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First-principle calculations of structural, electronic, optical and thermal properties of hydrogenated graphene

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ABSTRACT

First-principle calculations of the structural, electronic, optical and thermal properties of hydrogenated graphene have been performed for three stable structures: chair, boat and tricycle using the plane wave Pseudo-potential method within density functional theory (DFT). The band structure and density of states have been studied. The values of 19 parameters have been calculated for all three structures. Four parameters such as dielectric constants, birefringence, plasmon energy and Debye temperature have been studied for the first time. The calculated values are in good agreement with the available experimental and reported values.

1. Introduction

The silicon based semiconductor technology has reached to the maximum limits of performance improvements. In the recent past, a constant effort has been made by researchers to investigate new and non-traditional materials, which electronic properties can be controlled by electric field. In 2004, single paper on graphene made a revolution in science and technology published by Noveselov et al. [1]. Graphene has potential applications in cutting-edge classes of electronic devices because of high electron mobility and current carrying capacities in comparison to semiconductors [2–5]. Recently, comprehensive up-to-date reviews on the basic science of graphene has been given by several workers [6–8]. High speed graphene transistors operating at gigahertz frequencies have already been designed and developed [9–11]. Nowadays, major chip makers are planning to make an International Technology Roadmap for designing ICs based on graphene which is most promising material for post-silicon electronic [12]. The lack of an energy band gap of the semi-metal graphene limits the electronic applications precluding their use as FETs and other high speed switching devices. This has prompted researchers to seek different methods for developing band gap in graphene by adsorbing or doping other atoms in graphene called functionalization [13,14]. A two dimensional covalently functionalized graphene in which adsorbent atom is hydrogen is called hydrogenated graphene (graphane). After the hydrogenation, carbon atoms change from the sp^2 to sp^3 hybridization. The changes in the properties of graphene with hydrogenation are due to change in hybridization which changes the lattice constants, bond lengths, partial density of states (PDOS) and total density of states (TDOS). It plays an important role in creating energy band gap. Hydrogenated graphene has a perfect two-dimensional periodic structure characterized by a sp^3 hybridization, covalently bonded hydrocarbon with a C:H ratio of one. Many hydrogenated forms of graphene such as chair, boat, tricycle, stirrup and twist-boat have been developed. Out of these, three structures: chair, boat and tricycle are most stable. Therefore, we thought it would be of interest to further study the various properties of these three structures in detail. Graphane was first theoretically predicted by Sofo et al. [15] and afterwards experimentally demonstrated by Elias et al. [16] using Raman spectroscopy and transmission electron microscopy. Using molecular dynamics methods, mechanical properties of hydrogenated graphene allotropes [17], patterned arrangement regulated mechanical properties [18], surface hydrogenation regulated wrinkling and torque capability of hydrogenated graphene annulus under circular shearing [19], with tilt grain boundaries tuned by hydrogenation [20] and thermal characteristics of graphene nanoribbons endorsed by surface functionalization [21] have been studied by different workers. Recently, several workers have studied the structural, electronic, elastic and vibrational properties of graphane using first-principle calculations [22–25]. The electronic structure of graphane within density functional theory (DFT) [26] have been calculated using SIESTA code [27] and local density approximation (LDA) [28]. Anisotropic optical properties have also been studied using first-principle calculations [29]. Various elastic [30] and thermal [31] properties of graphane have been studied using the Quantum Espresso code. A review article covering the important aspect of graphane including its structural properties, fabrication techniques and potential applications have been given by Zhou et al. [32]. Theoretical analysis of mechanical

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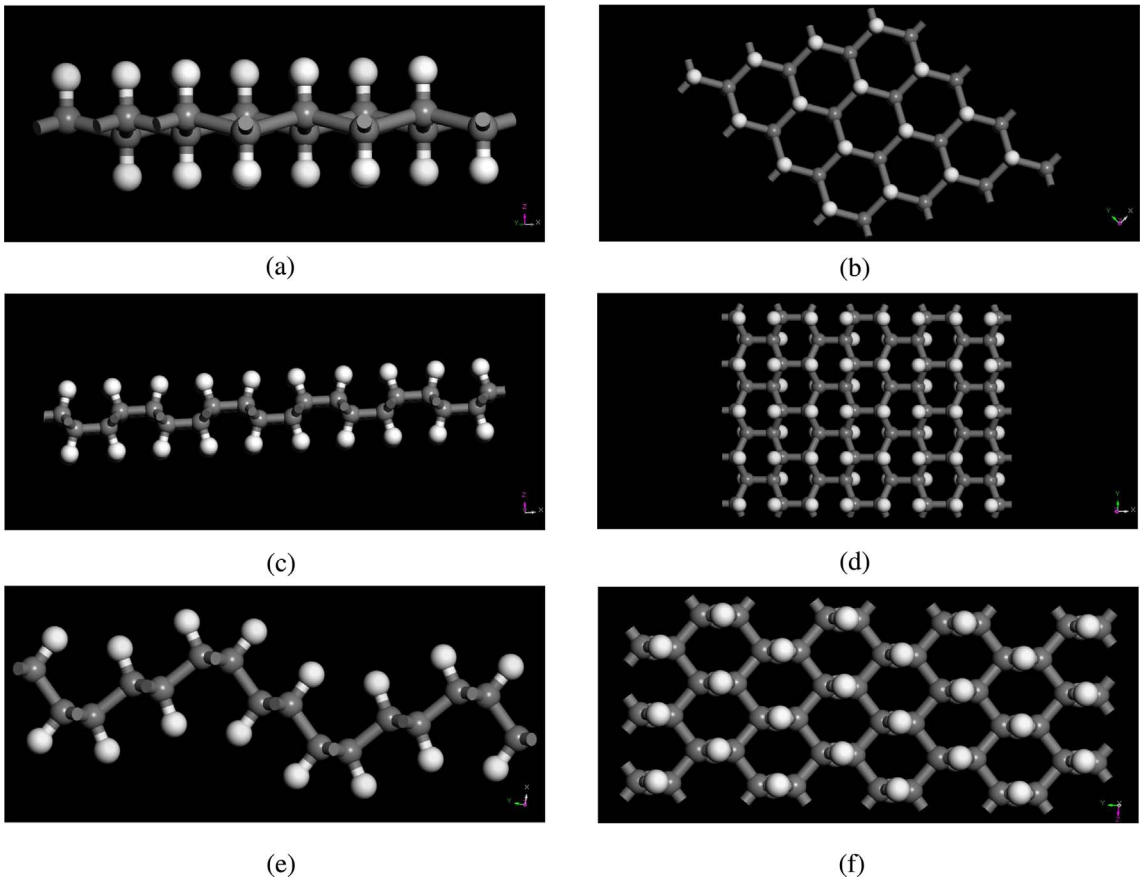

Fig. 1. Pictorial representation of graphane configurations in which hydrogen atoms are indicated by white circles and the carbon atoms by grey circles. (a) and (b) show the side and top view of chair configuration. (c) and (d) show the side and top view of boat configuration. (e) and (f) show the side and top view of tricycle configuration, respectively.

Table 1
Lattice constant (a), C–C bond length (d $_{C-C}$), C–H bond length (d $_{C-H}$), C–C–C bond Angle (θ_{C-C-C}), C–C–H bond Angle (θ_{C-C-H}), band gap energy (E_g), binding energy (E_b) of chair, boat and tricycle graphane configurations.

Parameters	Chair		Boat		Tricycle	
	This work	Reported	This work	Reported	This work	Reported
a (Å)	2.54	2.42[a], 2.516[b], 2.539[c], 2.54[d], 2.51[e]	4.435	4.272[b], 2.48[c],	21.360	15.0[g]
d_{C-C} (Å)	1.513	1.52[b], 1.536[c], 1.54[d], 1.52[e]	1.546, 1.609	1.52[b], 1.56[b], 1.543[c], 1.570[c], 1.54[d], 1.57[d],	1.562, 1.562, 1.559, 1.559	1.539[g], 1.541[g], 1.540[g], 1.541[g]
d_{C-H} (Å)	1.112	1.11[b], 1.104[c], 1.11[d], 1.12[e]	1.104	1.10[b], 1.099[c]	1.113, 1.114	1.108[g], 1.109[g]
θ_{C-C-C} (degrees)	112.01	110[a], 111.5[c], 111.5[d], 111.51[e]	113.182, 111.871	111.8[c], 110.7[d], 112.3[d]	109.1, 105.9, 107.7, 105.5	
θ_{C-C-H} (degrees)	107.407	110[a], 107.4[c], 107.4[d], 107.35[e]	107.432	107.0[c], 107.2[d]	113.552, 110.447	
E_g (eV)	3.424	3.5[b], 3.491[c], 3.42[e]	3.403	3.7[b], 3.374[c]	3.515	3.446[g]
E_c (eV)	25.5	27.65[e]	49.6		100.2	
E_b (eV)	3.852	2.8[f]	3.43		3.512	

[a] Experimental given in Ref [16].
[b] Ref. [15].
[c] Ref. [23].
[d] Ref. [22].
[e] Ref. [24].
[f] Ref. [25].
[g] Ref. [48].

properties have been discussed by Peng et al. [33]. Recently, the authors have studied the various properties of $ZnSiP_2$ [34], $ZnGeP_2$ [35] and other chalcopyrites [36] using first-principle calculations, and I-III-VI_2 semiconductors using solid state theory of plasma oscillations [37]. In this paper, structural, electronic, optical and thermal properties of three different structures of graphane: chair (C), boat (B) and tricycle (T) have been studied using the first-principle calculations within the density functional theory (DFT). The values of 19 parameters such as lattice constant (a), bond lengths (d_{C-C} and d_{C-H}), bond angles (θ_{C-C-C} and θ_{C-C-H}), energy gap (E_g), cohesive energy (E_c), binding energy (E_b), dielectric function $\varepsilon(\omega)$, refractive index $n(\omega)$, birefringence $\Delta n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, conductivity $\sigma(\omega)$,