Grüneisen Parameter and Its Related Thermodynamic Parameters Dependence on Size of Si Nanoparticles

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1. INTRODUCTION
In the last two decades, the size of materials came into a nanometric scale, which lead dramatically increase of surface to volume ratio and correspondingly changes of physical, chemical and mechanical properties. To understand these properties and related physical bases, which are the necessary promises for correct industrial application, theoretical considerations on these size dependent phenomena become important due to partly absence of accurate measurement techniques on these properties of materials [1]. Nanoparticles (NPs) and nanowires (NWs) NPs and NWs mean solo nano-sized particles with free surfaces and have attracted increasing attention in the materials community since their electronic, optic, catalytic, mechanical and thermodynamic properties are significantly altered from those of either the bulk or a single molecule, where NWs is an extremely thin wire with a diameter on the order of a few nanometers or less and NPs is a small object that behaves as a whole unit with respect to its transport and properties in the size range between 1 to 100 nanometers [2,3]. Among these properties; mass density and bulk modulus having a large impact on other physical constant and playing an important role in material growth, homogeneity and porosity [4-7].

The Grüneisen parameter provides fundamental basis for studying thermal and elastic properties of solids [8-11]. In recent years, Omar and his group published several articles on thermal properties of nanoscale size solids [12-15]. Calculations of lattice thermal conductivity on Si nanowires by the use of
modified Debye model gave an inverse dependence of Grüneisen parameter $\gamma(r)$ with the nanowires diameter where the effects of electron concentration as a crystal imperfection in calculations is not taken into account [12,13]. While calculations of lattice thermal conductivity for GaN and GaAs nanowires with the effects of electron concentration gave a decrease of $\gamma(r)$ with the decrease of nanoparticles size [14,15]. With the miniaturization of a solid down to nanometer scale, the property characterization such as thermal and mechanical of the solid are no longer constant but change with variation of size. In this work as a request for calculating $\gamma(r)$, the size dependence of lattice thermal expansion $\alpha_t(r)$, Molar volume $V_m(r)$, Bulk modulus $B(r)$ and specific heat $C_v(r)$ will also be calculated with that of $\gamma(r)$.

2. METHOD OF CALCULATIONS

In the quasiharmonic approximation and assumption of a perfect crystal, the anharmonicity give rise to a major component of Grüneisen parameter in crystals, according to the relation [16, 17]:

$$\gamma(\infty) = \frac{3 \alpha_t(\infty) V_m(\infty) B(\infty)}{C_v(\infty)}$$

(1)

where $\alpha_t(\infty)$ is the bulk lattice thermal expansion, $V_m(\infty)$ is bulk molar volume, $B(\infty)$ is the bulk modulus and $C_v(\infty)$ is the bulk specific heat capacity which is assumed to follow Debye model. The amount of variation in the Grüneisen parameter depends on the structure of the material and the nature of interaction between atoms [18]. To calculate the nanoscale Grüneisen parameter $\gamma(r)$, Eq. (1) is modified to the state:

$$\gamma(r) = \frac{3 \alpha_t(r) V_m(r) B(r)}{C_v(r)}$$

(2)

where $\alpha_t(r)$ is the nanoscale lattice thermal expansion and is calculated from the following relation for tetrahedral semiconductors [19]

$$\alpha_t(r) = \left(\frac{0.021}{r_m(r)}\right) - \left[0.0256 \left(\frac{d_{mean}(r) - d_o}{d_o}\right)^3\right]$$

(3)

where $d_o$ is the mean bond length for diamond and is equal to (1.545Å), $d_{mean}(r)$ a nanoscale mean bond length, it is calculated from the relation $d_{mean}(r) = h - \Delta d_{mean}(r)$ where $\Delta d_{mean}(r)$ is the increase in the mean bonding length and can be calculating according to the following relation [20]:

$$\Delta d_{mean}(r) = \Delta d_{mean}(r_c)e^{-\left(\frac{r-r_c}{1.545}\right)^2}$$

(4)

Recalling $\Delta d_{mean}(r_c)$ as the maximum increase in the mean bond length and for Si is equal to (0.0988) by using $\delta h = h - \Delta d_{mean}(\infty)$, where $\Delta d_{mean}(\infty)$ is equal to 0.235nm [20] and $r_c$ denotes a critical radius at which all atoms of the particle are located on the bulk surface which is calculated from $r_c = (3 - D)h$, in this relation $D = 0$ for NPs and D=1 for nanowires (NWs) [21], $\beta$ is the best fitting parameter to the curve of nanometric size dependence melting point which is equal to (2.5) for Si. In Eq. (3), $T_m(r)$ is the nanoscale size dependent melting temperature as [20]:

$$\frac{T_m(r)}{T_m(\infty)} = \left(\frac{V(r)}{V(\infty)}\right)^{\frac{1}{2}} e^{\left(\frac{-R S_m(\infty) - R}{S_m(r) - s R}\right)}$$

(5)

Where $R$ is the ideal gas constant equal to (8.314 J.K$^{-1}$.mol$^{-1}$), $S_m(\infty)$ is bulk overall melting entropy, $V(\infty)$ is the Bulk lattice volume and $V(r) = a^3(r)$ is the nanoscale
lattice volume. The values of $\alpha(r)$ are calculated from the relation [19],

$$\alpha(r) = \frac{4}{3} \frac{d_{\text{mean}}(r)}{r^3}$$  \hspace{1cm} (6)

Fig. (1) shows $T_m(r)$ along with the related experimental values of NPs for Si, the calculated results agree well with the experimental results [22]. The input parameters required are given in Table (1). The nanoscale lattice specific heat $C_v(r)$ in Eq. (2) which is assumed to follow the Debye model is calculated according to the following relation [23]:

$$C_v(r) = \frac{9}{\pi} \frac{R}{\theta_D(r)} \int_0^\infty \frac{x(r)^2 dx(r)}{(x(r)^2 + 1)^{3/2}}$$  \hspace{1cm} (7)

where $x(r) = \frac{\theta_D(r)}{T}$ and $\theta_D(r)$ is the size dependent Debye temperature, it is calculated from the relation on the basis of the proportional relationship of $\theta_D(\infty)^2 \propto T_m(\infty)$ temperature [24], under the assumption that the size in the relation can be extended to $r$ [25,26] as:

$$\theta_D(r) = \theta_D(\infty) \left( \frac{T_m(\infty)}{T_m(r)} \right)^{1/2}$$  \hspace{1cm} (8)

According to Eq. (7), the specific heat $C_v(\infty)$ is a proportional quantity of $\theta_D(\infty)$, then the decrease in $\theta_D(r)$, will follow by the increase of $C_v(r)$ as shown in Fig. (2)

Upon structure miniaturization to the nanometer regime, the bulk modulus $B(\infty)$ similar to other parameters is no longer constant but changes with the shape and size of the solid. The relation for the bulk state is modified to a nanoscale size bulk modulus $B(r)$ form as [18, 27]:

$$B(r) = v_s^2(r) \rho(r)$$  \hspace{1cm} (9)

where $v_s(r)$ is the nanoscale size dependent sound group velocity and is calculated from the relation [28]:

$$\frac{v_s(r)}{v_s(\infty)} = \frac{\theta(r)}{\theta(\infty)}$$  \hspace{1cm} (10)

where $v_s(\infty)$ is the bulk sound group velocity and $v_s(r)$ is in a nanoscale state. For a system consisting of low-dimensional crystals, according to excess volumes as a function of dislocation density and grain size from
published papers, the theoretical volume $V(r)$ and mass density $\rho(r)$ of nanocrystalline material can be expressed as [29, 30]:

$$\rho(r) = \rho(\infty) \frac{V(\infty)}{V(r)} \quad (11)$$

where $\rho(\infty)$ is the bulk density. The molar volume $V_{mol}(\infty)$ is a lattice volume multiplied by Avogadro’s number. For the case of nanoscale, $V_{mol}(r)$ is calculated from [18, 21]:

$$V_{mol}(r) = N_A V(r) \quad (12)$$

The nanoscale size dependence for $B(r), \rho(r), V_m(r)$ and $\gamma(r)$ are shown in Figures (3), (4), (5) and (6). The figures show that the lattice thermal expansion, molar volume and bulk modulus drop while the specific heat rise when the size is decreased as shown in Fig. (2).

**Table (1):** The relevant data used in the calculations

| Parameters | Si |
|------------|----|
| $\alpha_1(\infty)/10^{-6}$ [19] | 3.73 |
| $T_m(\infty)/K$ [19] | 1685 |
| $B(\infty)/N.m^2 \times 10^{10}$ [31] | 9.8 |
| $S_m/\text{J.K}^{-1}\cdot\text{Mol}^{-1}$ [20] | 30 |
| $h/\text{nm}$ [20] | 0.3338 |
| $C_p(\infty)/K^1$ [23] | 19.388 |
| $V_m(\infty)/\text{m}^3\cdot\text{Mol}^{-1} \times 10^{-5}$ [32] | 1.205 |
| $\rho(\infty)/\text{Kg.m}^3 \times 10^3$ [33] | 2.329 |
| $\alpha(\infty)/\text{nm}$ [33] | 5.431 |
| $\theta(\infty)/K$ [23] | 692 |
| $\nu_g(\infty)/\text{m.sec}^{-1}$ [23] | 6524 |

**Figure (3):** Bulk modulus for Si nanoparticles and nanowires dependence on the size compared with the results of MDS [34].

**Figure (4):** Mass density for Si nanoparticles versus size of nanoparticles.

**Figure (5):** Molar volume as a function of the size of Si nanoparticles.

**Figure (6):** Grüneisen parameter as a function of the size of Si nanoparticles.
3. ANALYSIS OF RESULTS:

Size effects influence the thermodynamic parameters. Experimental evidence of the size-dependent heat capacity was recently reported for metallic nanoclusters and nanostructured dielectrics [35-37]. According to Equation (7), the specific heat $C_v(r)$ is a proportional quantity with $\theta_B(r)$, then the decrease in $\theta_B(r)$ according to the Eqs. (8) and (5), it will follow by the increase of $C_v(r)$ as shown in Fig. (2). For group IV elemental semiconductors, the melting point $T_m(r)$ will follow by a systematic dependence with their $B(r)$ as shown in Figure (7). According to this phenomenon, the smaller size for nanoparticles (NPs) which corresponds to a lower melting point, $T_m(r)$ should consequently give a smaller bulk modulus $B(r)$ as it is the case in Fig. (8). The value of $B(r)$ results obtained is compared to the available computer simulation results based on molecular dynamic simulations (MDS), where MDS is a computer simulation method for studying the physical movements of atoms and molecules [34] of Si nanowires (NWs), and have the same trend variation, while MDS gives higher values as it is clear from the Fig. (3). Such a dependence is related to non-variable lattice parameter in MDS. In the size range the nanoscale size unit cell volume is sensitively larger than the bulk.

On the other hand, the Density is known to be a size-independent property of materials. Generally, density can be varied by changing either the pressure or the temperature. Recently, it has been observed experimentally that mass density is size-dependent property of nanomaterials, such as in the case of Au nanocrystals [38], it was found that density decreases with the thickness of the layer in nanometer range which is less than 20nm due to the higher fraction of free volume in Au nanoclusters. At size 5nm, the density value of Si nanoparticles is found to be 1.472 gm.cm$^3$ compared to 2.329 gm.cm$^3$ for bulk; this is largely due to the variation in the surface to volume ratio which leads to increase in mean bond length. The results obtained have the same trend with the available experimental results for Au nanocrystals. Thus, the increasing of mean bond length leads to the change in mass density as we have found in this work and it is shown in Figure (4). The figure shows that the $\rho(r)$ decreases with the reduction of their sizes which leads to decrease in bulk modulus.

From the physical point of view, the calculated nanoparticles size dependence of Grüneisen parameter $\gamma(r)$ on the parameters $\alpha_1(r)$, $B(\infty)$ and $V_{m21}(r)$, will be explained according to as: It is well known that, Grüneisen parameter is a function of anharmonicity part of lattice vibration, in this case the dependence Grüneisen parameter in Fig. (6) could be referred to the decrease of lattice anharmonicity as the nanoparticle size decreases. For this case, the decrease in nanoparticles size will follow by the increase of their bond length [20], which according to the principals of energy tight binding model reduces the lattice interaction. In this case, lower lattice vibration gives lower values of $\gamma(r)$. Thus, it leads to a less anharmonicity vibration and Fig. (6) indicates such hypothetical dependence. The zero values of $\gamma(r)$ represents a zero anharmonicity at about 5nm particles diameter, which leads to a structure deformation. However, in previous published works, at almost this size, and for several elements such as Au and Cu, the structure change from crystalline to that of molecular like form [39,40]. Furthermore, the shape of the curve for $\gamma(r)$ is similar to that of the temperature dependence of $\alpha_1$, that is the lattice thermal expansion of Si [20]. Depending on these precise parameters, where both are represented by the anharmonicity part in the...
lattice vibration, their shape should be represented by this phenomena. Moreover, the reduce in nanoscale size has an effect on the lattice anharmonicity and according to the results obtained by Omar [39], the low temperature shape of $\alpha_1(\infty)$ could be due to the structure change and so for $\gamma(r)$ in this work.

![Figure (7): Bulk modulus versus melting temperature for different IV elements.](image1)

![Figure (8): Bulk modulus versus melting temperature versus for Si nanoparticles.](image2)

4. Conclusions
When the material sizes reduces to a nanoscale range, the Grüneisen parameter no longer remains constant but accordingly changes and play an important role as size effect dominates. The relation used to correlate molar volume, bulk modulus and Grüneisen parameter for the bulk solid found to be work well for the case of nanoscale size solids. According to the definitions of Grüneisen parameter which corresponds to the vibrational anharmonicity, its zero value should represent the disappearance of anharmonicity and that consequently the break bonding in nanoscale.

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