Integrating Silicon In Armchair Graphene Nanoribbon For Solar Cell Applications

Preetika Sharma\(^*\) and Gaurav Sapra\(^1\)

\(^1\)Assistant Professor, UIET, Panjab University, Sector 25, Chandigarh, INDIA-160025
* preetikamadhav@yahoo.co.in

Abstract. Solar power is not only free but also infinite and use of solar energy indeed has many advantages. Thus, solar technologies are greatly studied for producing low cost and better versions of existing devices that can be integrated in the existing photovoltaic (PV) systems. Many such devices like the solar powered curtains and clothes, cases for laptop and other electronic products are being produced. Silicon today is of course being used rapidly as a PV material for solar cell. However, a continuous effort has been made to use graphene for high efficiency solar cell applications and its use. Graphene on the other hand, is not very good at collecting the electrical current produced inside the solar cell but researchers are looking appropriately on this material. Many ways to modify graphene for this purpose are being studied. Solar cell requires semiconductor materials for exhibiting photovoltaic effect. As graphene is zero band gap material, hence, armchair graphene nanoribbons (AGNR) that are semiconducting are being looked up for solar cell applications. Therefore, in this present work, various attempts have been made to investigate the electronic bandgap by using AGNRs in solar cells. The in-depth analysis of electronic properties has been done where band structure, density of states and geometrical stability on the basis of transmission of energy has been examined. Further, AGNR doping with silicon has been performed in which we have replaced the carbon with silicon. Initially, we started with one-silicon atom as a dopant and then went upto 4 silicon as dopant and the variations has been compared. Thus, through fine analysis, the use of doped AGNRs in solar cells is investigated.

Keywords: AGNR, Pristine Graphene, Solar Cell

1. Introduction

Solar energy is an economical, abundant and a sustainable source of energy. Solar energy systems rely on solar cells. Solar cells are made using pn junction made by a crystalline material such as silicon, germanium, gallium arsenide etc. These cells are connected in series to form an array of PV systems. They convert sun energy into electrical energy. These PV systems are a lot beneficial as they save a lot in electricity expenses as well as they are promoting green environment. This helps in reducing global warming. The materials required for solar cell must have high electrical conductivity and should be highly transparent. However, metals have high conductivity but they are not transparent. High transparency is needed to allow maximum light absorption so as to convert photons to electrons\(^[1]\). Semiconductors are the materials that are used in solar cell applications. These materials directly convert the light into electricity. The current is carried by either holes or electrons. Also highly doped semiconductors are transparent. They have bandgap. But for transmission of visible range, the value of bandgap should be greater than 3eV. This can be achieved in silicon. However, the transparency of silicon is a hindrance and hence, searches for better materials are needed. Thus, how good a semiconductor will perform as solar absorber or a collector, the study is governed by its bandgap.

Since last ten years, a lot of effort has been put on the PV applications. Much research and enhanced
development has been focused to find new materials and enhanced cell structural designs. In particular, scientists and research organizations are searching materials that are similar or better performers than silicon semiconductors and its compounds (in its various types, namely, mono crystalline, polycrystalline, and amorphous silicon). However, as silicon is easily available in abundance and therefore its cheaper in terms of production and fabrication, there is a lot more to know about new materials that will replace them in PV industry. Some of the new materials searched include organic diodes, semiconductors, graphene and its composites, thin-film semiconducting materials that include CdTe etc. The main area of focus is on the novel material called graphene. It is made of carbon atoms that are arranged in the form of hexagonal lattice [2,3]. It is not only a strong material but also completely transparent making it perfect for absorption of light and used for solar cell applications.

The evolution of solar cells technologies is usually divided into three generations [4]. The first generation consist of mono crystalline/ polycrystalline silicon wafers. The second generation is on thin-film semiconductors that include the amorphous silicon such as CdTe, CIGS etc. The third generation of solar cells consist of new materials that result in very cheap fabrication cost and production expenses. This generation thus yield high efficiencies and consist of dye sensitized solar cells (DSSCs), multijunction solar cells (MJSCs), organic solar cells (OSCs), quantum dot sensitized solar cells, perovskite solar cells (PSCs) etc. The classification of solar cells discussed is shown below in Fig. 1.

![Classification of solar cell](image)

**Figure 1.** Classification of solar cell

**Graphene Nanoribbons (GNR) based solar cells:**

Graphene has good and potential applications in high-performance electronic devices, circuits such as photosensors, and smart applications. It has great electronic properties that include high carrier mobility, high carrier saturation velocity, excellent thermal conductivity, high mechanical strength, transparency, good thickness, and flexibility and versatility. This all makes graphene a great choice for advanced future applications. One such strongly needed application in future that whas become the need of the hour is the use of solar energy rather than conventional energy. For this, new solar cell technological design are needed [4]. In particular, as graphene has a unique integration of many properties such as high electrical conductivity and high optical transparency in visible and near-infrared regions, this gives it the tremendous ability to be used as the active layer for many metal and semiconductor junction based solar cells. Not only this, it is also reported that graphene solar cells have been also fabricated on various substrates. The commonly used are the silicon and compound semiconductors like cadmium disulphide. Further, many heterojunction photovoltaic devices have also been fabricated in form of nanowires where good
efficiency has been achieved. This has been made possible by using the combination of one-dimensional (1D) structure and physical characteristics of 1D nanowires. Graphene nano ribbons (GNRs) were also introduced as a theoretical model and it was examined through its edge and nanoscale size effect [5]. As electronic components are becoming ever smaller, the industry is gradually approaching the limits of what is achievable using the traditional approach with silicon as a semiconductor material.

Graphene nanoribbons (GNRs) are extremely amazing new materials that are being used for variety of applications. These applications range from electronic to thermoelectronic uses. They have tremendous role in mechanically robust thin films, high efficiencies in various devices, capacitors, nano batteries, photo detectors, diodes, transistors, integrated circuits and many more [6]. Among all the applications, the highest potential is seen in the feature of GNR is the tuneability. It can change its properties and can modify to perform more applications. These properties are a function of their precise atomic structure. Hence, it is important to exploit the GNRs to the fullest. Their two basic edge structures, namely zigzag and armchair, and these edge structures have been intensively studied and it is seen that their electronic and magnetic depend on the structure. The difference between the electronic property of zigzag and armchair GNRs has been reported. It is reported that the band gaps of zigzag GNRs are smaller than those of armchair GNRs, and the band gap increases with increasing size of the GNR [6]. Armchair nanoribbons show width-dependent band gap and also the band gap produced is inversely proportional to the width of the GNR.

2. Computational Work

This work includes the calculation of the structural properties and equilibrium geometries of GNRs both pristine and doped. This study is based on the first principle calculation that is based on density functional theory [7-8]. An AGNR is taken first as pristine and then silicon as dopant is substituted. The concentration of silicon dopant is varied for 2%, 4%, 6% and 8%. The pristine structure and doped structures are shown in Fig 2(a-e). All geometrical structures are optimized by using density functional theory (DFT). Each carbon and silicon atom in the structure is relaxed at less than 0.05 eV/Å³. The electronic properties for pristine and doped AGNRs are studied using Atomistix Tool Kit (ATK). The local density approximation (LDA) is used in order to represent the exchange correlation potential. The Double Zeta polarized basis set has been chosen for all atoms when the geometries have been optimized. The structural systems are analysed with 1 × 1 × 10 uniformly placed K points. The cut off energy is 75 Hartree which is set for all the structures. All the carbon atoms on the edges are saturated with H atoms for stability in structures.

3. Results And Discussions 3.1 Structures of pristine and doped armchair graphene nanoribbons are shown in Fig 2 (a-e)

In order to investigate the behavior of pure and doped AGNR, it is very important to see and study the electronic properties of structures. For this, optimization of all geometrical structure of pristine AGNR along with its electronic properties that include the band structure, DOS and transmission spectrum are calculated. Fig 2(a-e) shows all geometrical structures in which the bond length between two carbon atoms is 1.42 Å and bond length between carbon and hydrogen atom is 1.10 Å. Further, the effect of silicon dopant on the electronic properties of AGNRs is investigated. All the AGNRs with different silicon doping concentrations are studied. The doping concentration is varied so that the energy gap of AGNRs can be engineered for various applications. Due to doping phenomena, formation of the carbon–silicon bond occurs. The carbon atoms in the ribbon are then replaced randomly in the structure with silicon atoms for the study. The variation of band gap, DOS, transmission spectrum and total energy are observed and then compared with the pristine AGNR. It is reported that silicon doping opens the band gap in graphene and increases its optical conductivity. Hence, AGNRs are seen promising materials for PV applications.
Figure 2. Optimised geometrical structure of a) pristine armchair graphene nanoribbon, b) one doped silicon armchair graphene nanoribbon, c) two doped silicon armchair graphene nanoribbon, d) three doped silicon armchair graphene nanoribbon and e) four doped silicon armchair graphene nanoribbon.
The geometrical stability of all the considered nanostructures of AGNR is investigated based on the total energy which is presented in Table 1.

**Table 1. Calculation of total energy for various structures optimized.**

| S. No | Structures | Total energy   |
|-------|------------|----------------|
| 1.    | Pristine   | -5867.549304   |
| 2.    | One doped  | -5885.620916   |
| 3.    | Two doped  | -5903.905452   |
| 4.    | Three doped| -5921.958995   |
| 5.    | Four doped | -5939.494712   |

The total energy of the optimized structure of any combination on the different AGNR systems is calculated. Further, on doping, the total energy increases in negative side, confirming the stability of the structures. Also not much change in total energy is observed which shows the structures are not much disturbed due to doping. The total energy is calculated as the sum of kinetic and potential energy for the structure. Strong interaction between AGNR and dopant is attributed to more value of total energy ($E_{\text{total}}$). In case of pristine, the total energy for pristine is -5867.549304eV/atom. The total energy calculations are done using the software VNL ATK. The pseudopotentials and basis set chosen is very crucial for energy calculations and it very much dependent on the elements included in your system whether its bulk or a molecule.

### 3.2 Band Structures

#### 3.2.1 Pristine Structure

AGNR provide continued miniaturization and performance enhancement in devices. We have investigated the electronic band structure of an undoped GNR [9-10]. It shows that a nanoribbon always show a gap in its electronic spectrum. A band gap of 1.2eV is observed. It is reported that a bandgap of 1.1 eV is capable of absorbing about 75% of the solar rays. Many polymers have bandgaps greater than 2 eV and hence they only harness about 30% of the photons which can be converted into electrons. Therefore, attempts are done to observe the ideal band gap needed for photovoltaic phenomena. Another important requirement is the need of direct band gap materials. In case of a material which has an indirect bandgap, there a photon and phonon both should take part in transition from the valence band to the conduction band. Due to this, direct bandgap materials show stronger light emission and better absorption properties. In this paper, we are observing electronic bandgap which is not only ideal for solar cell but also is a direct bandgap. Upon studying the pristine, we see for silicon dopant in AGNRs. We can observe that as silicon dopant is added, the band gap starts decreasing.
Figure 3. Band structure of a) pristine AGNR, b) 2% silicon doping in AGNR, c) 4% silicon doping in AGNR, d) 6% silicon doping in AGNR and e) 8% silicon doping in AGNR.
3.3 Density of states

3.3.1 Pristine Structure

![Figure 4](image_url)

**Figure 4.** Plot shows density of states in structures w.r.t energy (eV) for a) pristine structure, b) 2% silicon doping in AGNR, c) 4% silicon doping in AGNR, d) 6% silicon doping in AGNR and e) 8% silicon doping in AGNR.

Fig. 4(a) shows the calculation of density of states of AGNR for pristine structure. The plot show an energy gap around Fermi level. Introduction of silicon dopant in armchair graphene nanoribbon (AGNR) is done. As a result, metallic character is enhanced upon silicon doping which is seen in following plots. The plots
shown below gives the presence of more conduction bands justifying the enhancement of metallic character upon doping.

Fig. 4(b) shows the calculation of density of states of AGNR for 2% silicon doped structure. Here the dopant is added with the concentration of 2% silicon. It is seen in the plot that as dopant is added, the metallicity has increased. The presence of more states and also the widening of the states shows the increased conduction in the structure due to doping.

Fig. 4(c) shows the calculation of density of states of AGNR for 4% silicon doped structure. Here the dopant remains same but the concentration is now increased to 4%. It is seen in the plot that as dopant is increased from 2% to 4%, the metallicity also increases. Regarding the states and their widening, it has also conveyed the increase in the metallic character.

Fig. 4(d) shows the calculation of density of states of AGNR for 6% silicon doping. In this structure, the widening of the states is increased and also it is observed that the height of the transmission peak is also increased. From this observation, we can suggest increase in metallic character with additional doping concentration.

Fig. 4(e) shows the calculation of density of states of AGNR for 8% silicon doping. Here the dopant concentration is now increased to 8%. With widening of the states and increased height of the transmission peak, increased conduction in the structure can be seen. The high peak value shows highly transmission material structure.

3.4 Transmission Spectrum Analysis:

Finally, the transmission spectrum of pristine AGNR and silicon doped AGNR are obtained from DFT simulations. The transmission spectrum of the structures is shown in Fig. 5(a-e). As it can be seen from Fig. 5(a-e), the plots give variation of the transmission coefficient with respect to energy [10].

The transmission spectra are plotted to justify the level of transmission that can see in DOS plots. These transmission peaks indicate the transmission pathways that are available for transmission. They show the path for the charge carriers at different applied voltages. Fig. 5(a) shows the transmission in a pristine AGNR. As it can be compared with DOS, it is seen that a band gap is observed in the material.
Figure 5. Transmission coefficient w.r.t energy (eV) for a) pristine structure, b) 2% silicon doping in AGNR, c) 4% silicon doping in AGNR, d) 6% silicon doping in AGNR and e) 8% silicon doping in AGNR

Here, in Figure 5(b), through 2% silicon doping, the change in transmission has been obtained. The enhanced metallic character is seen as the silicon dopant is added in pure structure of AGNR.
Figure 5(c) shows the transmission plot for 4% silicon dopant in AGNR. The change in transmission has been obtained. The enhanced metallic character is seen as the silicon dopant concentration is increased.

Figure 5(d) shows 6% silicon doping in AGNR. The change in transmission obtained is seen.

Therefore, in all figures, we see that when AGNRs are doped with silicon, they do change their properties and characteristics. It can be noticed that passivated nanoribbons have more stable structure. The transmission clearly justifies the transition of semiconductor towards metallic state.

4. Conclusions and Future Scope

Solar cells appear to be more promising and show great potential while being used with new materials such as graphene or graphene composites. They are steadily being improved in terms of efficiency and parameters. The main challenge lies in finding suitable material which can provide ideal band gap as well as direct band gap for solar cell operation. So for this, the effect of silicon doping on band gap parameter is investigated. The variation in band gap parameter led to transition from semiconductor to metallic state. An ideal band gap is tried to achieve which is a direct band gap also thus fulfilling ideal conditions for solar cell operation. The electronic behaviour of graphene nanoribbon is seen through density of states and transmission spectrum. To make ideal solar cells, suitable materials are needed. Hence, the trajectory of these solar energy panels is upwards and the keep a room for further development.

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