Effect of silicon dopant on mechanical properties of monolayer graphene

V K Majeti*, A Roy, K K Gupta and S Dey
Department of Mechanical Engineering, National Institute of Technology Silchar, India
E-mail: vamsimajeti10@gmail.com

Abstract: The exceptional qualities of graphene have drawn the attention of many researchers and scientists. It has exhaustive real-life applications, ranging from mechanical and medical domain to electronic fields. The significant properties of graphene can be tailored by chemical functionalization methods. By incorporating foreign atoms, the properties of pristine graphene can be modified. Molecular dynamics (MD) simulations are carried out to conduct tensile tests on square-shaped graphene doped by silicon. The fracture strength, failure strain and Young’s modulus are measured on graphene doped by silicon. The carbon atoms in the graphene sheet are replaced randomly with silicon atoms for this simulation and the variation of mechanical properties are observed by comparing with the pristine form of graphene. The properties such as Young’s modulus, fracture strength and failure strain are found to reduce with the increase of doping intensity. During chemical vapour deposition (CVD) method as silicon atoms are likely to replace the carbon atoms, it may promote the electronic properties but in the present study, it is found to decline its mechanical properties due to increase in silicon doping concentration. As a result, it is therefore suggested to consider the effect of silicon dopants in the applications of graphene.

Keywords: Graphene, molecular dynamics, LAMMPS, silicon dopant.

1. INTRODUCTION

The discovery of new materials is generally sought for gaining new age of applications over time. The furtherance in upcoming fields of research and solutions to problems of ongoing research can be overcome by the development of such new materials[1]. Out of all, only a few materials are gained significant attention in various fields of applications. Graphene is one of such materials which has exciting and remarkable attributes such as its 2D structure of one carbon atom thickness, lightness with exceptional electronic and mechanical properties[2,3]. This uniqueness in characteristics led graphene to the forefront of material science[1]. Graphene as the pristine form is a monolayered structure with a periodic and uniform arrangement of carbon atoms in a hexagonal honeycomb-style[4]. This sp² bonded aromatic structure of graphene results in an immense strength of about two hundred times the strength of steel[1]. Earlier, it is presumed that graphene does not exist due to its instability concerning the formation of curved structures such as fullerene, nanotubes but various attempts were made to produce the graphene sheet [5]. Despite such attempts, the first successful method is mechanical exfoliation where in the planar few-layer graphene(PFLG) is synthesized.

Graphene is regarded as a promising material by industrial and academic researchers[6] which attracted a wide area of applications such as NEMS, nano-electronics, nanocomposites[5,7], electrodes and chemical sensors[5]. Electronics devices is another major application due to its linear current-voltage characteristics and sustainability at huge currents(>10⁸ A/cm²). Shen et al. [8]
explored the application of graphene in the biomedical field ranging from drug/gene delivery, biological sensing and antibacterial materials to biological imaging. Perreault et al. [9] stated that owing to its single carbon atom thickness, graphene has the specific surface area of 2630 m$^2$/gram, which is very high, thus making it best candidate for processes containing adsorption. Also, the efficiency of conventional photocatalytic materials can be enhanced by composites of semiconductors and graphene. Graphene can also be used in electrochemical energy devices like fuel cells, metal-air batteries and biosensors [10].

An ample amount of techniques are carried out for the synthesis of graphene since the first successful attempt. Novoselov et al. [11] extracted few layers graphene films from graphite by mechanical exfoliation process to perform a study on electronic properties of few-layer graphene (FLG). This extraction method is defined as a highly reliable process and graphene as the best possible metal for metallic transistor application. Reina et al. [12] presented an economic way of producing graphene. They synthesized a continuous graphene film from single layer to few layers by ambient pressure chemical vapour deposition (CVD) method on evaporated polycrystalline Ni. This method gives the flexibility to transfer the produced graphene sheets to different substrates. Apart from these methods, graphene can also be produced by chemical reduction and electrochemical reduction methods. Stankovich et al. [13] used graphite oxide (GO) to produce graphene sheets. Graphite oxide is exfoliated into individual graphene oxide sheets followed by chemical reduction, produced graphene sheets. Shao et al. [14] stated the electrochemical method of producing graphene as the green strategy. They produced graphene sheets by electrochemically controllable reduction of graphene oxide and observed that the properties are quite different from chemically reduced graphene. It is also stated that the graphene produced by this method enhances the activity in the applications of energy storage, biosensors and electrocatalysis. Schniepp et al. [15] presented a process to produce bulk quantities of graphene sheets by an optimized combination of graphite oxide and thermal treatment. Individual graphene sheets are split from graphene oxide by extreme rapid heating of completely oxidized graphite. Strupinski et al. [16] developed a method for chemical vapour deposition of graphene on SiC substrates.

Experimental studies on graphene have been done extensively. For instance, Lee et al. [17] measured the elastic property and failure strength of a graphene membrane by nano-indentation in an atomic force microscope. These results established graphene as the strongest material ever. Tsai et al. [18] investigated Poisson's ratio, shear modulus and Young’s modulus of the graphene layer and graphite flakes (containing several graphene layers) using molecular dynamics simulations. The results showed that graphite flakes exhibit lower moduli than graphene. Robertson et al. [19] reported on advances in atomic resolution imaging of graphene. It was observed that the structure of graphene has deviated from the pristine form. The vacancy defect, impurity dopants and edges are also explored. Zandiatashbar et al. [20] presented work on the effect of sp$^3$-defect and vacancy defect on the pristine form of graphene. The results showed that elastic modulus in graphene is maintained at sp$^3$-defect however failure strength is decreased by 14% only. Unlike the sp$^3$-defect, vacancy defect produced a considerable drop in the mechanical properties of graphene. Huelmo et al. [21] reported that silicon dopants from the substrate replace the carbon atom in the graphene more preferably thus creating new material.

From this section of the study, the importance of graphene is illustrated and it is observed that plenty of studies are conducted on graphene in both theoretical and experimental ways. The properties of graphene can be modified by doping with foreign material like silicon as it is observed that silicon atoms in SiC substrate are likely to replace the carbon atom positions in graphene in CVD method[21]. Considering these statements as the purpose of the present study, the effect of doped silicon atoms on the mechanical properties of the graphene sheet (employing MD simulation by intentionally incorporating silicon atoms at random positions of carbon atoms in monolayer graphene sheet) is examined. The subsequent detailed discussion on simulations and quantitative comparison of
mechanical properties of silicon doped graphene with pristine graphene is reported.

2. MODELLING AND SIMULATION

Molecular dynamics is a versatile technique in estimating deformations, temperature effects and failure mechanisms[4]. This section describes the methodology adopted for atomic simulation of pristine and doped graphene sheets. In the present study, Young’s modulus, fracture strength and failure strain are investigated by performing atomic simulations on the system. The non-equilibrium molecular dynamics simulation approach is adopted to determine the mechanical properties of the system. Tersoff potential is chosen to define the inter-atomic energy between C-C and Si-C atoms. Accuracy of the system’s behaviour depends on the potential file.

Molecular dynamics is a computer simulation process that analyzes the physical movement of atoms in the system which has an interaction over a defined period of time. It uses classical mechanics to define the movement of atoms.

\[ F_i = m_i \frac{\partial U}{\partial r_i} \]  

(1)

Here, \( F_i \) is the atomic force acting on the atom \( i \) and is defined by the derivative of inter-atomic energy \( U \) which is defined in potential file stated above. MD is a cyclic process in which the state of an atom at the previous time step is used to determine the state of the atom during next time step. Tersoff style potential represents three-body potential between atoms that define interatomic energy as

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

(2)

Where, \( V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})] \)  

(3)

Here \( V_{ij} \) is the potential energy of the system. \( f_A \) and \( f_R \) represent the attractive and repulsive pair potential respectively while \( f_C \) represents the cut-off function. This further calculates the energy of all the surrounding atoms of atom \( i \) within the cutoff radius. \( b_{ij} \) represents bond coefficient and \( r_{ij} \) is the interatomic distance between atom \( i \) and atom \( j \). \( f_A \) and \( f_R \) are defined as

\[ f_R = A e^{-\lambda_2} \]  

\[ f_A = -B e^{-\lambda_1} \]

where \( A, B, \lambda_2 \) and \( \lambda_1 \) are the parameters of two-body interaction.

A square-shaped pristine form of graphene (Figure 1) with an edge length of 7.2nm comprises of 2040 carbon atoms is created in VMD(visual molecular dynamics)[22] software. The model is then exported to Avogadro software[23] where the carbon atoms at random positions are replaced by silicon atoms. Doping concentration is defined as the percentage of carbon atoms replaced by silicon atoms in a pristine graphene sheet. A widely used molecular dynamics simulation software LAMMPS(Large-scale Atomic/Molecular Massively Parallel Simulator) [24], developed by Sandia laboratories is adopted to carry out the simulations. Metal units are chosen and periodic boundary conditions are applied in all the three-dimensions. A timestep of 0.001 ps (picosecond) is chosen for each iteration of the simulation. The first and foremost step after importing the model to LAMMPS, is the minimization of the total energy of the system, carried out by conjugate gradient (cg) method. The system is then equilibrated using Nose Hoover thermostat[25,26]. The temperature of the system is maintained at 300K throughout the simulation. Conditions for uniaxial deformation are maintained by Nose Hoover thermostat and barostat and a strain rate of 0.001/ps(iso-strain method) is applied in the armchair direction of the system. OVITO(Open Visualization Tool) [27] is utilized to visualize the simulations.
3. RESULTS AND DISCUSSION

3.1. Validation of the model
The present model of graphene is validated by the reports of previous studies on the pristine form of graphene at 300K. In this regard, molecular dynamics simulations are carried out using the Tersoff potential of SiC to determine Young’s modulus, fracture strength, failure strain of the graphene. The results came out to be in good agreement with the past literature[28-30] as furnished in Table 1.

Table 1. Validation for the mechanical properties of a pristine SLGS

|                        | Fracture strength (GPa) | Young’s modulus (TPa) | Failure strain |
|------------------------|-------------------------|-----------------------|----------------|
| Ni. and Z. et al. (Tersoff-Brenner)[28] | 180.0                   | 1.13                  | 0.3248         |
| Ansari et al. (MD Tersoff-Brenner) [29]   | 123.0                   | 0.79                  | 0.2330         |
| Zhang and Gu (MD AIREBO) [30]            | 115.9                   | 1.09                  | 0.1380         |
| Present study (MD Tersoff)                | 210.3                   | 1.15                  | 0.3223         |

3.2. Mechanical properties of pristine and silicon doped graphene
Simulations are carried out on pristine and silicon doped graphene sheets at a strain rate of 0.001/ps. During this, stress vs strain curves were plotted for all the doping concentrations as furnished in Figure 2. From these stress vs strain curves, fracture strain, fracture strength and Young’s modulus are extracted for the study. Figure 3 describes the dependence of the properties on doping concentration.

Figure 2. Stress-strain curve of monolayer graphene at various doping concentrations.
From Figure 2, the linear relationship between stress and strain can be observed up to certain lower values of strain. So, the young’s modulus at 2.5% strain is considered for the present study. Yielding of the pristine graphene starts at 25% strain where the stress is almost constant while the strain increases considerably. Young’s modulus of pristine graphene is 1.15 TPa and the fracture strength and failure strain are 210.3 GPa and 32.23% respectively. It is revealed that fracture strength and failure strain are dependent on doping concentrations of Si. A significant decrease in failure strain and fracture strength is observed compared to its pristine form. It is noticed that the yield area covered by the doped graphene is relatively less and the material has failed at a strain value much lower than the failure strain of pristine form.

Figure 3 shows the variation of fracture strength, failure strain and Young’s modulus with doping concentrations. At 0.5% doping concentration, the fracture strength and failure strain decreased by 16.78% and 25.78% respectively but as doping concentration is increased further, the similar rate of reduction is not observed. At 2% doping concentration, fracture strength and failure strain are decreased by 21.9% and 29.25% respectively. A decrease in Young’s modulus is noticed with the increase in doping concentration. At 2% concentration, Young’s modulus is reduced by 12%. So, it is inferred that by incorporating silicon atoms, graphene sheet became much softer and weaker.

4. CONCLUSIONS

In the present study, the effect of doped silicon atoms on the mechanical properties of the square-shaped graphene sheet is examined. MD simulations are carried out to perform the tensile tests on monolayer graphene at 0.5%, 1%, 1.5%, 2% silicon doping concentrations. The sheet is loaded at a strain rate of 0.001/ps in armchair direction. Variations in fracture strength, failure strain and Young’s modulus are plotted against silicon doping concentrations. The results indicated a significant change in the properties of graphene with doping. As the doping concentration is increased, a decrement in the properties is observed.

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