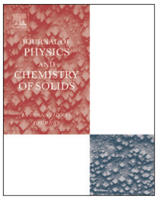
Journal of Physics and Chemistry of Solids 83 (2015) 32–39

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Shape dependent magnetic and optical properties in silicene nanodisks: A first principles study

Suman Chowdhury, Palash Nath, Debnarayan Jana*

Department of Physics, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata 700009, W.B., India

ARTICLE INFO

Article history:
Received 3 December 2014
Received in revised form
24 February 2015
Accepted 18 March 2015
Available online 18 March 2015

Keywords:
Silicene
Nanodisks
Density functional theory

ABSTRACT

We report the optical anisotropy of four differently shaped silicene nanodisks within the framework of density functional theory in the long wavelength limit ($q \to 0$). The calculations of density of states of all these nanodisks reveal clearly that zigzag trigonal (ZT) nanodisk has the maximum magnetic moment of $3.969\mu_B$. Further, the calculations related to optical properties indicate that the static value of real part of the dielectric constant and the real part of the refractive index assume maximum values for diamond shaped (DS) nanodisk in perpendicular polarization of the applied external electromagnetic (EM) field. However, in case of parallel polarization, significant changes in the static real part of dielectric constant and static refractive index are observed. Zero reflectivity is noticed around 3 eV and 5 eV for all nanodisks in parallel polarizations. Electron energy loss spectroscopy study reveals a presence of strong (intense) peak at 9 eV in perpendicular polarizations for all nanodisks. All these study may shed light on device fabrication in nano-opto-electronic technology and material characterization techniques.

1. Introduction

Graphene, a 2D material due to its unique electronic band structure has fostered to fascinating phenomena like massless Dirac fermion physics and quantum Hall effect [1–3]. Besides, its high carrier mobility and easy control of charge carriers have made it a promising candidate for next generation electronics. However, its lack of a non-zero finite band gap has forced it unsuitable in logic and high speed switching devices because the current in such a case can never be turned off completely. The band gap opening in graphene can be introduced by patterning graphene into nanoribbons [4–6], chemical functionalization with O, H, halogen atoms [7,8], B and N atoms [9–15], strain engineering [16,17], substrate interaction [18–21], and Stone–Wales defects [22–26]. However, the structures produced are not very much compatible with the existing silicon based industry. Silicene, a monolayer of Si atoms forming graphene like honeycomb lattice has recently attracted attention to researchers as a fascinating two-dimensional material beyond graphene. Being the allotropes of Si, these materials possess similar electron transport properties like graphene [27] and it has the added advantage being easily interfaced/integrated with the present Si based nano-electronic devices, thus promoting silicene as a better candidate than graphene. Moreover, due to the mixing of sp^2 and sp^3 hybridization, the typical buckling amplitude (~ 0.44 Å) is quite significant and in such a structure, the band gap can be easily tailored by applying transverse external static electric field [28] which is quite compatible with the experimental situation.

Silicene being a very soft material, its structure can be easily distorted upon adsorption of various atoms. In particular, adsorption of oxygen adatoms has been an interesting topic because this may lead to growth of monolayer silicon oxide. Recently, the oxygen dissociation and the adsorptions of dissociation induced oxygen atoms on free standing silicene have been studied by first principles calculations [29] and the calculations have indicated that free standing silicene is indeed unstable in oxygen. Thus, it is necessary to protect the silicon atoms from exposing to oxygen for using silicene as good electronic device. The reactivity of silicene over graphene indicates the easier fabrication in epitaxial growth under ultra-high vacuum [30]. In fact, it has been demonstrated that silicene can be grown epitaxially on silver surface (Ag (111)) [31]. The oxidation effects on (4×4) silicene on Ag (111) have showed [32] that the silicene oxide structure is a disordered one with a semiconductor like band structure. Besides, the metallic surface states arising due to hybridization of Si and Ag decay due to oxygen adsorption. These effects have also been experimentally verified by scanning tunneling microscope (STM) and angle resolved photo-emission spectroscopy (ARPES). The design of an effective encapsulation layer on the silicene has been

---

* Corresponding author.
E-mail address: djphy@caluniv.ac.in (D. Jana).

http://dx.doi.org/10.1016/j.jpcs.2015.03.017
0022-3697/

demonstrated [33] from the Raman spectra of Al_2O_3 capped silicene on Ag (111). Further, the strong chemical reactivity of silicene has promoted Özcelik et al. to predict [34] a stable single layer honeycomb like silica known as $h\alpha$ silica. Its stability has been verified both from positive values of phonon frequencies and the variation of free energy with temperature. It is believed that this proposed materials along with its derivatives may serve as a novel composite for future nanoelectronics [34].

Vacancy defects in single-layer graphene and silicene exhibit unusual interesting electronic and magnetic properties [35] emerging from their honeycomb structures and rotation symmetries. Recently, we have demonstrated [36] the magnetism of silicene under mono-vacancy, divacancy and substituted atoms such as Al and P. The first-principles calculations indicate the highest magnetic moment for divacancy situation while zero magnetic moment for mono-vacancy and 2 Al doped situations. We have also studied the optical properties of silicene nanosheet with varying concentrations of Al and P [37]. It is to be noted that unlike graphene, silicene is a topological insulator which can be characterized by full insulating gap with helical gapless edges [38]. Due to gapless nature of 2D graphene, considerable attention has been focused on to reduced dimensional nanostructure. Nanodisks are basically materials in nano-meter scale having closed edges. Graphene nanodisks have been constructed from several benzenes [39]. Furthermore, nanodisks are thought to be an integral block for the construction of various types of nanoribbons. In particular, it has been demonstrated [40] that trigonal zigzag graphene nanodisk possesses half-filled zero energy states and they are metallic as well as ferromagnetic in nature. Zero dimensional nanodisks have been proposed to be ideal for nano- and spintronic devices [43]. Sony and Shukla [44] have studied the optical absorption spectra of various graphene nanodisks by using Pariser–Parr–Pople (PPP) model. Electronic properties of honeycomb silicene nanodisks have been studied by Kikutake et al. [45] taking into account the edge states. In particular, the authors have [45] found the counting rule of the zero-energy states and constructed the low-energy theory of zigzag triangular silicene nanodisks. Motivated by the electronic properties of graphene nanodisk and the magnetic property of single layer graphene and silicene, we are interested here to study the electronic and optical properties of silicene nanodisks of various shapes within the framework of density functional theory (DFT). In particular, electron energy loss spectroscopy (EELS) and optical absorption spectroscopy are indeed convenient and broadly used characterization techniques for materials. EELS study will indicate the effective collective excitation (plasmonic) modes in the system. Thus, optical properties of such anisotropic nanodisks are very important and essential for designing and characterizing various opto-electronic devices. Recently, a distinctive change of electron energy loss function of silicene multilayers on silver (Ag) substrate has been noticed with the variation of thickness of Ag [46]. In this paper, we demonstrate the shape dependent magnetic and optical properties of silicene nanodisk in the long wavelength limit ($q \to 0$).

2. The methodology

In this work, we have used well-tested Troullier–Martin norm [47], conserving pseudopotentials, in fully separable Kleinman and Bylander form for silicon. The calculations have been performed in the framework of DFT [48–50], within the generalized gradient approximation (GGA) according to Perdew, Burke, Ernzerhof (PBE) [51] parameterization implemented in SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [52–54] code. A large simulation box of dimension $25 \times 25 \times 25$ Å^3 is considered to avoid any interaction between its periodic image along all directions. The double ζ plus polarized basis set is employed through out the whole range of systems. A 300 Ry mesh cutoff has been used for the reciprocal space expansion of the total charge density. Brillouin zone (BZ) has been sampled by using $24 \times 24 \times 1$ Monkhorst–Pack (MP) [57] of k points. All the simulations are performed using the diagonalization method. All the structures are optimized by minimizing the forces on individual atoms below 10^{-3} eV/Å using the standard conjugate-gradients (CG) technique. The convergence criteria for energy of self-consistent field (SCF) cycle is chosen to be 10^{-4} eV. Optical properties of any system [58,59] are in general calculated with the help of frequency dependent complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where ϵ_1 and ϵ_2 are respectively the real and imaginary parts of the dielectric function. First-order time-dependent perturbation theory is used for the calculations of dielectric properties in which dipolar transition matrix elements between occupied and unoccupied single electron eigenstates are computed, as implemented in the SIESTA code within Kohn–Sham (KS) formalism [52–54]. In the long wavelength limit ($q \to 0$) the imaginary part of the dielectric function [52–54,60,13] is given by

$$\epsilon_2(\omega) = \frac{2e^2\pi}{\omega\epsilon_0} \sum_{K,CB,VB} \left| \left\langle \psi_K^{VB} | \vec{u}\,.\,\vec{r} | \psi_K^{CB} \right\rangle \right|^2 \delta\left(E_K^{CB} - E_K^{VB} - \omega \right) \tag{1}$$

In expression (1), ω is the frequency of the electromagnetic (EM) radiation in energy unit. Ω represents the volume of the supercell and ϵ_0 is the free space permittivity. CB and VB represent the conduction band and the valence band respectively. $\vec{u}$ and $\vec{r}$ denote the polarization vector and position vector of EM field respectively.

Sufficient number of unoccupied states (above Fermi level) has been used for the calculations of dielectric spectra. To introduce the exchange and correlation effect, the self-consistent ground state DFT energies and eigenfunctions have been inserted into the dipolar transition matrix elements. In this way, we have calculated the imaginary part of the dielectric function ϵ_2, which is then used to calculate real part (ϵ_1) of dielectric function with the help of Kramers–Kronig (KK) transformations [55,56]. Optical calculations were carried out using $10 \times 10 \times 1$ optical mesh and 0.2 eV optical broadening. For parallel polarization the direction of the electric field is chosen to be incident parallel to the plane of the silicene nanodisks, whereas for perpendicular polarization the direction of the electric field is considered to be incident perpendicular to the plane of the nanodisks.

To calculate other related optical properties of four types of silicene nanodisks from $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ data we proceed as follows. The complex refractive index ($\widetilde{N}$) of any material is related to the complex dielectric function ($\epsilon(\omega)$) by the relation $\widetilde{N} = \sqrt{\epsilon(\omega)}$. From this, one can get the real as well as the imaginary part of the refractive index in the form $\widetilde{N} = n(\omega) + ik(\omega)$, where

$$n(\omega) = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2} \right)^{1/2}, \quad k(\omega) = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2} \right)^{1/2} \tag{2}$$

With the magnitude of $n(\omega)$ and $k(\omega)$, one can compute the reflectivity at normal incidence of EM wave of the system using the relation, the reflectivity and the absorption coefficient can be written respectively as

$$R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad \alpha(\omega) = \frac{2k\omega}{c\hbar} \tag{3}$$

where c represents the speed of light in vacuum and ω is in the energy unit. The direct measure of the collective excitation is the quantity called EELS. It is given by the relation $L(\omega) = \mathrm{Im}(-1/\epsilon(\omega))$ or in terms of ϵ_1 and ϵ_2, $L(\omega) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$.