Formation of Ag nanowires on graphite stepped surfaces. A DFT study

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ARTICLE INFO

ABSTRACT

We investigate the feasibility of obtaining silver nanowires on graphite stepped surfaces theoretically, using density functional theory calculations. Three layer slabs are used to model graphite surfaces with and without defects. Adsorption energies for Ag atoms on graphite surfaces were calculated showing the preference of Ag adatoms to locate on the steps, forming linear structures like nanowires. An analysis of the charge densities and projected densities of states for different structures is also performed.

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1. Introduction

The development of metallic nanowires has attracted much attention in recent years because of the interesting chemical, physical and mechanical properties that present these structures as well as for their potential applications in nanotechnology. Different methods have been employed to obtain nanowires [1]. One of them is electrochemical deposition in which the metal of interest can be electrodeposited into porous masks or the nanowire can be obtained by preferential deposition at the step edges of the highly oriented pyrolytic graphite (HOPG) [2]. In particular, Ag nanowires can be used as electrosensors for amines [3], or as the basis for more sophisticated nanostructures synthesis with other applications. There are extensive experimental results of the Ag-graphite system [4–9] as well as theoretical studies of Ag adsorption on graphite surfaces without defects [10–16]. These results are, at the same time, supported by scanning tunneling microscopy (STM) characterization of graphite substrates after Ag evaporation on this surface [17,18].

In this work, we employ density functional theory (DFT) calculations to evaluate the interaction between Ag atoms and (0 0 0 1) graphite surfaces without defects and with a step in the [0 1 0 0] direction. The latter system is similar to that found in Ag electrochemical deposits on HOPG, wherein the substrate is a surface composed of flat terraces and regions with steps. In a first stage, DFT parameters, such as cut off energy, *k*-point set, smearing function; were optimized for bulk graphite, by calculating known properties for the ground state and comparing the results with experimental data in the literature. Then, slab models were built for the surface with and without defects. For both types of surfaces, adsorption of Ag atoms was studied determining the most favorable sites for adsorption. Adsorption energies for systems with different geometrical configurations for the stepped surface were also evaluated in order to examine the feasibility of developing aligned structures such as nanowires on graphite stepped edges.

2. Computational method

DFT with calculations with Van der Waals corrections were performed using the Viena Ab-initio Simulation Package (VASP) [19–22], which employs a plane-wave basis set and a periodic supercell method. The generalized gradient corrected approximation (GGA) functional Perdew, Burke, and Ernzerhof (PBE) was used [23]. The Kohn–Sham equations were solved variationally using the projector-augmented-wave (PAW) method [24,25]. For the Van der Waals description, we adopt Grimme's DFT-D2 approach [26]. In order to test the validity of the method employed, some additional calculations were performed using the vdw-DF2 method to account for the Van der Waals forces [27] and the results compared with

Table 1
Surface energy calculation as a function of the number of layers, and dispersion energy of the slab (E_{vdw}).

Number of layers	Surface energy (J/m^2)	E_{vdw} (eV)
1	0.18	−0.11
2	0.18	−0.35
3	0.19	−0.59
4	0.19	−0.84
5	0.19	−1.09
6	0.19	−1.33
7	0.19	−1.58
8	0.19	−1.83
9	0.19	−2.08
10	0.19	−2.33
11	0.19	−2.57
12	0.19	−2.82
13	0.19	−3.07
14	0.19	−3.32

those previously obtained. Spin polarization was considered in all calculations.

For bulk calculations, DFT parameters like kinetic cutoff energy value (E_{cut}), k-points set and smearing function, were optimized. This task was carried out using the Methfessel–Paxton first order smearing approach, for the partial occupations of the electronic states near the Fermi level. For all calculations, we used a smearing width of 0.01 eV. Analysis of the system energy shows that the use of a $8 \times 8 \times 8$ gamma centered k-point grid to sample the Brillouin zone and $E_{cut} = 700$ eV, is enough for the total energy to converge to within 10 meV. Geometry optimizations were obtained by minimizing the total energy of the unit cell using a conjugated gradient algorithm to relax ions [28].

Slab models were employed for surface calculations. Surface energy was calculated for slabs with increasing number of layers in order to determine the number of layers necessary for our model. During calculations, DFT parameters previously obtained from bulk optimization and an $8 \times 8 \times 1$ k-points grid were used, concluding that three layers are enough to ensure surface energy convergence (see Table 1). Ooi et al. [29] calculated the surface energy of a graphite (0 0 0 1) surface for a slab with increasing number of layers. They employed the LDA approximation because the GGA approximation without the dispersion contribution fails to generate interplanar bonding. They found oscillating values in 0.075–0.085 J/m^2 range. These oscillations increase with the slab thickness, attributing this behavior to the inability of LDA to reproduce Van der Waals bonding. In our case the inclusion of the Van der Waals term to GGA made the surface energy converge with only a few layers. Eq. (1) was used for calculating the surface energy (σ), where E_{slab} is the total energy of the slab, n_c is the number of carbon atoms of the slab model, A is the surface area, and E_{bulk} is the energy per atom for bulk graphite.

$$\sigma = \frac{E_{slab} - n_c E_{bulk}}{2A} \qquad (1)$$

Details on the slab model will be given in the following sections.

Eq. (2) was used to calculate the adsorption energy (E_{ads}), where $E_{Ag_n/surf}$ is the energy of the graphite surface (with or without defects) with n Ag atom adsorbed, where $n = 1, 2, 3$ and 4, E_{surf} is the energy of the clean graphite surface (with or without defects) and E_{Ag} is the energy of an isolated Ag atom.

$$E_{ads} = E_{Ag_n/surf} - E_{surf} - nE_{Ag} \qquad (2)$$

With this definition a negative adsorption energy corresponds to a stable adsorption on the surface.

To evaluate the stability of growing Ag nanowires on the step, we define the nanowire formation energy, E_{nw}, as

$$E_{nw} = [E_{(Ag_n/Step)} + E_{(Surface)}] - [E_{(Ag_{n-1}/Step)} + E_{(Ag_1/Terrace)}] \qquad (3)$$

E_{nw} determines how easily an Ag_n nanowire is formed on the step from an Ag_{n-1} nanowire on the step and an Ag monomer adsorbed on the terrace. A negative value of this energy indicates a favorable tendency to the formation of a nanowire.

In order to analyze the electronic structure, the electronic charges on atoms were computed using Bader analysis [30] and the atom projected density of states (PDOS) was obtained by projection of the one-electron wave functions onto atomic Bader volumes.

3. Results

3.1. Bulk

In order to test the reliability of our calculations some properties were calculated and compared with experimental data from literature.

A geometry optimization was performed to determine lattice parameters of the graphite hexagonal crystal structure. The unit cell employed is shown in Fig. 1(a). Ion positions, cell volume and cell shape were allowed to simultaneously relax. The calculated lattice parameters are $a = 2.462$ Å and $c = 6.353$ Å. The parameter c is underestimated 5% respect to the experimental value ($a = 2.462$ Å, $c = 6.707$ Å) [31].

The calculated value for the bulk modulus, B, is 34.2 GPa which is in good agreement with experimental data [31–36]. B, was calculated by fitting the energies from a series of constant volume relaxations (i.e., all degrees of freedom except volume have been optimized) to the Birch–Murnaghan equation of state [37,38].

3.2. Clean surface without defects and with a step

The surface was modeled with a slab consisting of three carbon layers within a 4×4 unit cell and a vacuum spacing between slabs of about 22 Å, for the surface without defects (Fig. 1(b)). The size of the supercell is large enough to allow further study of the adsorbed species and the vacuum spacing ensures no interaction between slabs. Being a considerably large supercell, a $3 \times 3 \times 1$ gamma centered k-point-set was used, in this case. For the study of adsorption of more than 3 Ag atoms a larger supercell was employed.

Carbon atoms on the surface were allowed to relax in all directions for the top two layers, keeping the bottom layer fixed. No change in the positions of carbon atoms in the direction parallel to the surface was found, but only in the direction perpendicular to the surface, with an increase in the distance between layers of approximately 0.06 Å. The surface energy calculated was 0.20 J/m^2 which agrees with values reported in literature [39–41]. No magnetization of the surface was observed.

We also studied a stepped surface with the step in the [0 1 0 0] direction. To model the step, some atoms from the top layer of the slab were removed. Fig. 2 shows the 5×4 unit cell slab, used to model the stepped surface. The surface was allowed to relax, keeping the bottom layer fixed. No major change in the C–C bond distance between pairs of carbon atoms on the step was observed, compared to pairs of carbon atoms on the terrace. Spin calculations showed a significant value of the magnetic moment; it is believed that this is due to the decrease in the coordination of carbon atoms forming the step.

3.3. Ag on the surface without defects

The adsorption of Ag on the graphite surface without defects was studied. An Ag atom was placed at specific sites on the surface, and a geometry optimization was performed, allowing the system to relax in order to find the most stable position for Ag on the surface. Fig. 3 shows the different adsorption sites on the graphite surface studied labeled α and β (top sites), H (hollow site) and B (bridge