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Step barrier for gold adatoms and small clusters diffusing on graphite: An *ab initio* study

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We investigate, by means of *ab initio* calculations, the influence of graphitic monoatomic steps on the diffusion of gold adatoms and small clusters. We find that the presence of dangling bonds dramatically affects the adsorbates behavior. More precisely, graphite steps attract atoms and clusters diffusing on the upper terrace, creating a "negative" step barrier. However, if the step dangling bonds are passivated by hydrogen atoms, these defects recover a behavior similar to metallic steps, showing a repulsive barrier.

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Graphite surfaces represent a conveniently simple (i.e., atomically flat over micrometer and chemically inert) surface, which can be used as a model for understanding the behavior of atoms[1–5] and clusters[6–12] deposited on it. The graphite monoatomic steps can also be used as a natural surface defect which can act as a nucleation center to grow tailored nanostructures, such as nanowires.[8,13,14]

Before using these surfaces as templates for nanostructure growth, it is important to understand the effects of steps on the diffusion of atoms or clusters. The existence of a repulsive downhill step barrier for diffusion is well documented for metallic systems.[15–18] The physical rationale for this repulsive barrier lies in an "undercoordination" effect: when the atom reaches the step, it is no longer bonded to the upper terrace but not yet to the lower one. This produces a undercoordinated, unfavorable state of higher energy, and therefore a barrier at the step. However, the existence of a repulsive step barrier is a controversial question for semiconductor surfaces, which show complex surface reconstructions and dangling bonds.[19] Some semiconductor steps behave as metallic steps, while some other show no significant diffusion barrier.[20] Finally, there are examples of "negative" barriers,[21] i.e., steps that attract atoms diffusing on the upper terraces.

In this paper, we use *ab initio* calculations to predict the effect of graphitic monoatomic steps on the diffusion of gold adatoms and small clusters. The *ab initio* approach is important to reproduce the well-known dangling bonds of undercoordinated C atoms, which are not taken into account when describing the system with semi-empirical potentials such as Lennard-Jones.[12,22] Our results show that depending on whether the step is passivated or not, the diffusion barrier at the step is either positive or negative, both for an isolated atom or a small cluster. Such results are consistent with the variety of behaviors observed for semiconducting steps[20,21] and emphasize the key role played by dangling bonds.

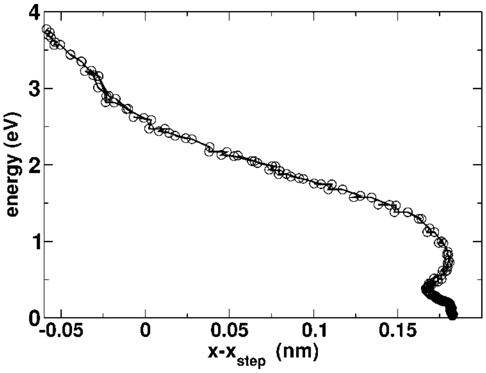

FIG. 1. A gold atom left on top of a graphite barrier spontaneously "descends" the step. X_{step} is defined as the position of the edge carbon atom closest to the gold one. The origin of energies is arbitrarily taken at the final state.

The runs were performed within a density-functional theory–local-density approximation (DFT-LDA) pseudopotential framework using the SIESTA package.[23] Standard norm-conserving pseudopotentials[24] were used for carbon and gold atoms, as in Ref. 25. We included semirelativistic effects for gold, since not taking them into account may affect the results: for example, the adsorption energy of a gold atom on a single carbon layer is 0.7 eV without relativistic effects and 0.9 eV once these are included.[5] The reason seems to lie in the sensitivity of the filling of the 6*s* and 5*d* energy levels to their (small) energy difference, the latter being affected by the relativistic corrections (see also Ref. 26).

We tried several bases sets for the quantum description of the electronic states. Gold atoms are described by a "DZP" (double-zeta + polarization) basis set, comprising two 5*d* and two 6*s* channels plus one 6*p* polarization multiplet. For carbon atoms we use a "cheaper" double-zeta (DZ) basis (consisting of two 2*s* and six 2*p* numerical atomiclike orbitals) for computational efficiency. Previous studies with these bases have shown that they satisfactorily reproduce the energies of carbon[27] and gold[25] systems. The calculations were carried out in the generalized gradient approximation (GGA)

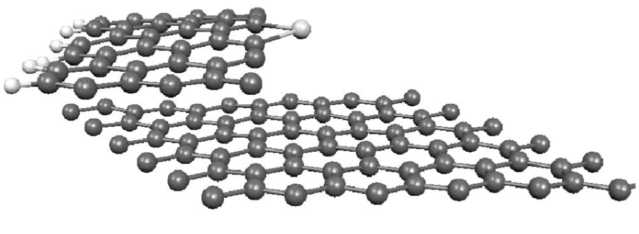

FIG. 2. Stablest position of a gold atom down a nonpassivated step.

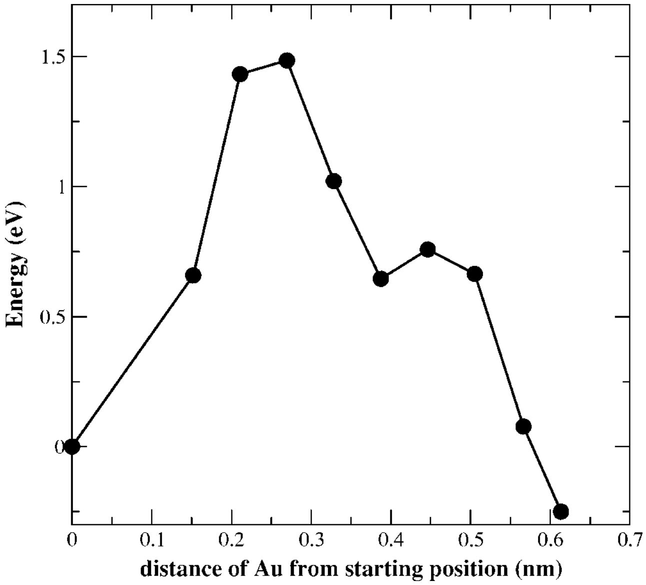

FIG. 3. Energies of the different configurations along the downhill diffusion for a gold atom on a passivated graphite step. We have taken the initial configuration energy as the origin. The *x* axis represents the distance of the atom measured from the initial position in nanometers.

within the Perdew-Burke-Ernzerhof functional.[28] We have shown elsewhere[5] that LDA leads to quantitatively different adsorption energies for gold on graphite, although the qualitative picture is similar. We have checked here that the physics is not modified by changing the functional, namely, the existence of barriers does not depend on the precise approximations adopted. Moreover, in Ref. 5, the diffusion barrier for an isolated gold atom on an infinite graphite sheet was shown to be identical—to within 0.01 eV—to the same value (0.05 eV) for both approximations. Finally, several important numerical values were tested against a change of electronic basis (namely, using a DZP description instead of a DZ one for carbon): the results were not affected by more than 15%.

The systems studied include two graphite layers (Fig. 4). The lower one comprises $(6\times6\times2)$ atoms with periodic boundary conditions so that no dangling bonds are present. The upper layer contains half of the atoms in the unit cell and is also fully periodic in the direction parallel to the step. In the perpendicular direction, two armchair edges are created: one is systematically passivated by hydrogen atoms to mimic the semi-infinite graphite, while the other edge (the "active" step) will be either passivated or not. The choice of the armchair edge, consisting of dangling carbon dimers, is justified by its larger stability as compared to the zigzag edge, composed of dangling atoms. We have verified that, approaching the armchair edge to the lower layer, it does not bind to it, so that the armchair edge is fully stable. As for gold, we have considered either isolated atoms or clusters made of five atoms.

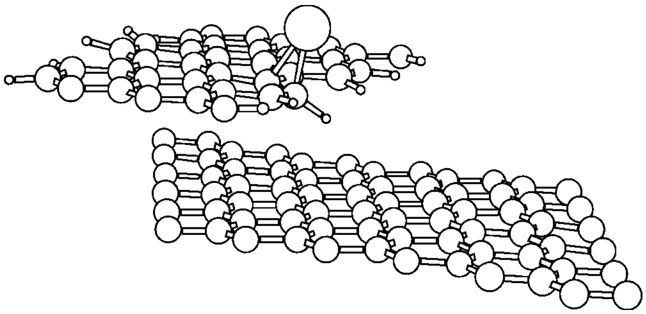

FIG. 4. A passivated barrier presents a barrier for downward diffusion. The figure shows the most unstable position along the best pathway, the transition state.

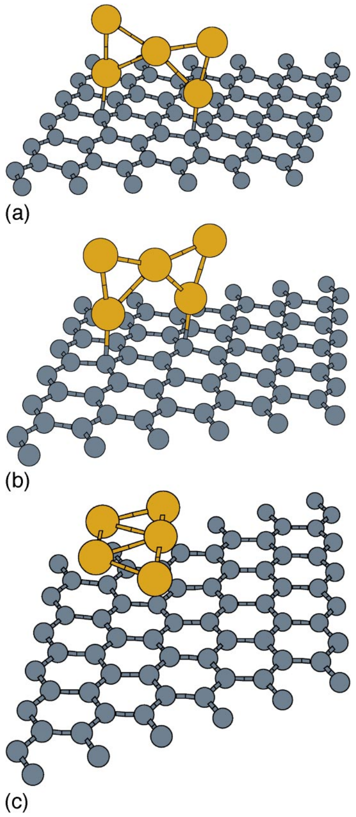

FIG. 5. Configurations of five-atom gold cluster adsorbed on an infinite graphite layer. (a) Stablest configuration; (b) metastable configuration, 0.17 eV higher than (a) [the difference between this configuration and (a) is a small rotation]; (c) metastable configuration, 0.49 eV higher than (a).

For the diffusion path and barrier, we used the nudged elastic band (NEB) approach.[29] In this method, a chain of "connected" configurations (nine in this study) between the initial and final geometries is allowed to relax towards the lowest energy pathway going through the saddle point of the transformation. The forces acting on the atoms of a given configuration are calculated with the SIESTA code branched to the NEB algorithm. Starting from a simple linear interpolation of the atomic positions of the initial and final states, the NEB algorithm relaxes the different configurations towards the best diffusion path, finding therefore the transition state and energy for the reaction under study. More technical details can be found in the abundant literature related to this method.[29]

We first investigate the influence of a step on the diffusion of a gold atom. Let us first recall that a gold atom diffusing

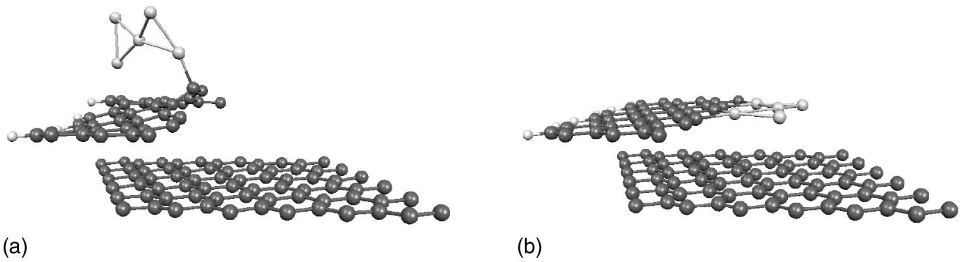

FIG. 6. A five-atom gold cluster left on top of a graphite barrier (a) spontaneously descends the step to reach a stable configuration (b).

on an infinite graphite substrate experiences a diffusion barrier of 0.05 eV, a result found previously with the same approach.[5] This value means that gold atoms deposited on a graphite substrate rapidly diffuse and find the surface steps. What happens when a gold atom reaches a step?

Figure 1 shows the energy of the system as a function of the distance to the step as obtained within a "zero-temperature" conjugate gradient minimization, the atom being initially located above the step. The energy becomes clearly lower and lower as the atom approaches the step and reaches its stablest position down the step (Fig. 2). It ends bonded to two carbon atoms belonging to two neighboring dangling C_2 dimers, with a gold to carbon distance of 2.16 Å (parallel to the graphite layers), which can be compared to the adsorption distance on an infinite graphite layer (2.5 Å). The distance between graphite layers being 3.3 Å, there is hardly any bonding between the gold atom and the lower layer. The carbon dimers, initially at a distance of 1.25 Å (characteristic of a double bond), open up to 1.31 Å, which means that part of the electrons engaged in C-C bonding have rehybridized with gold. As a result, we conclude that there is no step barrier for single atom diffusion. In particular, the gold atom is not reflected back as it is observed for metallic edges.

Since the gold adatom is clearly attracted by the step dangling bonds, to which it finally attaches, we have investigated what happens when they are passivated by H atoms. We find that the physics changes completely, since now the adatom experiences a huge step barrier $E_b = 1.5$ eV (Fig. 3). Clearly, the chemical reactivity associated with dangling bonds is no longer at work and the "classical" undercoordination effect for metallic surfaces is observed. Figure 4 shows the transition state for the passivated barrier crossing as obtained within our NEB approach. It should be noted that the 1.5 eV value means that, at room temperature, the adatom will never be able to cross the step [assuming an Arrhenius rate, $\tau = \tau_0 \exp(E_b/k_B T)$ taking a prefactor of $\tau_0 = 10^{-13}$, we find a waiting time of about 50 000 years].

Is the physical picture we have found for the adatom similar for a small gold cluster? We first investigated the possible adsorption configurations of a gold cluster deposited on a graphite substrate. Figure 5 shows several cluster geometries for a five-atom gold cluster deposited on an infinite graphite substrate: Figs. 5(b) and 5(c) show metastable configurations, while Fig. 5(a) shows the stablest configuration we have found. We have also studied the diffusion of the cluster (in the stablest configuration) on an infinite substrate or on the upper terrace, far enough from the step: we always find a barrier of 0.15 eV. The diffusive jump leaves the structure of the cluster unaffected, the two Au-C bonds being broken and reconstructed on the closest C atoms (at a C-C distance, i.e., 0.14 nm). The value of the diffusion barrier is small enough to allow clusters deposited on a graphite substrate to rapidly reach the steps at room temperature,[30] a fact that has been clearly confirmed by experiments.[8]

Let us now investigate the cluster behavior close to the steps. As for the single atom, we find that, in the case of a nonpassivated step, the cluster spontaneously descends the step, i.e. there is no step barrier. Figure 6(b) shows the relaxed configuration of the cluster, initially deposited on the step [Fig. 6(a)]. The energy gained by descending the step is 8 eV.

In the case of a passivated step, the cluster behavior is also similar to that of a single atom. Only the precise value of the barrier is affected, changing from 1.5 eV (single adatom) to 1.8 eV. Both results are obtained with a DZ basis and the GGA approximation. To check the accuracy of our cluster result, we calculated the barrier using the DZ-relaxed configurations but calculating the energy with a DZP basis (without relaxing the system again): we find a barrier of 1.6 eV, in good agreement with the previous value. Within an accuracy of ~20%, we find the step barrier is similar for both an isolated atom and a five-atom cluster.

Figure 7 shows the stable cluster position on the higher terrace (a) and the configuration on the lower terrace (c) in the passivated case. These configurations are chosen as the "start" and "end" configurations for the NEB path. The

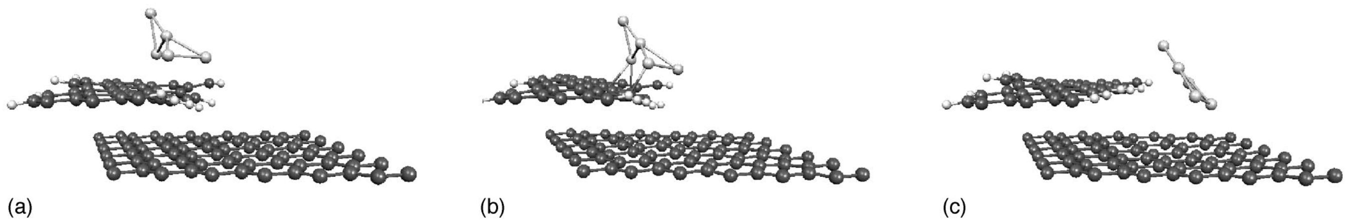

FIG. 7. A passivated graphite step presents a barrier for a cluster, shown here in the stable top position (a), the transition state (b), and the final, stablest position (c).

downhill configuration is 0.85 eV more stable than the high terrace one (see Fig. 8). After convergence of the NEB procedure, we obtain the transition state configuration above the step, shown in Fig. 7(b). Figure 8 shows the energies of the different NEB cluster configurations as the cluster crosses the barrier. The fourth point corresponds to the transition state shown in Fig. 7(b).

The behavior of single adatoms or small clusters seems to be equivalent: a step barrier for passivated steps and no barrier for "naked" steps. Clearly, dangling bonds favor step crossing, leading to a zero or a negative step barrier, as calculated in this paper, in agreement with several references.[20,21] Concerning the similar values of the step barrier obtained for the atom and the cluster, one can argue that in the case of the cluster, the undercoordination argument does not apply to all the atoms. Therefore, one should not expect a step barrier five times larger for the five atom cluster, as compared to the single-atom case.

The presence or not of a step barrier is important for nanowire preparation,[14,31,32] an active field nowadays. For nonpassivated steps, matter will adsorb from the upper and lower terraces, while for passivated steps only atoms or clusters arriving from the lower terraces are able to attach. In order to understand the formation of a whole nanowire, we project to calculate the change in step barrier produced by a gold adatom already attached to the step.

In this context, it is interesting to comment on a former result obtained by Jensen *et al.*[22] There, the energy of a large (250 atoms) gold cluster was calculated when crossing a (nonpassivated) step and a large step barrier (more than 1 eV) was found, in agreement with a result by Yoon *et al.*[12] It is important to note that in Refs. 12 and 22, the interaction was calculated from *empirical* potentials, which do not include the dangling bonds. Furthermore, the internal degrees of freedom of the cluster were not allowed to relax when crossing the step. The comparison between these results and those presented here is therefore not straightforward. One can argue that the semiempirical potentials used (Lennard Jones for the substrate) cannot reproduce the step dangling bonds (hence favoring a strong barrier), but also that such a large cluster cannot easily deform to lower its energy while crossing the step (with the opposite effect). An *ab initio* study on large clusters seems necessary, but is well beyond the present-day computer power. Experimental checks would be welcome. Finally, we have checked that a five-atom gold cluster is also attracted by a nonpassivated graphite vacancy island (having dangling bonds), the physical mechanism being the same as with the nonpassivated steps: the system lowers its energy (by about 10 eV) by passivating the dangling bonds created by the five-atom vacancy in the graphite. The already quoted studies—which use semiempirical potentials[12,22]—predict a repulsion of the cluster by the vacancies. Clearly, semiempirical potentials lead "graphite" steps behaving like passivated steps, even if no H atoms are adsorbed on the edges. Experimentally, the two types of steps might be observed, depending on the precise history of the samples (heating, exposure to hydrogen,…).

In conclusion, we find that graphite steps attract atoms and clusters diffusing on the upper terrace, creating a "negative" step barrier. However, if the step dangling bonds are passivated by hydrogen atoms, these defects recover a behavior similar to metallic steps, showing a repulsive barrier. The extrapolation to larger clusters containing hundreds of atoms is, however, not straightforward.

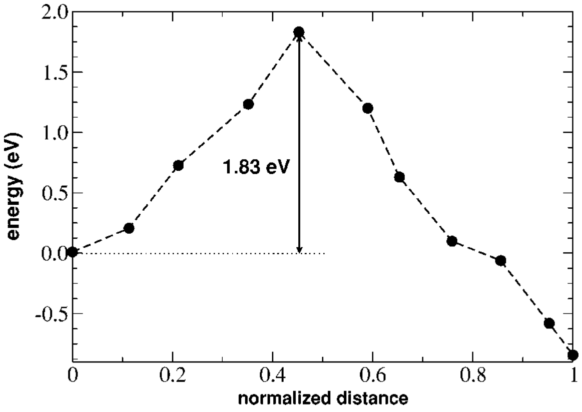

FIG. 8. Energies of the different configurations along the downhill diffusion for a five-atom gold cluster on a graphite step. We have taken the initial configuration energy as the origin. The *x* axis represents the distance of the cluster center of mass measured from the initial center of mass position (in the upper position), normalized by the final distance (in the lower configuration).

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