Exploring semiconductor substrates for Silicene epitaxy

Amrita Bhattacharya†, Saswata Bhattacharya†, Gour P. Das∗
Dept. of Materials Science, Indian Association for the Cultivation of Science, Kolkata-32, India
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We have carried out first-principles based DFT calculation on electronic properties of silicene monolayer on various (111) semi-conducting surfaces. We find that the relative stability and other properties of the silicene overlayer depends sensitively on whether the interacting top layer of the substrate is metal or non-metal terminated. The nature of silicene-monolayer on the metal terminated surface can be metallic or even magnetic, depending upon the choice of the substrate. The silicene overlayer undergoes n-type doping on metal terminated surface while it undergoes p-type doping on non metal terminated surfaces of the semiconductor substrates.

Keywords: Silicene, Planar Nanostructures, Density Functional Theory, Electronic Structure

From first principles calculations, the 2D mono-layers of Silicon, known as silicene, has also been predicted to be stable with graphene like semi-metallic characteristics viz. a linear dispersion relation at the K point. The epitaxial growth of Ag thin film on Si(111) substrate has been explored by experimentalists in the past. The limited intermixing between Ag thin film and Si(111) substrate, make the choice of substrate ideal, for the growth of Ag thin films, so, it was natural to conjecture a reverse case. Infact, the experimental evidence of formation of silicene on Ag(001), Ag(111), Ag(111) substrates has been reported by various groups. The formation of silicene on Ag(110) substrate has also been studied using first principles methods by A. Kara et al. More recently, evidence of epitaxial Silicene on non-silver ZrB2-0001 substrate and Ir(111) substrate has also been reported. Moreover, silicene monolayer on Ag(111) was found to undergo a phase transition to two types of mirror-symmetric boundary-separated rhombic phases at temperatures below 40 K by scanning tunneling microscopy. However, the possibility of existence of other suitable substrates for formation of silicene monolayer can not be ruled out and has not been exhaustively explored till date.

In this communication, we report from our first principles based calculations, the bonding, stability and electronic structure of silicene monolayer, when epitaxially grown on various Group II-VI and Group III-V semiconductor substrates. The nature of silicene monolayer on the metal terminated surface of these substrates can be metallic or even magnetic, depending upon the choice of the substrate. The silicene overlayer undergoes n-type doping on metal terminated surface while it undergoes p-type doping on non metal terminated surfaces of the semiconductor substrates.

Our calculations have been carried out using first-principles density functional theory (DFT) based total energy calculations. We have used VASP code with projected augmented wave (PAW) potential and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional within generalized gradient approximation (GGA). An energy cut off of 600 eV has been used. The k-mesh was generated by Monkhorst-Pack method and the results were tested for convergence with respect to mesh size. However, for the generation of the electronic density of states (DOS) and band structure plots, higher values of k-points were used. In all our calculations, self-consistency has been achieved with a 0 eV convergence in total energy. For optimizing the ground state geometry, forces on the atoms were converged to less than 0.001 eV/Å via conjugate gradient minimization.

The silicene unit cell has a buckled hexagonal planar geometry, with a lattice parameter of 3.84 Å and a homogeneous Si-Si bond distance of 2.29 Å throughout the sheet. The semiconductor substrates viz. AlAs(111), AlP(111), GaAs(111), GaP(111), ZnS(111) and ZnSe(111), that we have considered for epitaxial growth of silicene monolayer, have reasonably good lattice matching with that of silicene, as given in TABLE. In this work, we have only considered the direct lattice matched non-polar substrates. However, other substrate orientations may also be relevant and will be addressed in our future work.
TABLE I. Binding energy (in eV/atom) of Silicene monolayer to different semiconductor substrates having lattice constants close to that of silicene (3.84Å).

| Surface     | Lat. const.(Å) | BE Si@MT | BE Si@NMT |
|-------------|----------------|----------|-----------|
| AlAs(111)   | 4.0038         | 0.630    | 0.370     |
| AlP(111)    | 3.8544         | 0.685    | 0.910     |
| GaAs(111)   | 3.9974         | 0.475    | 0.880     |
| ZnS(111)    | 3.8249         | 0.570    | 0.675     |
| GaP(111)    | 3.8541         | 0.605    | 0.525     |
| ZnSe(111)   | 4.0076         | 0.440    | 0.540     |


study.

Therefore, the unit cell of the composite system consists of the silicene monolayer (having two Si atoms) placed on top of six layers of the substrate (having 12 atoms), with a vacuum slab of 20Å above it. It is to be noted here that in these substrates, the contact layer of the substrate that interacts with the silicene overlayer could either be non metal terminated (NMT) or metal terminated (MT), e.g. in ZnS(111), the interacting layer could be either S terminated or Zn terminated (FIG.1). If the contact layer is NMT, then the MT bottom layer in the unit cell does not need H-passivation (FIG.1b). However, if the contact is MT, then the lowest layer of the six layer substrate in the unit cell is NMT that needs to be passivated by hydrogen (FIG.1b), in order to avoid the effect of dangling bonds. The nomenclature used for designating an unit of NMT substrate is NM6M6, while the MT substrate is denoted as M6NM6H. For calculating the binding energy (BE) and magnetic interaction of the silicene monolayer with the semiconductor substrates we have used a 4×4 supercell. The BE of silicene monolayer to the MT and NMT surfaces of these substrates are summarized in TABLE-II.

For MT surface the BE values lie in the range of 0.56 ± 0.12 eV/atom (TABLE-I) which is comparable to that of silicene monolayer on Ag(111) substrate, for which our estimated value (0.52 eV/atom) is in good agreement with first principle result of P. Vogt et.al [17]. Thus, on comparing the binding energies of silicene to semiconductor MT/ NMT substrates with Ag(111), we find that they are close or comparable for metal terminated surfaces of GaAs(111), GaP(111), ZnS(111), ZnSe(111) substrates and non metal terminated surfaces of AlAs(111), GaP(111) and ZnSe(111) substrates (TABLE-I). Our calculations show that when the bulk substrate (both MT and NMT) is cleaved to certain number of layers, the top layer contains uncompensated dangling bonds and therefore, give rise to magnetic moment in the substrate (TABLE-II). We have estimated the magnetic moment of the substrate, before and after introduction of silicene monolayer which are given in TABLE-II. We would first discuss the behaviour of silicene with the NMT semiconductor substrates. When silicene mono-
TABLE II. Magnetic Moment/ unit ($\mu_B$) of the substrate (4×4), before and after introduction of Silicene monolayer on it. The subscript denotes the number of units in the substrate.

| System | Mag. Si2@NMT | Mag. MT | Mag. Si2@MT |
|--------|--------------|---------|-------------|
| $\text{Si}_2\text{Al}_6\text{As}_6\text{H}$ | 1.41 | 0.84 | 0.00 |
| (As6Al6)$_4$ | 1.45 | (Al6As6H)$_4$ | 0.00 |
| $\text{Si}_2\text{P}_6\text{Al}_6\text{H}$ | 1.42 | 0.80 | 0.00 |
| (P6Al6)$_4$ | 1.48 | (Al6P6H)$_4$ | 0.00 |
| $\text{Si}_2\text{Ga}_6\text{As}_6\text{H}$ | 0.75 | 0.65 | 0.00 |
| (As6Ga6)$_4$ | 1.26 | (Ga6As6H)$_4$ | 0.00 |
| $\text{Si}_2\text{Ga}_6\text{P}_6\text{H}$ | 1.39 | 0.78 | 0.86 |
| (Ga6P6)$_4$ | 1.49 | (Ga6P6H)$_4$ | 0.86 |
| $\text{Si}_2\text{Zn}_6\text{Se}_6\text{H}$ | 0.00 | 0.00 | 0.38 |
| (Se6Zn6)$_4$ | 0.64 | (Zn6Se6H)$_4$ | 0.38 |
| $\text{Si}_2\text{Zn}_6\text{S}_6\text{H}$ | 0.00 | 0.00 | 0.00 |
| (Zn6S6)$_4$ | 0.65 | (Zn6S6H)$_4$ | 0.00 |

TABLE III. Bader Charge Analysis of Silicon atoms of the silicene overlayer on MT and NMT substrates. +ve denotes electron lost while -ve denotes electron gained.

| MT System  | NMT System  | MT Atom | Charge | NMT Atom | Charge |
|------------|-------------|---------|--------|----------|--------|
| Si2As6Al6H | Si2As6Al6H  | Si1     | -0.0475| Si1      | +0.001 |
| Si2        | Si2         | -0.17   |        | Si2      | +0.33  |
| Si2As6P6H  | Si2P6Al6H   | Si1     | -0.06  | Si1      | +0.0375|
| Si2        | Si2         | -0.16   |        | Si2      | +0.225 |
| Si2As6As6H | Si2As6Ga6H  | Si1     | -0.005 | Si1      | +0.015 |
| Si2        | Si2         | -0.255  |        | Si2      | +0.2475|
| Si2Ga6P6H  | Si2P6Ga6H   | Si1     | +0.01  | Si1      | +0.055 |
| Si2        | Si2         | +0.225  |        | Si2      | +0.2125|
| Si2Zn6Se6H | Si2Se6Zn6H  | Si1     | +0.005 | Si1      | +0.0275|
| Si2        | Si2         | -0.015  |        | Si2      | +0.0575|
| Si2Zn6S6H  | Si2S6Zn6H   | Si1     | +0.2175| Si1      | +0.425 |
| Si2        | Si2         | -0.24   |        | Si2      | -0.2375|

The Fermi level at Γ point.

Results of the Bader charge analysis of Silicene monolayer on the MT semiconductor substrates is shown in TABLE III. In case of most of the MT substrates, electrons are transferred from the substrate to the silicene overlayer because of higher electronegativity of the Si atoms as compared to the contact metal atoms of the substrate. As a result of this the Silicene overlayer undergoes a substrate induced n-type doping [24, 25]. While only in case of MT GaP(111) substrate, electrons are transferred from silicon to the substrate [ie. in the opposite direction] which suggest a p-type doping in the silicene overlayer similar to NMT cases [20, 27].

For a better understanding of the p-type/ n-type doping of the silicene overlayer, we have estimated the work function (WF) of MT/NMT ($\phi_s$) surfaces of semiconductor substrates and compared it with that of free standing silicene monolayer ($\phi_{fl}$). For $\phi_s > \phi_{fl}$, electrons are expected to transfer from silicene overlayer to the substrate, thereby leading to a p-type doping of the silicene overlayer. On the contrary, if $\phi_{fl} > \phi_s$, then electrons should be transferred from the substrate to the silicene overlayer leading to n-type doping. The results of our calculations shown in FIG 3 reveals that for MT substrates the WFs are consistently lower than that of free standing silicene (4.5 eV) with the exception of MT GaP(111) substrate (which is reverse to the other MT cases as also seen from the Bader analysis of TABLE III). However, for NMT surfaces the trend is just reverse leading to the p-type doping. This is just reverse leading to the p-type doping. From the layer projected DOS plot of FIG 2 the difference between the substrate induced p-type and n-type doping of the silicene overlayer can be observed. In case of GaP(111), the p-type doping of the silicene overlayer is accompanied by shift in Fermi level towards the valence band (FIG 2) while in the case of n-type doping (FIG 2, c and d) the Fermi level shifts towards the conduction band. This type of p-type or n-type doping in silicene-substrate composite system could be useful for band gap engineering of bilayer silicene following the case of bilayer graphene [28, 29].
FIG. 2. Layer projected DOS plot and electronic band dispersion of Silicence on: (a): Ga terminated surface of GaP(111). The blue and red dotted bands corresponds to the spin up and spin down components of Si respectively. (b): Ga terminated surface of GaAs(111) substrate. The blue dotted bands corresponds to those of Silicene. (c): Zn terminated surface of ZnS(111) substrate. (d): Zn terminated surface of ZnSe(111) substrate. The spin down band (blue dotted) corresponds to the conduction band only while the spin up band (red dotted) has contribution in both the valence band and conduction band at the Fermi level giving rise to half metallic behaviour.

FIG. 3. Comparison of work function of MT(111) and NMT(111) semiconductor substrates. The dotted line corresponds to the work function of freestanding silicene monolayer

In conclusion, we report from our first principles based calculations, the bonding, stability and electronic structure of silicene monolayer, when epitaxially grown on various Group II-VI, Group III-V and Group IV semiconductor substrates viz. AlAs(111), AlP(111), GaAs(111), GaP(111), ZnS(111) and ZnSe(111). We find that the relative stability and other properties of the silicene overlayer depends sensitively on whether the interacting top layer of the substrate is metal or non-metal terminated. The binding energy of silicene monolayer to the metal terminated surfaces of these substrates are estimated to be range in the 0.56 ± 0.12 eV/atom. The introduction of silicene monolayer on the NMT surface of all these semiconductor substrates, leads to enhancement in the magnetic moment of the composite system. However, the behavior of silicene on MT surface of semiconductor substrates can be metallic, magnetic or semi-metallic depending on the choice of substrate. It undergoes substrate induced p-type doping on NMT substrates while n-type doping on MT substrates [with an exception of GaP(111)] depending upon its charge transfer with the substrates.

† presently affiliated to Fritz-Haber-Institut der Max Planck Gesellschaft, Faradayweg 4-6, Berlin-14195, Germany.

*Corresponding Author Email id: msgpd@iacs.res.in

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