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Influence of antisite defect upon decomposition of nitrous oxide over graphene-analogue SiC

Ali Ahmadi Peyghan [a], Morteza Moradi [b,*]

[a] Young Researchers and Elite club, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[b] Materials and Energy Research Center, Semiconductors Department, P.O. Box 31787-316, Karaj, Iran

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ABSTRACT

Using density functional theory including dispersion correction, we have studied adsorption of nitrous oxide (N_2O) molecule on the pristine and antisite defected graphene-like silicon carbide (*h*-SiC) in terms of energetic, geometric and electronic properties. The N_2O is weakly adsorbed on the pristine sheet releasing energies in the range of 14.2 to 28.9 kJ/mol. Electronic properties of the pristine *h*-SiC are not influenced by the adsorption process. It is predicted that the N_2O molecule can strongly interact with the Si-antisite defected sheet (D_{Si}) in such a way that its oxygen atom diffuses into the surface, releasing an N_2 molecule. The energy of this reaction is calculated to be about 540.1 kJ/mol and the electronic properties of the D_{Si} are slightly altered.

1. Introduction

Nitrous oxide (N_2O) is an important component of the earth's atmosphere that has gained significant attention of late due to its environmental effects [1]. Due to its long life, of approximately 150 years, in the atmosphere, it is a potent greenhouse gas (ca. 310 and 21 times greater warming potential than carbon dioxide and methane, respectively) and is involved in the depletion of stratospheric ozone [1–5]. N_2O is produced by both natural and anthropogenic sources. Biological processes in soils and oceans are the primary natural sources of N_2O. The anthropogenic sources include agriculture (fertilizer production), nitric acid production, adipic acid production, fossil fuel combustion (stationary and mobile), biomass combustion and sewage treatments [4]. Nitric acid production is currently believed to be the largest industrial source of N_2O emissions [6]. Thus, a reduction in anthropogenic N_2O emissions is urgently required, and catalytic direct N_2O decomposition is considered the most effective and economic method to achieve this target [7].

Carbon nanotubes (CNTs) were identified for the first time by Iijima in 1991 as by-products of arc discharge experiments [8]. They are light and flexible, have a high elastic modulus, and show electronic properties that are dependent on their diameters and chiralities [9]. In addition to CNT, there are also some other nanotubes found experimentally such as silicon carbide (SiC) [10–12]. The outstanding properties of SiC including physical, chemical, and thermal properties enable it to be employed in high temperature, high frequency, and harsh environments [13]. There are some differences between silicon and carbon, for example, Si has lower electronegativity, weaker bonds (except when bonded to very electronegative atoms), kinetically more reactive, larger atomic radius, etc. These differences lead to differences in the properties of silicon compared with carbon. A great amount of experiment and theory has demonstrated that the existence of defects, such as Stone–Wales defects, vacancies, antisite, and pentagon–octagon in graphene and nanotubes can drastically change their properties [14–17].

By the analogy with CNTs, SiC nanotubes (SiCNTs) can be considered to be formed by rolling SiC sheet (*h*-SiC). In a previous study it was reported that the most stable structure of planar *h*-SiC forms graphene-like [18]. Banerjee et al. [19] have reported that the upper energy levels of the valence band (near Fermi energy) are primarily contributed by the p-orbital of carbon atoms, and the p-orbitals of Si atoms form the lower energy of the conduction band. Sun et al. have indicated that instead of being a semimetal as graphene, the infinite periodic *h*-SiC is a semiconductor; its armchair ribbons are nonmagnetic semiconductors while its zigzag nanoribbons exhibit magnetic metallicities [20]. *h*-SiC with sp^2 bond may be implied in electronic devices in future. In contrast to the half-metal behavior of graphene, *h*-SiC possesses polar Si–C bond and wide band gap [21], which promises the potential application of *h*-SiC in this silicon age of the semiconductor. The electronic and magnetic properties of the *h*-SiC have been extensively studied [22].

In nanostructure research, molecular interaction (e.g. of carbon monoxide, nitrogen monoxide, methane and so forth) with the nanostructure surface is a subfield of considerable interest due to potential applications such as storage, pollutant dissociation, and sensor [23–26]. However, most of gases are found physisorbed on suspended pristine graphene. The reactivity of graphene is often adjusted by doping with other elements or topological defects [27]. Zhang et al. [28] have investigated

* Corresponding author. Tel.: +98 912 2467683.
E-mail address: 2m.alborzi@gmail.com (M. Moradi).

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adsorption mechanisms of single oxygen on pristine and antisite-defected SiCNTs. It was found that the SiCNTs with antisite defect are more reactive than perfect nanotube for adsorbing oxygen atoms. Here, we have tried to find the answers of the following questions: (1) whether there is a potential possibility of *h*-SiC serving as a suitable surface for N_2O dissociation or not; (2) if not, what is the strategy that can be applied to improve the applicability of *h*-SiC to N_2O dissociation?

2. Computational methods

We selected an *h*-SiC consisted of 39 Si and 39 C atoms, in which the end atoms have been saturated with hydrogen atoms to reduce boundary effects. The full geometry optimizations and property calculations on the pristine and antisite defected *h*-SiC in the presence and absence of a N_2O molecule were performed using three parameter hybrid generalized gradient approximation using B3LYP functional augmented with an empirical dispersion term (B3LYP-D, [29]) with 6-31G basis set including the d-polarization function (denoted as 6-31G (d)) as implemented in the GAMESS suite of program [30]. GaussSum program [31] has been used to obtain the density of states (DOS) results. The B3LYP density functional has been previously shown to reproduce experimental properties and has been commonly used in nanostructure studies [32,33]. We have defined adsorption energy in the usual way as:

$$E_{ad} = E\,(\text{h-SiC}) + E\,(N_2O) - E\,(N_2O/\text{h-SiC}) + E_{BSSE} \quad (1)$$

where E (N_2O/*h*-SiC) corresponds to the energy of the *h*-SiC in which the N_2O has been adsorbed on the surface, E (*h*-SiC) is the energy of the isolated sheet, E (N_2O) is the energy of a single N_2O molecule, and E_{BSSE} is the energy of the basis set superposition error which was calculated using counterpoise correction method [34,35]. To investigate the electronic charge changes through the *h*-SiC, the net charge-transfer (Q_T) between N_2O molecule and the sheet is calculated by Mulliken analysis which is defined as the charge difference between the N_2O molecule adsorbed on the *h*-SiC and an isolated N_2O molecule.

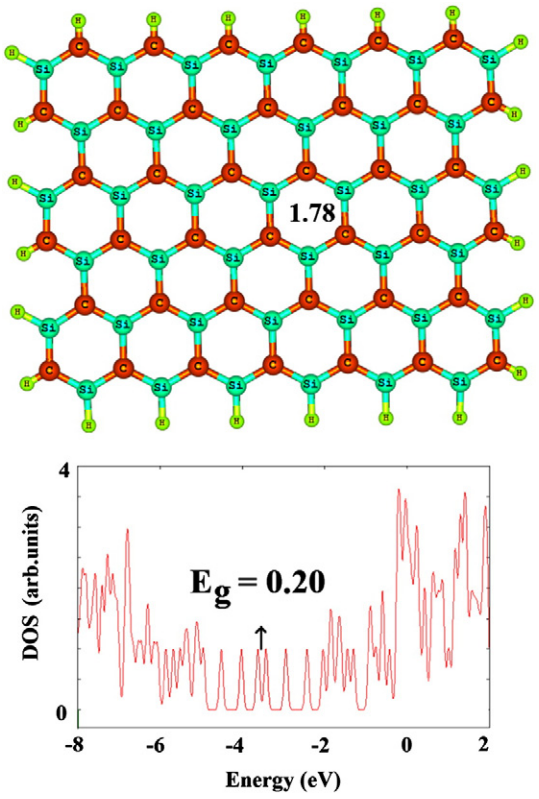

Fig. 1. Structure of optimized *h*-SiC and its density of state (DOS) plot. Bonds are in Å.

3. Results and discussion

3.1. N_2O adsorption on pristine h-SiC

The optimized structure and geometry parameters of the pristine *h*-SiC are shown in Fig. 1, in which Si–C bond length is 1.78 Å, in good

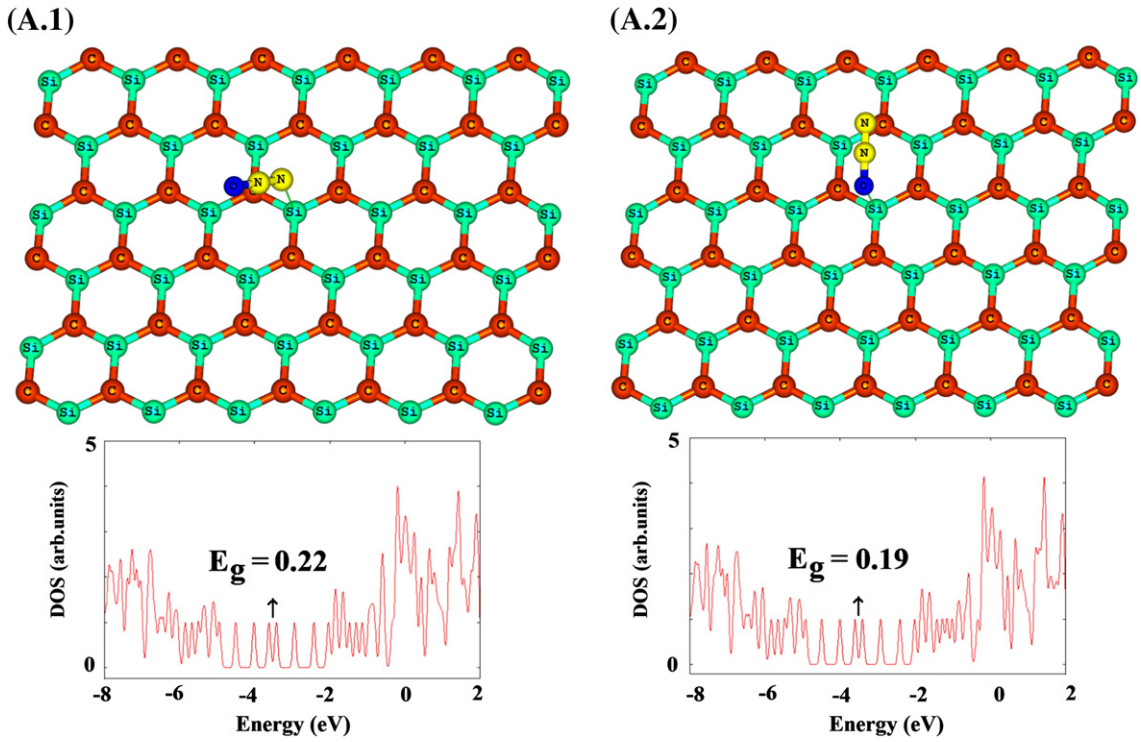

Fig. 2. Structures of optimized N_2O/*h*-SiC and their density of state (DOS) plot. Bonds are in Å.