Carbon 117 (2017) 246–251

Contents lists available at ScienceDirect

Carbon

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

Investigation on the contact between graphdiyne and Cu (111) surface

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ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form
14 February 2017
Accepted 28 February 2017
Available online 28 February 2017

Keywords:
Graphdiyne
Copper surface
Interface
Bonding strength
Charge transfer
Density of state

ABSTRACT

Since graphdiyne has been proved with excellent physical properties and successfully synthesized on copper foil, understanding its contact with copper surface is of great significance for its applications. Here, we investigate the interfacial structural, mechanical and electronic properties of the contact between graphdiyne and Cu (111) surface through first principles calculations. The most stable interface structure is confirmed according to interfacial binding energies. The interface rigid peeling process is simulated to obtain the interfacial bonding strength. Different kinds of interfacial interactions are found by the results of charge density and density of state. With interface distance decreasing, charges are transferred from the copper surface to the upper layer graphdiyne, and different bond interactions occur between surface Cu atoms and graphdiyne, which make the contact between graphdiyne and copper surface more tightly and provide a bridge for charge transfer at the interface. The results are hoped to be helpful to understand the contact between graphdiyne and copper surface and predict the performance of related nanoelectronics.

1. Introduction

As a single atomic layer two-dimensional material isolated from graphite in 2004 [1], graphene has attracted much interest due to its unique properties [2]. However, the intrinsic zero band gap becomes an impediment for its applications in semiconductor devices, and there are still lots of challenges to effectively open a large band gap although much efforts has been made [3–5]. Recently, graphdiyne, a carbon allotrope which has a similar symmetry with graphene and has butadiyne linkages between two nearest neighbor hexagonal rings, has been grown on copper surfaces with a large area of 3.61 cm^2 and a nature semiconductor property with conductivity of 2.516×10^{-4} Sm^{-1} [6]. First principles calculations indicate that it has a nature band gap of 0.46 eV [7] and a carrier concentration of 2.74×10^{11} cm^{-2} for holes and 1.62×10^{11} cm^{-2} for electrons [8]. Due to the two-dimensional structure and remarkable electronic, optical and mechanical properties [9–14], graphdiyne is expected to be a new carbon nanomaterial applied in fields such as field emission devices [15], solar cells [16], photocatalytics [17] and field effect transistors [18].

As key elements in nanodevices, interfaces are of great interest to researchers [17–25]. In view of the fact that the realization of functional graphdiyne-based devices is based on the contact with substrate materials and graphdiyne films is grown on copper substrate, the understanding of the contact between graphdiyne and copper surface is of important basic significance. However, as the key elements to connect graphdiyne with substrate materials, there was very limited research specifically targeted the contact interface between graphdiyne and copper surface.

Here, we implement first principles calculations based on density functional theory (DFT) to specifically investigate the interfacial structural, mechanical and electronic properties of the contact between graphdiyne and copper surface. We separate the graphdiyne layer rigidly from the copper (111) surface and study their interfacial bonding properties. The most stable interface structure is confirmed according to interfacial binding energies. Different kinds of interfacial interactions are found combining the results of charge density and density of state, and the bonds at interface make the contact between graphdiyne and copper surface more tightly and provide a bridge for charge transfer.

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http://dx.doi.org/10.1016/j.carbon.2017.02.097
0008-6223/

2. Results and discussion

2.1. Interfacial structural

Considering that the copper has the same symmetry and appropriate lattice constants with graphdiyne by its (111) surface, the contact interface is formed by placing the monolayer graphdiyne on the Cu (111) surface. Fig. 1a shows the periodic supercell of the interface structure, in which the structure boxed in the red frame is the unit supercell. The interface distance is defined as the distance between the first layer copper and graphdiyne film as shown in Fig. 1b. To combine the graphdiyne layer and the Cu (111) surface with atoms on staggered positions and make the composite structure with periodic symmetrical geometry, three types of stacking configurations are taken into account to form the contact between graphdiyne respectively named as top, hcp and fcc configurations shown in Fig. 1c, d and e. For different stack configurations, binding energies between graphdiyne and Cu (111) surface is defined as

$$E_b = \frac{E_{G-C} - (E_G + E_C)}{A} \quad (1)$$

where E_{G-C} is the total energy of the interface structure, E_G and E_C are energies of separated monolayer graphdiyne and copper substrate respectively, A is the contact area of a unit supercell of 90.524 Å^2. Fig. 2a shows relationships between the interface distance and binding energy for different stacking configurations by separating the monolayer graphdiyne rigidly from the copper substrate without geometry relaxations. It can be seen that the fcc configuration provides the most stable state, with a minimum binding energy of −0.053 eV/Å^2 at the interface distance of 1.91 Å. Then results of the hcp configuration is very close to the fcc configuration with the minimum binding energy of −0.051 eV/Å^2 and the interface distance of 1.93 Å. The top configuration reaches the minimum binding energy of −0.049 eV/Å^2 at the interface distance of 2.03 Å, which are far from the results for fcc and hcp configurations. It can be observed that relative positions between

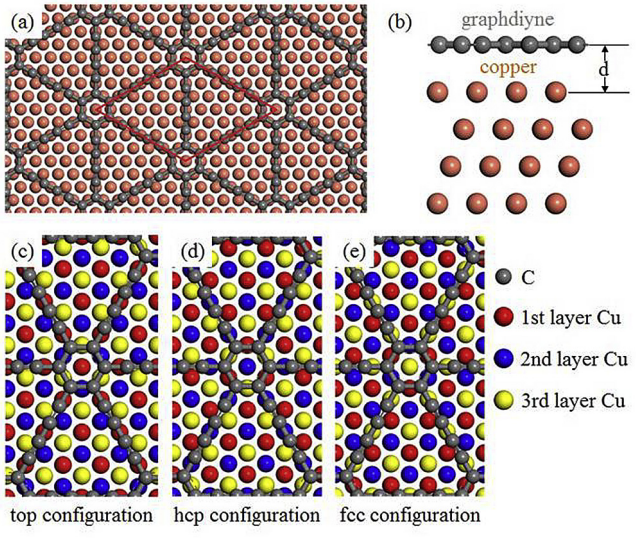

Fig. 1. Structure of the interface between monolayer graphdiyne and Cu (111) surface. (a) is the top view of the interface. The structure boxed in the red frame is the unit supercell. (b) is the side view of the unit supercell, *d* is the interface distance. (c), (d) and (e) are the top views of top, hcp and fcc configurations, respectively. Grey balls are carbon atoms, red, blue and yellow balls are respectively copper atoms in the first, second and third layer. (A colour version of this figure can be viewed online.)

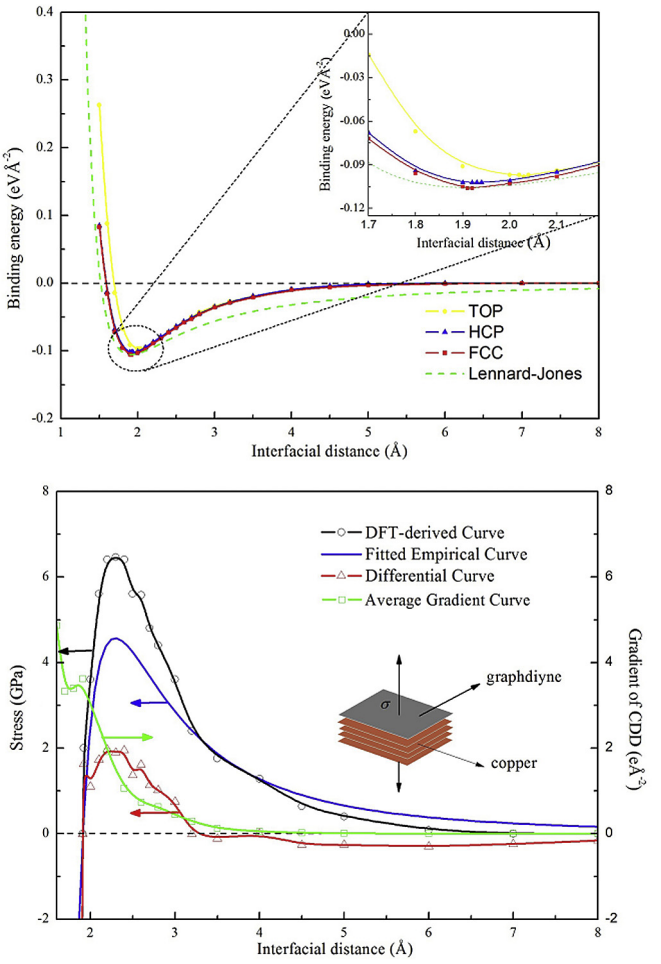

Fig. 2. (a) is the relationship between binding energies and interface distance for different stacking configurations. The dashed line is the L-J fitting curve based on the fcc curve. (b) is the change of bonding strength and gradient of CDD during the interface peeling process. The curve in red is the difference between DFT-derived and fitted empirical curves. (A colour version of this figure can be viewed online.)

first layer Cu atoms and C atoms in graphdiyne are the same for both fcc and hcp configurations, which indicates that main interactions are between graphdiyne and first layer Cu atoms. Compared with different stacking orders, it can be found that fcc and hcp configurations both have nine surface Cu atoms just below π bonds of graphdiyne in a unit supercell and they stay at similar binding energy levels, while the top configuration is with no surface Cu atom just below π bonds and it is less stable than other two configurations. The minimum binding energy of the fcc configuration is a little lower than that of the hcp configuration, with the fact of that there are more second layer Cu atoms just below π bonds of graphdiyne in the fcc configuration than in the hcp configuration. Hence, we can assume that the interfacial bonding strength largely depends on interactions between p_z-orbitals of graphdiyne and *d*-orbitals of surface Cu atoms, which is similar to the strong chemical contact between graphene and metals [20–22], while the potential profiles do not show the single-well feature in the graphene-copper system [25]; and Cu atoms in the second layer also has a weak influence on the upper layer graphdiyne. The single-well binding energy feature implies that the physical contact between graphdiyne and copper surface might be significantly weaker compared with the chemical contact.

An interlayer binding energy curve to describe the interfacial