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A Calorimetric Study Assisted with First Principle Calculations of Specific Heat for Si-Ge Alloys within a Broad Temperature Range *

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Calorimetric measurements are performed to determine the specific heat of Si-x at.% Ge (where x = 0, 10, 30, 50, 70, 90 and 100) alloys within a broad temperature range from 123 to 823 K. The measured specific heat increases dramatically at low temperatures, and the composition dependence of specific heat is evaluated from the experimental results. Meanwhile, the specific heat at constant volume, the thermal expansion, and the bulk modulus of Si and Ge are investigated by the first principle calculations combined with the quasiharmonic approximation. The negative thermal expansion is observed for both Si and Ge. Furthermore, the isobaric specific heat of Si and Ge is calculated correspondingly from 0 K to their melting points, which is verified by the measured results and accounts for the temperature dependence in a still boarder range.

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The thermophysical properties of semiconductors have attracted considerable attentions in the fields of solid physics, thermodynamics, heat storage, phase transition, and so on.[1–3] The study of specific heat facilitates the commercial applications related to the physical characteristics in at least three aspects: (1) thermal management, which has been a primary challenge to electronics;[4] (2) novel semiconductor materials design, various applications have been put forward different requirements for thermophysical properties;[5,6] (3) fundamental researches, the reliable specific heat data is necessary to thermal physics and semiconductor physics, including heat transfer and thermodynamics.[7,8] Accordingly, an in-depth knowledge of specific heat is of great importance in both industrial applications and scientific research for semiconductor materials. Si, Ge and their alloys play irreplaceable roles in semiconductor industries.[9,10] The practical applications are highly dependent on thermophysical properties, especially for the specific heat. Nevertheless, a comprehensive specific heat study of Si-Ge alloys is still very limited.

The correlation among the specific heat, temperature and composition is significantly helpful to explore the effect of electrons and lattice vibration within Si-Ge alloys, especially for low temperatures and high temperatures, and thus guiding the potential applications. Some electronic devices, such as polar expedition equipment, spacecraft sensors and components based on Si-Ge alloys, require for low working temperature under extraordinary conditions.[11–13] In these cases, the specific heat change in low temperatures causing the unstable performance for electric components cannot be ignored. Thus, in addition to the conventional temperature, the study of specific heat of semiconductor at low temperatures holds practical significance.

In this Letter, we investigate the specific heat of Si-Ge binary systems in a much broad temperature range by experimental measurement and first principle calculations. The calorimetric measurements on Si-Ge alloys in the temperature range of 123–823 K (−150–550℃) are performed. Moreover, the specific heat at constant volume C_V, bulk modules B and thermal expansion α of Si and Ge are calculated via first principles calculations in combination with the quasiharmonic approximation (QHA). Ultimately, the isobaric specific heat C_p is calculated from 0 K to their melting temperatures.

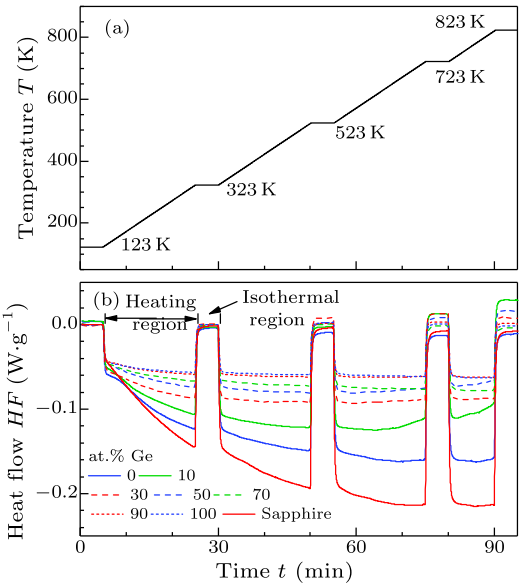

Fig. 1. Experimental process during calorimetric measurements. (a) Sample temperature versus time. (b) Heat flow versus time.

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In the experiments, the Si-x at.% Ge (where $x = 0$, 10, 30, 50, 70, 90 and 100) alloys were prepared from 99.9999% purity Si and 99.9999% purity Ge in an arc-melting furnace. A differential scanning calorimetry equipment (METTLER DSC1) was applied to perform the calorimetric measurements from 123 to 823 K. The alloy was cut into slices to obtain good thermal contact with the high-purity standard aluminum pan. Then, it experienced a heating process at a constant rate of 10 K/min and was held isothermally for 5 min, and then heated to the next temperature, as shown in Fig. 1(a). Then, the isobaric specific heat $C_{\rm p}$ of samples can be obtained by

$$\frac{m_{\rm sam}C_{\rm p,sam}}{HF_{\rm sam}} = \frac{m_{\rm spr}C_{\rm p,spr}}{HF_{\rm spr}}, \quad (1)$$

where the subscript sam and spr refer to Si-Ge alloy sample and sapphirine standard sample, respectively, HF is the heat flow during calorimetric measurements, and m is the mass.

For the calculations, using the QHA, the lattice vibrational specific heat at constant volume of a system $C_{\rm V}$, can be expressed by[14–16]

$$C_{\rm V} = \sum_{\boldsymbol{q},\lambda} k_{\rm B}\left[\frac{\hbar\omega_{\boldsymbol{q},\lambda}}{k_{\rm B}T}\right]^2 \frac{\exp(\hbar\omega_{\boldsymbol{q},\lambda}/k_{\rm B}T)}{[\exp(\hbar\omega_{\boldsymbol{q},\lambda}/k_{\rm B}T)+1]^2}, \quad (2)$$

where $k_{\rm B}$ is the Boltzmann constant, $\hbar$ is the reduced Planck constant, and $\omega_{\boldsymbol{q},\lambda}$ is the phonon frequency. The sum is taken over all phonon branches λ and wave vector $\boldsymbol{q}$.

To access the isobaric specific heat of the lattice, the finite displacement method was applied using the PHONOPY code.[17,18] Since the difference of energy per Si or Ge atom between 2×2× 2 and 3×3× 3 supercell is less than 0.005 eV, the 2×2× 2 supercell containing 64 atoms was chosen. The density functional calculations combined with the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were employed using the VASP code[19,20] to calculate the static energy and the force constant matrix of the system under the periodic boundary condition. Then, the phonon densities of state (DOS) around the equilibrium volume at 0 K were obtained. Consequently, the equilibrium volumes at different temperatures were obtained according to the Helmholtz free energy-volume curve. Then, the bulk modulus B and volume thermal expansion α can be derived easily. Thus, the isobaric specific heat of lattice, $C_{\rm p}$, can be calculated from

$$C_{\rm p} = C_{\rm V} + \alpha^2 BVT. \quad (3)$$

The heat flows of alloys and standard sample in the DSC measurements are illustrated in Fig. 1(b). The temperature plateaus around 0, 25, 50, 75 and 90 min represent the isothermal regions, where the measured system was kept at 123, 323, 523, 723 and 823 K, respectively. Except for the isothermal regions, the heat flow of standard sample decreases continuously as the temperature increases. The heat flow of alloys is similar to that of the standard sample. It continuously drops during the heating region but approaches to a constant for most alloys. This indicates that the alloys are endothermic during the heating region. Moreover, the rates of endothermic reaction for most of the compositions, which are proportion to the specific heat, are nearly a constant at high temperatures. However, the heat flow for Si-50 at.% Ge and Si-10 at.% Ge increases slightly at high temperatures. It is suggested that the rate of endothermic reaction drops in the high temperate range for these two compositions.

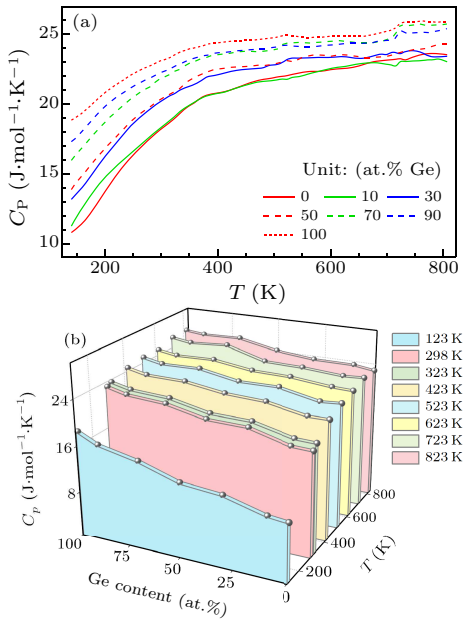

Fig. 2. The measured specific heat of Si-Ge alloys: (a) $C_{\rm p}$ of different compositions versus temperature, and (b) $C_{\rm p}$ at different temperatures versus Ge content.

The measured specific heat $C_{\rm p}$ is illustrated in Fig. 2(a). For all the compositions, the specific heat increases drastically at low temperatures and nearly a constant in the high temperature range. It is found that there is a positive correlation between the specific heat of alloys and the Ge content at low temperatures. However, when the temperature is higher than 400 K, the compositions with lower Ge content, especially for Si-70 at.% Ge, exhibit higher specific heat. To clarify the relationship between the specific heat and the compositions, $C_{\rm p}$ of different Ge content is presented in Fig. 2(b). The specific heat increases linearly with the rise of Ge content. Nevertheless, the slope of the curve becomes smaller with the rise of temperature. The specific heat value of pure Ge at 123 K is 18.24 J·mol^{-1}·K^{-1}, more than 2 times larger than that of Si, 9.09 J·mol^{-1}·K^{-1}. At room temperature 298 K, the specific heats for Ge and Si rise up to 23.09 and 18.41 J·mol^{-1}·K^{-1}. With the increasing temperature, the difference between them becomes smaller. The specific heats of Ge and Si at 823 K are 25.99 and 23.53 J·mol^{-1}·K^{-1}. There exists only 9.47%

difference.

The specific heat of solid alloy consists of the electronic contribution and the lattice vibrational contribution. Generally, most electrons have much lower energy than ground state Fermi energy $E_{\rm F}^0$. Their thermal excitation is negligible due to the Pauli exclusion principle. Only the electrons whose energies are around $E_{\rm F}^0$, contribute to the specific heat. Thus the electronic contribution to specific heat is far smaller than the lattice vibrational contribution. However, at low temperatures, the specific heat of the lattice vibrational contribution decreases rapidly. In this case, the electronic contribution may be considered. To evaluate their contribution, the thermophysical properties, including the specific heat of lattice are calculated.

At the beginning of the calculation, the geometry optimization was performed on diamond Si and Ge. The calculated lattice constant for Si is 5.4662 Å, with only 0.67% deviation between the reported value, 5.43 Å.[21] For Ge, the calculated and reported lattice constants are 5.7752 and 5.66 Å.[22] There exists 2.04% difference. By the integral of phonon density of state, the specific heat at 0 K equilibrium volume, $C_{\rm V,0}$, was calculated, as shown in Fig. 3(a). There is a violent increase of $C_{\rm V,0}$ before 400 K for both Si and Ge. When the temperature reaches 400 K, the specific heat changes slowly and converges to 24.76 J·mol^{-1}·K^{-1} and 24.83 J·mol^{-1}·K^{-1}, respectively.

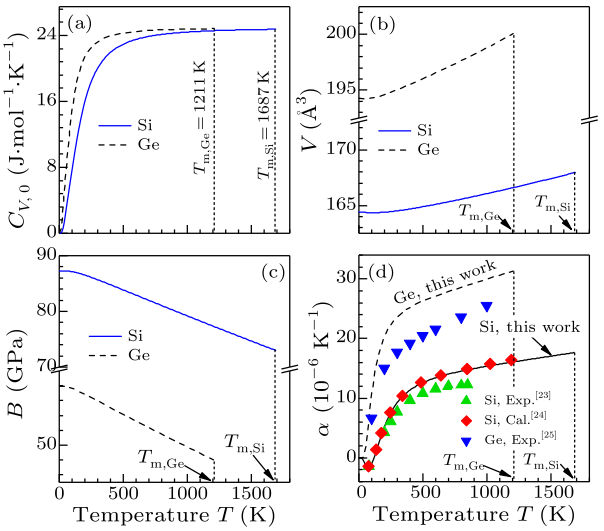

Fig. 3. The calculated thermophysical properties versus temperature for Si and Ge lattices at zero pressure. (a) The specific heat at constant volume, (b) the equilibrium volume, (c) the bulk modulus versus, and (d) the thermal expansion coefficient.

To obtain the temperature-dependent equilibrium volume, the Helmholtz free energies at different temperatures were calculated in 13 volumes that contain: a ground state equilibrium volume, four compressions and eight expansions. The energy-volume curve was fitted, and the equilibrium volume, which corresponds to the lowest free energy at a specific temperature, is presented in Fig. 3(b).

The equilibrium volume of Si 2 × 2 × 2 supercell at 0 K and 0 Pa is 164.37 Å^3. With the rise of temperature, the volume decreases until 118 K, which implies the negative thermal expansion of Si. When the temperature is higher than 118 K, the volume continuously rises to 167.70 Å^3. The same calculation was performed to Ge. The volume of Ge 2 × 2 × 2 supercell hardly changes before 100 K, which is around 194.25 Å^3. This suggests that the thermal expansion of Ge nearly equals 0 K^{-1} before 100 K. With the rise of the temperature, the volume increases linearly till the melting temperature.

The bulk modulus B and volume thermal expansion α of Si and Ge were calculated as shown in Figs. 3(c) and 3(d). The tendencies of the bulk modulus of Si and Ge are nearly identical. After a short plateau, they both decrease linearly with the rising temperature. The negative thermal expansion for both Si and Ge is observed at low temperatures. The reported thermal expansion coefficients of Si and Ge[23–25] are also demonstrated in Fig. 3(d). The calculated thermal expansion coefficient of Si is no more than zero until the temperature rises to 118 K, which agrees well with the first principle results calculated by Argaman *et al.*[24] The lowest calculated thermal expansion for Si is -1.57×10^{-6} K^{-1} at 74 K. This nearly coincides with the measured lowest value -1.55×10^{-6} K^{-1} at 79 K.[23] The calculated thermal expansion of Ge agrees well with the experimental results reported by Slack *et al.*[25] at 100 K. Moreover, there is a tiny temperature range (0–31 K) where Ge exhibits negative thermal expansion. The lowest thermal expansion appears at 22 K, which is -1.2×10^{-7} K^{-1}. The negative thermal expansion for Si and Ge could be interpret as that at low temperatures, the transverse acoustic modes exhibit negative Grüneisen parameters in most of the Brillouin zone, triggering the anomaly of thermal expansion. With the rise of temperature, the normal high frequency longitudinal acoustic and optical modes become dominant, leading to the disappearance of the negative thermal expansion.[24] However, both the calculations for Si and Ge deviate from the experimental data as the temperature is enhanced.

According to Eq. (3), the isobaric specific heat at zero pressure was calculated and illustrated in Fig. 4. The measured and reported specific heat of Si and Ge are also displayed. Both the calculated results increase rapidly from 0 K, and then change slightly at high temperatures. For Si, the calculated specific heat nearly equals the measured value in the present work at 123 K. With the rising temperature, the difference between them becomes larger. At 298 K, the calculated specific heat value for Si is 20.07 J·mol^{-1}·K^{-1}, exhibiting 1.66 J·mol^{-1}·K^{-1} difference between the measured value. Meanwhile, at 300 K, the calculated specific heat is 20.13 J·mol^{-1}·K^{-1}, 0.45% larger than the value given by Ref. [26]. Despite the tiny difference, the tendencies of both the experiment and calculation are

identical.

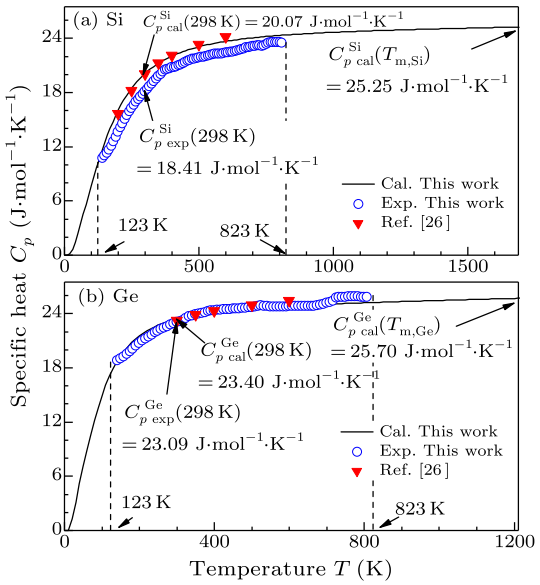

Fig. 4. The calculated isobaric specific heat of Si and Ge lattices versus temperature: (a) Si and (b) Ge.

For Ge, the calculated curve nearly coincides with that of the experiment in this work. At 298 K, the calculated and the measured results are 23.40 J·mol^{-1}·K^{-1} and 23.09 J·mol^{-1}·K^{-1}, respectively. There exists only a 1.34% difference. Moreover, the calculated result agrees well with the reported value. The specific heat for Si and Ge at their melting temperature is quite close, with the values of 25.25 J·mol^{-1}·K^{-1} and 25.70 J·mol^{-1}·K^{-1}, respectively. The difference between them is less than 1.78%. From this comparison it can be seen that the calculated results of Si and Ge are in good agreement with the measured data in the corresponding temperature range. Therefore, it can be concluded that the lattice vibrational contribution dominates the specific heat of Si and Ge in the temperature range of 123–823 K. In addition, the calculations provide a much border temperature range of specific heat of lattice. Thus, the calculated isobaric specific heat value of Si and Ge can be employed when they are required.

In summary, the specific heat increases drastically at low temperatures, while nearly a constant at high temperatures for all the compositions. It increases linearly with the rise of Ge content. Meanwhile, the specific heats at constant volume, equilibrium volume, thermal expansion and bulk modulus of Si and Ge are determined. The negative thermal expansion is observed for Si and Ge when the temperature is lower than 118 K and 31 K, respectively. The specific heat of lattice at zero pressure from 0 K to the melting temperatures of Si and Ge is calculated. The calculated and measured results are nearly identical, which indicates that the lattice vibrational contribution dominates the specific heat of Si and Ge lattices in the temperature range of 123–823 K.

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