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The size dependence of the diamond–graphite transition

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Abstract. The transition between nanometre-scaled diamond and graphite as well as the corresponding thermodynamic functions are discussed based on the temperature–pressure phase diagram of carbon including the contribution due to surface effects. As a result, the equilibrium transition size between diamond and graphite as a function of temperature and the thermodynamic function for the transition are obtained. It is found that as the size and temperature decrease, diamond becomes more stable than graphite. The obtained result is consistent with the reported experimental results on the chemical vapour synthesis of nanometre-sized diamond under ambient pressure.

Regarding the equilibrium phase diagram of carbon it is understandable that the graphite-to-diamond transition occurs at high temperature and high pressure. However, it is observed that nanometre-sized diamond (nano-diamond) is also obtained at low temperature and low pressure [1, 2], i.e. under conditions where bulk diamonds are a metastable modification of carbon crystals. Moreover, it is found that the diamond phase that initially formed as a nanocrystalline phase with a grain size below 3 nm transforms into graphite at larger size [1, 2]. These results suggest that nano-diamond is energetically preferred compared to nanometre-sized graphite (nano-graphite) and that the relative stability of diamond compared to graphite is a function of size [3–7]. The stability of diamond with a diameter (d) of about 3–5 nm has been calculated by several theoretical efforts [3–7]. One of them has further established the dependence of the equilibrium temperature on the size of diamond at zero pressure where the largest diameter of 15 nm at 0 K is obtained [5]. Recently, these theoretical calculations have been confirmed by experimental results where nano-diamonds with $d = 5$ nm are observed to be unstable against the transition into graphite, while nano-diamonds with $d = 2.5$ nm still exist after an annealing procedure at and above 1073 K which is a mean temperature of crystallization by the CVD method [8]. Below 1073 K, the nano-diamonds with $d = 5$ nm are stable and the diamond-to-graphite transition does not occur [8]. This experimental result implies again that the equilibrium size of diamond is temperature dependent.

With regard to the observed size dependence of the relative stability of the two carbon modifications, it seems reasonable to consider the additional pressure contribution due to the curvature of the nanometre-sized particles [6]. In this paper, simple model calculations based on the extrapolation of the bulk diamond–graphite equilibrium phase boundary in the temperature–pressure diagram to the nanometre size region will be employed to estimate the

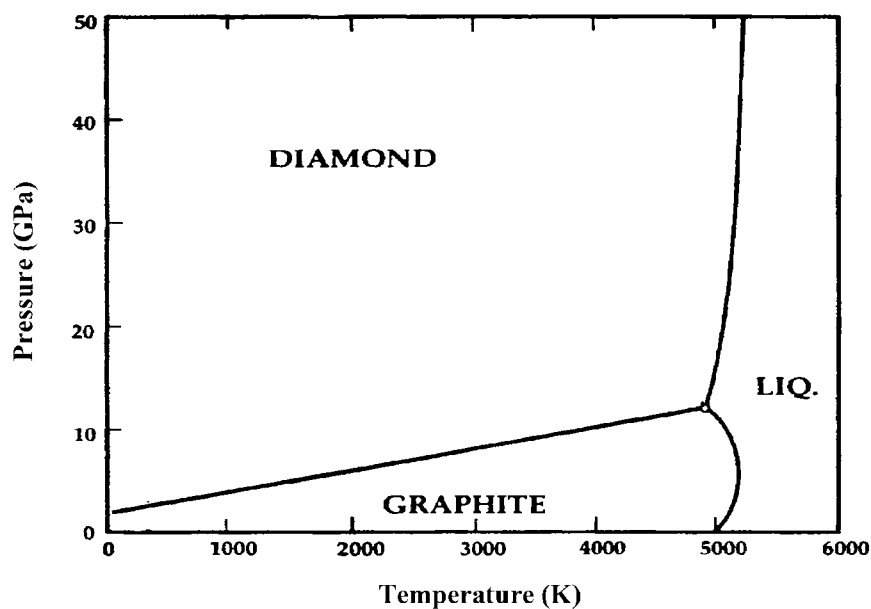


Figure 1. The temperature–pressure phase diagram of carbon [1].

relative stability of the two modifications with respect to the system size. The extrapolated phase boundary is calculated according to the Laplace–Young equation taking the experimental values for the bulk phases into account. As a result, a similar equilibrium size for the graphite–diamond transition is obtained as was found both experimentally [8] and theoretically [3–7]. Moreover, the thermodynamic functions for diamond–graphite transition is estimated on the basis of the Clausius–Clapeyron equation. Further, the model calculation indicates an explanation for the experimental observation that under ambient pressure a direct transition from nano-graphite to nano-diamond is not observed, but a reverse transition is very easy.

According to the phase diagram of carbon, which is shown in figure 1, the transition pressure function $P(T)$ for the diamond–graphite transition is given as [1]

$$P = 1700 + 2.06T \quad (1)$$

with the external pressure, P in MPa and the temperature, T in Kelvin. Equation (1) is determined by the two terminating points of the graphite–diamond boundary in the phase diagram of carbon that are (1700 MPa, 0 K) and (12000 MPa, 5000 K), respectively [1]. Thus, $dP/dT = (12\,000 - 1700)/5000 = 2.06$. The latter is the graphite/diamond/liquid triple point [1, 9–10]. The two points are connected by a straight line, which has been established by thermodynamic calculations based on the measured physical properties of graphite and diamond in the temperature range from 300 K to 1200 K and by experiments on the graphitization of diamond [1].

In order to estimate the contribution of the size-dependent internal pressure, some assumptions have to be made. Under the assumption of spherical, quasi-isotropic nanocrystals, the additional curvature-induced pressure, P_a is given by the Laplace–Young equation [6] as:

$$P_a = 4\gamma/d \quad (2)$$

with a diameter, d of the order of several nanometres and the surface free energy of crystalline carbon, γ . Due to this additional pressure P_a , the external pressure P necessary

for the transition of nano-graphite to nano-diamond decreases by the same amount. Thus, $P + P_a = 1700 + 2.06T$ is obtained for the size dependent phase boundary. From equations (2) and (1) and considering that during the low-temperature and low-pressure synthesis of diamond, $P \approx 0$ [6], one obtains:

$$d = 4\gamma / (1700 + 2.06T). \quad (3)$$

To calculate the equilibrium size of diamond with graphite, $\gamma_D = 3.7 \text{ J m}^{-2}$ [2, 6] for diamond is taken, which is a mean value for the surface energy of different faces. In fact, two limiting cases of γ_D have theoretically been calculated as 6.17 J m^{-2} for the (100) face and 2.55 J m^{-2} for the (111) face [7]. Although there is the above uncertainty for γ_D [2–7], regarding quasi-isotropic crystals, the uncertainty in γ_D only leads to a linear change of d in terms of equation (3). For graphite, a value of $\gamma_G = 3.1 \text{ J m}^{-2}$ has been given [2, 6]. At equilibrium, the diamond and the graphite should have the same pressure. To avoid this difference between γ_D and γ_G ,

$$\gamma = (\gamma_D + \gamma_G) / 2 \quad (4)$$

is taken with $\gamma = 3.4 \text{ J m}^{-2}$ while $(\gamma_D - \gamma) = (\gamma - \gamma_G) < 0.1 \gamma$. As a first order approximation, this difference of pressure for nanocrystals is neglected in the following calculation.

The calculated result in terms of equation (3) is shown in figure 2. For comparison, some theoretical and experimental results are also indicated in the figure. The transition size of nano-diamond decreases from about 8 nm at 0 K to 3 nm at 1500 K. Note that our result not only corresponds to the experimental results for the diamond–graphite transition at 1073 K [8] and 1300 K [11], but shows also a reasonable agreement with existing theoretical predictions [3–7].

However, it should be noted that the diamond–graphite transition in the two directions may follow different kinetics. Since $\gamma_D > \gamma_G$ [3, 4, 6, 7, 12], the diamond-to-graphite transition is expected to be accelerated on the surface of the nano-diamond due to the decreases of γ and thus P_a during the formation of graphite on the surface of diamond, which is similar to a solid-to-liquid transition with nil hysteresis. For the graphite-to-diamond transition, the benefit on the decrease of γ does not exist although P_a increases when the transition occurs on the surface of graphite. Thus, the transition cannot be initiated on the surface, which results in a more restricted nucleation process within the crystal with a large hysteresis that is similar to a solid–solid transition. This transition can only take place at conditions far from equilibrium and is thus not observed during annealing of graphite under ambient pressure.

Since the lattice constant of diamond is 0.357 nm [13], the diameter of the atoms in the diamond lattice is about 0.09 nm. Assuming that a critical nucleus has about 100 atoms [14], the diameter of the nucleus is thus only about 0.5 nm (a discussion on the diameter of the critical graphite nucleus is similar). Since the size of the critical nucleus is located within the stability field of diamond (see figure 2), a higher nucleation possibility and growth rate exist at lower temperature for diamond compared to graphite. However, during a CVD process, the difference of energetic states between vapour carbon and diamond or graphite is much larger than that between diamond and graphite [1]. Although the nucleus of graphite is metastable in comparison with that of diamond, it still can form during the CVD process (the existence of hydrogen will decrease the activation energy of the vapour–diamond transition and accelerate the transition although it is not a necessary condition for this transition [4, 15]). It should be noted that the above prediction is not in conflict with the existence of nano-graphite within a diamond thin film since now grain boundaries are sp^2 bonding, which is the same for both graphite and diamond [15]. In other words, at once a thin film is formed, the nano-graphite is

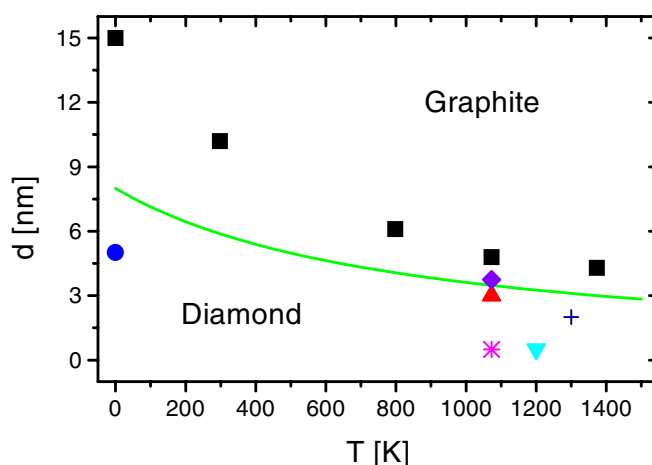


Figure 2. The size–temperature transition diagram of carbon at zero pressure where the solid line shows the model prediction of equation (3). The theoretical and experimental results are also plotted in the figure. The symbol ● denotes the theoretical estimation based on the surface energy difference between diamond and graphite [3]. The symbol ▲ presents the theoretical calculation based on the consideration that the surface atoms are terminated by hydrogen atoms, which implies that the transition is related to a CVD method [4]. Thus, the temperature is assumed to be the mean temperature with the CVD method [5]. The symbol ■ gives the theoretical calculation in terms of the charge lattice model [5]. The symbol ▼ is the theoretical result calculated by the chemical potential of carbon, where the stable diamond cluster has 104 atoms [6]. Since the lattice constant of diamond is 0.357 nm [13], the diameter of the atoms in the diamond lattice is about 0.09 nm. Thus, the corresponding diameter of the cluster is about 0.4 nm. The symbol ◆ is based on the experimental observation that diamond crystals with a diameter of 5 nm are transformed into graphite while diamond crystals with a diameter of 2.5 nm still exist [8]. We assume that the equilibrium size is mean value of 2.5 nm and 5.0 nm, that is 3.75 nm at 1073 K. The symbol + shows an experimental result where the nano-diamond transforms to onion-like carbon with a size of 2 nm [11]. Although the transformed product of the onion-like carbon has a lower Gibbs free energy than the graphite [11], which indicates that the equilibrium transition size between diamond and graphite is larger than 2 nm, it still shows some kind of instability of the nano-diamond. Moreover, the location of a nucleus during the chemical vapour deposition is also shown in the figure as *.

also stable within the thin film due to the change of surface energy to grain boundary energy which is the same for graphite and diamond.

Moreover, according to the Clausius–Clapeyron equation [16],

$$H = (dP/dT)(V_G - V_D)T \quad (5)$$

where H is the transition enthalpy in J mol^{-1} , $dP/dT = 2.06 \text{ MPa K}^{-1} = 2.06 \text{ J cm}^{-3} \text{ K}^{-1}$ (see above) and V_G and V_D are the molar volumes of graphite and diamond having sizes of 5.298 and 3.417 in $\text{cm}^3 \text{ mol}^{-1}$, respectively [3]. Thus, we have $H = 3.87 T$. Through $S = H/T$, $S = 3.87 \text{ J mol}^{-1} \text{ K}^{-1}$ where S is the transition entropy. It is interesting that Gamamik [5] has used a temperature-dependent transition entropy where $S = 3.37 \text{ J mol}^{-1} \text{ K}^{-1}$ at room temperature and $S = 4.59 \text{ J mol}^{-1} \text{ K}^{-1}$ at 1073–1373 K, which contributes partly to the decrease of equilibrium size of the diamond–graphite transition. The mean value of the above data is $3.98 \text{ J mol}^{-1} \text{ K}^{-1}$, which is similar to our result of $S = 3.87 \text{ J mol}^{-1} \text{ K}^{-1}$.

In summary, we have introduced a simple method to calculate the size-dependent diamond–graphite transition temperature by applying the Laplace–Young equation to the bulk diamond–graphite phase diagram. The obtained equilibrium temperature increases as the size of the nano-diamond decreases. The calculated results are consistent with the theoretical

predictions and existing experimental evidence obtained by low-temperature and low-pressure synthesis of diamond.

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