Influence of point and linear defects on thermal and mechanical properties of germanium nanowire: a molecular dynamics study

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Abstract
In the nanoscale dimensions, semiconductor nanowires such as germanium nanowires (GeNWs) are appropriate candidates for using field-effect transistors, Josephson junctions, sensors and so on. However, such uses require detailed knowledge of the physical properties of GeNW. Thus we investigated the thermal conductivity and stress-strain diagram of GeNW with lattice vacancy and linear imperfection. Non-equilibrium molecular dynamics simulation as numerical method was employed in this research. The three body Tersoff potential was employed to describe interaction between germanium atoms in GeNW. Two types of defects, point and linear, were applied to the nanowire. The Nose–Hoover thermostat was employed to control temperature of the system. We then studied thermal conductivity and Young's modulus in three crystallography directions [100], [110] and [111]. Our MD results showed that in the case of 8% point vacancy, the thermal conductivity decreased greater than 70% and Yong’s modulus decreased about 25% for three crystallography directions.

Introduction
Semiconductor materials specially silicon nanowire (SiNW) and germanium nanowire (GeNW) are important key building blocks that were used widely in nano-electronic devices [1–4], lithium batteries [5–7], sensors [8, 9], power sources [10]. We know that the thermal and mechanical properties of these nanowires significantly differ from the bulk [11, 12]. Therefore, the manufacturability of these nanowires requires the characterization of the thermal and mechanical properties such as Young’s modulus and thermal conductivity. In addition, application of semiconductor nanowires in environments with tensile or shock stresses requires their precise knowledge of mechanical and thermal properties. Mechanical properties of semiconductor nanowires were already investigated [13–17], for instance silicon-based materials for the development of Li-ion batteries. On the other hand, some materials such as metal oxides and alloys (Si or Sn-based and Ge-based materials) were used as a suitable material for lithium batteries [18–21]. The main hindrance for the application of these materials is the volumetric expansion, which can damage anode-cathode structure during charging-discharging cycle. To avoid unfavourable process such as volumetric expansion, nano-scale materials can be used [5, 22]. Silicon and germanium materials have the potential to be used in energy storage devices for their unique properties [5, 23–30].

Thermal conductivity of these materials is also important [31, 32]. The management and conduction of heat in nanoscale devices is an important issue which has attracted the attention of scientists around the world. Elimination of extra heat is a vital subject for further development in nano-electronic industries. Nanomaterial application for heat conductivity were already studied by many researchers [33–36]. During the production of nanowires, defects and vacancies occur influencing their physical properties, such as Young’s modulus and thermal conductivity [37, 38].

In this study, we calculated thermal conductivity and Young’s modulus of GeNW with two types of defects, vacant lattice sites and linear imperfection in three crystallographic directions, [100], [110] and [111]. The non-
equilibrium molecular dynamics simulations were employed to explore these properties. The results of this investigation can facilitate the development of nano-sized instruments and Li-batteries.

Computational method
In this study, all of non-equilibrium molecular dynamics (NEMD) simulations were carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [39] (http://lammps.sandia.gov). The considered GeNW has a radius of 20Å and a length of 200Å. We investigated three crystallography directions, [100], [110] and [111], which these directions were along GeNW longitudinal axis. In order to study influence of defect on physical properties of GeNW, the two types of defects were considered, (a) point vacancy and (b) linear vacancy. To vacancy generation, the germanium atoms were removed randomly from GeNW (figure 1(a)). Point vacancy considered 1, 2, ..., 8% of GeNW and physical quantities calculated for every defect percent. Moreover, for modelling linear vacancy, a cylindrical region with diameter 6Å on GeNW axis with various lengths were removed (figure 1(b)). The mentioned length changed up to 170Å. Linear vacancy lengths were set 50, 70, 90, 110, 130, 150 and 170Å. In our non-equilibrium molecular dynamics simulations, the three body Tersoff [40] potential was picked up as implemented in LAMMPS package for germanium. The Tersoff potential has functional form as follow:

\[
E = \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij}
\]

\[
V_{ij} = f_c(r_{ij}) \left[ f_A(r_{ij}) + b_{ij} f_A(r_{ij}) \right]
\]

\[
f_c(r) = \begin{cases} 
1 & r < R - D \\
\frac{1}{2} - \frac{1}{2} \sin \left( \frac{\pi}{2} \frac{r - R}{D} \right) & R - D < r < R + D \\
0 & r > R + D 
\end{cases}
\]

\[
f_A(r) = A \exp(-\lambda_A r) \\
b_{ij} = (1 + \beta \zeta_{ij}) \frac{1}{\tau}
\]

\[
\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) \exp [\lambda_A^m (r_{ij} - r_{ik})^m]
\]

\[
g(\theta) = \gamma_{ij} \left( 1 + \frac{c^2}{d^2} + \frac{c^2}{d^2 + (\cos \theta - \cos \theta_{ij})^2} \right)
\]

where, \(f_A, f_R, \) and \(f_c\) are attractive function, repulsive function and switching function respectively. Moreover the term \(b_{ij}\) includes three-body interactions. The summations in the potential are over all neighbors \(j\) and \(k\) of atom \(i\) within a cut-off distance \((=R + D)\). The coefficients of the three-body Tersoff potential for germanium atoms are shown in table 1.

NEMD simulations for mechanical and thermal properties were done initially in NVE ensemble using Langevin thermostat [41] for reaching system to equilibration situation for 1ns. The time step for all simulation was considered 1fs. Verlet integration was used to integrate equation of motion.

Figure 1. (a) Point and (b) linear vacancy of GeNW. In both the vacancy collared by gray, linear vacancy was generated by removing cylindrical region with diameter 6Å.
To obtain Young’s modulus of the GeNW, we let the system to evaluate in NVT ensemble by using Nose-Hoover thermostat \[^{42}\] for control temperature at 300 K for all simulations. Then, by applying tensile loading (by constant velocity 0.1 Å ps \(^{-1}\)) to one end of GeNW along longitudinal axis. The other end was fixed during simulation time. For evaluating the stress on the GeNW, it needs to calculate stress on the individual atoms according to equation (7),

\[
S_{ij} = m v_i^2 v_j^2 + \frac{1}{2} \sum_{n=1}^{N} \left( F_{i}^{n} F_{j}^{n} + F_{j}^{n} F_{j}^{n} \right)
\]

where \(i\) and \(j\) indicate \(x, y, z\). The first term is kinetic energy contribution for atom \(i\). The second term is pairwise energy contribution where \(n\) loops over the neighbors of atom \(i\). Also \(r_{ij}\) and \(r_{j}^n\) are the positions of the 2 atoms in the pairwise interaction, and \(F_i\) and \(F_j\) are the forces on the 2 atoms resulting from the pairwise interaction. After calculation of \(S_{ij}\) for each atoms (here \(i\) and \(j\) are \(z\)), because longitudinal axis of nanowire placed on \(z\) axis), we sum \(S_{zz}\) over all atoms in nanowire and then divided by nanowire volume to get stress on nanowire. Also, strain is equal to multiplication of velocity to elapsed simulation time. From slope of elastic region of stress-strain curve, Young’s modulus was obtained. The result of calculations will show in next section.

Now, to evaluate thermal conductivity of GeNW along longitudinal axis of nanowire, we have used Fourier’s law (\(\kappa = \kappa_{x} \frac{dl}{dz}\)). To generating temperature gradient and steady state of heat flux, we fixed two region at both ends of GeNW with 1nm width by setting zero force and velocity on those atoms. Then two other regions with same width in near fixed regions were selected as hot and cold regions. By applying NVT ensemble to the hot and the cold regions for 1ns, temperature of the hot and the cold regions were kept at 330 and 270K, respectively. After that, by averaging over 1ns, in the layers (with 1nm width) between the hot and the cold regions, the temperature gradient and heat flux were calculated.

**Results and discussion**

The Young’s modulus and Thermal conductivity of GeNW were determined using NEMD simulation in different conditions of crystal defects.

**Young’s modulus**

At first, we produced 1%, 4% and 7% point vacancies by removing Ge atoms within NW randomly. Then, the stress was applied along the axis of GeNW. The obtained stress-strain curves for GeNW including point vacancies were plotted in figure 2 for strain rate 0.1 Å ps \(^{-1}\) in the [100] orientation. As shown in this figure, both of failure point and fracture stress have been decreased with increasing vacancy percentage. We plotted stress-strain diagram in the figure 3 for linear vacancies. Three lengths of linear defects (50, 110 and 170 Å) were considered for simulation.

Both of the figures are relevant to [100] crystallography direction along NW axis. The slope of initial region (elastic region) of stress-strain curve obtains Young’s modulus. As seen in the figure 2 by increasing point vacancy defect the slopes of the curves diminish. So, by increasing defects, the GeNW becomes softer. On the other hand, we defined simple linear vacancy at figure 1. The stress-strain curve for linear vacancy was shown at figure 3 for [100] orientation. When length of linear vacancy is larger, it leads to a slightly larger fracture strain.
without a noticeable alteration in the failure point. Also, we explored Young’s modulus for both types of defects and [100], [110] and [111] crystallography directions. The results were plotted in the figures 3 and 4. As can be seen, both of defects lead to reduction in Young’s modulus. This behavior is common in nano-sized systems such as graphene [43, 44]. The rate of Young’s modulus reduction in the case of point vacancy defect was larger than that of the linear vacancy defect model. Decrement in Young’s modulus were about 27% and less than 5% for the point vacancy and the linear vacancy defects, respectively. Moreover, the effect of crystallography directions on Young’s modulus was studied. The results of non-equilibrium molecular dynamics have shown that [100] and [111] crystallography directions have the smallest and largest values, respectively [45] (figures 4 and 5).

The results of our work in compare with pervious researches
Vuong V et al are used first-principles DFT calculations to investigate the mechanical and electronic properties of the Si, Ge and Ge-core/Si shell NWs, along the [100] direction within the cross sectional size of 1.0 nm and 1.4 nm under the axial strain [46]. They found a fracture strain about 35% for Ge nanowire with 1.4 nm and a reduction of a fracture strain with increase of radius. In our study the radius of NW is 2 nm and the obtained fracture strain is about 20%, so our results are in good agreement with this research. Based on several empirical potentials, Kang and Cai [47] have used the molecular dynamics simulation to investigate the brittle and ductile
fracture of the Si and Ge NWs based on Tersoff potential. The nanowire has diameter 5nm and length 50 nm, (in our work radius is 2nm and length 20 nm). The fracture happen in a fracture strain about 35% that have a good agreement with our results. Theoretical calculations with real-space pseudo potentials constructed within density-functional theory are employed to calculate mechanical and electronic properties for [100], [110], and [111] germanium nanowires up to 2.7 nm in diameter [48]. They found the Young’s module of 100, 140 and 150 GP for [100], [110] and [111] direction respectively. That are in good agreement with our results. Ma et al investigate the mechanical properties for Si and Ge NW using DFT calculation and experiment [49]. Their results show the fracture strain of Ge NW happens about 30% employing DFT calculation and about 8% in experimental. The results for fracture strength and fracture strain are in good agreement with our study. Also the results of pervious MD study using Tersoff potential are in good agreement with DFT calculation. Comparison our results and experimental results show the fracture stress is somewhat higher than the existing experimental estimates (between 5–15 GPa) [48–50] and has a fracture of 4%–10% [49, 51]. This may be attributed to two reasons. First, the NW in this simulation contains no surface defects whereas grown NWs may have surface roughness [52, 53] that can reduce the fracture strength. Second, the imposed strain rate in this simulation is several orders of magnitude higher than that in real experiments. This is due to the fundamental limitation on the time scale of MD simulations. Given these two reasons, the high fracture strength predicted by this simulation is not very surprising.
Table 2 shows the Mechanical properties of SWCNT, SiNW and GeNW. According to table 2 the Young’s modulus of SiNW is higher than of GeNW, while its fracture strength is typically lower than of GeNW. The Young’s modulus of SWCNT is about 10 times higher than SiNW but fracture strength of SWCNT is in order of Si and Ge NWs.

| Material          | Elastic modulus (GPa) | Tensile strength (GPa) | Failure strain (%) |
|-------------------|-----------------------|------------------------|--------------------|
| SWCNT/MWCNT [54]  | 1000                  | 11−63                  | 5−12               |
| Si NW             | 187 [55], 210 [56], 158 [57] | 12 [58]               | 7                  |
| Ge NW             | 106,112 [59]          | 18 [60], 15 [59]       | 15,17 [60]         |

Figure 6. Thermal conductivity of GeNW, (a) for point vacancy defects and (b) linear vacancy defects.

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Thermal conductivity
Another property that were extracted here, is thermal conductivity along longitudinal axis. As mentioned in the computational method section, after generating a temperature gradient and steady heat flux across longitudinal axis of GeNW, we have averaged temperature in middle layers and heat flux for 1ns and then calculated thermal conductivity from Fourier’s law. Influence of both types of defect as well as crystallography directions were explored. Same as Young’s modulus, point vacancy defect has greater effect on thermal conductivity than linear vacancy defect. This is because of phonons passing through GeNW can more scatter than from linear vacancy defect. As shown in figure 6(a), when 8% point vacancy defect was generated, thermal conductivity dropped over 85% in comparison to the perfect case for three orientations. On the other hand, for linear defect, maximum of 28% reduction in the thermal conductivity was observed (figure 6(b)). These findings should help engineers to tune these quantities for their own applications.
There is another notable point in magnitude of thermal conductivity versus crystallography orientation. As it was seen in figure 6 for \{110\} orientation thermal conductivity was larger than others and \{100\} orientation was less than any other direction.

The obtained thermal conductivity is one order of magnitude smaller than bulk-Germanium. The nanowire with the largest cross section has the largest phonon mean free path as the surface to volume ratio decreases. The smaller cross-sectional areas increase the surface to volume ratio, so that more phonons are diffusely reflected at the surfaces. Since the phonon mean free path is significantly reduced in smaller wires, so thermal conductivities are also much less [61]. Since the length of nanowire in our study is much less than the phonon mean free path of bulk Ge, which is about 300 nm at 300 K, the nanowire length dramatically reduces the effective phonon mean free path in the nanowire, which reduces its thermal conductivity.

Conclusion

We have tried to explore thermal and mechanical properties of germanium nanowire with vacancy defect including point and linear defects. The obtained results in both defects show that the Young’s modulus and thermal conductivity decrease with increasing defect percentage. We saw the effect of crystallographic orientations \{100\}, \{110\} and \{111\} on the properties. Simulation results showing point defects in comparison with linear defects have a greater effect on thermal conductivity and Young’s modulus. These results can be useful in development of Li-batteries and tune these quantities for nano-sized systems. Further studies are necessary to determine the effects of these defects on other thermal and mechanical properties for application of GeNW in nanotechnology.

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