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## LETTER TO THE EDITOR

## Phase stability of electronically excited Si nanoparticles

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### Abstract

It is well established that the melting temperature,  $T_m$ , of nanoparticles decreases when their size decreases. In Si and similar materials, it is also known that electronic excitation leads to a decrease of  $T_m$ . Here, the cumulated effect of size reduction and high electronic excitation is studied theoretically. It is shown how, in the thermodynamical limit, both effects combine.

The processes occurring in a semiconductor nanoparticle under electronic excitation or light illumination are of great interest. Indeed, in a number of nanotechnologies, electron injection and transport or light emission are part of the fabrication process, the characterization procedures or the function of the nanosystems [1, 2]. It has been known for a long time that electronic excitation is responsible for a modification of the cohesive properties of semiconducting materials, like Si. At very high electronic excitation, this leads to a softening of the covalent bonds, responsible for a decrease of the melting temperature [3, 4] or a transition to a new kind of liquid state [5, 6]. In bulk material, this is observed under very short laser irradiation (about 100 fs) due to the very short relaxation time of electrons. At longer laser irradiation times (some picoseconds and above), ordinary thermal melting takes place [7].

An order of magnitude of the electronic concentration,  $p$ , for a noticeable modification of the melting temperature,  $T_m$ , has been evaluated theoretically for the case of Si [4]. It turns out that  $T_m$  decreases by about 10% when  $p \approx 10^{21} \text{ cm}^{-3}$ . Turning to the nanoparticle, this is equivalent to one electron per spherical nanoparticle of radius 0.6 nm. It corresponds to the injected electron density in nanodots and other nanosystems.

At such dimensions, the electronic and optical properties of nanoparticles are known to differ from the ones of the bulk material [8]. The electron and hole states are shifted. The net result is that the optical band gap increases when the size of the nanoparticle decreases.

At the nanometre size, other effects also take place. Indeed, nanoparticles are characterized by the fact that the ratio of the number of surface to volume atoms is not small. It is then obvious that the effects of the surface on the cohesive properties of the particle cannot be neglected. This is seen in various situations, like the well known size-dependent melting point depression [9]

and other phase transitions [10] of nanoparticles. Since the surface tension depends on the chemical environment, it is obvious that the melting point variation depends on it, as observed experimentally for various cases [11–13].

Since the theoretical work of Pawlow [14] in 1909, various models have been devised to describe the variation of the melting temperature with the radius,  $R$ , of the particle [15–20] and their shape [21–24]. It turns out that  $T_m$  decreases when  $R$  decreases, following:

$$T_m = T_{m,\infty}[1 - \alpha/(2R)],$$

$T_{m,\infty}$  is the bulk melting point.  $\alpha$  is constant for a given material. For inorganic materials,  $\alpha$  is positive, between 0.4 and 3.3 nm [17, 20]. Again, the decrease of  $T_m$  is noticeable when  $R$  is in the nanometre range.

Given the fact that the cohesion of nanoparticles is affected by both size and electronic concentration, it is interesting to study how both effects combine.

The reasoning is based on the calculation of the temperature variation of the isobaric free energy of the involved phases,  $G(T)$ . Let  $N$  be the number of atoms in the particle. Let us consider relatively large particles, where (1)  $N$  is such that the thermodynamical arguments remain valid, (2) the surface of the particle may be characterized by a single value of the surface tension. These conditions are met when the radius of the particle is equal to or larger than about 3 nm, and the particle is either ‘rounded’ or, conversely, presents the shape of a regular polyhedron with one kind of facet [24]. At a fixed temperature, the total Gibbs free energy for a particle of  $N$  atoms is given by:

$$NG = NG_\infty + fN^{2/3}\gamma, \quad (1)$$

where  $f$  is a geometrical factor depending on the shape of the particle. The term ( $fN^{2/3}$ ) is equal to the number of surface atoms.  $\gamma$  is the surface tension related to one atom (i.e. the surface tensions divided by the number of surface atoms). For most inorganic materials,  $\gamma$  remains nearly constant when  $T$  varies.  $G$  and  $G_\infty$  are the particle and bulk energies per atom, respectively.

Phase transitions occur at the temperature where the difference between the  $G$  s of the two involved phases is zero. Let us consider the case of melting. The melting temperature is  $T_m$ . Since, near  $T_m$ , we are well above the Debye temperature of the solid, the specific heat is approximately constant. Hence, one has:

$$(G_l - G_c)_\infty = C - BT, \quad (2)$$

where  $C$  and  $B$  are constants for a given material. The subscript  $\infty$  states that we are dealing with very large materials, i.e. with  $R$  much larger than the interatomic distance. At a fixed temperature, the total Gibbs free energy difference for a particle of  $N$  atoms is given by:

$$N(G_l - G_c) = N(G_l - G_c)_\infty + fN^{2/3}(\gamma_l - \gamma_c). \quad (3)$$

This dependence is a function of the values of the surface tensions of the liquid,  $\gamma_l$ , and the crystal,  $\gamma_c$ . Since  $R$  is proportional to  $N^{1/3}$ , one obtains:

$$T_m = T_{m,\infty} + f(\gamma_l - \gamma_c)/BN^{1/3} = T_{m,\infty}[1 - \alpha/(2R)], \quad (4)$$

where  $T_{m,\infty}$  is the bulk melting temperature. The term ( $f/N^{1/3}$ ) is directly proportional to the ratio of surface to volume atoms.

When the semiconducting material is electronically excited, the electrons modify the interatomic bond strength. In Si and similar materials, the bonds are softened by electronic excitation. Assuming that the electron–hole plasma is uniformly distributed in the system, it turns out that the mean phonon frequency decreases like [4]:

$$\omega = \omega_0(1 - \beta p). \quad (5)$$

In this equation,  $\beta$  is a constant for a given material and  $p$  is the concentration of electron–hole pairs ( $p = P/N$ ;  $P$  is the total number of electron–hole pairs of the particle). The mean phonon frequency is proportional to the Debye temperature,  $\theta$ :

$$\theta = \theta_0(1 - \beta p). \quad (6)$$

The bulk normal Debye temperature is  $\theta_0$ . In Si,  $\beta^{-1} \approx 9 \times 10^{21} \text{ cm}^{-3}$ .

Although the origin of melting is still subject to discussion, it refers to the phonons. Hence the contribution to  $G$  in equations (1)–(3) is the phonon one. When  $T > \theta_0$ , the total energy of the lattice is given by:

$$G_{c\infty} \approx 3kT - a\theta_0. \quad (7)$$

The constant  $a \approx 1k$ . In the following, it is further assumed that the liquid is not changed under electronic excitation. The reason is that we consider the case of Si, where it is known that the liquid phase is metallic. This is valid for some other semiconductor materials (Ge, III–V compounds).

$\gamma_c$  is also affected by the electronic excitation.  $\gamma_c$  is related to the interatomic bond strength,  $U$ .  $U$  is the sum of a metallic ( $M$ ) and a covalent contribution [25]:

$$U = M + U_0(1 - \beta p). \quad (8)$$

Therefore, one may rewrite:

$$\gamma_c = \gamma_1 + \gamma'(1 - \beta p). \quad (9)$$

Introducing the previous equations into equation (3), one obtains:

$$N(G_1 - G_c) = N(G_1 - G_{c\infty} - k\theta_0\beta p) - fN^{2/3}\gamma'(1 - \beta p). \quad (10)$$

Given that  $(G_1 - G_c) = 0$  at  $T_m$ , one obtains:

$$T_m = T_{m,\infty}[1 - \alpha(1 - \beta p)/(2R) - \beta' p] = T_{m,\infty}[1 - \alpha/(2R) - \beta'' P/R^3 + \beta''' P/R^4]. \quad (11)$$

This equation tells us that the effect of the electron–hole pair on  $T_m$  is proportional to  $p$ , i.e. the electron–hole pair density.

For Si,  $\alpha$  has been calculated to be 1.88 nm [17] or 0.8454 nm [20].  $\beta' \approx 4$  [17] or, for a spherical particle,  $\beta'' \approx 0.017 \text{ nm}^3$ . This means that, for  $R = 2 \text{ nm}$ ,  $\alpha/(2R) = 0.47$  or 0.21;  $\beta''/R^3 = 0.02$ ;  $\beta'''/R^4 \approx 0.01$ –0.004. Thus, for this value of  $R$ , the effect of the size is more important (by a factor of 10) than the effect of one electron–hole pair. Or the effect of size is equal to one of about 10 electron–hole pairs. The two contributions are equal for  $P = 1$ , at  $R = 0.13$  or 0.20 nm. These values compare with the bulk Si–Si distance (0.234 nm), so that the particle is no longer spherical and the thermodynamics is no longer valid. In other words, the model is valid when  $R \geq 2$ –3 nm, as noted previously.

In the present model, it is assumed that the electron–hole plasma is spatially uniform. However, at low  $R$ , this is not necessarily the case. Indeed, when dealing with the electronic properties of nanoparticles, one important parameter is the exciton Bohr radius,  $a_B$ .  $a_B = 4.3 \text{ nm}$  for Si. It turns out that our present thermodynamical approach is valid when  $R \geq a_B$ . Under this condition, the electron–hole plasma density is no longer uniform. The system is quasi-zero-dimensional [8]. The energy levels are discrete, and described by atomic-like wavefunctions. They look like (but not exactly) wavefunctions of electrons and holes in a quantum well. It might then be expected that the phonon modes and the surface tension are also modified by this effect. Indeed, the fact that the electrons and holes wavefunctions are atomic-like implies that the density of the electron–hole ‘plasma’ is not the same at the surface as in the core. Moreover, it depends on the value of  $P$ . Hence, at the present stage, the evaluation of the surface density appears to be difficult. Hence the effect on  $\gamma_c$ . Further work

is necessary to obtain a quantitative evaluation of the effect of the surface tension. Whatever this is, it might be expected that the present model gives correct orders of magnitude.

In summary, it turns out that the electronic excitation of Si nanoparticles leads to a decrease of the melting temperature. This adds to the effect of the size reduction.

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