagonal (SH). The $Si_V - Si_{VI}$ transition was first observed at 34 GPa.[5] It was found later that Si_{VI} is stable from 37.6 to 41.8 GPa and has the same structure as the X phase of the alloy $Bi_{0.8}Pb_{0.2}$.[11] Further compression results in the $Si_{VI} - Si_{VII}$ transition at 40–42 GPa.[5,11,12] Si_{VII} has the hexagonal close packed (HCP) structure. Its transition to Si_X, with face centered cubic (FCC) structure, was found at 79 ± 2 GPa.[11,12]

Mc Mahon, *et al.*[13,14] reported that an orthorhombic phase Si_{XI} (space group Imma) exists between the β-tin and SH phases. The possibility of this phase was considered earlier in theoretical calculations.[15,16] Mc Mahon *et al.*[14] simplified this phase transition by describing the two phases in terms of a common orthorhombic cell. The Imma structure turns into the β-tin structure when $a = b$, and becomes the SH structure when $b/c = \sqrt{3}$.

The high temperature part of a silicon phase diagram has been investigated less intensively. Melting of Si was studied by differential thermal analysis up to 5 GPa by Jayaraman *et al.*,[17] by Lees and Williamson up to 6 GPa,[18] resistometrically up to 12 GPa by Brazkin *et al.*,[9] and by Bundy up to 13 GPa.[4] Kinetics of $Si_I - Si_{II}$ transition at high temperatures

was investigated by Bundy.[4] As a result of these studies, the P-T phase diagrams of silicon shown in Fig. 1 were proposed. The coordinates of the $Si_I - Si_{II} - Si_L$ triple point (Si_L-liquid phase) were estimated to be 11.5 GPa and 1003 K,[19] and the P/T slope of the $Si_I - Si_{II}$ equilibrium line was claimed to be negative[4] or positive.[9,19]

It is obvious that the high temperature region of P-T phase diagram of silicon has not been studied sufficiently. The positions of the $Si_I - Si_{II}$ equilibrium line, the Si_{II} melting line, and the $Si_I - Si_{II} - Si_L$ triple point have only been roughly estimated. There is no information on coordinates of other triple points. There were no studies of the structure of the phases Si_{II}, Si_{XI}, and Si_V at high temperatures, and the positions of the $Si_{II} - Si_{XI}$ and the $Si_{XI} - Si_V$ equilibrium lines are unknown. The goal of this paper is to fill out these gaps by performing *in situ* x-ray study of Si at pressures up to 15 GPa and temperatures 298–1073 K, and collecting data on phase transitions and structure of various phases, and to obtain a more comprehensive P-T phase diagram of silicon.

II. EXPERIMENTAL TECHNIQUES

In situ x-ray diffraction experiments were conducted in the T-cup 6-8 apparatus[20] at the superconducting beamline
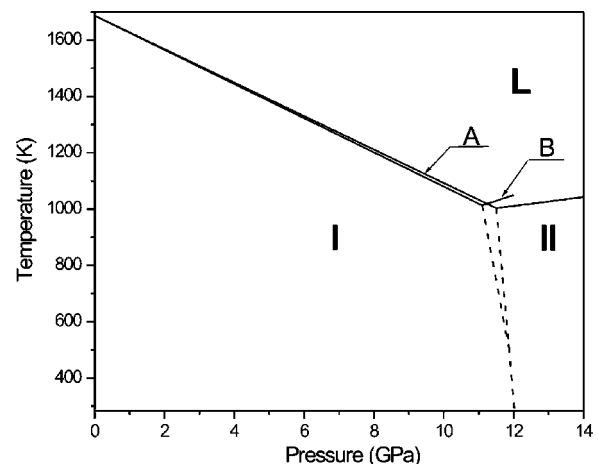

FIG. 1. P-T phase diagrams of silicon. A-Tonkov (Ref. 19), B-Brazhkin *et al.* (Ref. 9). Dashed lines denote assumed positions of the $Si_I - Si_{II}$ phase equilibrium line.

X17B1 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The experiments were carried out using tungsten carbide cubic anvils of 10 mm in size with a 2 mm truncation size. Three surfaces around truncation were tapered at about 2°. The pressure medium was made of a mixture of amorphous boron and epoxy resin. For a detailed description of cell assembly used in our experiments see Ref. 20. Layers of silicon and $NaCl+BN_h$ pressure calibrant (BN_h is hexagonal boron nitride) were placed between two Re stripe heaters. Temperature was measured by a W/Re26%−W/Re4% thermocouple, and pressures were calculated from Decker's equation of state for NaCl.[21] The uncertainty in pressure measurements was estimated to be less than 0.2 GPa.[22] The incident x-ray beam, collimated to dimensions of 100 μm × 100 μm, was scattered at the fixed angle of $2\theta = 6.213°$ and collected in an energy range up to 100 keV with a Ge solid-state detector. Typical duration for collecting a diffraction pattern with acceptable resolution was 200–250 s.

Si powder from Alfa Aesar of 99.999% purity was used in the experiments. Two different runs were made using the same cell design and materials. X-ray diffraction patterns of the Si sample and $NaCl/BN_h$ pressure calibrant were recorded at each point. Data collection was done at selected temperatures and constant ram load.

In the first experiment, run A, we kept the cell at room temperature and increased pressure by steps up to 15.5 GPa. In the second experiment, run B, an initial pressure of 6.6 GPa was applied at room temperature. After that we increased the temperature to 573 K and changed the pressure in small steps until we reached 14.4 GPa. Next the pressure was reduced to 8.9 GPa and then temperature increased to 773 K and we repeated the pressure buildup. During pressure loading and unloading the temperature remained constant. The pressure buildup was repeated at 973 K. After reaching 12.8 GPa we kept the constant ram load and increased the temperature in steps of 5 degrees to the maximum value of 1073 K.

III. RESULTS AND DISCUSSION

Structure of different phases was determined from x-ray patterns; examples are depicted in Figs. 2 and 3. This data allowed us to make a map of various phases observed in runs A and B, see Fig. 4. During compression, regardless of the temperature, silicon transformed in the following order: $Si_I \rightarrow Si_I + Si_{II} \rightarrow Si_{II} \rightarrow Si_{XI}$. Decompression at 573 K and 773 K resulted in the opposite sequence of phases: $Si_{XI} \rightarrow Si_{II} \rightarrow Si_I + Si_{II} \rightarrow Si_I$. The $Si_{II} - Si_{XII} - Si_{III}$ transition was observed only at room temperature decompression in the end of run B. At room temperature the I–II transition is very sluggish. The Si_{II} peaks were first observed at P = 10.5 GPa, while the Si_I peaks completely disappeared at 13.4 GPa, compare Fig. 2(b) and Fig. 2(c). The region of coexistence of the Si_I and Si_{II} phases decreased significantly at high temperatures. At T = 573 K the onset and completion of the I–II transition were detected at 10.4 GPa and 12.4 GPa, respectively. At T = 773 K the transition started at about 10.6 GPa and was completed at P = 11.7 GPa. At T = 973 K the pressure differ-
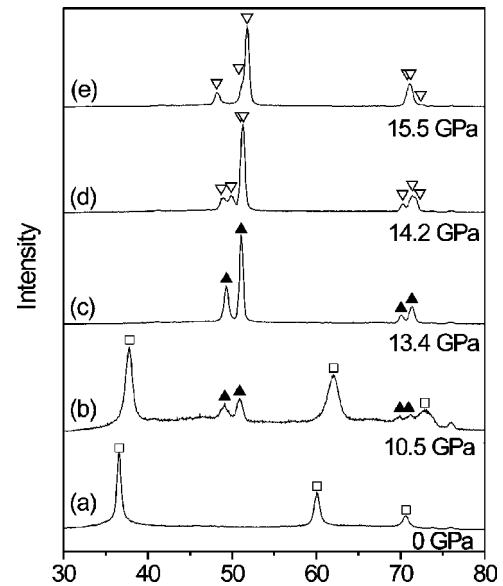

FIG. 2. Selected x-ray spectra of Si as a function of pressure at T = 298 K, run A. □-Si_I (111), (220), and (311) peaks, ▲-Si_{II} (200), (101), (220), and (211) peaks, ▽-Si_{XI} (200), (002), (101), (011), (220), (211), and (121) peaks. The peaks of each phase, in this and next figure, are listed in left to right sequence.

ence between these two points further narrowed. The Si_{II} peaks were first detected at P = 10.5 GPa and at P = 10.8 GPa the pattern consisted almost entirely of Si_{II} peaks, compare spectra (a) and (b) in Fig. 3. We concluded that the $Si_I - Si_{II}$ equilibrium point at this temperature is at P = 10.5 ± 0.2 GPa. Such a small pressure interval of transition is typical for the proximity of the triple point. Consequently, we concluded that the pressure coordinate of the $Si_I - Si_{II} - Si_L$ triple point is 10.5 ± 0.2 GPa. The value of the
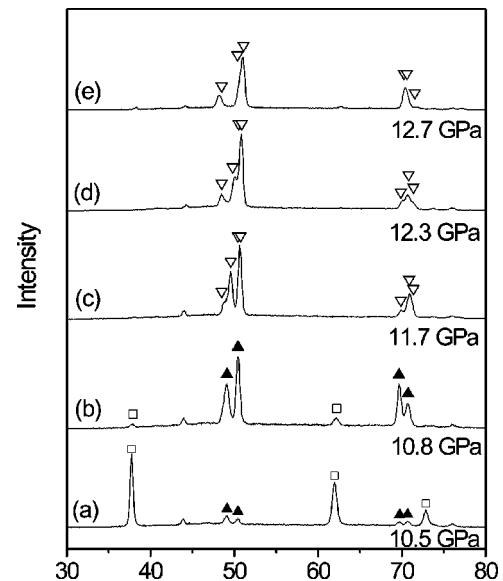

FIG. 3. Selected x-ray spectra of Si sample as a function of pressure at T = 973 K from run B. □-Si_I (111), (220), and (311) peaks, ▲-Si_{II} (200), (101), (220), and (211) peaks, ▽-Si_{XI} (200), (002), (101), (011), (220), (211), and (121) peaks.
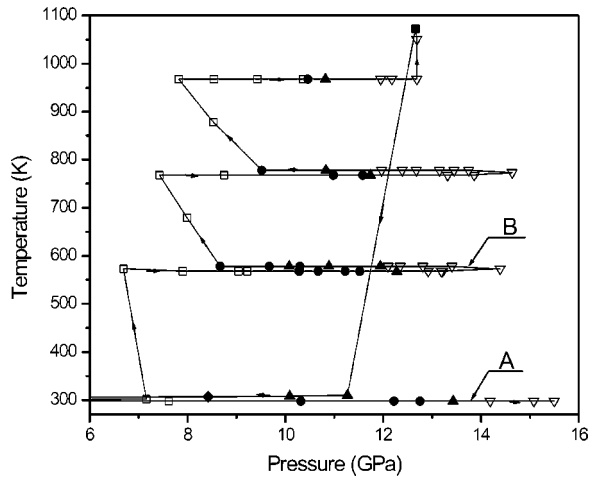
FIG. 4. P-T paths in runs A and B and observed phases of Si. $\square$-Si_I, $\bullet$-Si_I+Si_{II}, $\blacktriangle$-Si_{II}, $\triangledown$-Si_{XI}, $\blacksquare$-Si_L, $\diamondsuit$-$Si_{II}+Si_{XII}$. Points obtained during compression and decompression cycles correspond to the same temperatures and are arbitrarily offset to guide the eye.

triple point temperature is less obvious. In our experimental runs we used relatively large temperature steps and we can only estimate that this value is greater than 973 K. Based on data published by Tonkov,[19] we estimate that the triple point temperature is 1003 ± 20 K.

At each temperature, the Si_{II} phase transformed into the Si_{XI} phase soon after the I–II transition was completed, see Fig. 4. The typical feature of this phase is the shift of the (002) peak towards low energy (large d-spacing) due to increase of its cell parameter a. Detail description of the process was offered by McMahon and coworkers.[13,14]

Based on obtained results, we prepared a modified phase diagram of silicon shown in Fig. 5. The melting lines of silicon phases were drawn based on the following assumptions. The $Si_I - Si_{II} - Si_L$ triple point is at $P = 10.5 \pm 0.2$ GPa and $T = 1003 \pm 20$ K. The pressure region from ambient pressure to 6 GPa has been well studied, and according to Tonkov,[19] the average slope of the Si_I melting curve in this range is 60 K/GPa. Our results indicate that the slope probably increases slightly with further increase of pressure to
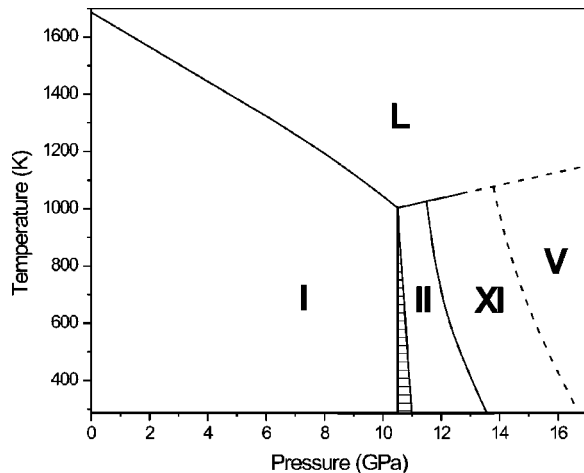
10.5 GPa. The melting temperature of Si_{XI} at 12.7 GPa is 1053 K, and the average slope of the Si_{II} and Si_{XI} melting lines in the 10.5–12.7 GPa region is 23 ± 5 K/GPa. This result indicates that the position of the $Si_{II} - Si_{XI}$ melting curve is about 40 K higher than that proposed in Ref. 19. The I–II phase equilibrium line position is difficult to estimate. Shear stresses and stress concentration at the grain contact zones influence the pressure of the onset of the I–II transition.[4,23] Therefore, in Fig. 5 the shaded triangle depicts the area where the equilibrium line may exist according to our results and data from Refs. 4, 7, and 13. The II–XI phase boundary has a negative dT/dP slope, and its absolute value decreases with growing temperature. We estimated that the position of the $Si_{II} - Si_{XI} - Si_L$ triple point is $P = 11.5 \pm 0.3$ GPa and $T = 1025 \pm 20$ K. According to our estimation the Si_{XI} phase has a broad region of stability of the width of about 3 GPa in the whole studied temperature range. The position of the XI–V phase boundary was estimated by extrapolation of the c/b and b/a axial ratio dependencies of the Imma lattice at 298 K, 573 K, 773 K, and 973 K to pressures, at which they reach the values 0.577 and 0.936,[5,7] typical for the primitive hexagonal lattice of the Si_V phase. The estimated position of the $Si_{XI} - Si_V - Si_L$ triple point is $P = 13.8 \pm 0.5$ GPa and $T = 1078 \pm 40$ K.

IV. CONCLUSIONS

The results of x-ray diffraction studies enabled us to draw a detailed P-T phase diagram of silicon in the pressure interval 0–15.5 GPa. We determined that the $Si_I - Si_{II} - Si_L$ triple point is located at $P = 10.5$ GPa. We also found the position of the $Si_{II} - Si_{XI}$ equilibrium line and coordinates of the $Si_{II} - Si_{XI} - Si_L$ triple point, and estimated the $Si_{XI} - Si_V$ equilibrium line and the $Si_{XI} - Si_V - Si_L$ triple point. The Si_{XI} phase is stable within a wide pressure region of the width of about 3 GPa, which, according to our estimation, does not vary significantly with temperature. To the contrary, the pressure interval of Si_{II} stability extensively narrows with increasing temperature from 298 K to 973 K.

FIG. 5. Proposed P-T phase diagram of silicon.

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