Effect of pressure on melting temperature of silicon

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Abstract
The melting temperature–pressure (T_m–P) phase diagram for both bulk and
nanocrystalline silicon is predicted by using the Clapeyron equation, where the
pressure-dependent volume difference is modelled by introducing the effect of
surface stress induced pressure. The predictions are found to be consistent with
other theoretical results.

1. Introduction

As the principal materials used for solid-state electronic and photovoltaic technologies,
crystalline and amorphous forms of silicon are well studied materials, although new
structures and properties are still being discovered [1–4]. The structural phase transition in
semiconductors under pressure has been a subject of considerable experimental and theoretical
research activity in recent years [5]. It has been found that the melting temperature, $T_m(P)$, of
stable bulk Si in the diamond structure decreases as the pressure, P, increases, or $dT_m/dP < 0$
since $\rho_l > \rho_s$, where ρ denotes the density and the subscripts l and s represent the liquid and
crystal phases, respectively [6–9]. This phenomenon is also present in the T_m–P phase diagram
of nanocrystalline (NC) Si [9].

Since high-temperature and high-pressure experiments on Si are difficult, with poor
measurement accuracy, the available data need further theoretical confirmation. A classic
way to determine the T_m–P curve is the Clapeyron equation, in the following form [10]:

$$dP = \frac{H_m(T_m, P)}{\Delta V_m(T_m, P) T_m}\, dT_m \tag{1}$$

where $H_m(T_m, P)$ denotes the molar melting enthalpy and $\Delta V_m(T_m, P)$ the molar volume
change during melting, where Δ denotes the change. Equation (1) is useful in many respects,
particularly in the description of the joint rate of change of the primary variables of pressure and

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temperature (dT_m/dP) along the phase equilibrium lines, and also in estimating the derived properties of molar enthalpy and molar volume of transition. However, one is frequently interested in knowing the relationship between the equilibrium values of P and T_m instead of their mutual rate of change. This leads us to try and integrate equation (1). Since both $H_m(T_m, P)$ and $\Delta V_m(T_m, P)$ are functions of pressure and temperature, and the necessary separation of variables cannot be accomplished in any direct and known manner, the integration of equation (1) has been carried out through approximate methods ever since the equation was first established in the 19th century [10]. When $\Delta P = P - P_0$ and $\Delta T_m = T_m - T_{m0}$ are small, $H_m(T_m, P) \approx H_m(T_{m0}, P_0)$ and $\Delta V_m(T_m, P) \approx \Delta V_m(T_{m0}, P_0)$ with minor error, where P_0 denotes zero pressure and T_{m0} is the bulk melting temperature under P_0 [10]. However, if ΔP and ΔT_m are larger, then exact functions of $H_m(T_m, P)$ and $\Delta V_m(T_m, P)$ must be known [10]. Thus, successful application of Clapeyron equation for the T_m–P phase diagram depends on establishing accurate $H_m(T_m, P)$ and $\Delta V_m(T_m, P)$ functions.

There are also other theoretical approaches for predicting the T_m–P curve, such as the latest two-state model to estimate volume change or to reproduce the T_m–P phase diagram by considering the free energy [9]. However, the model is only a first step in interpreting this type of behaviour, where some approximations have not been justified [9].

Recently, a thermodynamic model for surface stress f has been established that is based on a consideration of the size dependence of the solid–liquid interface energy [11–13]. In terms of the model, a relationship between the surface stress induced internal pressure P_i and T_m may be determined, which makes it possible to determine the $\Delta V_m(T_m, P)$ function.

In this paper, the Clapeyron equation associated with f is introduced to estimate the $\Delta V_m(T_m, P)$ function as well as the T_m–P phase diagram for NC Si and bulk Si. It is found that the model's prediction is in agreement with other theoretical results.

2. Model

To solve the Clapeyron equation, $H_m(T_m, P) \approx H_m(T_m)$ and $\Delta V_m(T_m, P) \approx \Delta V_m(P)$ are assumed as a first-order approximation [10], which lead to a simplification of equation (1):

$$dP = \frac{H_m(T_m)}{\Delta V_m(P) T_m} \, dT_m. \tag{2}$$

In equation (2), the $H_m(T_m)$ function is determined by the Helmholtz function, $H_m(T_m) = G_m(T_m) - T_m \, dG_m(T_m)/dT_m$, where $G_m(T_m)$ denotes the temperature-dependent Gibbs free energy difference between the solid and liquid. For semiconductors, $G_m(T_m) = H_{m0} T_m (T_{m0} - T_m)/T_{m0}^2$, where H_{m0} denotes the bulk molar melting enthalpy at T_{m0} [14]. Thus,

$$H_m(T_m) = H_{m0}(T_m/T_{m0})^2. \tag{3}$$

In equation (2), $\Delta V_m(P) = (V_l - V_s) + (\Delta V_l - \Delta V_s)$, where $\Delta V_s = -V_s P_s \kappa_s$ and $\Delta V_l = -V_l P_l \kappa_l$ and the compressibility is $\kappa = -\Delta V/(VP)$. If P_l can be expressed by P_s, which is simplified as P, then the $\Delta V_m(P)$ function is obtained.

To find a relationship between P and P_l, a spherical particle with a diameter D is considered. According to the Laplace–Young equation, $P = 4f/D$ and $P_l = 4\gamma/D$ for the particle in a solid state or in a liquid state, respectively [11–13], where γ denotes the surface energy [11]. Thus, $\Delta V_m(P)$ is size-dependent, which is induced by the distinction of the surface properties between a solid interface and a liquid interface relating the difference between γ and f [11]. Essentially, γ describes a reversible work per unit area to form a new surface, while f denotes a reversible work per unit area under elastic deformation, which is equal to the derivative of γ with respect to the strain tangential to the surface [11–13]: for

the solid, $f \neq \gamma$; for the liquid, $f = \gamma$. Thus, $\Delta V_l = -V_l P(\gamma/f)\kappa_l$ because $P/P_l = f/\gamma$. Then,

$$\Delta V_m(P) = V_l - V_s + [V_s\kappa_s - V_l(\gamma/f)\kappa_l]P, \tag{4}$$

where f has been expressed as [11–13]

$$f = (h/2)[3S_{vib}H_{m0}/(\kappa_s V_s R)]^{1/2}, \tag{5}$$

where h is the atomic diameter, R is the ideal gas constant, and S_{vib} is the vibrational part of the overall melting entropy S_m. Equation (5)—without any free parameter for surface stress f—was established by considering the relationship between the size-dependent solid–liquid interface energy $\gamma_{sl}(D)$ (where D denotes the diameter of the crystal) and f [11]. The predicted f values in terms of equation (5) are in agreement with the known experimental results and the theoretical results obtained from the first-principle calculations or from elastic continuum mechanics calculations [11]. Considering that the present theoretical and experimental results are only semi-quantitative while equation (5) does not need any detailed considerations regarding the usually unknown surface states, equation (5) is useful for determining the $\Delta V_m(T_m, P)$ function and the T_m–P phase diagram, with the note that the surface effects of atoms (ions) have been determined by using the measured thermodynamic amounts shown in (5) [11].

Integrating P from 0 to P and T_m from T_{m0} to T_m in terms of equations (3) and (4), i.e. $\int_0^P \{V_l - V_s + [V_s\kappa_s - V_l(\gamma/f)\kappa_l]P\}\,dP = (H_{m0}/T_{m0}^2)\int_{T_{m0}}^{T_m} T_m\,dT_m$, yields,

$$T_m(P) = T_{m0}\sqrt{1 + \{2(V_l - V_s)P + [V_s\kappa_s - V_l(\gamma/f)\kappa_l]P^2\}/H_{m0}}. \tag{6}$$

Although the above discussion regarding P is related to the internal pressure P_i, it may be extended to the general case for the pressure effect on T_m. This may be illustrated as follows. Let P denote the sum of P_i and the external pressure P_e, namely

$$P = P_i + P_e. \tag{7}$$

When $P_e \approx 0$ then $P = P_i$. This is the case of the size-dependent melting of NC. When $P_i \approx 0$ and $D \to \infty$, then $P = P_e$. This is the usual situation of the pressure-dependent melting of bulk crystals. Since any pressure source should have the same effect on materials properties, it is assumed that equation (6) is applicable for bulk crystals.

Note that equation (6) is also applicable for NC if T_{m0} in equation (6) is substituted by the size-dependent melting temperature at zero pressure, $T_{m0}(D)$. Thus, the melting temperature for NC Si is a function of the both size and pressure. The value of $T_{m0}(D)$ may be determined in terms of the size-dependent amplitude of the atomic thermal vibrations of nanocrystals, according to Lindemann's criterion for melting in the following form [15]:

$$T_{m0}(D) = T_{m0}\exp\left(-\frac{2S_{vib}}{3R}\frac{1}{D/D_0 - 1}\right), \tag{8}$$

where $D_0 = 6h$ for particles where all atoms of the particles are located on their surfaces. Since $T_{m0}(D) < T_{m0}$, then $T_m(P)$ for NC Si is lower than that for bulk Si over the full range of pressure change.

3. Results and discussion

Figure 1 presents a comparison between the model predictions of equation (6) associated with (5) and other theoretical results for the T_m–P diagram for bulk and NC Si [9]. As is shown in the figure, the Clapeyron equation—without any adjustable parameter—may predict the
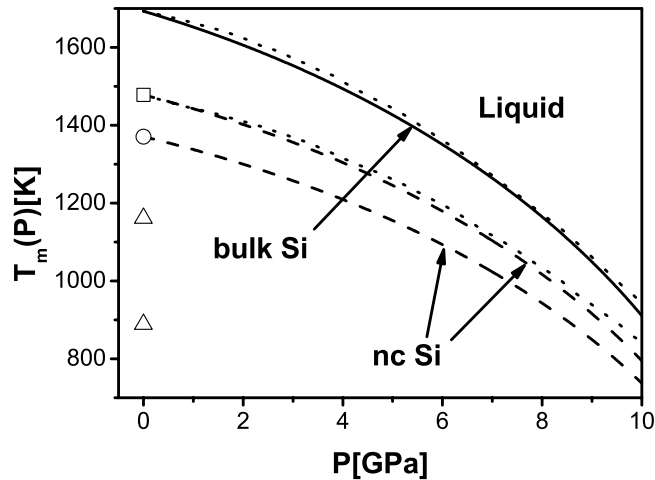
Figure 1. A comparison of the model predictions of equation (6) associated with (5). In the figure, the solid curve denotes the melting of bulk Si. The two dash curves show the melting of NC Si where the corresponding $T_{m0}(D)$ values, denoted as □ (1478 K) and ○ (1371 K), are obtained from other theoretical results [9] and equation (8), respectively. For comparison, two dotted curves give the theoretical results for melting of both bulk and NC Si [9]. The symbol △ denotes the experimental results of $T_{m0}(D)$ for NC Si under ambient pressure with $D = 5$ nm [16]. The necessary parameters in equation (6) are as follows: $T_{m0} = 1693$ K [9]; $H_{m0} = 50\,550$ J mol^{-1} [17]; $S_{vib} = 6.7$ J mol^{-1} K^{-1} [18]; $h = 0.2352$ nm [19]; $\gamma = 0.865$ J m^{-2} [20]; $\kappa_s = 1.02 \times 10^{-11}$ Pa^{-1} (determined by $\kappa_s = 1/B_s$, where $B_s = 97.7$ GPa is the bulk modulus [21]); $\kappa_l \approx 1 \times 10^{-10}$ Pa^{-1} as a first-order approximation under higher pressure [22]; $V_s = M/\rho_s = 12.066 \times 10^{-6}$ m^3 mol^{-1} (where $M = 28.09 \times 10^{-3}$ kg mol^{-1} is the molar weight [17] and $\rho_s = 2.328 \times 10^3$ kg m^{-3} [22]); $V_l = M/\rho_l = 10.93 \times 10^{-6}$ m^3 mol^{-1} (where $\rho_l = 2.57 \times 10^3$ kg m^{-3} [22]); f is determined by equation (5); and $T_m(P)$ is in K and P is in GPa. To guide the eye, three arrows indicate the corresponding melting temperatures of bulk Si and NC Si.

$T_m - P$ phase diagram accurately even when $P \rightarrow 10$ GPa, due to the successful determination of the $H_m(T)$ and $\Delta V_m(P)$ functions. The prediction of equation (6) has little difference compared to other theoretical results when P is small. This is because the cited κ_l value is measured under a larger value of P, which in turn implies that κ_l is a weak function of pressure. When $P > 10$ GPa, the model prediction also differs a little from other theoretical results, since the limitation of equation (5) is $D > D_0 = 6h = 1.4112$ nm. This leads to the applicable pressure range being smaller than 10.5 GPa in terms of equation (5) [15]. It is known that, on pressurization (beginning at 7–8 GPa at ambient temperature), the diamond structure of Si undergoes a well characterized sequence of a first-order transition to β-Sn structured Si [2], which finishes at 10–12 GPa [2, 23]. Thus, before equation (6) becomes invalid, the above melting transition is also absent [9]. Note that the success of equation (6) implies that both the assumptions—that H_m is essentially a function of temperature and ΔV_m is essentially a function of pressure—are reasonable.

The melting temperature of NC Si is lower than that for bulk Si due to the size effect [15], as shown in the figure. Moreover, the slope of the $T_m - P$ curve for bulk Si is larger than that of the corresponding nanocrystals, which can be implied by rewriting equation (2) as $dT_m/dP = \Delta V_m(P)T_m/H_m(T_m)$, where $dT_m/dP \propto T_m$. Since $T_m > T_m(D)$, then $dT_m/dP > dT_m(D)/dP$.

As shown in the figure, the value of $T_{m0}(D)$ that is obtained from equation (8) is within that of the theoretical and experimental results. The predicted $T_m - P$ curves for NC Si for

various $T_{m0}(D)$ values are different, since $T_m(P) \propto T_{m0}(D)$ in term of equation (6), where the other parameters are the same. However, the trend for the melting temperature to decrease as the pressure increases is similar, for the same reason.

4. Conclusion

In summary, the Clapeyron equation has been introduced to estimate the T_m-P phase diagram of bulk and NC Si by introducing the effects of surface stress induced pressure. It is found that, as P increases, T_m drops more strongly for bulk Si than for NC Si. The model's predictions are in agreement with other theoretical results.

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