Int. J. Nanosci. Nanotechnol., Vol. 17, No. 3, Sept. 2021, pp. 141-145

Effect of Size and Shape on Thermo-Elastic Properties of Nano-Germanium

Pratyay Chattopadhyay[1,*], G. R. Patel[2] and T. C. Pandya[1]

[1]Department of Physics, St. Xavier's College (Autonomous), Ahmedabad-380009, Gujarat, India
[2]Department of Physics, Government Science College, Sec-15, Gandhinagar-382415, India

(*) Corresponding author: pratyay10@gmail.com
(Received: 15 July 2020 and Accepted: 06 May 2021)

Abstract

Germanium is a semiconductor with varied applications in the field of nanoscience and other fields of science. With known information about the bulk properties of germanium, an effort has been made to investigate the characteristics of germanium when it is in nanoscale size. The effective use of germanium and its compound in nanotechnology and other fields requires an intensive study of the thermo-elastic properties in nano scale. Effect of size and shape on the melting temperature, thermal expansivity, and bulk modulus has been studied for pure nano germanium. An attempt has been made to compute Young's modulus using two different formalisms. A comparative study of both the formalisms with experimental values is presented in this work. The comparative study for Young's modulus brings out the most suitable formalism for germanium nano crystal to calculate this modulus.

Keywords: *Melting point, Thermal expansivity, Bulk Modulus, Young Modulus, Nanosolid.*

1. INRODUCTION

Germanium is a very important semi-conductor material found on the earth [1, 2]. Although not readily available, like its silicon counterpart, it still has various uses in transistors, integrated circuits, etc. Though its bulk properties have been known to many for ages, investigation to understand the properties of nano solid had been started recently [3]. The use of nanomaterial is vast and has got many real-life applications [4]. The effect of size and shape plays a very important role to understand the thermoelastic properties of the nanomaterial.

The unavailability of experimental data for the size and shape dependence on the thermodynamic properties of semiconducting nanomaterials led us to investigate the effect of size and shape on the thermodynamic as well as thermoelastic properties of nanosolids. In the present communication, size dependency of melting point, bulk modulus, and coefficient of volume thermal expansion and Young modulus of nano-germanium has been reported. Two different theoretical formalisms [5, 6] have been used to compute the ratio of Young modulus of nano germanium to bulk germanium. Our predicted results are compared with the available results [7,8]. A comparative study of both formalisms is presented in the present work.

2. METHODOLOGY

The variation in the melting point against the size of nano-solids can be understood using the W.H.Qi model [9]. This model has predicted the size dependent melting temperature of nanoparticles, nanowires and nanofilms. Melting temperature of nanosolid based on the Qi model reads as follows

$$T_{mp} = T_{mb}\left(1 - \frac{N}{2n}\right) \qquad (1)$$

where *n* is the total number of atoms in a nanosolid and the total number of atoms on the surface of the nanosolid is N. Here T_{mp} and T_{mb} are the melting temperatures of the nanosolid and the corresponding bulk material respectively. The value of ratio N/n depends upon the shape and size of the nanosolid and the expressions of N/n for spherical nanosolids, nanowires and nanofilms have been tabulated in Table 1 [9].

Table 1. *N/n for three different types of nanosolids. Here d and D are the diameter of the atom and nanoparticles respectively. For the disk-like nanosolid l and h are the diameter of nanowire and width of nanofilm respectively.*

Nanosolid	N/n
Nanosphere	$4d/D$
Nanowire (h>>1)	$(8/3)(d/l)$
Nanofilm (l>>h)	$(4/3)(d/h)$

The coefficient of volume thermal expansion of nanosolids based on R. Kumar et al. model [10] and also given in [11] reads as follows.

$$\alpha_{nm} = \alpha_b \left(1 - \frac{N}{2n}\right)^{(-1)} \qquad (2)$$

where α_{nm} and α_b are the coefficients of volume thermal expansion of nanosolid and corresponding bulk material respectively.

Equation of isothermal bulk modulus developed by Pandya et al. [3] reads as follows

$$B = B_0\left(\frac{V}{V_0}\right)\left(1 + (B_0' + 1)\left(1 - \frac{V}{V_0}\right)\right) + B_0\left(\frac{V}{V_0}\right)\left(\frac{(B_0'+1)}{2}\left(1 - \frac{V}{V_0}\right)^2\right) \qquad (3)$$

where B_0 is the isothermal bulk modulus at zero pressure, B_0' is the pressure derivative of bulk modulus. V_0 is the volume at zero pressure and V is the volume at pressure P.

To compute the ratio of Young modulus, of nano-crystal to bulk crystal, two different formalisms [5,6] have been used. Following Qi model [9] S. Patil et al. [5] proposed the expression for Young modulus of nanosolids which reads as follows:

$$\frac{Y_{nm}}{Y_{bm}} = exp\left(\pm\frac{S_{vib}-1}{\frac{r}{r_0}-1}\right) \qquad (4)$$

Here Y_{nm} and Y_{bm} are the young modulus of the nanosolid and corresponding bulk value respectively and r_0 is the critical radius at which all the atoms of the nano-crystal are located on the surface [5]. The value of `r_0' is given by [5,12]

$$r_0 = (3 - d)h \qquad (5)$$

where *h* is the atomic diameter and d=0 for spherical nanosolids, d=1 for nanowires and d=2 for nanofilms [12]. Ratio [5] of mean square displacement of atoms on the surface and that in the interior of the nanosolid can be derived from the vibrational entropy expression and is given by

$$S_{vib} = \left(\frac{2S_{nm}}{3R}\right) + 1 \qquad (6)$$

Here *R* is the ideal gas constant and S_{nm} is nano melting entropy given by [13, 16]

$$S_{nm} = S_{mb} + \left(\frac{3R}{2} ln\left(1 - \frac{N}{2n}\right)\right) \qquad (7)$$

Here S_{mb} is the bulk melting entropy given as $S_{mb}=H_{mb}/T_{mb}$ [13, 16]; H_{mb} is melting enthalpy for bulk materials and T_{mb} is the bulk melting temperature. The value of the ratio N/n can be obtained from Table 1. Using the approach adopted by G. Patel et al. [6] the ratio of Young modulus can be computed as follows

$$\frac{Y_{nm}}{Y_{bm}} = 1 + \left(1 - \left(1 - \frac{(\beta)(S)A}{6}\right)\right) \qquad (8)$$

where β is material constant [6,14] and S is the shape factor [6,15] of the material. `A' is the surface to volume ratio [6,14].

3. RESULT AND DISCUSSION

Using eq. (1) the melting temperatures for nano-germanium have been evaluated and the predicted results for spherical nanosolids, nanowires and nanofilms are

reported in Figure 1. Figure 1 provides a comparative study of variation of melting temperatures against the size of the nanosolid. In Figure 1 we have included our predicted results for the nanosolids having size less than 13nm because for the nanosolids having higher size our results are analogous to their corresponding bulk counterpart.

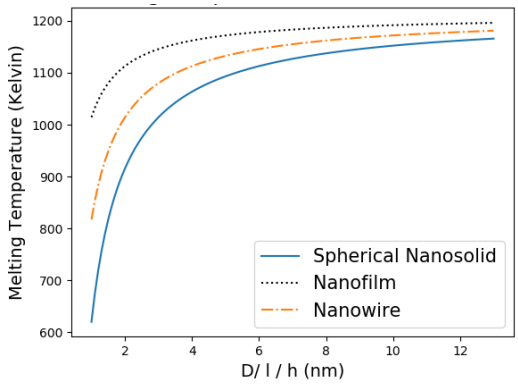

Figure 1. *Variation of melting temperatures of nanogermanium for spherical nanosolid (D nm), nanowire (l nm) and nanofilm (h nm) shapes against the size.*

It is found that the melting temperature decreases as the size of nanosolid decreases and the trend of variation in melting temperature is almost similar for different shapes. It is found that effect of shape on the melting temperature is significant in the case of spherical nanosolid. Variation in melting temperature is noteworthy for smaller particles. At nano-level the surface to volume ratio increases drastically, resulting in alteration of the thermodynamic and thermal properties. At the nanoscale range as the size of the particle decreases melting temperature depresses. This is due to the enhanced surface to volume ratio at the nanoscale size. At the size below 20nm surface to volume ratio increases considerably so the number of atoms on the surface increases. On the surface 50 percent of the bonds are dangling bonds that causes in the reduction of melting temperature considerably below 20nm size.

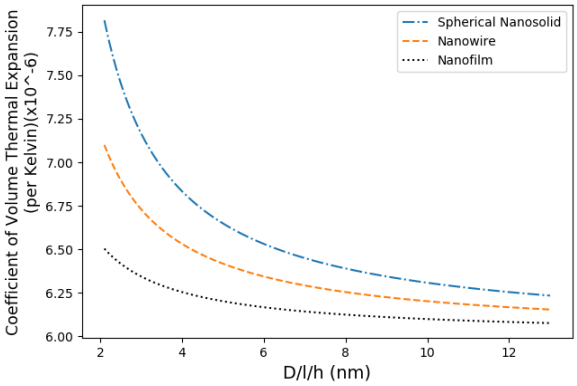

Figure 2. *Variation of coefficient of volume thermal expansion of nanogermanium for spherical nanosolid (D nm), nanowire (l nm) and nanofilm (h nm) shapes against the size.*

Using eq. (2) the coefficient of volume thermal expansion for nanogermanium has been computed. The predicted results for spherical nanoparticles, nanowires and nanofilms are shown in Figure 2. The variation in the coefficient of volume thermal expansion (α) for the nanosolids is significant for the size less than 10nm for all the shapes. In this range, it is found that (α) increases as the size of the nanosolids decreases. Results of the coefficient of volume thermal expansion (α) for nanosolids having a size greater than 10nm are similar to the results of their corresponding bulk counterparts for all the cases.

The variation of isothermal bulk modulus against compression, calculated using eq. (3), is shown in Figure 3. The input parameters used for the computation of isothermal bulk modulus are tabulated in Table 2.

Table 2. *Input parameters used for the computation of bulk modulus.*

B_0'	B_0' (GPa)	Particle Size
4	112	13 nm
4	92	49 nm
3	74.9	Bulk Germanium

Our results on the study of compressibility of nano germanium

demonstrate that nano size samples are less compressible than bulk materials which are in agreement with the Hall-Patch effect [3]. Our results indicate that bulk modulus increases with decrease in particle size, which may be the effect due to the larger surface between grains in nanosized particles that provides energy leading to the increase in hardness. Hence it is found that nanogermanium gradually hardens with an increment of pressure.

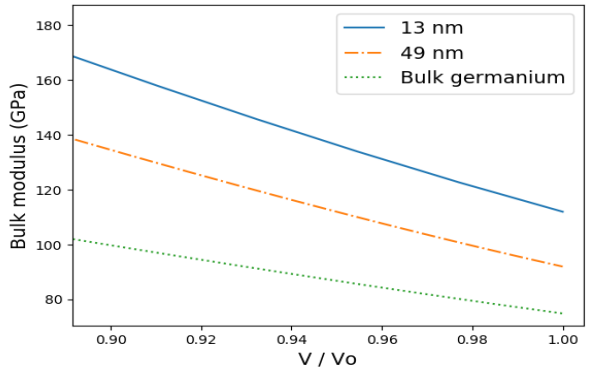

Figure 3. *Bulk modulus versus volume compression for germanium and nanogermanium having spherical shape.*

The predicted results for the ratio of Young modulus of nanosolids to the bulk solid computed using eq. (4) and eq. (8) are compared in Figure 4. As the size decreased of nanowire surface to volume ratio increases and number of atoms on the surface increases so on the surface interatomic distance decreases which enhances tangential force resulting into the increment of young modulus.

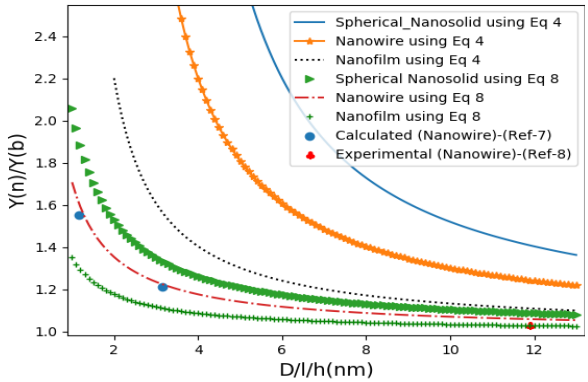

Figure 4. *Ratio of size-dependent Young modulus of nanosolid to bulk Ge computed using (4) and (8)*

For the case of nanowire, it is found that the predicted results of the ratio of Young modulus using eq. (8) are in good agreement with the available experimental finding [13] and other available computed results [7]. It is found that results obtained by Patil et al [5] formulation deviate largely as compared with the work of G. Patel et al. [6]. Patil's formulation is based on Lindemann's criterion of melting. Patel and co-workers have used a liquid drop [14] model to derive the empirical relation between Young modulus and the size of nano solids. With reduction in size the binding energy increases and because of this increase in the binding energy the Young modulus increases with reduced size. This large difference between the results of these two formalisms is observed because each of the formalism is based on different assumptions.

4. CONCLUSION

It is concluded that the melting temperature decreases as the size of nanosolid decreases. We have found that nano size samples are less compressible than bulk materials. Nanogermanium gradually hardens with an increment of pressure and the coefficient of volume thermal expansion of nanosolids increases with decreasing size for all different shapes.

In the present work, two different formalisms are critically analysed by studying the thermoelastic properties of nano germanium. It is found that the Young modulus of nanosolids decreases as the size of nanosolid increases, the reason being the binding energy of nanogermanium. These predictions may be of current interest to the researchers engaged in the experimental studies and this model may be applicable to binary semiconductors.

ACKNOWLEDGEMENT

The authors express their sincere thanks to the referees for their valuable

suggestions for the improvement of the paper content.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERRENCE

1. Yonenaga Ichiro, "4-Germanium crystals in Single Crystals of Electronic Materials: Growth and Properties", *Woodhead Publishing*, (2019) 89-127.
2. Crain, J., Ackland, G. J., Clark, S. J., "Exotic structures of tetrahedral semiconductors", *Rep. Prog.Phys*., 58 (1995) 705-754.
3. Pandya, Tushar C., Shaikh, Aasim I., Bhatt, Apoorva D., "Particle-size effect on the compressibility of nanocrystalline germanium", *AIP Conf. Proc.*, 1349 (2011) 413-414.
4. Stark W. J., Stoessel, P. R., Wohlleben, Hafner, W., A., "Industrial applications of nanoparticles", *Chem. Soc. Rev.*, 44 (2015) 5793-5805.
5. Patil, S. D., Shinde, P. B., Takale, M. V., "Effect of size and shape on Young's modulus of nano-structured Ag by Lindemann's criterion", *International Journal of Chemical and Physical Sciences*, 3 (2014) 150-154.
6. Patel, Ghanshyam R., Pandya, Tushar C., "Effect of size and shape on Young modulus of semiconducting nanosolids", *AIP Conference Proceedings*, 1837 (2017) 040024 (1-3).
7. Yang, Po-Yu., Ju, Shin-Po., Lai, Zhu-Min., Hsieh, Jin-Yuan., Lin, Jenn-Sen., "The mechanical properties and thermal stability of ultrathin germanium nanowires", *Royal Society of Chemistry Advances*, 6 (2016) 105713.
8. Smith, Damon A., Holmberg, Vincent C., Korgel, Brian A., "Flexible germanium nanowires: Ideal strength, room temperature plasticity, and bendable semiconductor Fabric", *American Chemical Society NANO*, 4 (2010) 2356-2362.
9. Qi, W. H., "Size effect on melting temperature of nanosolid", *Physica B: Condensed matter*, 368 (2005) 46-50.
10. Kumar, Raghuvesh, Sharma, Geeta, Kumar, Munish, "Size and temperature effect on thermal expansion coefficient and lattice parameter of nanomaterials", *Modern Physics Letters B*, 27 (2013) 1350180 (1-11).
11. Jaiswal, R., Pandey, B., Mishra, D., and Fatma, H., "Thermo-physical Behaviour of Nanomaterials with the Change in Size and Shape", *International Journal of Thermodynamics*, 24 (2021) 1-7.
12. Jiang, Q., Aya, N., Shi, F. G., "Nanotube size-dependent melting of single crystals in carbon nanotubes", *Appl. Phys. A*, 64 (1997) 627-629.
13. Singh, Madan., Lara, Sekhants'o., Tlali, Spirit., "Effect of size and shape on the specific heat, melting entropy and enthalpy of nanomaterials", *Journal of Taibah University for Science*, 11 (2017) 922-929.
14. Nanda, K. K., Sahu, S. N., Behera, S. N., "Liquid-drop model for the size dependent melting of low-dimensional systems", *Phys. Rev. A*, 66 (2002) 1-8.
15. Qi, W. H., Wang, M. P., "Size and shape-dependent melting temperature of metallic nanoparticles", *Mater. Chem. Phys.*, 88 (2004) 280-284.
16. Jaiswal, R. L., Pandey, B. K., "Modelling for the study of thermophysical properties of metallic nanoparticles." *SN Appl. Sci.*, 3 (2021) 466.