Effect of doping and counterdoping on high-pressure phase transitions of silicon

<table>
<thead>
<tr>
<th>著者</th>
<th>J. J. Guo, D. Pan, X. Q. Yan, T. Fujita, and M. W. Chen</th>
</tr>
</thead>
</table>
| 声明 | 本声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明声明statement

doi: 10.1063/1.3457479
Effect of doping and counterdoping on high-pressure phase transitions of silicon

J. J. Guo, D. Pan, X. Q. Yan, T. Fujita, and M. W. Chen

1WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
2Department of Materials Physics and Chemistry, University of Science & Technology–Beijing, Beijing 100083, People’s Republic of China

(Received 11 May 2010; accepted 3 June 2010; published online 25 June 2010)

The influence of dopants and counterdopants on high-pressure phase transitions of silicon was investigated by high-pressure Raman microscopy. A small amount of dopants were found to dramatically influence the high pressure stability of silicon. The combination of doping and counterdoping provides an effective way to manipulate the critical pressures of the phase transitions, which offers unique insights on atomic mechanisms of high pressure phase transitions of Si.

Chemical doping by intentionally introducing impurities has been an important subject in solid-state physics because it is an imperative approach to improve the physical performances of semiconductors as a small amount of dopants can drastically affect the electrical properties of semiconductors. For example, the addition of boron to silicon in the proportion of one boron atom to $10^5$ silicon atoms can increase the conductivity of pure silicon by a factor of 1000. Dopants, such as B and P in Si, usually cause lattice strains because of the large atomic size mismatch, which influences the electronic properties of doped semiconductors and limits the solubility of dopants. Practically, counterdopants with an opposite atomic size disparity and neutral charge have been used to cancel out the lattice strains. For example, Ge is used as counterdopants in B-doped Si because the local strain induced by small B atoms is assumed to be compensated by large Ge atoms. In addition to the applications as semiconductor, recently heavily doped Si has been developed as an important structural and functional material used in microelectromechanical systems where both mechanical and electronic properties are required. It is known that Si undergoes a series of crystallographic phase changes at high stresses. Nevertheless, whether or not the chemical doping and counterdoping influence the high-pressure behavior of silicon remains poorly known.

In this letter, we investigated the high-pressure phase transitions of silicon with dopants and counterdopants by Raman spectroscopy combining with a diamond anvil cell (DAC). In addition to intrinsic single-crystal (111) Si, Ge-doped ($1.4 \times 10^{20}$ atoms/cm$^3$), B-doped ($1 \times 10^{19}$ atoms/cm$^3$), and B/Ge codoped with (5.6 $\times 10^{19}$ atoms/cm$^3$)/Ge (5.6 $\times 10^{19}$ atoms/cm$^3$) codoped single-crystal (111) Si wafers were also investigated. A mixture of methanol–ethanol (4:1) was used as the pressure transmitting medium. Si samples were examined by a micro-Raman spectrometer (Renishaw, U.K.) with an Ar$^+$ laser source (excitation wavelength: 514.5 nm). The power of laser was set to less than 5 mW to avoid the heating effect. The microstructure of pressurized samples was characterized by a spherical aberration corrected transmission electron microscope (JEM-2100F).

Figure 1(a) shows Raman spectra of undoped cubic silicon (Si-I) subjected to pressures ranging from 2.0 to 17.1 GPa. Increasing pressure gives rise to intensity drop and blueshift in the Si transverse optical (TO) band at $\sim 520$ cm$^{-1}$. As the Raman bands associated with the high-pressure metallic β-tin phase of Si (Si-II) are impalpable in the Raman spectra, the critical pressure of the transition from Si-I to Si-II is usually determined by the complete disappearance of the TO band of Si-I. For undoped single crystal Si, the TO band completely disappears at a pressure between 12.5 and 12.9 GPa. On release of the pressure, Raman bands were observed at $\sim 8$ GPa, suggesting that the metallic Si-II phase formed at high pressures undergoes further phase transitions between 7.9 and 8.2 GPa [Fig. 2(a)]. According to the literature, the band at $\sim 365$ cm$^{-1}$ can be assigned to rhombohedral Si-XII and the band at 465 cm$^{-1}$ is from bcc Si-III. In addition to the two strong peaks, several small Raman peaks corresponding to Si-XII and Si-III can also be observed between the two major peaks. These two

![Graphs showing Raman spectra](image)

**FIG. 1.** (Color online) High-pressure Raman spectra of (a) undoped; (b) B-doped; (c) Ge-doped; and (d) B/Ge codoped single-crystal Si during compression cycles.

---

$^a$Author to whom correspondence should be addressed. Electronic mail: mwchen@wpi-aimr.tohoku.ac.jp.
metastable crystalline phases have been reported to be simultaneously formed in a slow unloading process. It is worth noting that the high-pressure behavior of the undoped Si, including the critical pressures for loading and unloading phase transitions, is in good agreement with the results reported in the literatures. 

Figure 1(b) shows the high-pressure Raman spectra of B-doped Si during compression. Similar to the pure Si, the TO peak intensity at \( \sim 520 \text{ cm}^{-1} \) gradually decreases and the peak shifts to higher frequencies with the increase in pressures. It is evident from Fig. 1(b) that the phase transition of B-doped Si takes place between 14.0 and 14.5 GPa, which is obviously elevated in comparison with that of the undoped Si at \( \sim 12.5 \) GPa. As the pressure is released, the Raman bands corresponding to Si-XII and Si-III emerge at approximately 10 GPa [Fig. 2(b)], which is also much higher than the undoped Si crystals at \( \sim 7.9 \) GPa. The improved transition pressures clearly demonstrate that the B doping leads to higher critical pressures for both compression and decompression cycles.

In view of the atomic radius of B (0.88 Å) is significantly smaller than that of Si (1.17 Å), the substitute B atoms generate high local tensile stresses that may act as negative external pressures to the Si lattices for the elevated high-pressure phase transitions. To evaluate this assumption, we investigated the high-pressure performances of Ge doped Si. Since the atomic radius of Ge is larger than that of Si, if the assumption is correct, the local compressive stresses should supplement the applied pressures and lead to the decrease in the critical transitions pressures. However, the same elevated trend of the phase transition pressures were observed in the Ge doped Si during both compression [Fig. 1(c)] and decompression [Fig. 2(c)] cycles. The critical pressure for the Si-I to Si-II transition is between 13.3 and 13.8 GPa while the transition from Si-II to Si-XII and Si-III occurs between 9.3 and 9.0 GPa during unloading.

We also investigated the pressure-induced structural phase transitions in B/Ge co-doped Si. Similar successive phase transitions, analogous to those in pure Si, can be observed as shown in Fig. 1(d). The critical pressure of the phase transition from Si-I to Si-II is between 12.9 and 13.0 GPa. This value is close to that of undoped Si but apparently lower than those of B-doped and Ge-doped Si. During the decompression process, the Raman bands corresponding to Si-XII and Si-III appear at a pressure between 8.6 and 8.3 GPa [Fig. 2(d)], again which is very close to the values of undoped Si. The critical pressures during loading and unloading were summarized in Table I. Interestingly, the phase transitions in B/Ge co-doped Si occur at considerably lower pressures than those of B-doped and Ge-doped Si. The intermediate critical pressure values of B/Ge co-doped Si shows the compensation effect of counterdoping. In general, high-pressure phase transitions are driven by the difference in thermodynamic free energy between two phases, which is closely correlated with the chemical compositions of materials. However, the obvious changes in the critical pressures caused by very low concentrations of B and Ge, particularly the compensation effect of B/Ge co-doping, suggest that the influence of doping on Si high pressure phase transition may not originate from thermodynamic effect and, instead, the kinetic effect arising from the resistance of the phase transitions may play a key role.

We employed high-resolution electron microscopy (HREM) to characterize the microstructure of a pressurized Si sample that was recovered from a DAC experiment with the maximum loading pressure of 12.1 GPa. As shown in the Raman spectra of Fig. 3(a), Si-I partially transforms into Si-II during loading and the recovered sample contains three phases, i.e., Si-I, Si-III, and Si-XII [Fig. 3(b)]. Figure 3(c) shows a HREM image in which the Si-I and Si-III can be identified. The interfaces between the two phases show a coherent or semicoherent relation along with dislocations in the vicinity of the interfaces. Although the Si-III and Si-XII phases do not directly transform from Si-I, the retained crystallographic relationship indicates that the transformations from Si-I to Si-II and Si-II to Si-III/Si-XII are via a displacive phase transition. For example, the diamond-type Si-I to \( \beta \)-Sn type Si-II transition can be accomplished by the distortion of a diamond unit cell through stretching along [100] and [010] and strongly compressing along [001], which can bring the Si atoms rearrangement with an increase in the coordination number from four to six. During the displacive phase transitions, the large distortion of structure unit cells needs to be mediated by interfaces and interface dislocations. The local stress fields produced by the doping atoms, regardless of compression or tension, interfere with the motion of the interfaces and dislocations, which can significantly push the phase transition to higher pressures.

From Vegard’s law that the Ge induced lattice expansion...
accommodation, the lattice contraction coefficient is larger for elastic compensation in B/Ge codoping Si compared with the density of Si. Since the concentrations of the dopants are ultralow, only one B atom in several thousands of Si atoms. The strain compensation in B/Ge codoping Si most likely due to the local volume compensation by introducing Ge atoms as the neighbors of B atoms to form Ge–B clusters. For elastic accommodation, the lattice contraction coefficient can be calculated based on the linear model or volumetric model:

\[ \beta_1 = \left( 1 - \frac{r_{\text{Ge}}}{r_{\text{Si}}} \right)^N \]  
\[ \beta_2 = \frac{1}{3} \left( 1 - \left( \frac{r_{\text{Ge}}}{r_{\text{Si}}} \right)^3 \right) N^{-1} \]

where \( r_{\text{Ge}} \) and \( r_{\text{Si}} \) are the covalent radii of the dopants and silicon atoms, respectively, and \( N \) is the density of lattice sites in Si. According to Eqs. (1) and (2), B and Ge dopants induce the lattice contraction and lattice expansion, respectively, and the simultaneous codoping of Ge and B can cancel out the lattice strains. For complete strain compensation by codoping, Ge/B ratio would be 5.8 and 4.3 for linear and volumetric model, respectively. In an earlier work by Maszare and Thompson, a ratio of 6.45:1 was experimentally derived for complete strain compensation, whereas Hirayama et al. obtained Ge–B ratio is 4:1. In the present high pressure study, however, the critical pressure of the codoped Si with a Ge/B ratio of 5.6:1 is slightly higher than that of undoping Si, which means the local strains caused by B doping are almost completely compensated. In other words, the tensile strain induced by doping one B atom into the Si matrix could be compensated by codoping 5.6 Ge atoms, which bring about the compressive strains. The result shows a good agreement with the linear calculation model.

In summary, the atomic size disparity between foreign atoms and Si atoms plays a key role in the high pressure stability of single crystal Si. The quantitative correlation between critical transition pressures and the concentrations of doping and counterdoping elements offers unique insights on the micromechanisms of high-pressure phase transitions of Si and effect of counterdoping.

**FIG. 3.** (Color online) Microstructure characterization of pressurized B/Ge codoped Si recovered from DAC. Raman spectra during a compression (a) and decompression (b) cycle. (c) HREM micrograph of the recovered sample containing Si-I parent phase and pressure-induced Si-III phase. The inset shows a semicoherent interface between Si-I and Si-III with periodic interface dislocations.