

**FIRST PRINCIPLE CALCULATION OF ZIGZAG GRAPHENE
NANORIBBONS WITH TITANIUM AND ZIRCONIUM
TERMINATION**

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CERTIFICATE

This is to certify that this dissertation, entitled **First principle calculation of Zigzag graphene nanoribbons with Titanium and Zirconium termination**, is the authentic work carried out by **Mr. Vinay Kumar Kohli (2K13/NSE/11)** under my guidance and supervision in partial fulfillment for award of degree of **Master of Technology (M. Tech) in Nuclear Science and Engineering** by Department of Applied Physics in Delhi Technological University (Formerly Delhi College of Engineering), Delhi during the year 2013-2016.

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I, hereby, declare that the work being presented in this dissertation, entitled **First principle calculation of Zigzag graphene nanoribbons with Titanium and Zirconium termination**, is an authentic record of my own work carried out under the guidance of **Dr. Nitin K. Puri**, Asst. Prof. Applied Physics Department, Delhi Technological University (Formerly Delhi College of Engineering), Delhi. The work contained in this dissertation has not been submitted in part or full, to any other university or institution for award of any degree or diploma.

This dissertation is submitted to **Delhi Technological University** (Formerly Delhi College of Engineering) in partial fulfillment for the **Master of Technology (M. Tech) in Nuclear Science and Engineering** during the academic year 2015-2016.

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ABSTRACT

We have investigated the stability and electronic properties of zigzag graphene nanoribbons (ZGNR) with Titanium and Zirconium termination using density functional theory. Stability has been analyzed on the basis of binding energy, and electronic properties are analyzed by band structure and density of state. We found that termination of Ti and Zr could be used to enhance metallicity in ZGNR, interesting results was found in case of Zr both edge termination which shows the highest binding energy than all other configurations.

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NOTATIONS

e	=	electron charge
ϕ_0'	=	electrostatic potential
E	=	Electric field
γ	=	relativistic gamma factor
c	=	speed of light
Γ	=	gamma function

Chapter 1

INTRODUCTION

1.1 Introduction: The Carbon gets its name from Latin root 'Caro' means coal. Fourth element in periodic table, Carbon is one the element having unique electronic structure, which makes possible hybridization to build up sp^3 , sp^2 , and sp networks. It is non-metallic in nature, and its electronic configuration makes it available up to four electrons to form covalent chemical bonds with other configurations atoms and molecules. Carbon has three isotopes occurring in nature ^{12}C , ^{13}C and a radioactive one ^{14}C . Carbon has highest number of allotrope than any other elements, which are all different than one and another. These are diamonds, graphite, graphene, fullerenes etc.

Graphite an allotrope of carbon has been known from ages, which is a natural occurring crystalline form of carbon. Graphene has simplest structure of Carbon atoms, its 2-D honeycomb lattice structure and only one atom thickness makes it at the paramount of interest around the world. Owing to its perfect 2-D structure, theoretically, graphene acts as a building block for all the other allotropes of carbon like Graphite, Carbon nanotubes, fullerenes; It means graphene could be rolled to make a nanowire, these 2D sheets when piled up one on another and graphite could be made etc.

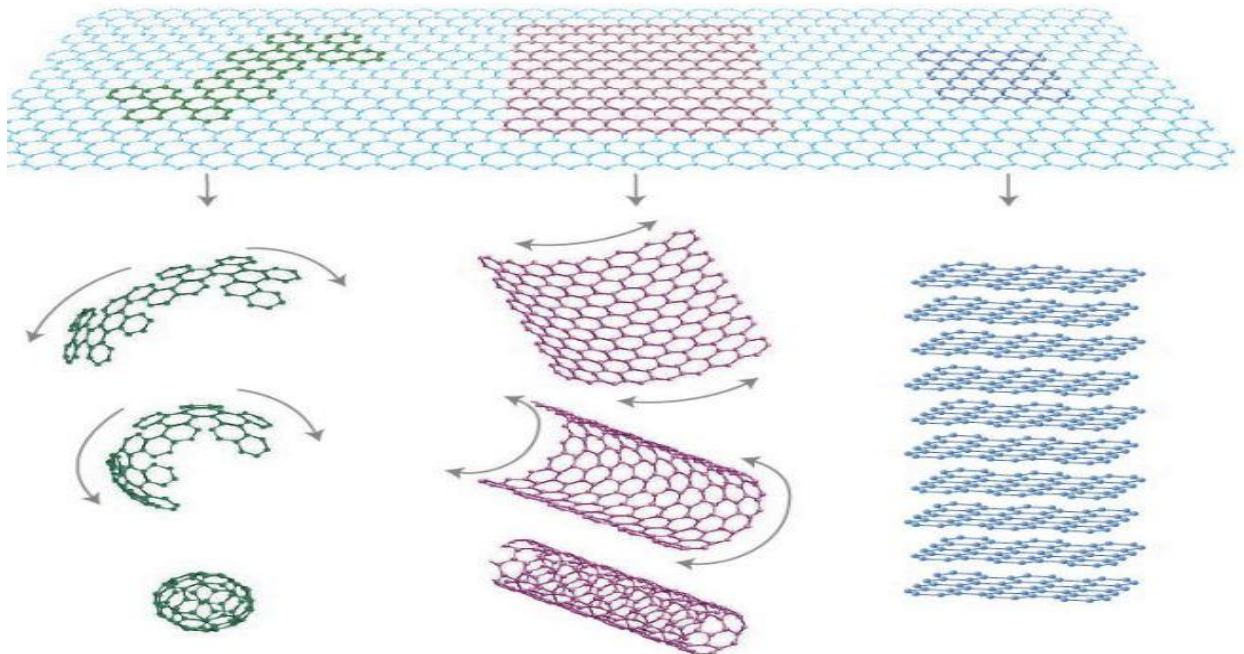


Figure 1 Graphene and other forms

The physical properties of graphite depends on its atomic structure, manner in which carbon atoms are arranged in 3-D, while its chemical properties depends on electron available in configuration for bonding with other atoms and structure. Graphite and diamond both are allotropes of carbon but have different atomic structure, which gives rise to different properties. In case of diamonds p-orbitals forms sp^3 bonds and in case of graphite forms sp^2 bond and a free electron is available. Graphite is nothing but graphene 2-D sheet stacked together, every sheet of graphite make Vander-walls bonds with another sheet. Carbon in graphene makes covalent bonds with other atoms showing sp^2 hybridization. The idea of perfect 2D material only one atom thickness goes back to half a century when the arguments given by Landau and Peierls in 1935 that a perfect 2-D crystal could not exist because it will be thermodynamically unstable. But in 2004 this belief was broken by the experimental discovery of graphene by giem et all. It was found that Graphene is stable and exhibits high crystal quality, and exceptional electronic properties.

Wallace et. all were the first to calculate the band structure of graphene in 1947. After that few properties of graphite has been studied but in 1991 Iijima et. all, made first carbon nanotubes in laboratory, which provides a new inspirations to researchers. Proper full time research in graphene was inspired after 2004 when Novoselov and giem rediscover the graphene nanoribbons, and studied the electronic and physical properties of graphene. Prior to this a little has been known about the electronic properties of graphene. This invention leads to 2010 noble prize in physics. With this Graphene has shown a great number of researches theoretical and experimental in this field. Some of important works includes new methods to modify the properties of graphene by termination of molecule, by insertion of atoms on graphene, growth of free standing graphene by Boehm et all, growth of graphene on metal surface epitaxial by Bommel et all. Exceptional physical and electronic properties of graphene are due to its special lattice structure. The band structure of graphene is unusual with the valence and the conduction bands meeting at a point at the six corners of the Brillouin zone near these crossing points these points are called Dirac points. As a result of the linear energy-momentum dispersion relation, at the Dirac points an electron has an effective mass of zero and behaves more like a photon than a conventional massive particle whose energy-momentum dispersion is parabolic. The tight-binding calculation of the band structure of graphene is based on Schrödinger equation. At low

energy levels, however, charge carrier transport can be described in a more natural way by using the Dirac equation.

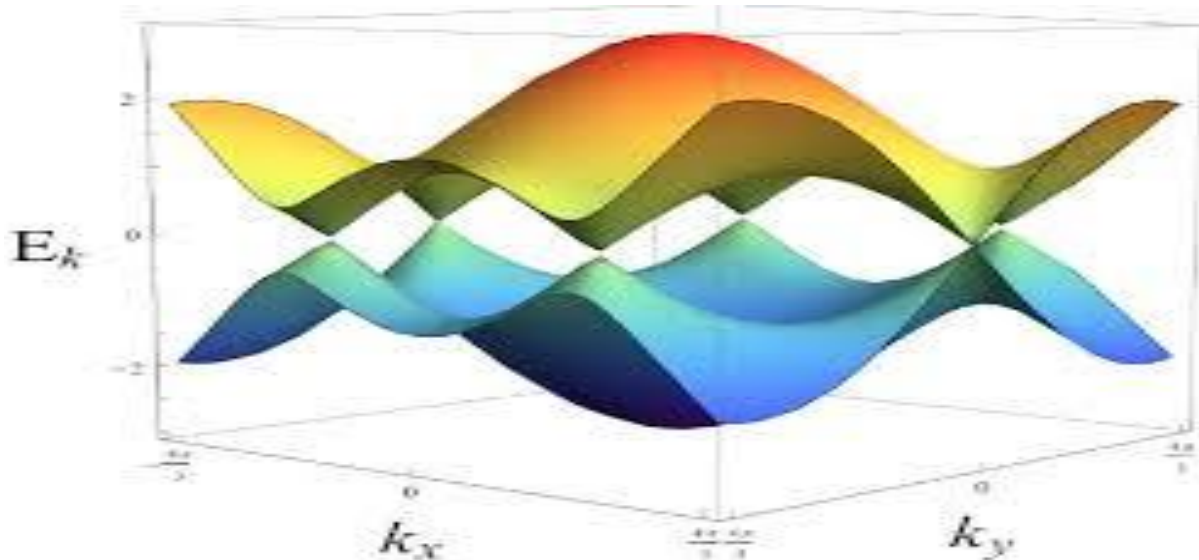


Figure 2 graphene BAND structure

These properties are very interesting that graphene has been enjoying the centre stage among all 2D material. To use graphene as building block in electronic industry we need to understand the I/V characteristics.

1.2 Characterisation of Graphene Nanoribbons: Carbon atoms in graphene are arranged in honey comb lattice, atoms makes sp^2 hybridization. Graphene nanoribbons are strip carved from graphene 2-d sheet. Lattice of graphene looks like two triangular sublattice, with carbon to carbon bond length of 1.42\AA . In its unit cell two carbons is attached with angle of 120° . Mechanical properties are due to contribution of one S orbital and two P orbital of carbon atom. Graphene sheet could be strip out in three ways namely Zigzag (0, n), Armchair (m, 0) and chiral (m, n). As shown in figure these three different kinds of edge state they have different electronic properties.

Zigzag GNR

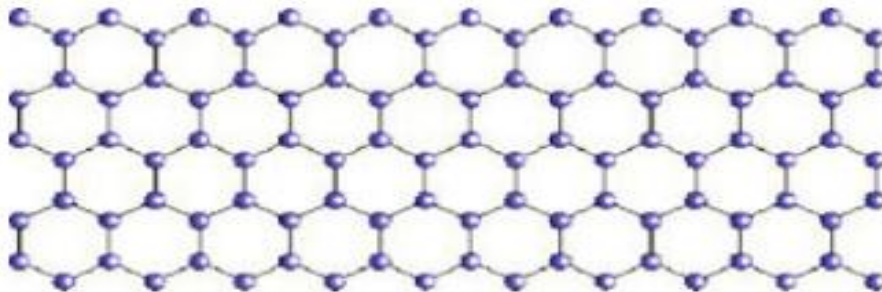


Figure 3 Zigzag graphene nanoribbons

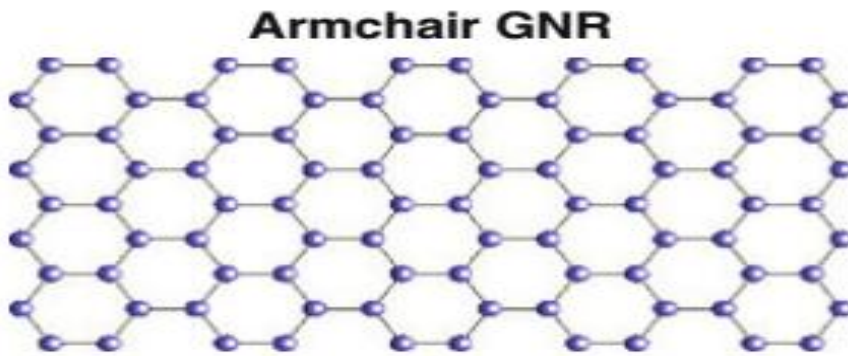


Figure 4 Armchair graphene nanoribbons

It is also observed that graphene has width dependent properties. Zigzag graphene nanoribbons are metallic in nature where armchair graphene nanoribbons could be semiconductor to half metal depending on termination. Band gap is found in AGNR where ZGNR has zero band gaps. These band gaps could be tailored as per need with different functionalization group, as transition metal which show vast opportunity in the field of semiconductor technology.

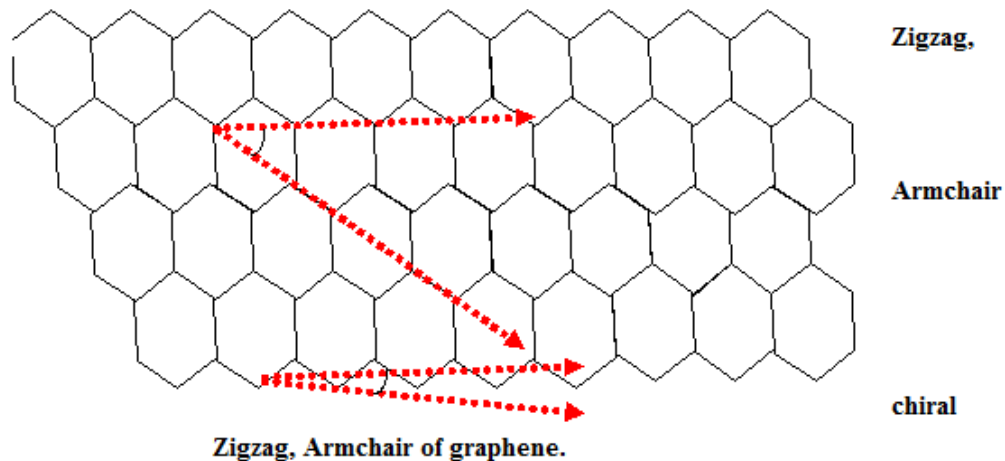


Figure 3 Graphene Honeycomb lattice

There are many characterization techniques to identify between zigzag and armchair graphene nanoribbons, some of these are given below.

1.2.1 Optical Microscopy: In Graphene discovery it is important to use suitable substrate material cause graphene is very sensitive in most of cases. SiO_2 is most common type of substrate used. In this silicon wafer deposited graphene adds a small optical path to the Fabry-Perrot created by the SiO_2 layer on silicon. By adjusting the thickness 90 to 300nm the reflected light

intensity is found maximum at 550nm. The short optical path added by graphene as thin as monolayer can easily be seen. The choice of substrate and its thickness is very important as even 5% change in the thickness of Si substrate could make it impossible to find the 2D structure. Other than Si wafer researchers has used other materials as Si₃N₄ and blue light, Si wafer and Al₂O₃ etc. It is seen that monochromatic light is suitable for optical contrast of graphene.

1.2.2 Atomic Force Microscopy (AFM): Atomic force microscopy is a powerful technique to verify the results from optical microscopy in case of graphene. AFM was one of the techniques used to verify that the flakes found optically were one atom thick monolayers of graphite. A single layer of graphene on crystalline layer graphene shows a typical of 0.4nm thickness in intermittent contact AFM mode. Although AFM is too slow and limited in lateral scan size to be used as a primary identification method and in spite of the extra apparent height, AFM soft imaging modes are the best to monitor the topological quality of substrate-supported graphene samples during the successive steps of device processing.

1.2.3 Transmission Electron Microscopy (TEM): The output of TEM is significantly improved than the optical microscopy. With new techniques to make graphene are used TEM has been very useful in its characterization. With the advent of colloidal methods to produce graphene sheets as well as improvement of device characteristics in unsupported graphene, TEM has been used as a structural characterization tool for suspended that can span magnification imaging as well as atomic scale details. Electron diffraction studies can be used to qualitatively distinguish a monolayer from a bi-layer.

1.2.4 Raman Scattering: Raman scattering is a fast and non-destructive technique useful in seeing the electron-phonon interaction, which implies a high sensitivity to electronic and crystallographic structures. It is very useful in structural investigation of carbon material and in particular nanotubes. In carbon materials Raman spectra shows similar features in the range of 800-2000 cm⁻¹ region, which is also of interest graphene.

1.3 Production of Graphene: The theoretical aspect of graphene was realized a decade ago, all it needed was experimental verification that it is possible to create it in laboratory. In 2004, a giem et. All were able to produce single layer graphene in laboratory. Which led to find new techniques to synthesize the graphene? Even though for more than a decade graphene has

been produced by mechanical exfoliation. One of the major challenge researchers are facing is that how to make high quality graphene for experiment. The production of high quality monolayers graphene is still a challenging job for researchers.

Among many methods for synthesis there's still a lot of work to be done, as we today all the techniques have some limitations. Even we could reduce the number of defects in the nanoribbons, yet these techniques are feasible for mass production. In 2004 Giam et al, produced graphene using mechanical cleavage method. This success has inspired many researchers around the world and new techniques to produce high quality mono layer and multilayer graphene has been found. These different techniques has there pros and cons. We want pure 2-d graphene because, it is seen that defects in graphene plays an important role in affecting the transport properties of electrons. Monolayer and multilayer graphene: there are many techniques used for the synthesis of monolayer and multilayer graphene. It is important to produce monolayer graphene as electronic properties need to be observed for different width of graphene. Some of methods which are used for synthesis are given here.

1.3.1 Mechanical Exfoliations: The good thing about Graphite is that its weak Van der Waals bonds make it easy to exfoliate graphene from it. With the force of $300\text{nN}/\mu\text{m}^2$ it is possible to exfoliate graphene; even an adhesive tape can give this much of force. When scotch tape is used to peel off the surface of graphite, a small layer of graphite is remain on the tape. After repeating this process many times few layer graphene could be produced. This technique is called scotch tape technique or mechanical exfoliation. This is the same technique used by Novoselov and Giam 58[1] for their research first time. Mechanical exfoliation has been used by many researchers around the world. The important thing about the technique is choice of substrate. It is found the Si/SiO₂ maximize the visual contrast for single layer graphene. Graphene in 300 nm SiO₂ is appeared to be yellow to bluish as the thickness of graphene is decreases. Thickness of 10nm gives the purple color contrast. One of the short coming of using mechanical exfoliation is that residue of glue remains in substrate, this effect the mobility of charge carrier in the substrate. This could be improved by baking in presence of hydrogen or argon at 200°C for an hour. This technique is well suited for research purpose as the graphene produced is few layers thick and still useful for scientific studies.

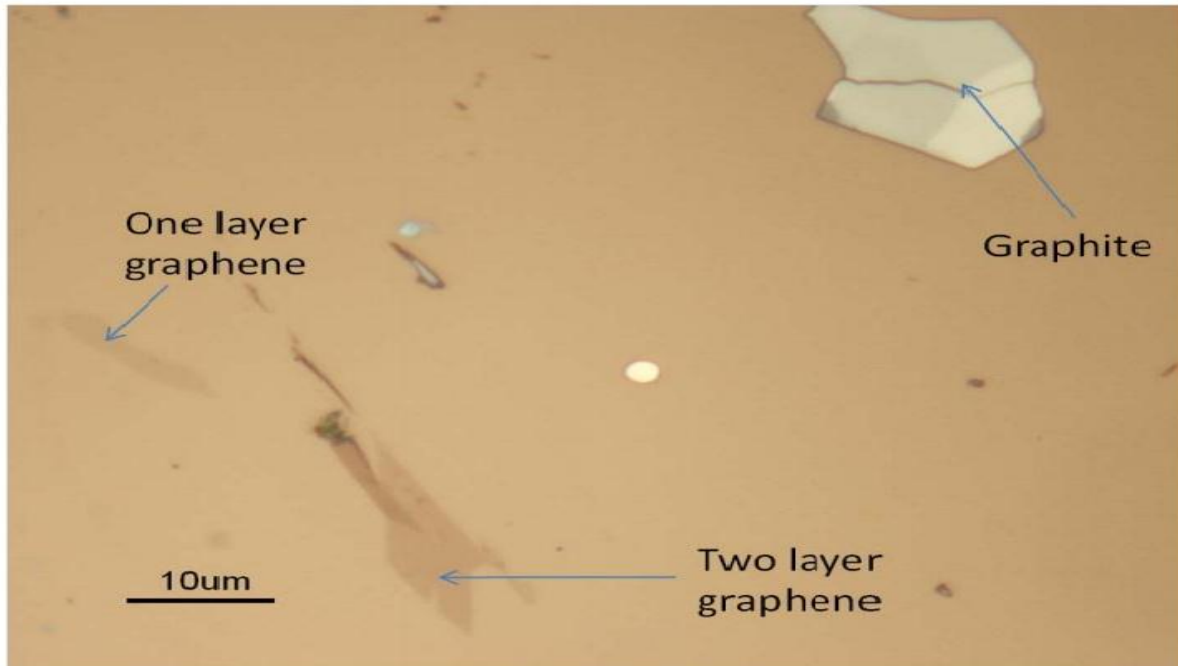


Figure 6 Mechanical exfoliation

1.3.2 Epitaxial Growth: In this technique monolayer graphene could be grown on a silicon carbide crystal. When silicon carbide is heated up to 1300 °C in vacuum, it goes through silicon sublimation, and graphitization. This controlled sublimation produces a graphene layer over the SiC wafer. Monolayer graphene grows on the Si side and few layers on the C side of the substrate. Yet these results may vary according to environmental conditions like temperature, pressure, etc. Temperature plays an important role to control the thickness of graphene. This technique is simpler than others. Even the quality of graphene produced is not very good. The electronic properties of few-layer graphene could vary because graphene grows simultaneously at different locations.

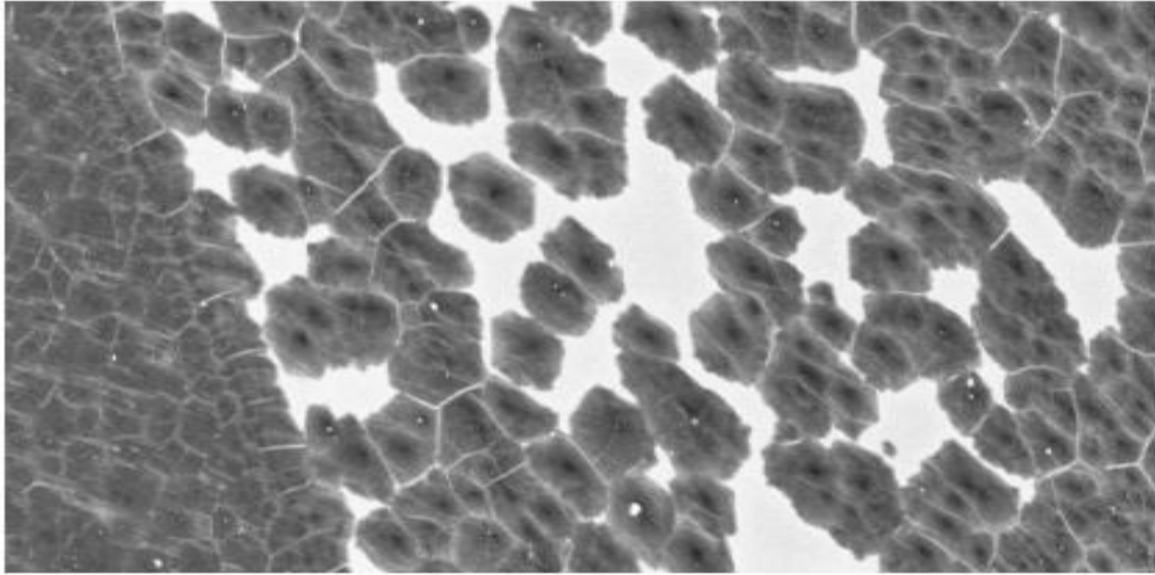


Figure 4 Epitaxial growth of graphene flakes

1.3.3 Chemical Vapour Deposition (CVD): CVD is most common method used for graphene production. In CVD, a gaseous mixture is directly came contact with substrate with heating gaseous particles are decomposes on substrate. Generally gaseous mixture of H_2 , CH_4 and argon is used at $1000^\circ C$ and Ni as wafer substrate. CH_4 decomposes on Ni and H_2 evaporates. Carbon diffusion takes place into Ni and after cooling it down a thin layer of graphene grown.

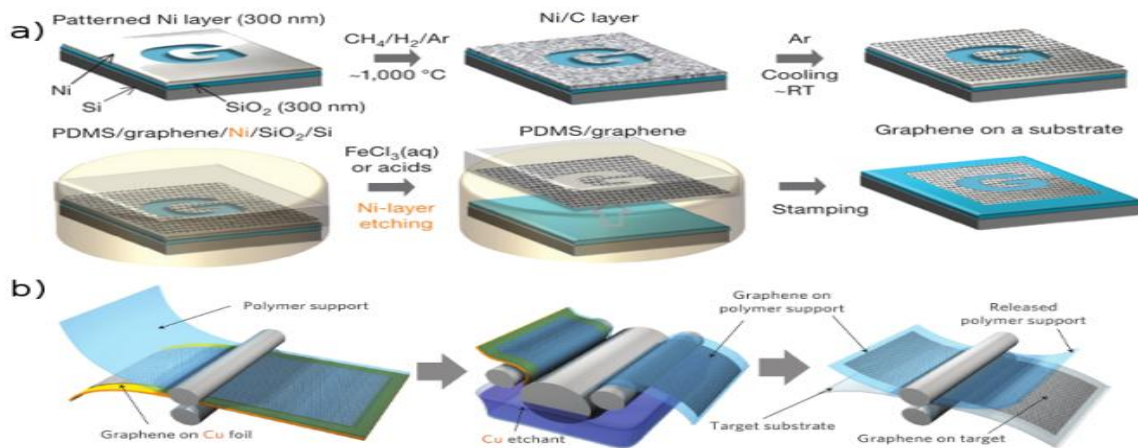


Figure 5 CVD methods

1.3.4 Graphene on Nickel: Transition metal has been used in many methods to grow graphene. In order to grow graphene nickel, pro crystalline Ni On Sio₂/Si crystal is annealed temperature is varied from 900-1000C in Ar and H₂ environment. The H₂ and Ch₄ exposure helps Carbon atoms to dissolve on Ni in solid solution form. After that the film is cooled down in presence of Ar. Ni has high C solubility at high temperature, but solubility decreases with lowering the temperature. In the process of cooling down Carbon atom precipitate in Ni surface as graphene.

1.3.5 Graphene on Copper: To grow graphene in Cu we need 25micrometer () thickness of cu foil. Heating of cu foil up to 1000C in presence of hydrogen and after that H₂/CH₄ is used to begin the growth of graphene. By this method graphene is found growing in cu foil, which is then slowly cool down to room temperature. The reason we use cu is because C has low solubility in Cu, which is a useful property to grow monolayer graphene. Ruoff et all used was among first to use this method. This method now has been used around the world for its benefits as high quality graphene, transfer properties etc.

1.4.6 Arc Discharge: Graphene could be fabricated using arc discharge of graphite in hydrogen environment. The reason behind using hydrogen is to passivized any dangling bond of carbon from making closed structure. We need suitable condition to grow the graphene, as high current (>100A), high voltage (>50V) and high pressure (>200Torr). This is a useful method to make boron doped and nitrogen doped graphene. In order to make doped graphene, H₂+diborane and H₂+ammonia is used. It was observed that discharge in presence of air could be used to make ~100-200 nm sheets. Air pressure is very important in the process.

1.4 Applications of Graphene: Graphene is most sought after future material, because of its unique physical and electronic properties. As new techniques to make graphene on bulk are coming day by day, the day is not far when we will be using graphene in every sector of our like. Due to its versatile application, it touches many fields of human life. Its potential use in display devices which not only will be light weight but its life will be enhanced considerably. Graphene uses in electronic, solar, medical devices will revamp the whole industry and will make them more productive and fruitful.. Initially when graphene was produce for first time it was very costly around \$100,000,000/cm². After few years of enhancing the productivity of exfoliation

techniques companies are now able to cut down the price to \$100/cm², which has made possible that many other companies could use graphene in research and development. Hong et. all was the first to make graphene using chemical vapor deposition (CVD) technique. In order to ignite new interest in graphene application European Union had made a Consortium in 2013 only for the research related to graphene applications, with more than 7 European universities and private sector companies. To give an overview of current and future application, some of the important application and uses of graphene has been discussed here

1.4.1 Application in Electronic: Electronic industry had seen exponential growth in few decades. It is predicted that in upcoming years it will not be able to keep up with the Moore's law, which says that every two year number of transistor in chip doubles. Graphene is one of the prospective materials which could revamp the electronic industries owing to its high charge carrier mobility which is around 2000 cm²/V.s at room temperature. Recently many researchers around the world have been using graphene to make transistors. IBM has reported in 2009 that it has made a field effect transistor using graphene. Charge carrier mobility of graphene is temperature independent between 10K to 100K. It is observed that electron and holes mobility is almost same in graphene.

1.4.2 Application in Optics: Graphene is one of the most promising future materials in optics. Graphene will revolutionize many sectors of optoelectronics these includes LED screen, touch screen etc. The amount of light absorbed by graphene could be changed by modifying the Fermi level. It was observed that graphene has light transmittance of 97% which makes it perfect material for optoelectronics purpose. Conductivity of graphene is also an important factor in its application. Today we are using a composite material indium tin oxide (ITO) in touch screen displays. In upcoming future it is predicted that graphene will replace the ITO. When graphene will be used in touch screen it will be possible to make flexible and more durable screens.

1.4.3 Application in Medical: The medical application of graphene is yet to realize. But researchers have been trying to use graphene as reinforced material for bio degradable bone tissues. It has been observed that a small quantity of graphene could enhance the mechanical flexibility and strength of Nano composite used. Other fields where it could be used is drug delivery agent, biomedical engineering etc.

1.4.4 Application in Sensors: Graphene has been studied for sensor purpose. The 2D structure of graphene makes it exposed the whole sheet to the detecting environments absorbed atoms and molecules. The efficiency of gaseous sensor could be increased considerably by using graphene coating in its surface. When absorbed atom is catches by graphene it causes loss of conductivity in detecting material due to its high electrical conductivity it's easy to detect these changes in graphene.

CHAPTER 2

COMPUTATIONAL DETAILS

2. Atk Vnl: We have used in our calculation Atomistix Toolkit Virtual Nano Lab software developed by Quantum wise. Atomistix is modeling software for atomic scale. Atomistix is further developed from TranSIESTA-C, which is an advanced version of TranSIESTA and McDCal. SIESTA is previous version of ATK VNL. Density functional theory and non-equilibrium green functions are used in atomistix toolkit. Atomistix One of the major advantages of using ATK VNL is that it has various modules which are very useful in simulation of nanostructure. We could make a nanostructure, analysed it with helpful numerical techniques. Atk Vnl is developed in such a way that it could solve Equation of Quantum mechanics using advanced software architecture and numerical techniques. Electronic properties of a many body systems are solved using Density functional theory. Atk is main calculation kernel, which executes the scripts. In atk vnl scripts could be modified by users which allows for virtual experiments. Graphene has been centre of interest among researchers because of its unusual physical and chemical properties. Properties of solids are function of its quantized ground states. In low dimension systems a charge particle is confined to 1D and 2D. If an Ambipolar field is applied to pure graphene it is observed that charge carriers of graphene could be inverted between electrons and holes. The mobility of electron is found more than $20,000 \text{ cm}^2/\text{V}_s$ at room temperature. Graphene shows anomalous quantum hall effect even at room temperature. Schrodinger equation is quite suitable to describe the electronic properties of condensed matter system. But in case of graphene charge carrier behave like particle without mass these properties could be described using Dirac equation correctly. These charge carriers are called as massless Dirac fermions.

2.1 Density Functional Theory (DFT): DFT is an exceptionally powerful computational method to calculate the electronic structure of many body systems. In quantum mechanics all the information of a system are defined from its wave function. This wave function could be calculated by shordinfer equation, for one body system it's easy to calculate but for many body systems it's very difficult. DFT is based on two theorems given by Hohenberg and kohn in 1964.

The Hohenburg-Kohn Theorem I: This states that for many body interacting systems ground states properties are determined by electron density. $V_{\text{ext}}^1(\mathbf{r})$ and $V_{\text{ext}}^2(\mathbf{r})$ are two external potential, $n(\mathbf{r})$ is the ground state density, \hat{H}^1 and \hat{H} are two Hamiltonian and ψ and ψ^1 are two normalize wave functions.

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle.$$

This equation states that no ψ could give energy less than it's \hat{H} . On rewriting the equation we get the equation given below.

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \int d\vec{r} \left[V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r}) \right] n_0(\vec{r})$$

$$\langle \Psi^{(1)} | \hat{H}^{(2)} | \Psi^{(1)} \rangle = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle + \int d\vec{r} \left[V_{\text{ext}}^{(2)}(\vec{r}) - V_{\text{ext}}^{(1)}(\vec{r}) \right] n_0(\vec{r})$$

On changing the labels and add the last two equations which gives.

$$E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}$$

This is a contradiction. So there could not be two $V_{\text{ext}}(\mathbf{r})$ which gives same density. Which means that N and $V_{\text{ext}}(\mathbf{r})$ determine all the properties of ground states?

The Hohenburg-Kohn Theorem II: "A universal function which gives the ground states gives the lowest value of function". The external potential is determined by electron density. energy sd function of density is given as:

$$E[n] = T[n] + E_{\text{int}}[n] + \int V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{II} \equiv F[n] + \int V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{II}$$

$F[n]$ is a universal function.

Ground states density given as:

$$E^{(1)} = E[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle.$$

$$E^{(1)} = E[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)}.$$

This shows that energy functional is minimized by the correct ground state energies.

The Kohn-Sham Formalism: The equation given by hohenburg-kohn could not be implemented directly. Kohn-Sham put forward the practical realization of DFT. The basic idea of

Kohn-sham approach was to replace the interacting many-body system with an auxiliary system of non-interacting particles having the same ground state. The total energy functional can be written as:

$$E[n] = \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + T_S[n] + \frac{1}{2} \int d^3\mathbf{r}d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}$$

Where, V_{ext} is the external potential, T_S is the kinetic energy term of the hypothetical non-interacting electrons. The third term is the classical electrostatic energy (Hartree) of electrons and all the, many-body effects are grouped in exchange correlation E_{xc} term. The minimization of equation results into Kohn-Sham equation.

$$H_{KS}(\mathbf{r})\psi_i(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

Where V_{KS} is potential (external potential, Hartree potential, Exchange Correlation), Ψ_i is Eigen function corresponding to Eigen values. Ground state electron density is obtained as:

$$n(\mathbf{r}) = \sum_{i=1}^{occ} |\psi_i(\mathbf{r})|^2$$

The kinetic energy is given as

$$T_S[n] = \sum_{i=1}^N \epsilon_i - \int d^3r V_{eff}(r)n(\mathbf{r})$$

Total energy is obtained as:

$$E = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d^3\mathbf{r}d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d^3\mathbf{r} V_{xc}(\mathbf{r})n(\mathbf{r}) + E_{xc}[n]$$

Exchange Correlation Term: The key achievement of Kohn-Sham approach is to pin point the independent single particle kinetic energy and the classical Hartree term from the remaining interacting part exchange-correlation functional, which can be approximated in different ways.

Local Density Approximation (LDA): This type of exchange-correlation energy was proposed by Hohenberg and Kohn in their original DFT paper, where exchange correlation energy of a system is approximated with the same associated with the homogeneous electron gas.

Even though its simple its works well in some systems.. For any small region, the exchange-correlation energy is approximated by that for jellium of the same electron density. In other words, the exchange-correlation hole that is modelled is not the *exact* one - it is replaced by the hole taken from an electron gas whose density is the same as the local density around the electron. The interesting point about this approximation is that although the exchange-correlation hole may not be represented well in terms of its shape, the overall effective charge is modelled exactly. This means that the attractive potential which the electron feels at its centre is well described. Not only does the LDA approximation work for materials with slowly varying or homogeneous electron densities but in practise demonstrates surprisingly accurate results for a wide range of ionic, covalent and metallic materials.

General Gradient Approximation (GGA): An improvement over LDA was suggested by Hohenberg and Kohn by considering higher order density gradient expansion terms which is known as the gradient expansion approximation (GEA). However, the GEA fails as exchange hole does not integrate to -1 i. e. violation of the sum rule. In spite of its failure, it paved a way to construct GGA exchange correlation hole by real space cut-off of GEA exchange hole. With the introduction of an analytic function, known as the enhancement function GGA exchange correlation energy can be obtained by modifying the LDA energy density. The over binding problem of LDA is corrected by GGA along with improved results in atomic and molecular energies, bulk phase stability, magnetic properties etc. However, both LDA, GGA schemes are found inadequate to describe, for example, band gap of Mott insulators like transition metal, rare earth compounds.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Stability Analysis: Density functional theory is an excellent theory used in condensed matter physics to calculate and analyzed the electronic band structure of many electrons system. DFT has shown remarkable results using different Exchange correlation approximation which shows agreement with experimental results. In our simulation we have analyzed Graphene Nanoribbons having Zigzag edges with termination of two transition metals Titanium and Zirconium. We have investigated the electronic properties of pristine; Ti and Zr terminated zigzag graphene nanoribbons using density functional theory. In our simulation we have used non spin polarized structure for the sake of simplicity because when we add spin to atoms it becomes more complicated to compute and require good computational resources to do simulations.

For our present analysis we have considered two termination site one edge and both edge. In one edge termination one hydrogen atom is replaced. In both edge terminations both hydrogen are replaced with Titanium and Zirconium. Termination sites are depicted in figure 10. Figure 11 shows the one edge termination of width 8 ZGNR with Zr. Figure 12 shows the both edge termination of width 8 ZGNR with Zr. Termination sites plays an important role in graphene as well as the dopant or substituent used. Termination sites are shown in figure 10.

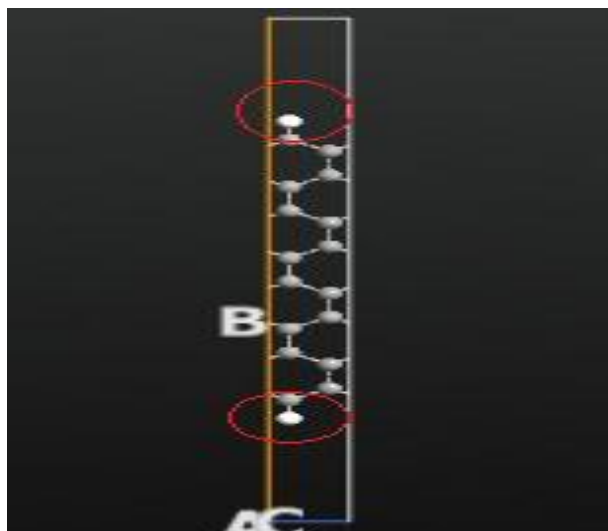


Figure 9 ZGNR with single edge termination

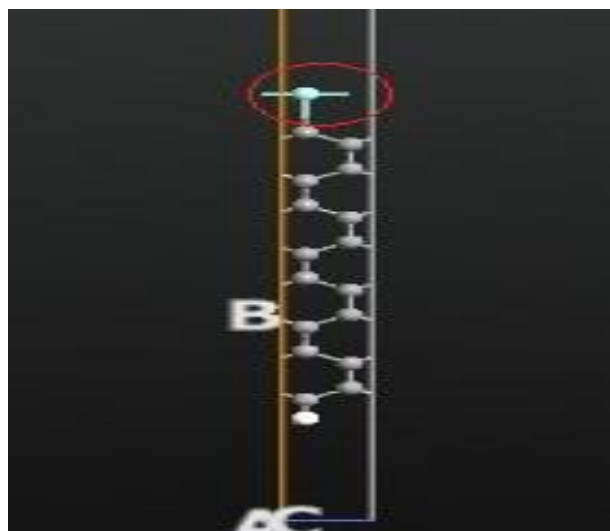


Figure 10 ZGNR with single edge termination

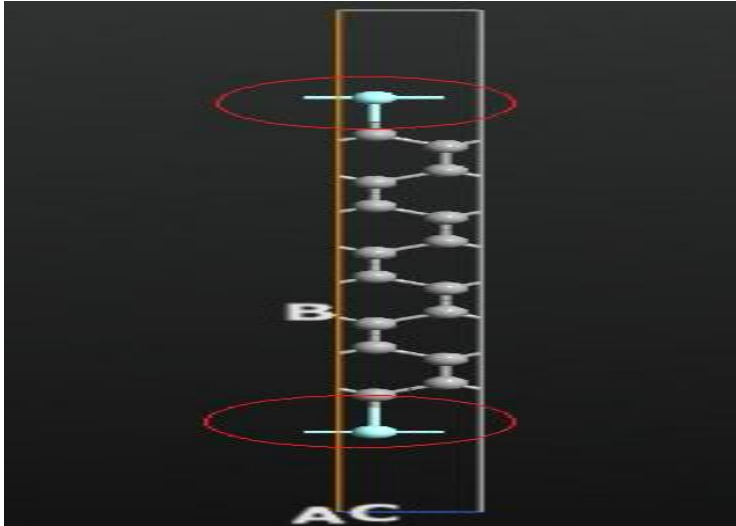


Figure 11 ZGNR with both edge terminations

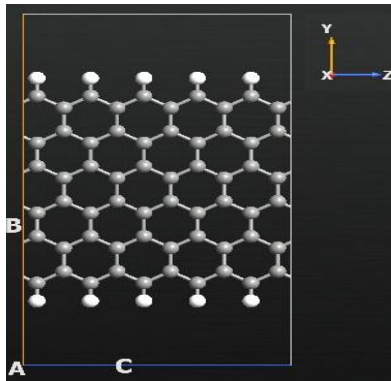


Figure 12 ZGNR

To analyse whether the structures are energetically stable or not, we need to compute the binding energy of all configurations. To calculate binding energy, we need to compute the total energy of ZGNR. First, we have calculated the ground state for pristine ZGNR with hydrogen termination. Then, we have calculated the total energy of one edge and both edge terminated ZGNR. Binding energy is calculated for all configurations, which gives information about the stability of configurations, whether they are stable or not. Binding energy is the amount of energy needed to break any structure into its constituent atoms. Negative binding energy implies the structure is stable, and positive binding energy implies the structure is not stable. We have used the formula given below to calculate the binding energy for all configurations:

$$E_b = -E(\text{Ti-ZGNR}) + E(\text{ZGNR}) + nE(\text{Ti}) - nE(\text{H})$$

Here $E(\text{Ti-ZGNR})$ = this is the total energy of Ti-terminated ZGNR (one edge/both edge)

$E(\text{ZGNR})$ = this is the total energy of pristine ZGNR (one edge/both edge)

$nE(\text{Ti})$ = this is total energy of titanium crystal per atom

n = is number of atom in titanium crystal

$nE(\text{H})$ = is total energy of hydrogen atom replaced

$E(\text{Zr-ZGNR})$ = is total energy of Zr terminated ZGNR (one edge/both edge).

Binding energy in tabulated form is given below:

Table 1 Binding Energy

Width	Binding energy (eV)			
	Ti one edge	Ti both edge	Zr one edge	Zr both edge
4	-0.193	-0.386	-0.778	-1.511
6	-0.199	-0.387	-0.791	-1.551
8	-0.194	-0.379	-0.774	-1.536

The calculation of Binding Energy From the binding energy analysis it is observed that the Ti and Zr terminated ZGNR are stable.

3.2 Electronic Properties: we have simulated electronic band structure of Ti and Zr terminated ZGNR having 4, 6, and 8width. Band structure of pristine ZGNR is compared with terminated ZGNR. It is observed that termination is a favorable way to perturb the electronic properties of ZGNR. Analyzing the band structure of all configuration it is clear that the all configurations with Ti and Zr termination are metallic in nature as the bands crosses the Fermi level.

When we terminate a ZGNR with titanium it was observed that C-Ti interaction creates new electronic states near Fermi level. These additional electronic states are due to electrons of C-3p which are responsible for enhancing the number of bonds crossing Fermi level observed in our Ti terminated ZGNR configuration. In case of single edge configuration we see the band increases to 3 but in case of both edge terminations we see that the band is increased to 5. Same result has been observed in case of zirconium. We could conclude on the basis of band structure that Ti and Zr termination in ZGNR is a good way to enhance metallicity GNR.

This is a representation of band structure of ZGNR width 4 pristine, one edge and both edge band structure. From the graph it's evident that when a ZGNR is terminated as one edge termination this results in enhancing the metallicity of ZGNR. In our case with one edge termination the number of bands crossing the Fermi level increases to 3. Initially in case of pristine it was 2. This additional band could be defined as contribution of Transition metal electrons to Carbon. In case of both edge terminations the number of bands crossing the Fermi level further increased to 5, these results shows that ZGNR are subject to termination sites and with only 2 termination sites the metallicity could be increased considerably. Same results have been observed in case of Zr termination where same numbers of band are increased. These results are same for width 4,6, and 8 of ZGNR.

Band Structure of 4 widths ZGNR with Ti termination:

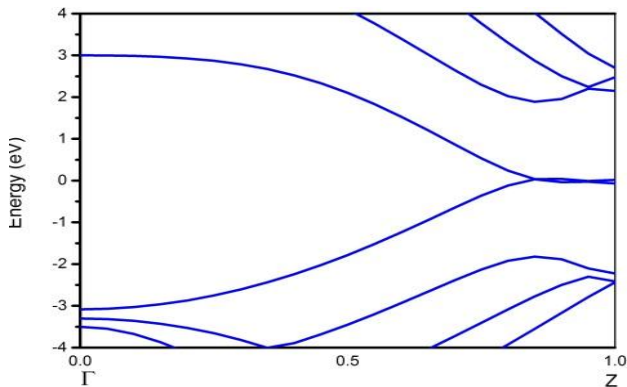


Figure 13 Width 4 Pristine

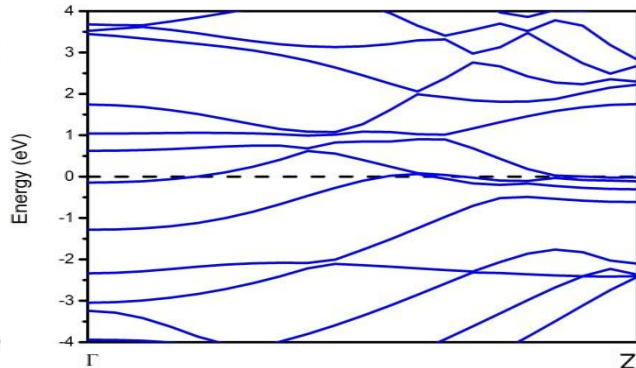


Figure 14 width 4 one edge Ti terminated

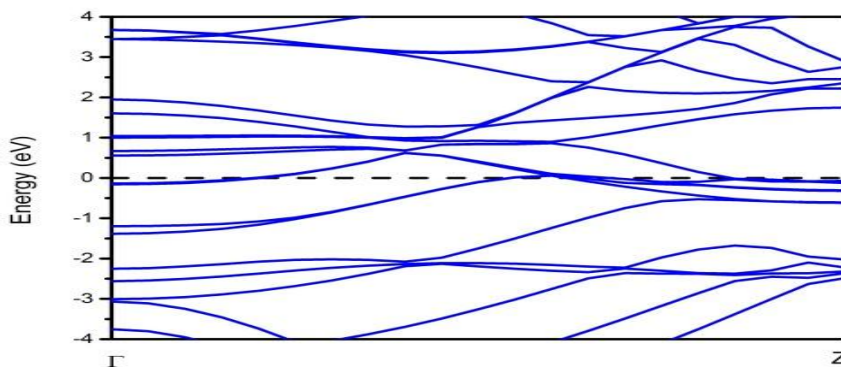


Figure 15 Width 4 both edge Ti terminated

Band structure of 6 widths ZGNR with Ti termination:

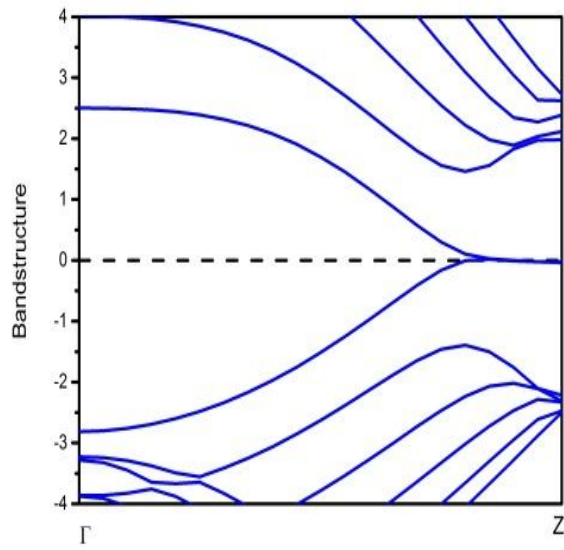


Figure 16 Width 4 Pristine

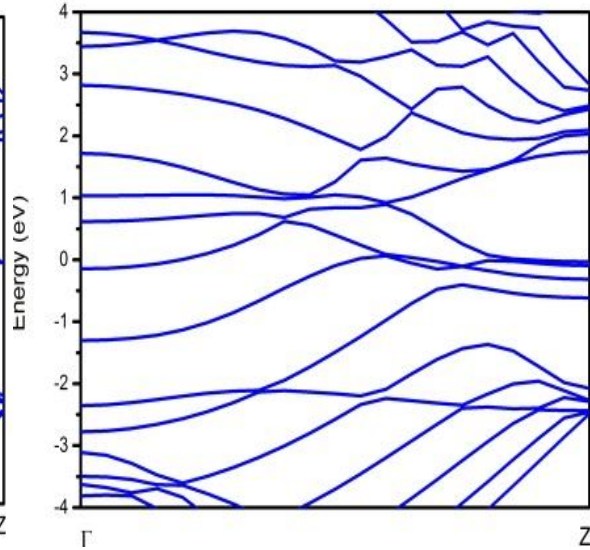


Figure 17 width 4 One edge Ti terminated

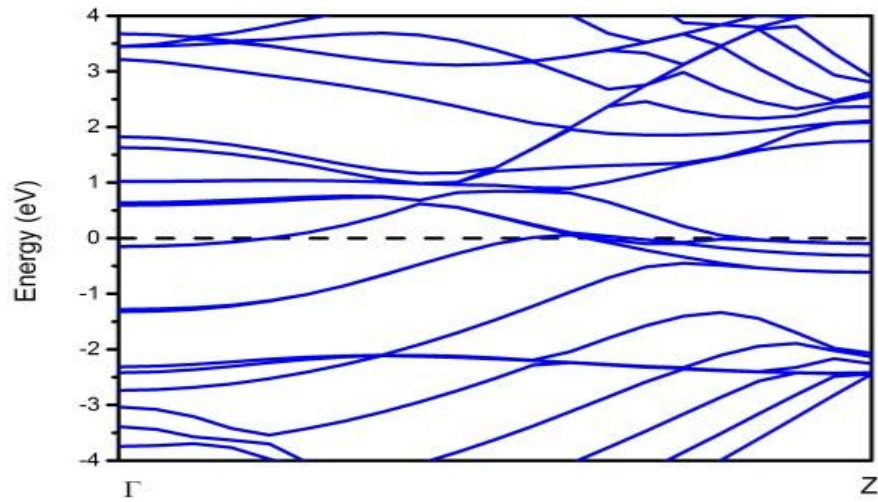


Figure 18 widths 6 both edge Ti terminated

Band structure of 8 widths ZGNR with Ti termination:

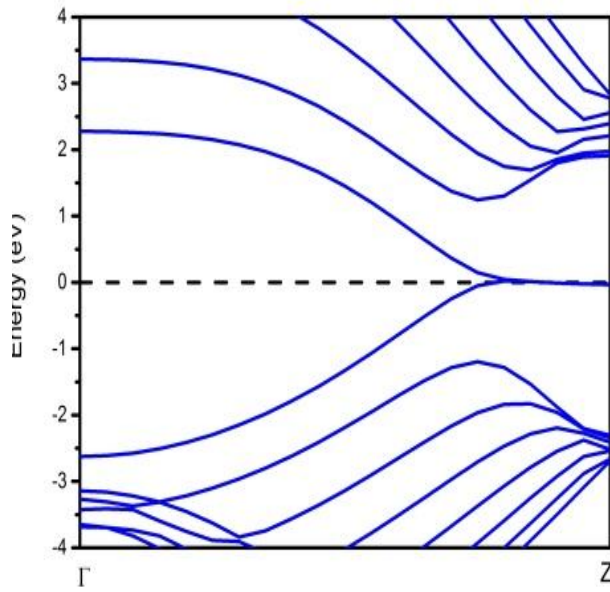


Figure 19 Width 8 Pristine

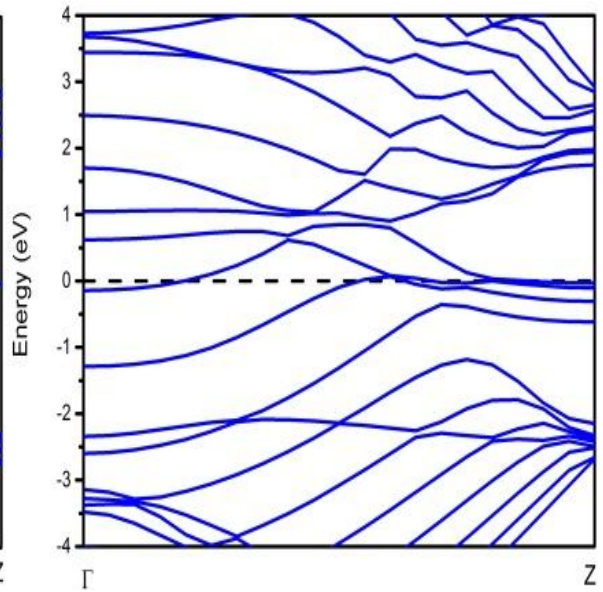


Figure 20 width 8 one edge Ti terminated

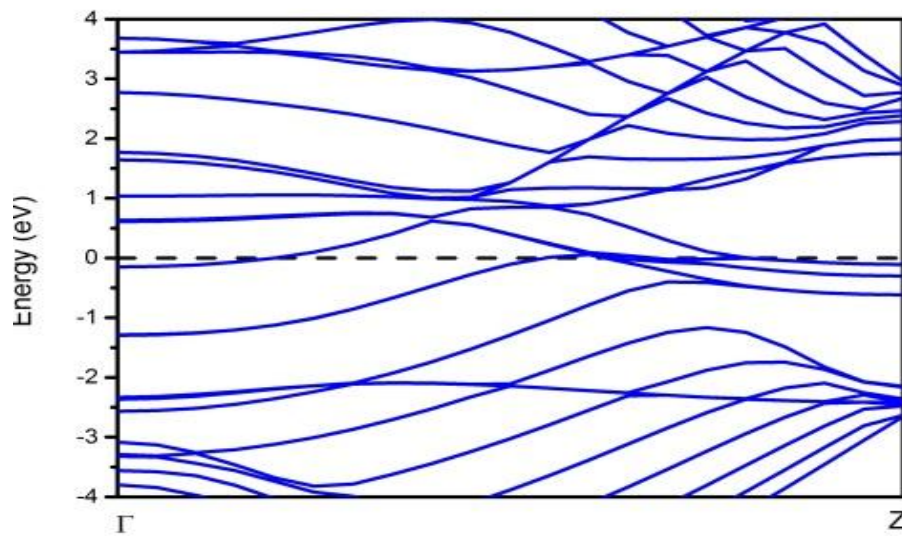


Figure 21 width 4 one edge Ti terminated

Band structure of 4 widths ZGNR with Zr termination:

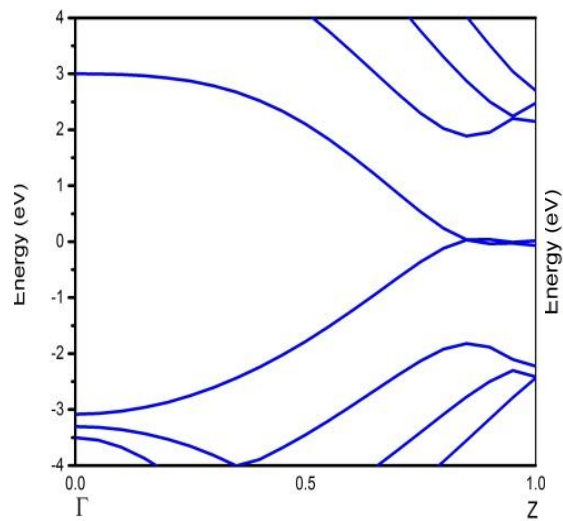


Figure 22 Width 4 Pristine

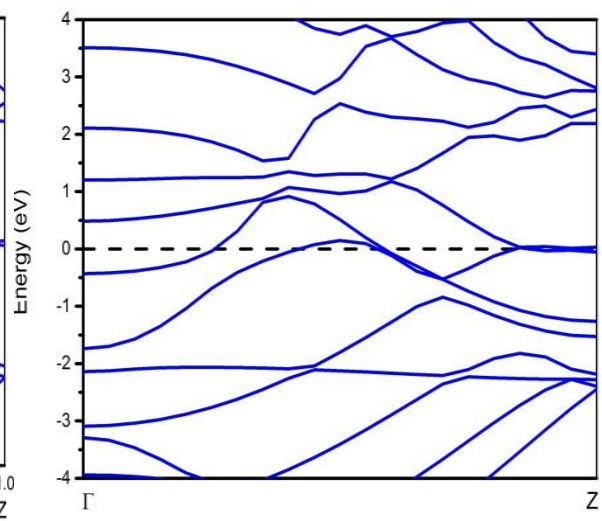


Figure 23 width 4 one edge Ti terminated

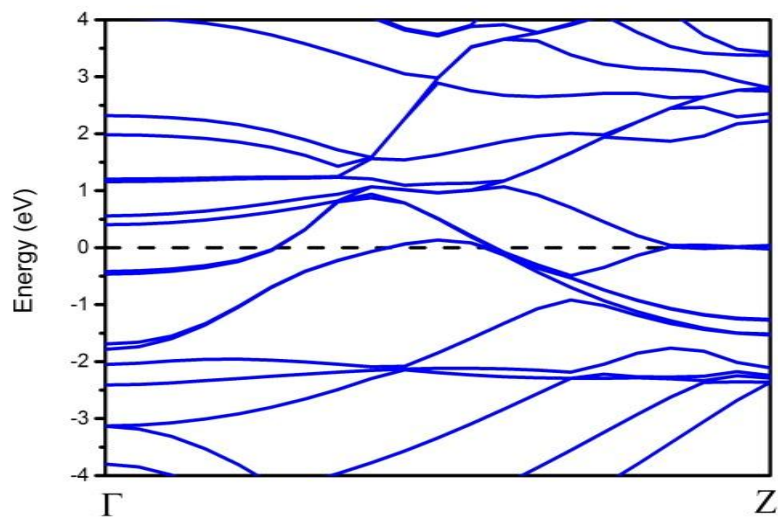


Figure 24 width 4 one edge Ti terminated

Band structure of 6 widths ZGNR with Zr termination:

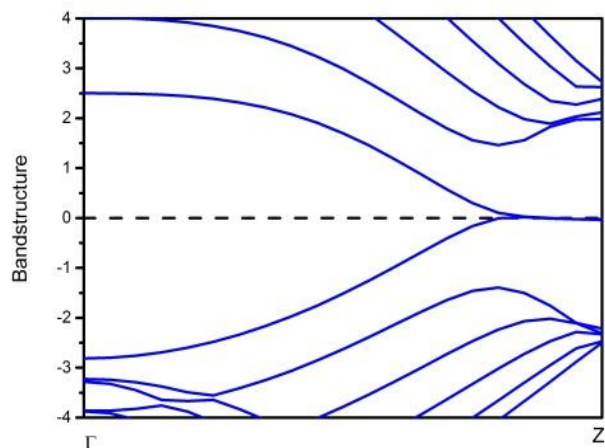


Figure 25 Width 4 Pristine

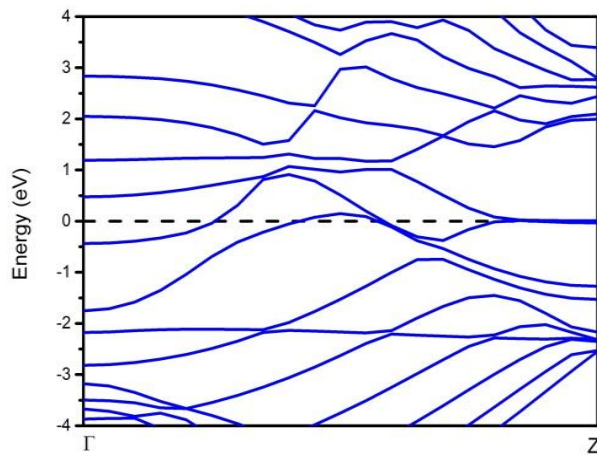


Figure 26 width 4 one edge Ti terminated

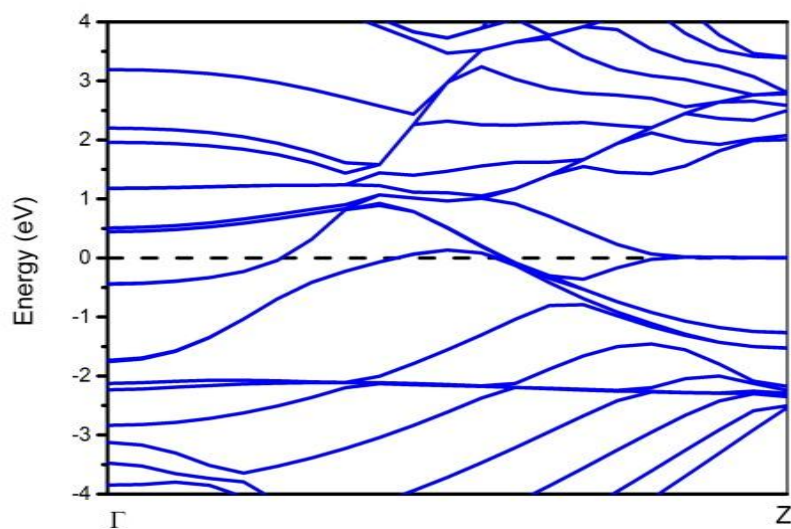


Figure 27 width 4 one edge Ti terminated

Band structure of 8 widths ZGNR with Zr termination:

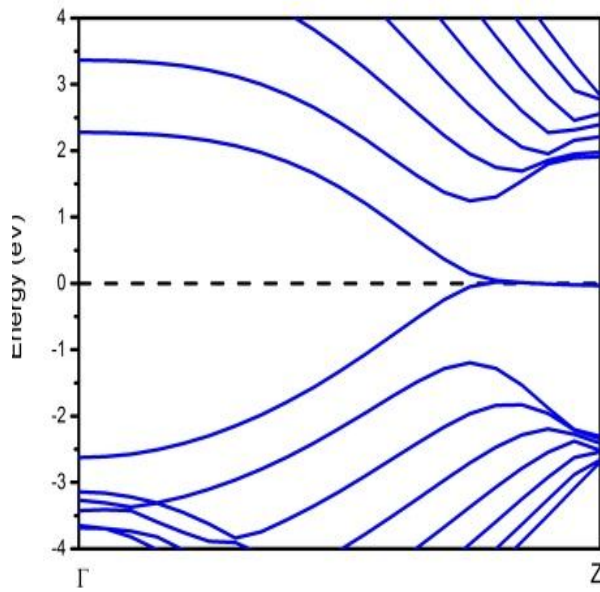


Figure 28 Width 4 Pristine

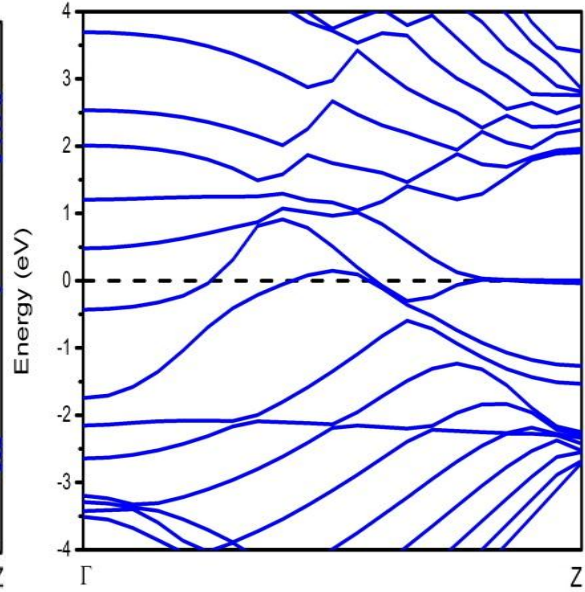


Figure 29 width 4 one edge Ti terminated

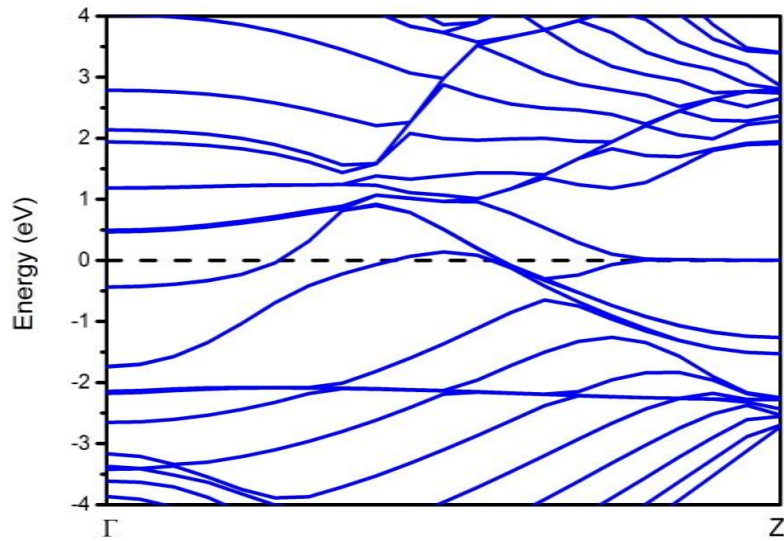


Figure 30 width 4 one edge Ti terminated

From the above band structure it is clear that number crossing the Fermi level can be increased by Ti and Zr termination. It was observed that termination sites also play an important role.

3.3 Density of State (DOS): In order to understand the electronic structure of ZGNR we have plotted total density of state (DOS) and projected density of state. DOS gives the

information about the electron that causes the effect of increase, metallicity. Larger the value of s, p, d orbitals larger will the share of termination in increasing metallicity.

In this DOS the contribution of p orbital is only significant, others orbitals have very less contribution so they are not included. We have calculated the density of states of our configuration and compare them with the pristine .To see the contribution of different orbital electron every orbit having some significant value at Fermi level has been used. DOS in case for width 4 pristine ZGNR show the major contribution of C-3p electrons. As the graph shows that in case of pristine the value is around 7 and in case of one edge termination this value increases to 25, this shows contribution of P orbitals.

DOS of ZGNR 4 width pristine:

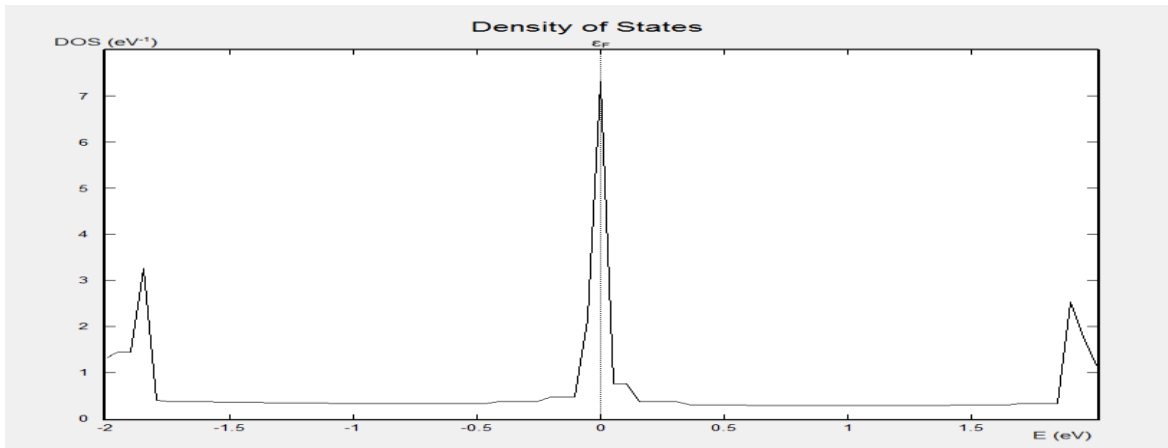


Figure 31 4 width ZGNR pristine DOS P orbital

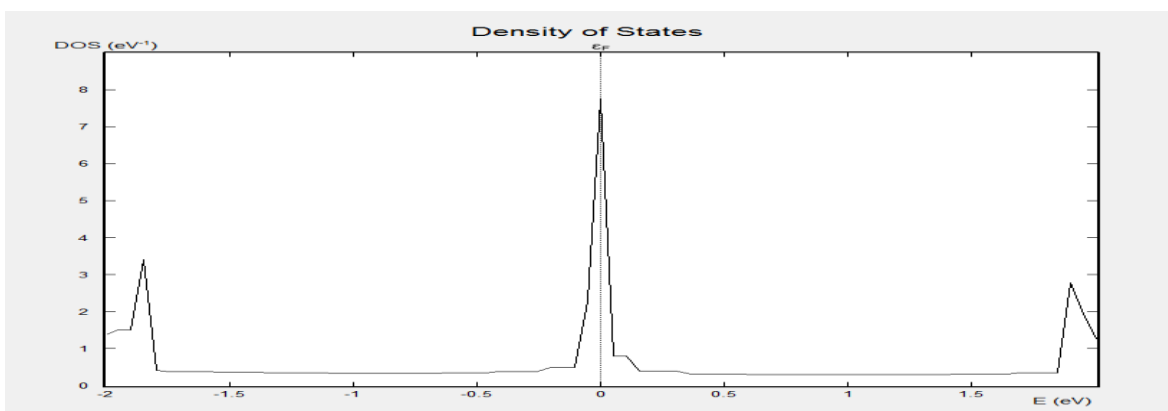


Figure 32 4 width ZGNR pristine Total DOS

DOS 4 ZGNR one edge Ti termination:

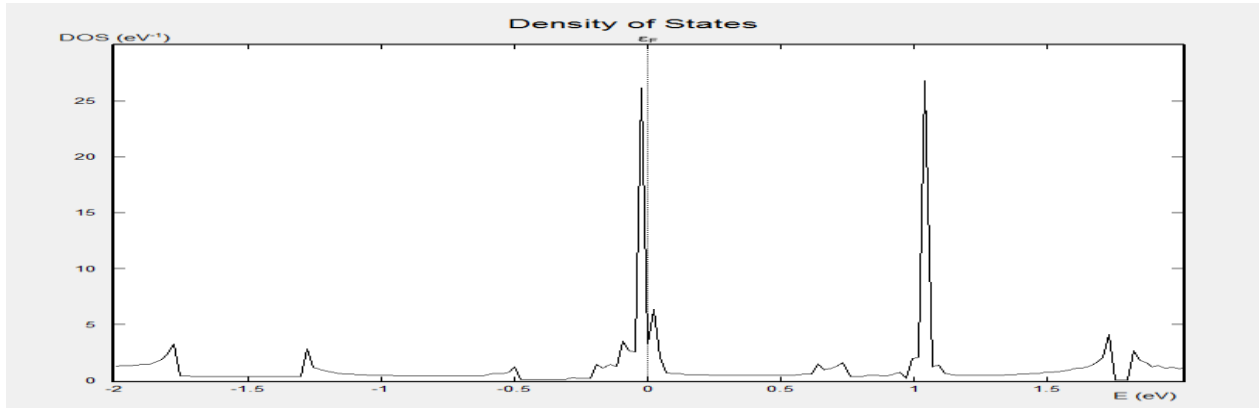


Figure 33 4 width ZGNR one edge DOS P orbitals

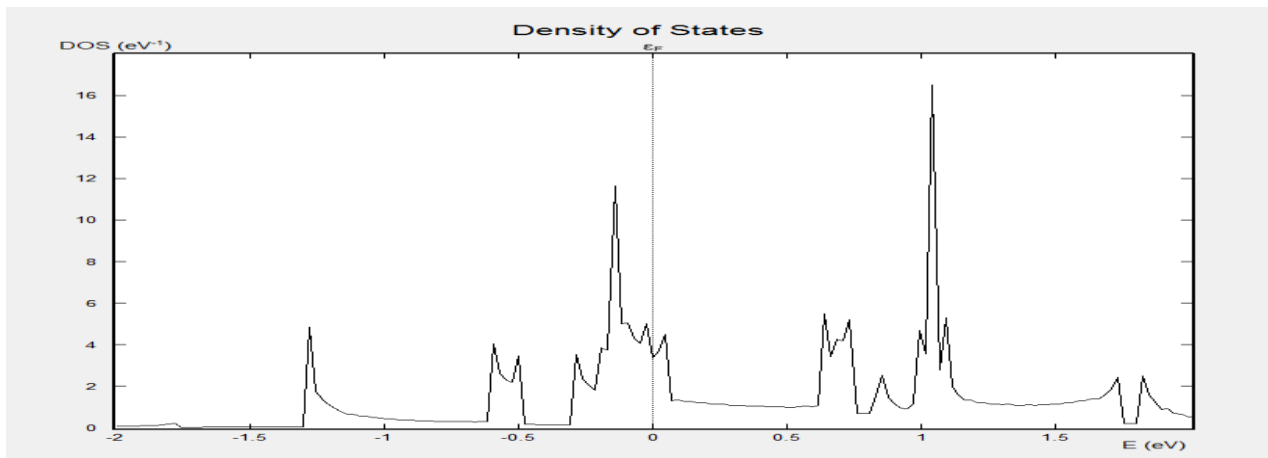


Figure 34 width ZGNR one edge DOS D orbitals

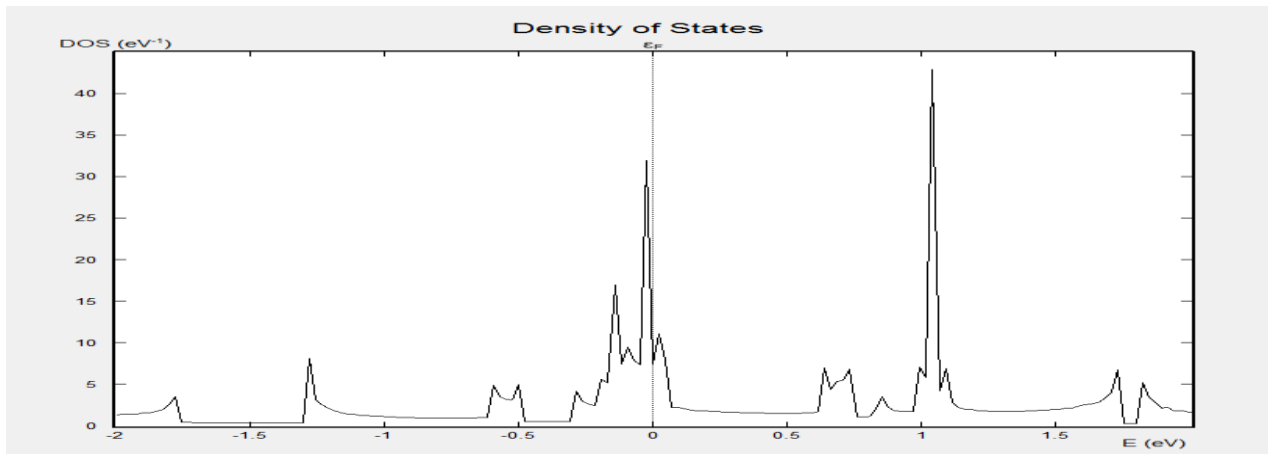


Figure 35 4 width ZGNR one edge Total DOS

The maximum contribution comes from p orbitals.

DOS 4 ZGNR both edge Ti termination:

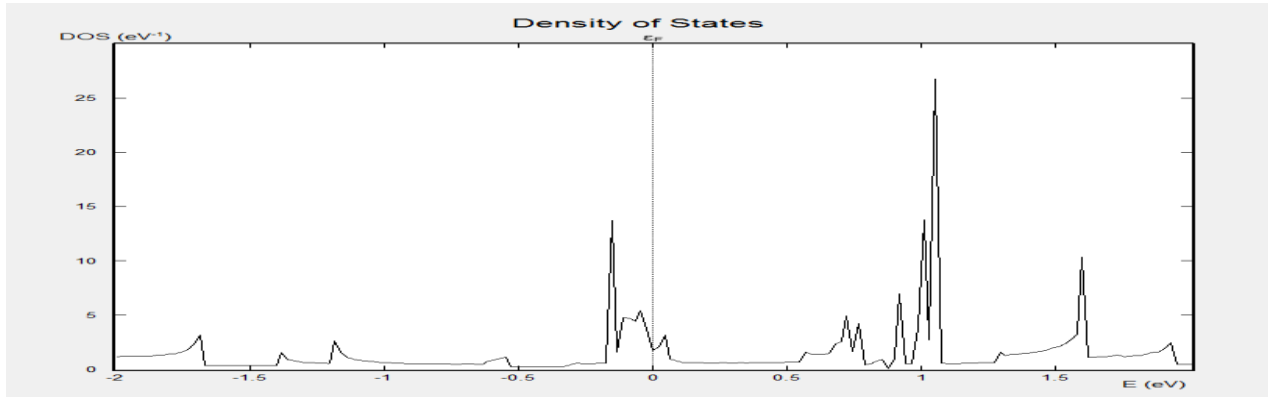


Figure 36 4 width ZGNR Both edge P DOS

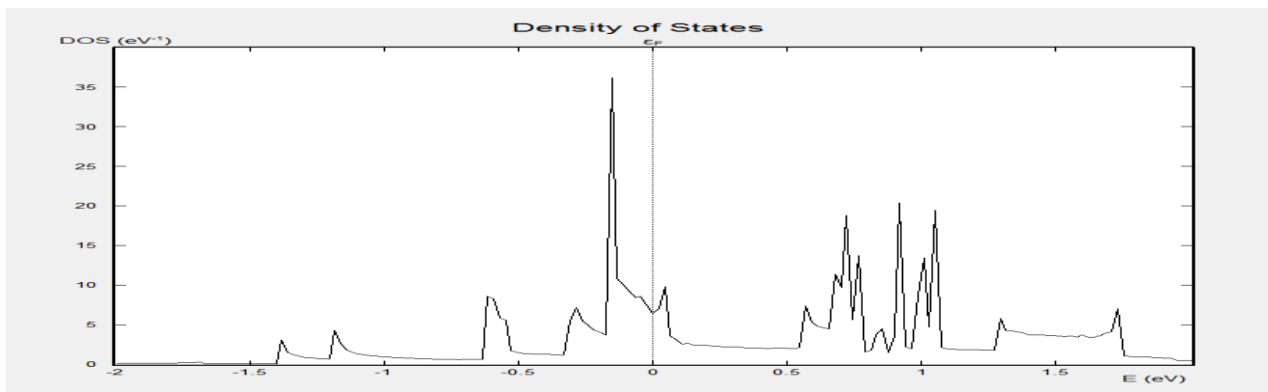


Figure 37 4 width ZGNR both edge D DOS

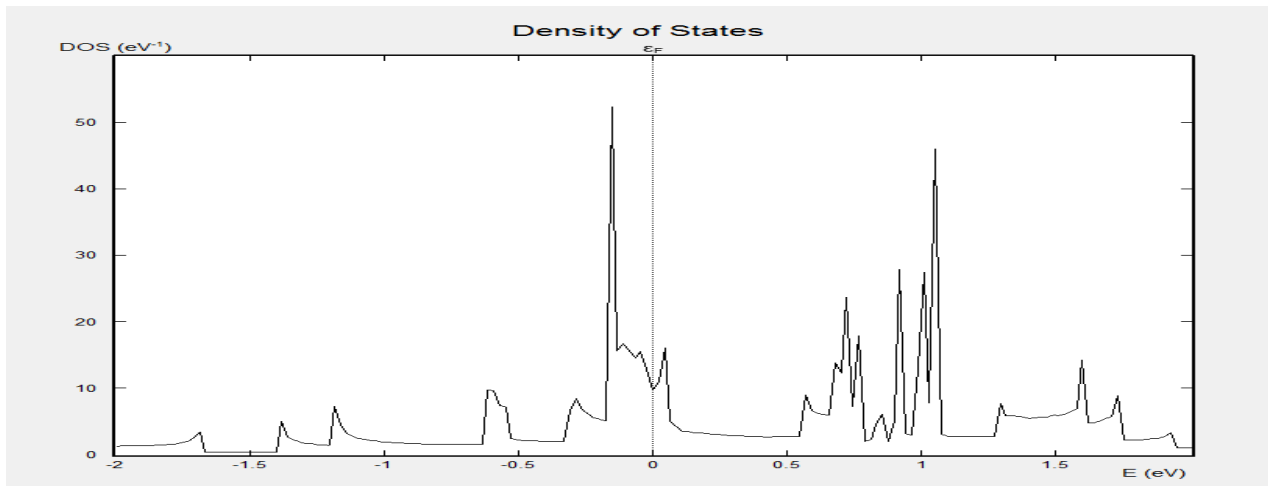


Figure 38 4 width ZGNR both edge Total DOS

The contribution is around on same range for P and d orbital.

DOS 6 ZGNR Pristine:

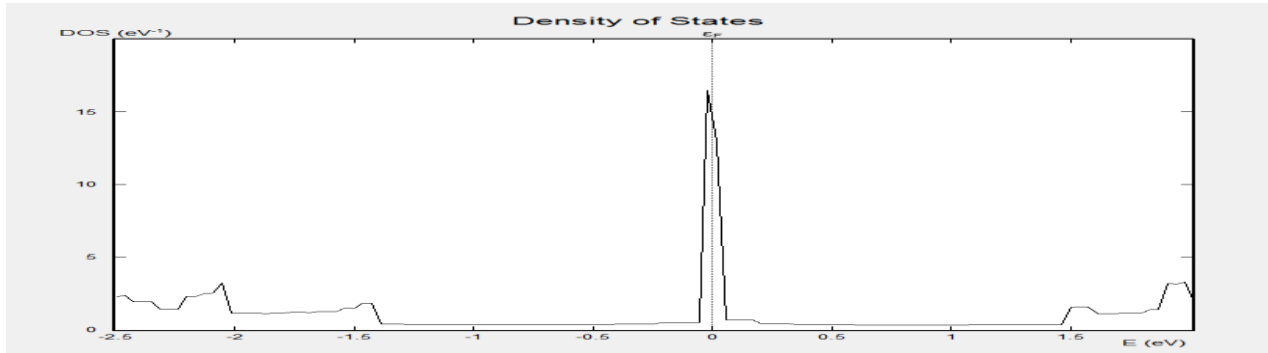


Figure 39 width 6 ZGNR Pristine P DOS

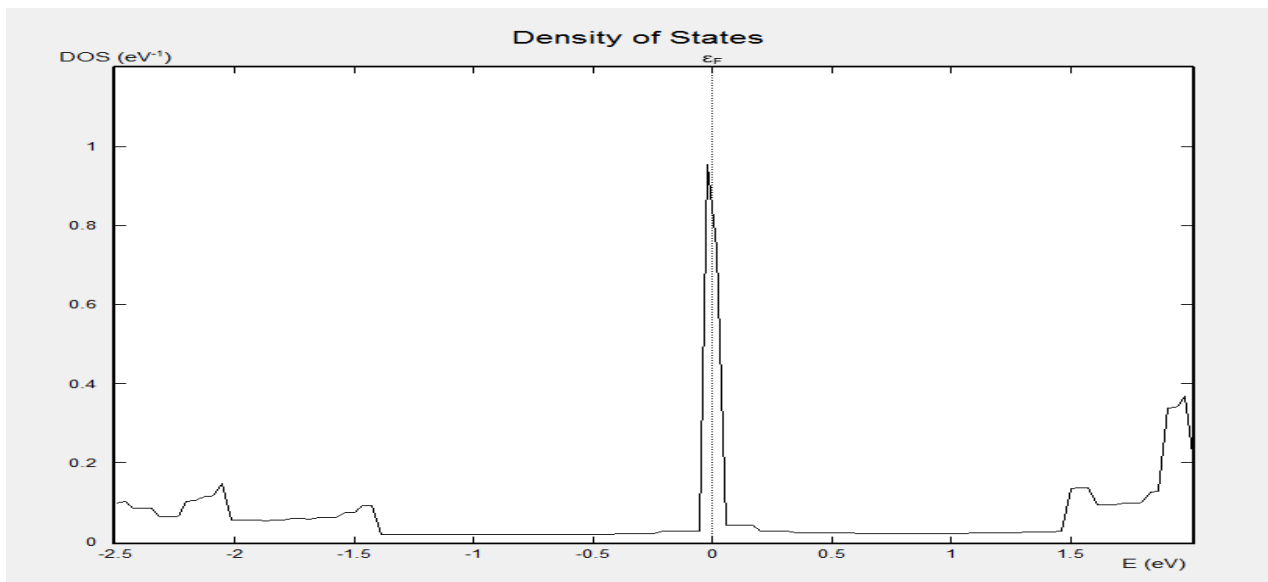


Figure 40 width ZGNR Pristine D DOS

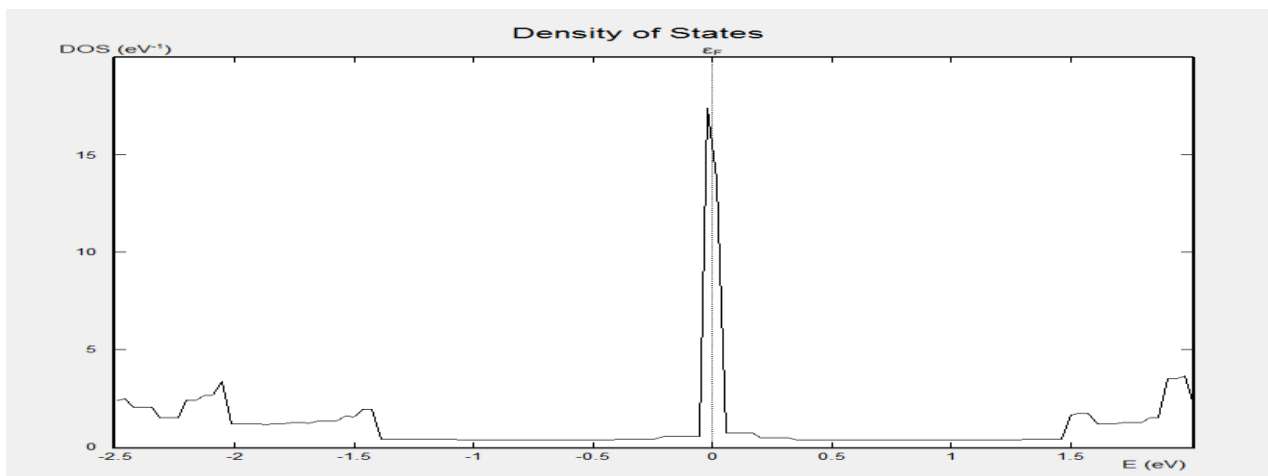


Figure 41 width ZGNR Pristine Total DOS

Only P orbital has some significant values. D orbital value is very less.

DOS 6 ZGNR one edge Ti termination:

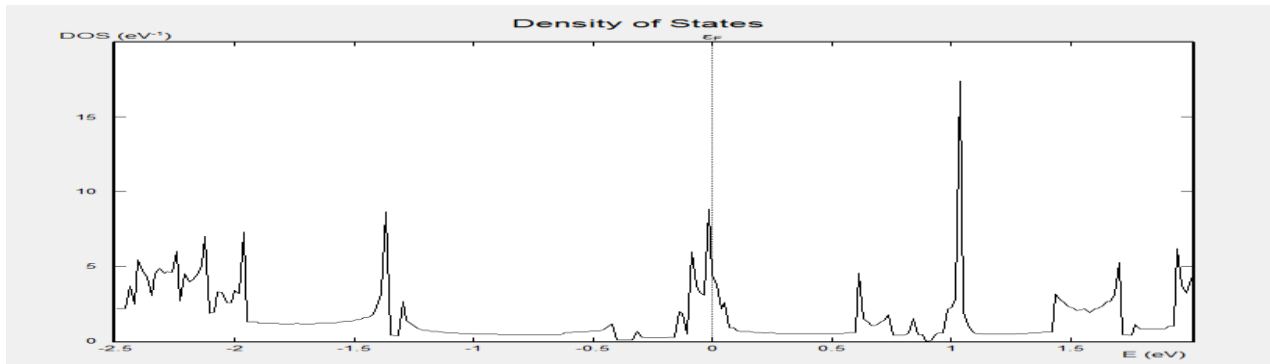


Figure 43 6 width ZGNR one edge P DOS

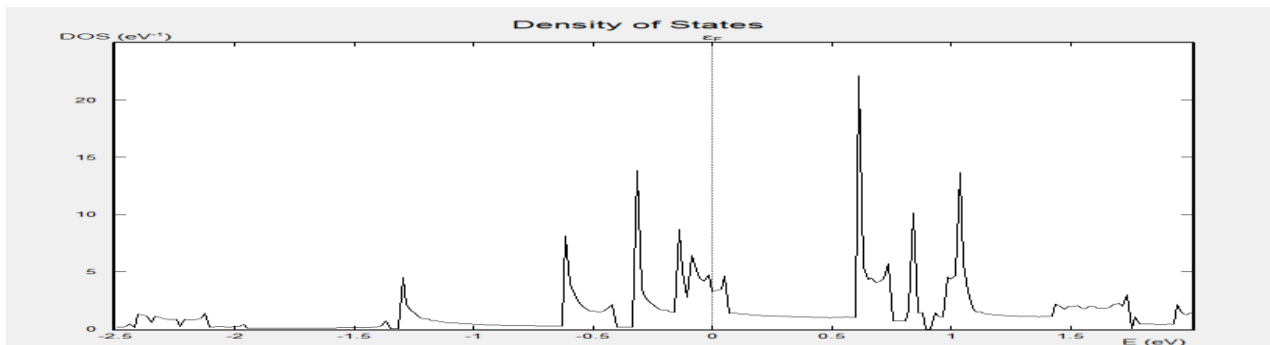


Figure 44 6 width ZGNR one edge D DOS

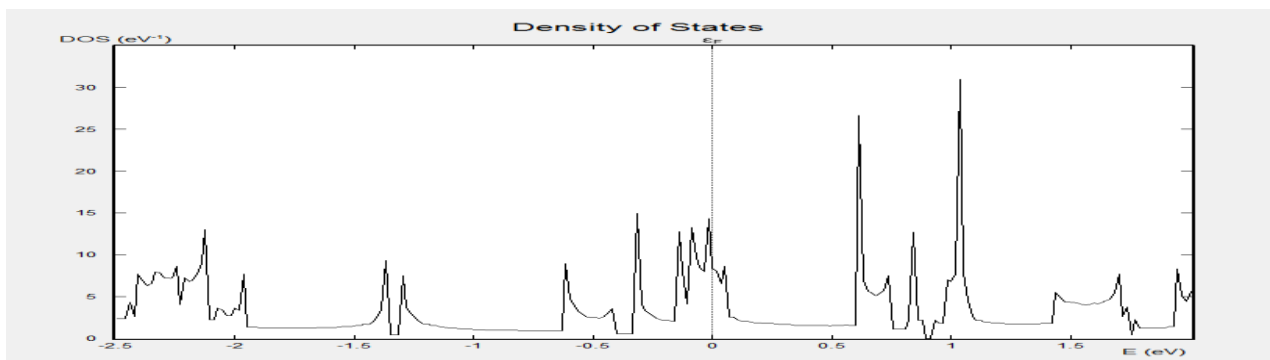


Figure 45 6 width ZGNR one edge total DOS

P and d orbitals both have around same values.

DOS 6 ZGNR both edge Ti termination:

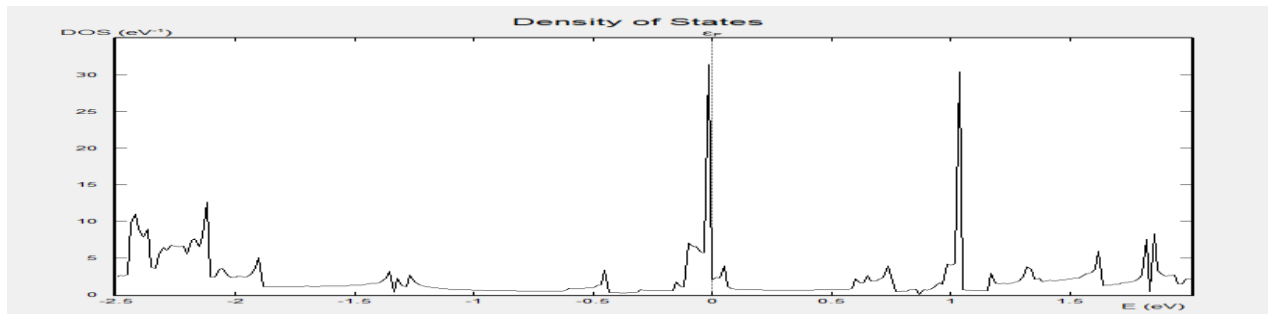


Figure 46 width ZGNR both edge S DOS

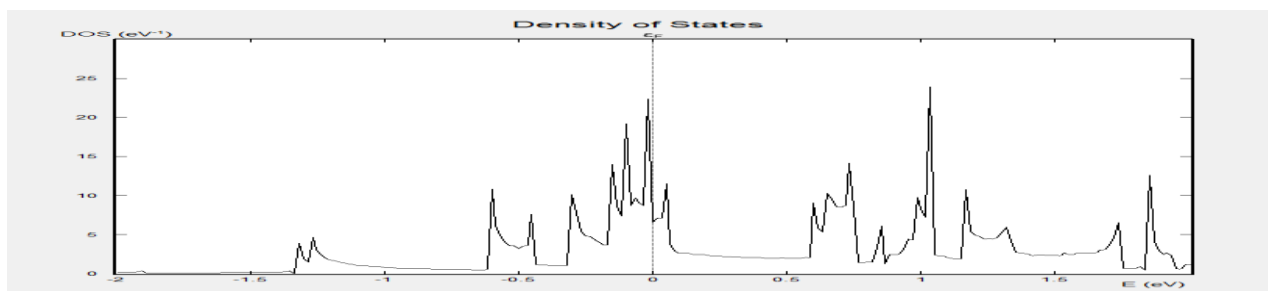


Figure 47 6 width ZGNR both edge D DOS

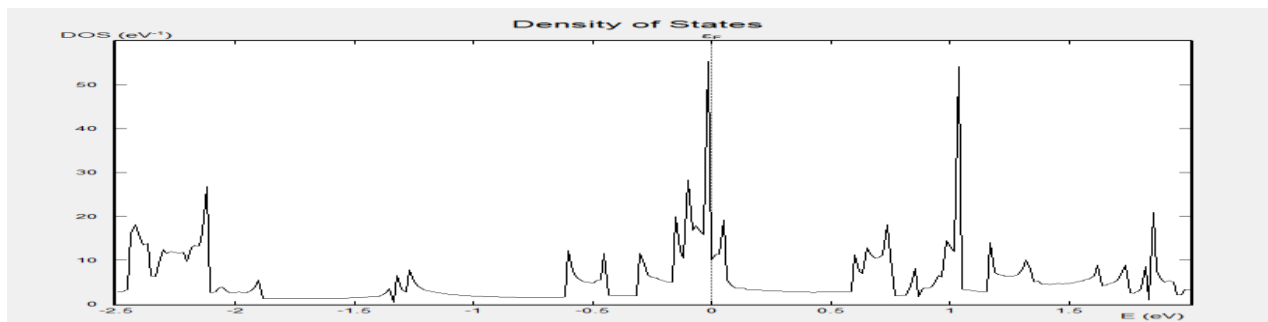


Figure 48 6 width ZGNR both edge total DOS

Both s and d contribution is significant. 6 edge was found more stable than others.

6 ZGNR Zr termination one edge:

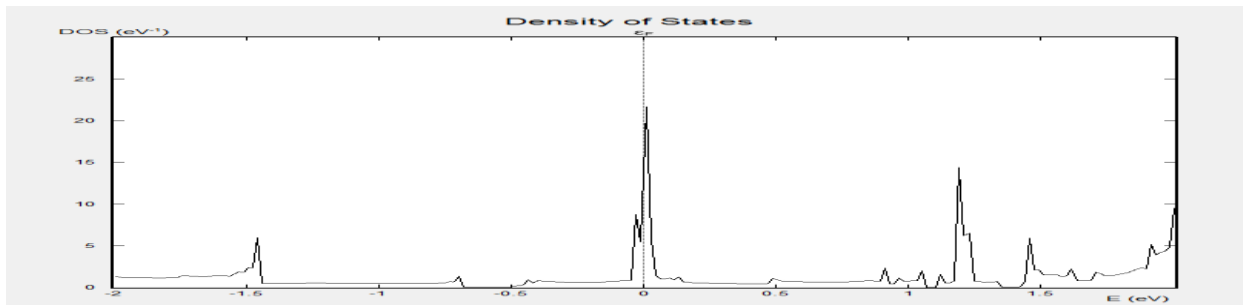


Figure 49 DOS P

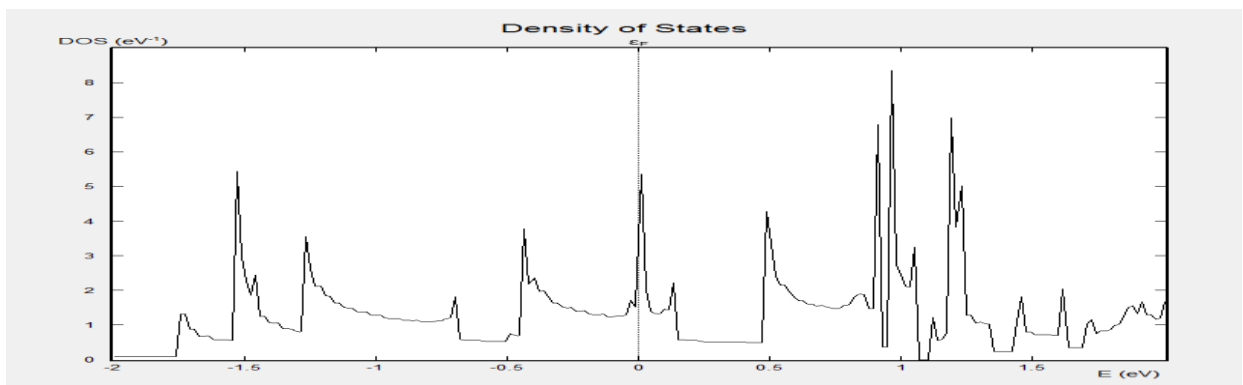


Figure 50 DOS D

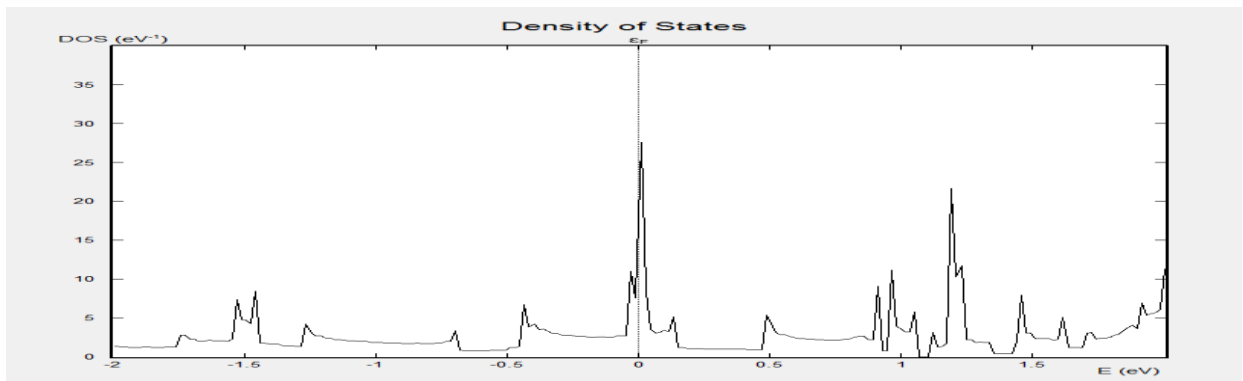


Figure 51 Total DOS

P orbital has significant contribution.

6 ZGNR Zr termination both edge:

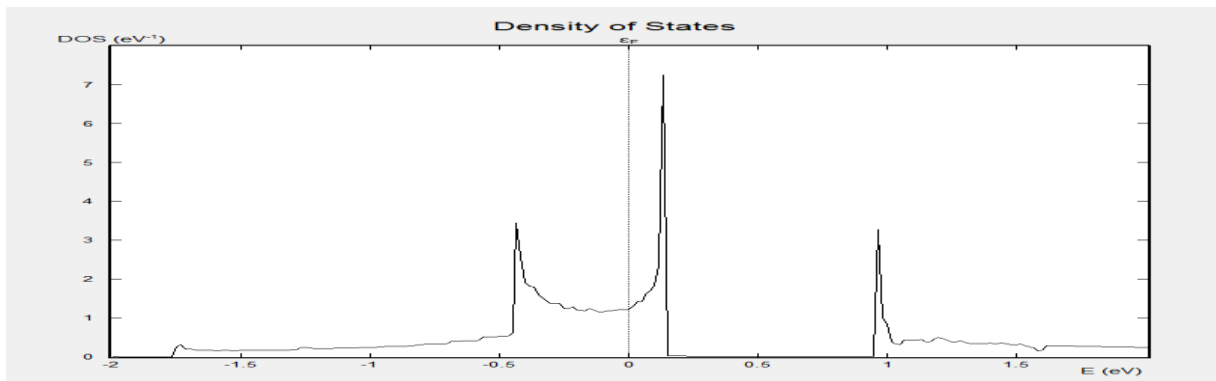


Figure 52 DOS S

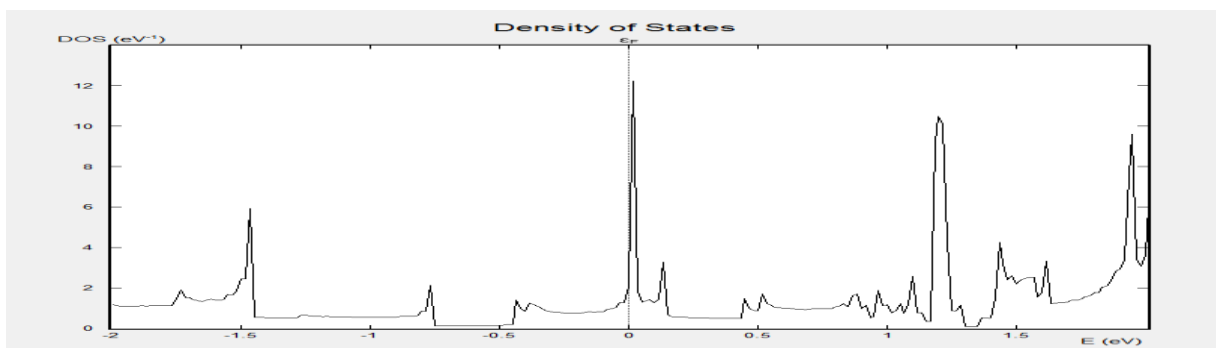


Figure 53 DOS P

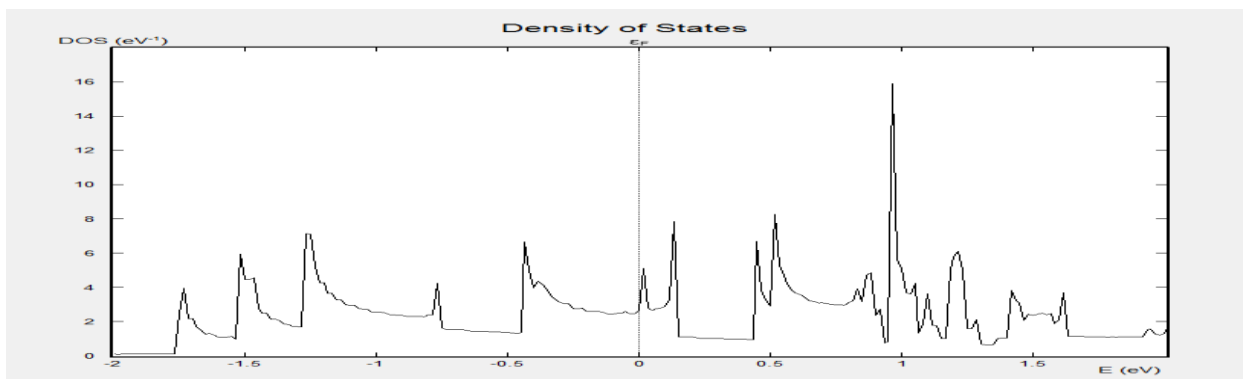


Figure 54 DOS D

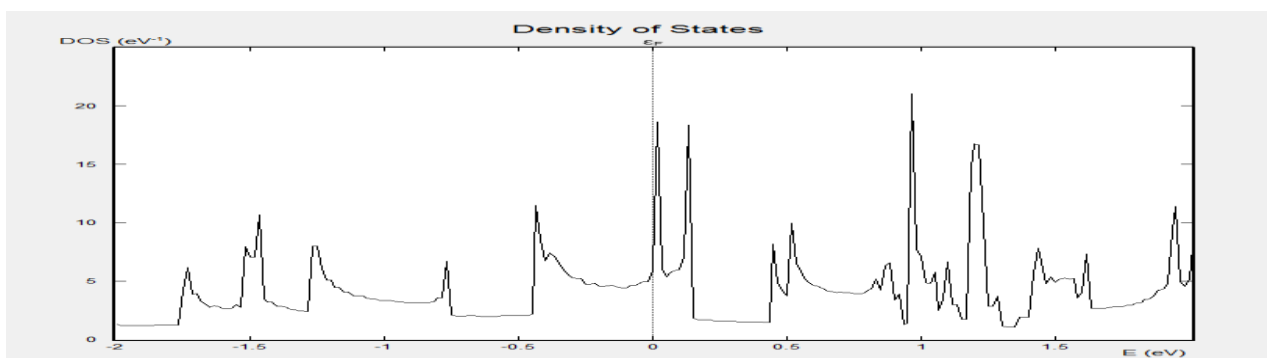


Figure 55 Total DOS

S, p, d Orbitals have very less values.

8 ZGNR Zr termination one edge:

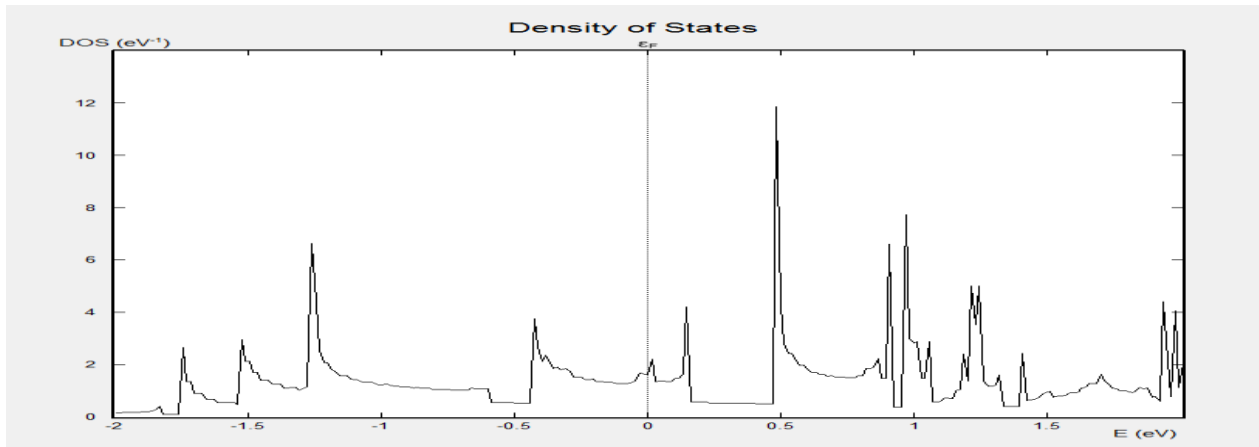


Figure 56 DOS P

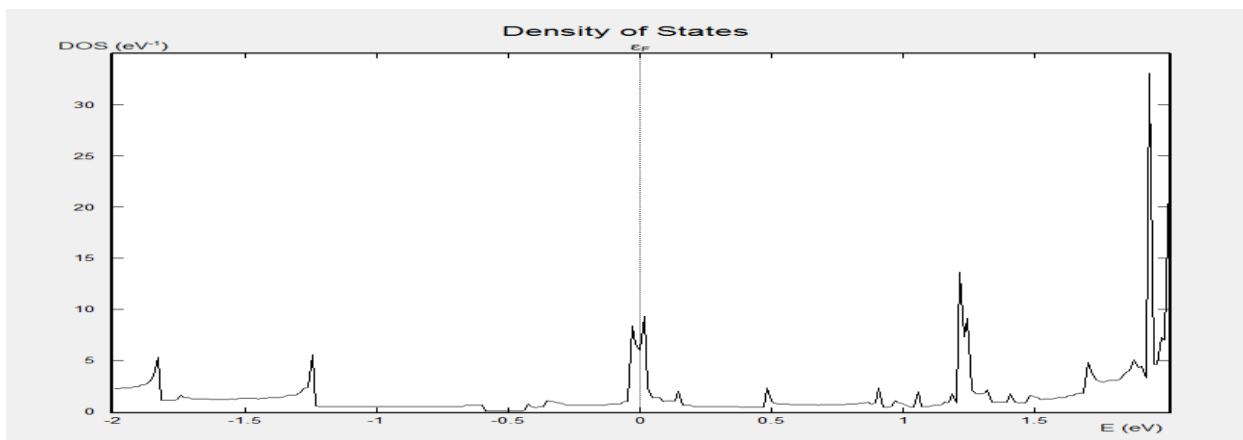


Figure 57 DOS D

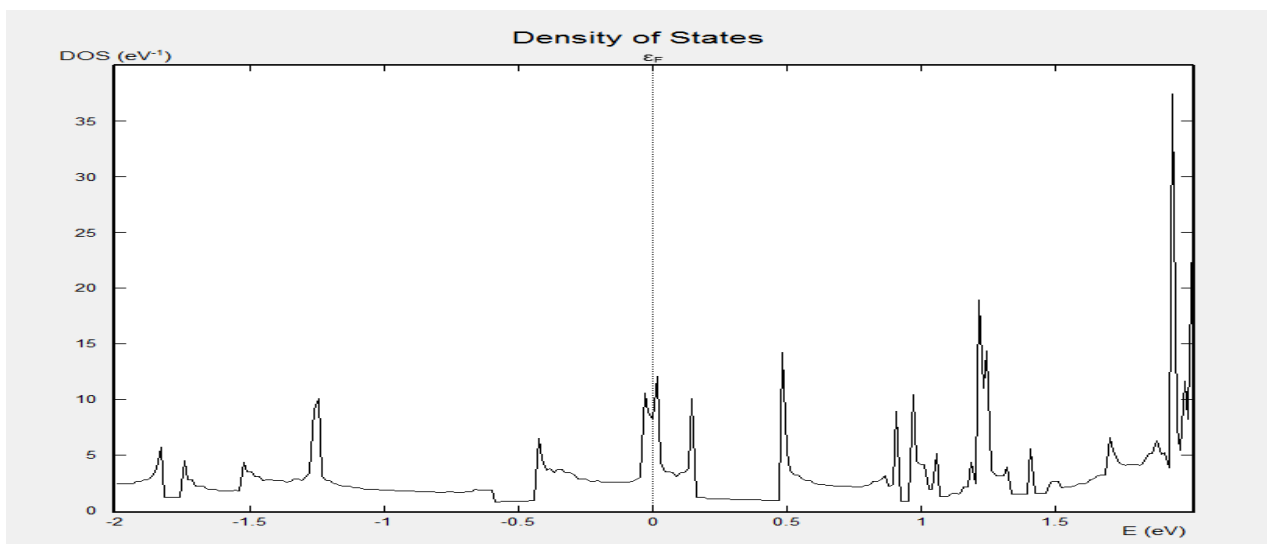


Figure 58 DOS Total

8 ZGNR Zr terminations both edge:

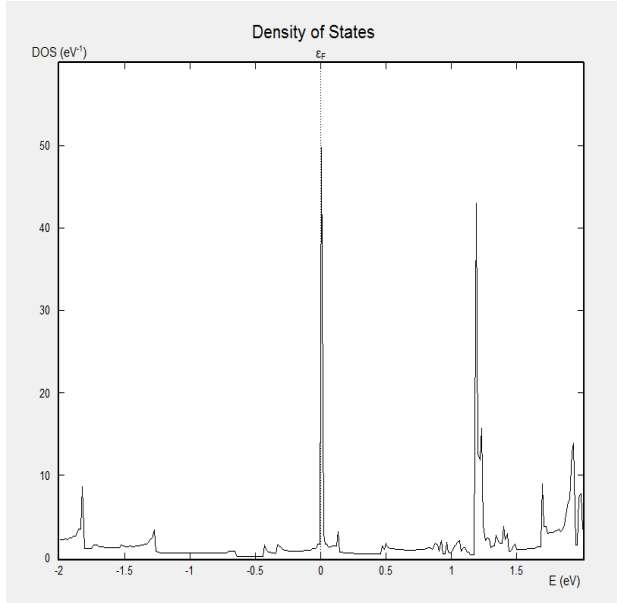


Figure 59 DOS P

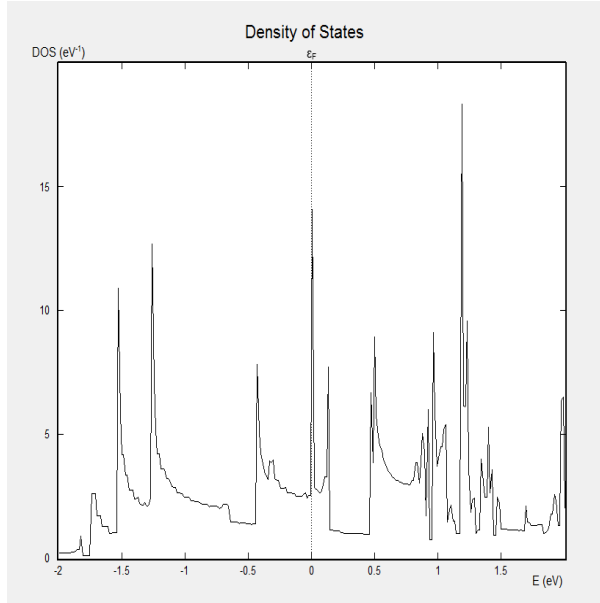


Figure 66 DOS D

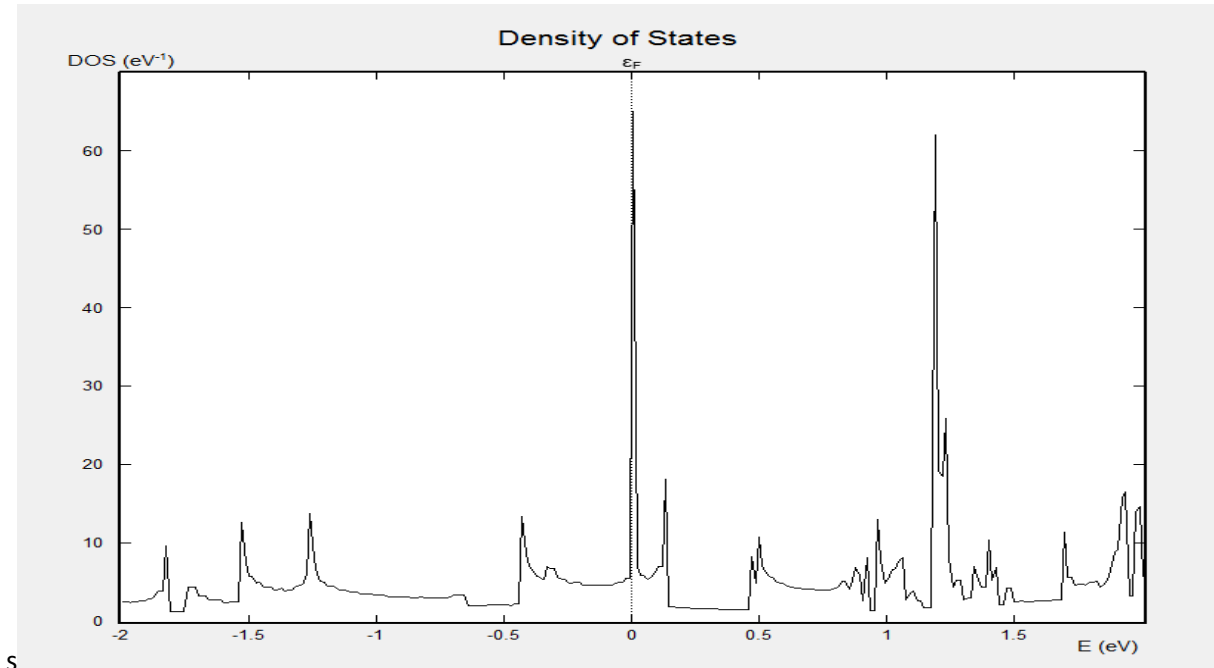


Figure 7 Total DOS

In this DOS the contribution of p orbital is only significantly larger than others. On comparing this with one edge it is clear that both edges are more metallic than one edge. To see the contribution of different orbital electron every orbit having some significant value at Fermi level

has been used. DOS in case for width 8 pristine ZGNR show the major contribution of 3p electrons. In case of one edge the p orbital contribution is very low than the both termination, this shows that

Both edge are more metallic than one edge.

CHAPTER 4

CONCLUSION

We investigated the effect of Titanium and Zirconium termination in ZGNR with the help of first principles calculation in DFT. We have investigated the electronic properties of pristine; Ti and Zr terminated. In our simulation we have used non spin polarised structure for the sake of simplicity because when we add spin to atoms it becomes more complicated to compute and requires good computational resources to do simulations. To analyse whether the structure are energetically stable or not we need to compute the binding energy of all configuration. We found that every ZGNR with Ti and Zr termination has negative binding energy which means they are stable. In this DOS the contribution of p orbital is only significant, others orbitals have very less contribution so they are not included. We have calculated the density of states of our configuration and compare them with the pristine .To see the contribution of different orbital electron every orbit having some significant value at Fermi level has been used.

Present analysis revealed that termination of ZGNR using transition metals (Ti/Zr) affects the stability and electronic properties of ZGNR considerably, and increased metallicity was observed. All the configurations were stable and both edge structures were found more stable than one edge in all configuration. The band structure in case of both edge terminations was found to have 5 bands crossing it. This was observed in both the cases Ti and Zr termination. In case of one edge termination the bond crossing the Fermi level is 3. We have only done our simulation for 4,6 and 8 width of zgnr, this could be increased to more numbers. Termination sites play an important role in graphene, so if we changed the termination to Doping and substitution we will observe very different properties. These properties than could be compare them with our results.

In future scope there are many possibilities like Ti and Zr termination could be used in Armchair nanoribbons, N chiral nanoribbons, Ti and Zr used as Doping and substitution could be used. More number of atoms could be analysed for more accurate. These other possibilities may take good amount of computational time. This observed increased metallicity can be used for Nano interconnects in Nano electronic and for sensor purpose.

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