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Gas adsorption on silicene: A theoretical study

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ABSTRACT

The adsorption of several common gas molecules on silicene has been studied using density functional theory (DFT). The most stable configurations, the corresponding adsorption energies, charge transfer, and electronic properties of several common gas molecules on silicene are thoroughly discussed. We find that silicene exhibits significantly high reactivity towards NO_2, O_2, and SO_2 with the adsorption energies being larger than 1.00 eV, suggesting its potential applications for the development of metal-free catalysts. Moreover, NO and NH_3 can be adsorbed on silicene with a moderate adsorption energy (0.35 and 0.60 eV), indicating that silicene could be a good NO or NH_3 sensor. Moreover, the band gap of silicene is opened upon adsorption of NO, O_2, NH_3, and SO_2 in various ways, while NO_2 adsorption makes silicene half-metallic nature. In addition, we find that the Stone–Wales defect and Ag(1 1 1) substrate can enhance the chemical reactivity of silicene. Our results may be useful not only to deeply understand the properties of silicene, but also to initiate one to further explore its potential applications in catalysis, gas detecting as well as electronics.

1. Introduction

Due to its unique mechanical and electronic properties, graphene has attracted enormous attention since it discovery in 2004 [1]. Potential applications of graphene in integrated circuits, transparent conducting electrodes, and hydrogen storage materials have been widely explored [2–6]. Recently, it has been reported that graphene is an interesting candidate for usage as a gas sensor because of its high sensitivity, which is ascribed to its high electron mobility at room temperature [7–10]. In particular, graphene is more suitable for device integration than carbon nanotube because the planar structure of graphene maximizes its interaction with adsorbates. Experimentally, it was shown that the sensitivity of graphene to NH_3, CO, and H_2O up to 1 ppb, and even the ultrahigh sensitivity of an individual molecule was suggested for NO_2 [6]. Other experiments [11] and calculations [12,13], however, show that these adsorbates are only physisobed on pristine graphene. In this sense, pristine graphene cannot detect the above gas molecules, since they do not bind or adsorb weakly on pristine graphene. To overcome this problem, the introduction of point defect or substitutional doping of impurity atoms into graphene is found to be an effective way to enhance the sensitivity of graphene to gas molecules [14–17]. For example, Dai et al. have suggested theoretically that B- and S-doped graphene could be a good sensor for NO and NO_2 [16]. However, in this proposed method, the sensitivity that graphene can provide is not fully achieved as only a very small portion of atoms on the graphene is reactive to gas molecules, since the corresponding dopant concentration is only 3.125% [16]. For practical applications, graphene-like materials with a large region are highly desired for detecting gas molecules as far as the sensitivity is concerned.

Silicene, a monolayer of hexagonally arranged silicon atoms [18], has been theoretically predicted [19–23] and experimentally synthesized [24–33]. Similar to its graphene counterpart, freestanding silicene exhibits essentially the same electronic properties according to density functional theory (DFT) calculations [18,19,34]. For example, the band structures of silicene resemble those of graphene, that is, π and π^* bands cross linearly at the Fermi level of the Brillouin zone, resulting in a massless Dirac fermions character of the charge carriers [35]. However, the differences in properties between silicene and graphene are very apparent: (1) the Si–Si bond length in silicene (2.29 Å) is much longer than that of the C–C bond in graphene (1.42 Å); (2) silicene possesses much higher chemical reactivity towards foreign adsorbates than graphene. This is expected, because there are sp^2-/sp^3-hybridized Si atoms in silicene, which is essentially different from the sp^2 hybridization of graphene. The π bonds in silicene come from the overlapping of $3p_z$ orbitals of Si atoms, while the overlapping of $2p_z$ orbitals of C atoms contribute to the π bonds of graphene [36]. Since the overlapping of $3p_z$ orbitals is relatively

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weak than that of $2p_z$ ones, the strength of π bonds in silicene should be very weak and are easily broken by the foreign species [37]. Though pristine silicene is a semimetal, the band gap in silicene monolayer can be opened up at the Fermi level by either applying external electric field or chemical functionalization with different functional groups [37–48].

To date, although the free-standing silicene sheets have not been isolated yet, silicene is believed to have a bright future and the relevant studies are in the stage of booming development. Experimentally, Ag surfaces have been used to grow and synthesize silicene nanoribbons and sheets [35,49]. For example, silicene nanoribbons on Ag(110) surface presented a magic width of 1.6 nm and aligned parallelly with each other in a well distributed way [21,27]. Especially, Vogt et al. have epitaxially synthesized large area silicon monolayer on Ag(111) surface [31], making the theoretical predicted silicene monolayer comes true. In addition, it was recently shown that the Dirac cone of silicene is destroyed at the *K*-point when epitaxially grown on Ag(111) [31,50–52], which is mainly attribution its lattice distortions and strong chemical interaction with Ag, resulting in strongly hybridized states [21].

In light of the high reactivity of silicene and the potential applications of graphene for the development of gas sensor and metal-free catalyst, we are very interested in the following questions: (i) can some common gas molecules be adsorbed silicene? (ii) If can, can silicene be used to detect or activate (catalyze) these gas molecules? (iii) How do the defects and substrates influence the adsorption of gas molecules on silicene? Hence, in the present work, we have studied the adsorption of several common gas molecules (CO, NO, NO_2, O_2, CO_2, NH_3, and SO_2) on silicene by

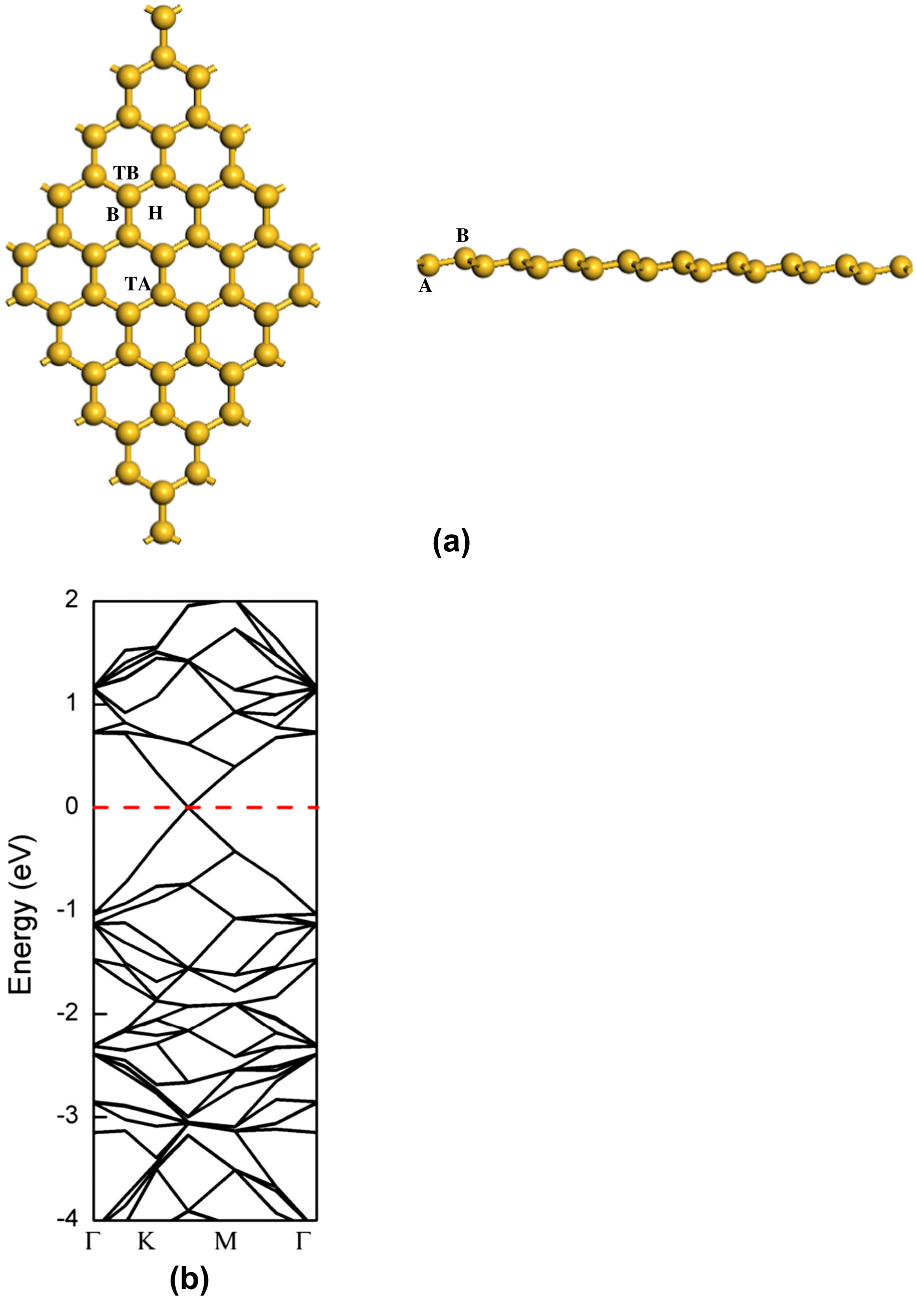

Fig. 1. (a) The buckled hexagonal structure of silicene, the four adsorption sites considered H, TA, TB, and B, and the sublattices A and B. (b) The band structure of silicene. The Fermi level is set to zero.