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Density functional study of silver clusters on a stepped graphite surface: Formation of self-assembled nano-wires

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Adsorption and diffusion of silver adatoms and clusters containing up to eight atoms on an HOPG substrate with an armchair step are studied using density functional methods. Step edges act as attractive sinks for adatoms and clusters. Diffusion barrier of an Ag adatom along the step edge is much larger than that on a clean terrace. At zero temperature, Ag clusters either distort or dissociate by forming covalent bonds with the edge C atoms. At 600 K, Ag_5 and Ag_8 clusters diffuse to the step edges, and then break up so as to maximize Ag-C bonds. The Ag atoms try to form a nanowire structure along the step edge. At such high temperatures, diffusion of clusters along the step edge involves diffusion of individual Ag atoms not bonded to the edge C atoms. Assumption of complete immobility of clusters trapped at step edges in the Gates-Robins model is not valid at high temperatures in this particular system.

1 Introduction

Metal clusters, in addition to being an interesting system of study for fundamental reasons, are useful in many applications such as catalysis, sensors etc. They can also be used as building blocks for novel materials in a bottom-up approach. Most of these applications require the clusters to be deposited on a substrate. In particular, studies of silver clusters deposited on highly ordered pyrolytic graphite (HOPG) substrates have attracted a lot of experimental attention. Ganz et al[1] were the first to study deposition of Ag (and also Au, Cu and Al) atoms and subsequent formation of clusters on HOPG. Later on, a number of studies have been reported by Palmer et al.[2–6]

Two different methods have been employed to put silver clusters on HOPG: (i) deposition of atomic vapor of silver, (ii) deposition of pre-formed clusters from a cluster source, either size-selected or otherwise. Silver atoms in an atomic vapor, after deposition on the surface, form clusters, whose diffusion and structure have been studied using scanning tunneling microscopy (STM) and scanning electron microscopy (SEM). As in all real surfaces, HOPG surface has defects, both point defects and atomic steps. The process of cluster deposition itself can also produce defects on the substrate. Structure of clusters both on the terraces of HOPG away from the step edges, and on the step edges have been studied in some detail in these experiments. Diffusion, and consequently, the final structures that the deposited atoms and clusters form depend on the experimental conditions: deposition rate, atom/cluster coverage of the substrate surface, temperature, impact energy of deposition etc. The major observations in these experiments relevant for the present study are as follows.

Deposition of silver atomic vapor produces clusters on the HOPG surface. Ganz et al[1] could identify single adatoms, dimers, small clusters containing three or more atoms, and two dimensional islands containing up to hundred atoms in their STM images. Francis et al[2,3], in their SEM images, found silver clusters after deposition of atomic vapor. At room temperature (20 °C) clusters were seen both on the wide terraces and step edges. No clusters were seen on the narrow terraces between two steps, and even on the wider terraces, there was a zone near the steps denuded of any clusters. Cluster density was found to be much higher at steps than on the terraces. The clusters formed large irregular shapes on the terraces, whereas at the steps the cluster sizes were smaller, varying between 1-10 nm. As the temperature was increased, no cluster nucleation was seen on terraces above 50 °C. In SEM images at 118 °C and 165 °C, no clusters were seen even on the wider terraces. All the clusters were found to be at the step edges. Some of the clusters at the step edges had dumbbell shapes. These observations imply that Ag adatoms and clusters diffuse easily on the clean terraces on HOPG at room temperature. They may be trapped at the defects on the terraces. Once they reach the steps, they can diffuse only along the step edges. But their mobility along the steps is lower compared to that on the terraces. At higher temperatures, they are not trapped at the terraces at all.

As for deposition of pre-formed Ag clusters on HOPG, we only discuss results obtained for low energy deposition. Most

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of the experiments studied clusters that are few to a few hundred, or a few thousand atoms large. Francis et al[2] deposited Ag clusters from a beam that contained clusters containing a few to a few hundred atoms. The lower limit of cluster size is not clearly mentioned, but the average cluster size was 160 atoms. In another set of experiments, Carroll et al[4] deposited Ag cluster anions containing 50, 100 and 400 atoms. Goldby et al[5] deposited Ag clusters containing 50-250 atoms, whereas in a separate study, Carroll et al[6] deposited size-selected Ag_{400} clusters. Ref[2] finds that the deposited clusters aggregate to form large particles, and these particles form large fractal-like islands on the terrace. Each fractal island contains about ten particles while each particle is composed of ten of the deposited clusters. Mean size of the particles on the steps is found to be much smaller, ~ 7 nm. Carroll et al, in ref[4] find that the clusters at the steps are larger than the deposited clusters. No clusters are seen on terraces near the steps. Refs[5] and [6] find that the particle size (particles are aggregates of clusters) at the steps is smaller than that on the terraces. Ref[6] also reports that there are many more clusters of incident size at the steps than at the terraces. All these facts again indicate that clusters have some mobility at the steps but that is lower than their mobility on the terraces. This prevents them from forming larger particles at the step edges.

While these experiments produce an overall picture of diffusion and aggregation of silver adatoms and clusters on HOPG, they cannot answer some of the details. For example, these experiments cannot give a detailed microscopic picture of diffusion of clusters on the terraces and at the step edges. Do step edges act as attractive sinks for adatoms and clusters? How do the atoms and clusters get trapped? How do they diffuse along the step edges, if at all? A model proposed by Gates and Robins has been used in ref[3] to describe growth of clusters at the step edges with limited success. This model assumes that a nucleus (two-atom cluster) and bigger clusters formed at the step edges by the incoming and diffusing atoms are completely immobile. Given that the model was not very successful for Ag clusters at the steps of HOPG, the details of diffusion of the clusters on this surface needs a closer look.

In this work we attempt to study the adsorption and diffusion of Ag adatoms and clusters near a step on a HOPG substrate using first-principles electronic structure methods. Recently, we have studied adsorption of these clusters on a clean defect-free HOPG substrate. However, a more realistic understanding of such systems requires a study of deposition of adatoms and clusters on a stepped surface. First-principles molecular dynamics calculations, as we perform here, of clusters containing a few tens or hundreds of atoms on substrates is beyond present computational capabilities. Therefore, we restrict our studies to adatoms and small clusters containing up to eight Ag atoms. Real surfaces contain steps than can be several atomic layers high. Again to keep the computations practical, we only consider monatomic steps in the work. While not exactly representing the experiments discussed above, (and we are not aware of any experiments of small size-selected Ag clusters on stepped HOPG) these studies will give an idea about adsorption and diffusion of small Ag clusters on the terrace and near the step edges of a HOPG substrate. This may help us understand some of the qualitative features of these experiments. Moreover, it can test whether the assumptions of the Gates-Robins model is valid in case of Ag/HOPG systems.

The rest of the paper is organized as follows. In section 2 we present the theoretical approach used for our calculations. In various subsection of section 3 we present the ground state structures and energetics of absorption of Ag_n ($n = 1-8$) clusters on the step edge of graphite at 0 K, diffusion of Ag_5 and Ag_8 on this substrate annealed at 600 K, and the electronic structure of a stepped HOPG with the step edge decorated by a self-assembled nanowire of Ag atoms. Finally we draw our conclusions in section 4.

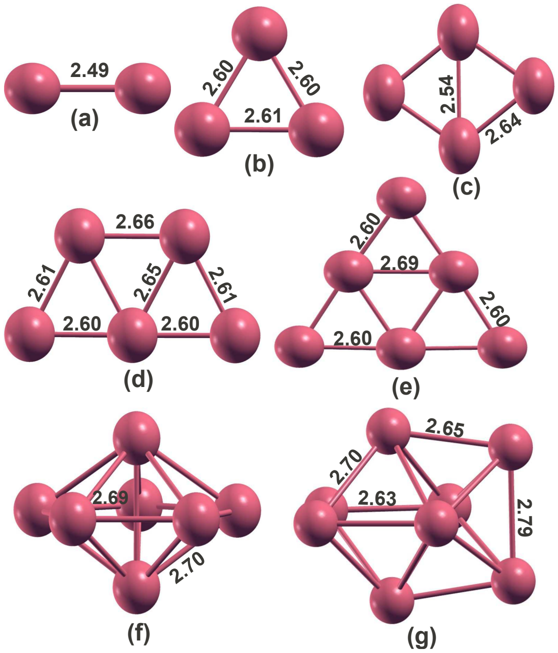


Fig. 1 The ground state structures of gas phase Ag_n clusters ($n = 2-8$).

2 Computational method

First principles electronic structure calculations within the framework of density functional theory (DFT) are performed using the plane-wave projector-augmented wave (PAW)[7,8] method as implemented in the Vienna ab initio simulation

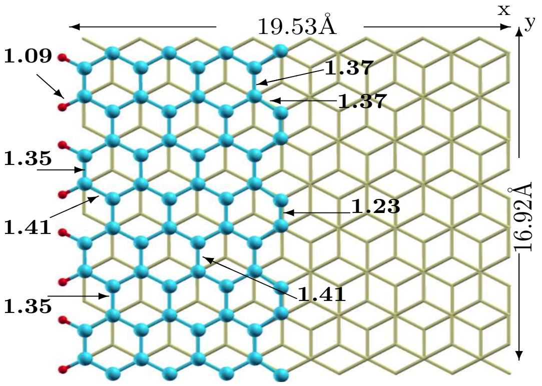


Fig. 2 Structure of the a relaxed graphite surface with an arm-chair step edge. Bottom two layers are periodic in *x* and *y* directions. The step edge is periodic only in the *y* direction.

package (VASP)[9–12]. An energy cutoff of 400 eV is used for the plane-wave basis set to represent the wave functions. The Brillouin zone integrations are performed using only the Γ-point as additional **k**-points do not change the computed results. We have used the local (spin) density approximation (L(S)DA) for the exchange-correlation energy functional due to the following reasons. Graphite is a layered material in which successive layers are held together by van der Waals forces. The usual semi-local functionals (GGA) within DFT are unable to capture these interactions. Although LDA also does not capture these interactions, it does produce a bonding between the layers, and a reasonable value for the interlayer binding energy. We have shown these in detail in a previous publication[13]. It was also shown that dispersion interactions have to be included for a proper description of bonding between Ag atoms and the C atoms on a clean graphite surface. But here our main aim is to describe the adsorption of Ag clusters over a stepped graphite substrate. Step C atoms have dangling bonds that lead to formation of strong covalent Ag-C bonds. Therefore, L(S)DA would be sufficient to describe this system, we believe. We have indeed found that L(S)DA and vdW-DF2 methods (the latter incorporates dispersion interactions) give qualitatively similar results for an Ag adatom and the Ag_2 dimer. Also, because of the increased computational cost of the vdW-DF2[14] calculations employed in ref[13], finite temperature MD calculations would have been difficult.

For bulk graphite our computed nearest neighbor (NN) C-C distance in the plane, and the distance between successive planes are 1.41 and 3.33 Å. These are slightly smaller than the experimental values[15] due to the over-binding nature of the LDA. The graphite substrate is represented in a repeated slab of three layers (AB stacking) with a vacuum of 15 Å. The monolayer step is created by cutting the top layer at the armchair edge as shown in Figure 2. This creates two armchair edges (as the system is periodic). One of these is passivated by hydrogen atoms to mimic the semi-infinite nature of graphite terrace and the other edge remains as it is. The bottom two layers extend in the *xy* plane and the step edge extends along the *y*-axis. Dimensions of the calculation supercell is 19.53 Å in the *x*-direction, and 16.92 Å along the *y*-direction (Figure 2). The distance between the step edge and its periodic image along the *x*-direction is 10.12 Å, which is sufficiently large to avoid any interaction between the step and the passivating H atoms at the other edge. Only the bottom layer was kept fixed, while the middle layer and step layer were allowed to relax.

For adsorption of Ag_n ($n = 1 - 8$) clusters, we considered many initial structures with different orientations of these clusters near the step edge, and optimized them to the nearest local minima using the conjugate gradient method. In many cases more than one initial structures relaxed to the same final structure. Relative stability of different adsorbed structures for a given cluster size is measured by their adsorption energies E_a on the substrate.

$$E_a = E(\mathrm{Ag}_n) + E(\mathrm{substrate}) - E(\mathrm{Ag}_n/\mathrm{substrate}), \quad (1)$$

where $E(\mathrm{Ag}_n)$ is the energy of an isolated Ag_n cluster in the gas phase, $E(\mathrm{substrate})$ is the energy of the stepped graphite substrate described above, and $E(\mathrm{Ag}_n/\mathrm{substrate})$ is the energy of the Ag_n cluster adsorbed graphite substrate. A larger adsorption energy implies a higher stability.

As mentioned in the Section 1, at low temperatures silver clusters have reduced mobility at the step edges, which indicates that there is an energy barrier for diffusion of adatoms and clusters along the steps. We try to have an estimate of the energy barrier for diffusion of an adatom along the step using the climbing image nudged elastic band (CINEB)[16] method. In our finite temperature MD calculations, the temperature is controlled by the Nośe-Hoover thermostat.[17–19]. The time step taken is 3 fs. We did not use hydrogen passivation of the dangling bonds in the MD simulations as a light element like H demanded a much smaller time step which made these calculations impractical. For these calculations, we increased the size of the supercell in *x*-direction to 24.67 Å so that the Ag atoms do not feel the presence of both the steps. Now the size of the simulation box is 24.67*Å* × 17.095 Å.

3 Results and discussions

In different parts of this section we will discuss the atomic and electronic structure of the graphite step edge, results for adsorption of Ag_n ($n = 1, 8$) clusters at 0 K, finite temperature dynamics of the Ag_5 and Ag_8 clusters on the surface, and finally the band structure of monoatomic chains of Ag atoms at the step edge.

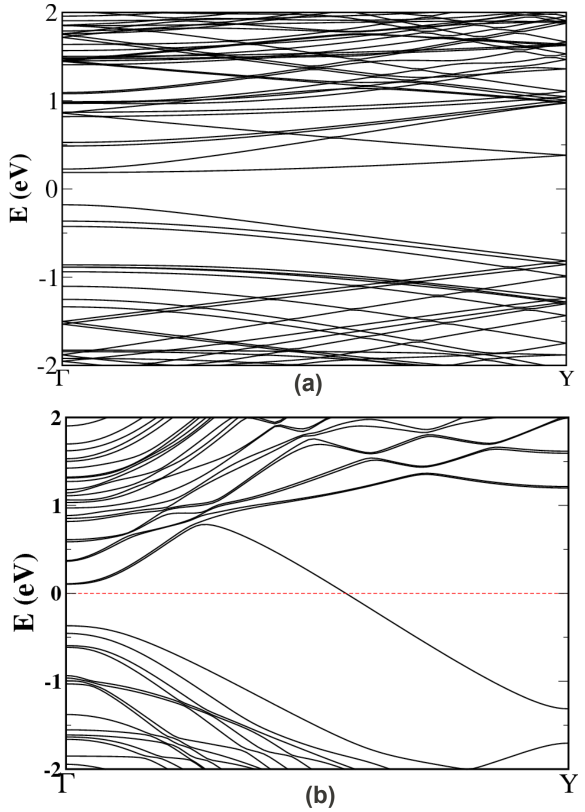


Fig. 3 Band structures of a reconstructed armchair step of graphite (a), and an ordered nanowire with one silver atom at each active site (b).

3.0.1 Band structure of a relaxed arm-chair step edge.

We first discuss the atomic and electronic structure of both un-relaxed and relaxed stepped HOPG substrates. In a clean graphite substrate each C atom is sp^2 hybridized, and is covalently bonded to three neighboring C atoms. One can have two different types of steps on the graphite-(0001) surface: a zigzag step and an armchair step. A zigzag step has two dangling bonds per edge C atom, while an armchair edge has one dangling bond per edge C atom. As a consequence, the formation energy of a zigzag step is larger than that of an armchair step. To have a rough estimate, we calculated the formation energies of zigzag and armchair edges in a graphene sheet, and these are 1.43 eV/Å and 1.34 eV/Å respectively. For an unrelaxed armchair step, the edge states associated with the dangling bonds cross the Fermi level and show a metallic character. However, a lower energy state is one in which pairs of step-edge C atoms dimerize to open up a gap in the band structure (Figure 3(a)). In the unrelaxed structure, the nearest neighbor (NN) C-C distance (the distance between an edge C atoms and its NN second-line C atom) at the armchair edge is 1.41 Å. After step-edge reconstruction, this distance becomes 1.37 Å. The distance between two NN C atoms in the second line also becomes 1.37 Å. C−C distance in the edge dimers is found to be 1.23 Å, which is very close to the length of the triple bond in acetylene (1.20 Å). The structure of the stepped graphite surface after this reconstruction, and all the relevant bond lengths are shown in Fig. 2.

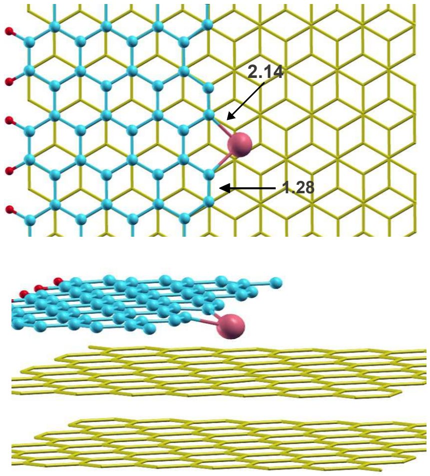


Fig. 4 Structure of a stepped graphite surface with single Ag adatom adsorbed at an active site. Top and bottom panels show top and side views.

3.0.2 Zero temperature adsorption of clusters

We now describe our results for deposition of Ag_n clusters on a stepped graphite surface at zero temperature in detail. Ground state structures of the isolated clusters up to Ag_8 calculated with L(S)DA are shown in Figure 1. All the clusters have the lowest spin state consistent with the number of electrons, as one would expect. Clusters with even number of electrons are all singlets while those with odd number of electrons are doublets. The molecular orbital containing the unpaired electrons in the odd-sized clusters are spread over the entire cluster, consistent with a 'metallic' bonding in these systems.

A silver adatom is very mobile on a clean graphite substrate[3,6], which means that it can rapidly diffuse until it finds a step edge. Once it reaches the step, it binds to two carbon atoms belonging to two neighboring step dimers (Figure 4) with an adsorption energy of 3.20 eV. We call this site the *active site* of the step. The Ag-C bond distance is found to be 2.14 Å, which is much smaller than the Ag-C distance of 2.36 Å (at the LSDA level) on a clean graphite layer. The adsorption energy is much lower ($E_a = 0.38$ eV) on a clean surface. This contrast between a clean surface and a step edge indicates that there is a covalent bond formation between Ag and C atoms in the latter while on the former the Ag atom is physisorbed through van der Waal's forces[13]. It is also worth noting here that the vdW-DF2 functional gives an adsorption energy of 1.33 eV for an Ag adatom at an active site. Although the vdW-DF2 adsorption energy at the step is lower than the LSDA value (which is usually the case[20]), it is much larger than the adsorption energy of an Ag adatom on a clean graphite, which is 0.21 eV[13]. These facts again indicate formation of covalent bonds. In its lowest energy position, the distance between silver atom and the carbon layer below is 2.65 Å, which is larger than the sum of atomic radii of Ag and C (2.35 Å). This indicates there is no direct bonding of the Ag atom with the lower layer. The C-C distance in the step dimers on either side of the Ag atom increases to 1.28 Å. Thus Ag-C bond formation weakens the C-C dimer bond. Ag-C bond formation can also be confirmed from the partial charge density plot which is given in the Figure S1 in the Supplementary Information. A large charge density between the Ag adatom and carbon atoms can be clearly seen.

In order to understand the nature of bonding between an Ag atom and the graphite substrate, we calculated the Bader charges[21–23] on all the atoms. There was a charge transfer of 0.4 e from the silver adatom to the C atoms. After adsorption of an Ag adatom, there is a moment of 0.98 μ_B in the system, which is very similar to the clean graphite case. In case of the clean surface, all the moment was on the Ag adatom[13]. In the present case, spin density is localized on the edge C atoms that are second neighbors of the Ag atom (Figure S2). The carbon atoms which are bonded to the Ag atoms partly saturate their dangling bonds due to the Ag-C bonding. In this process the dangling bonds of the second neighbor carbon atoms become unsaturated giving rise to an overall moment of 0.98 μ_B. Adsorption energies, magnetic moments and charge transfer (from the clusters to the substrate) for all cluster sizes studied in this work are presented in Table 1.

Table 1 Adsorption energies, magnetic moments and charge transfer from the cluster to the graphite substrate in the lowest energy structures of Ag clusters adsorbed on an armchair step edge on HOPG.

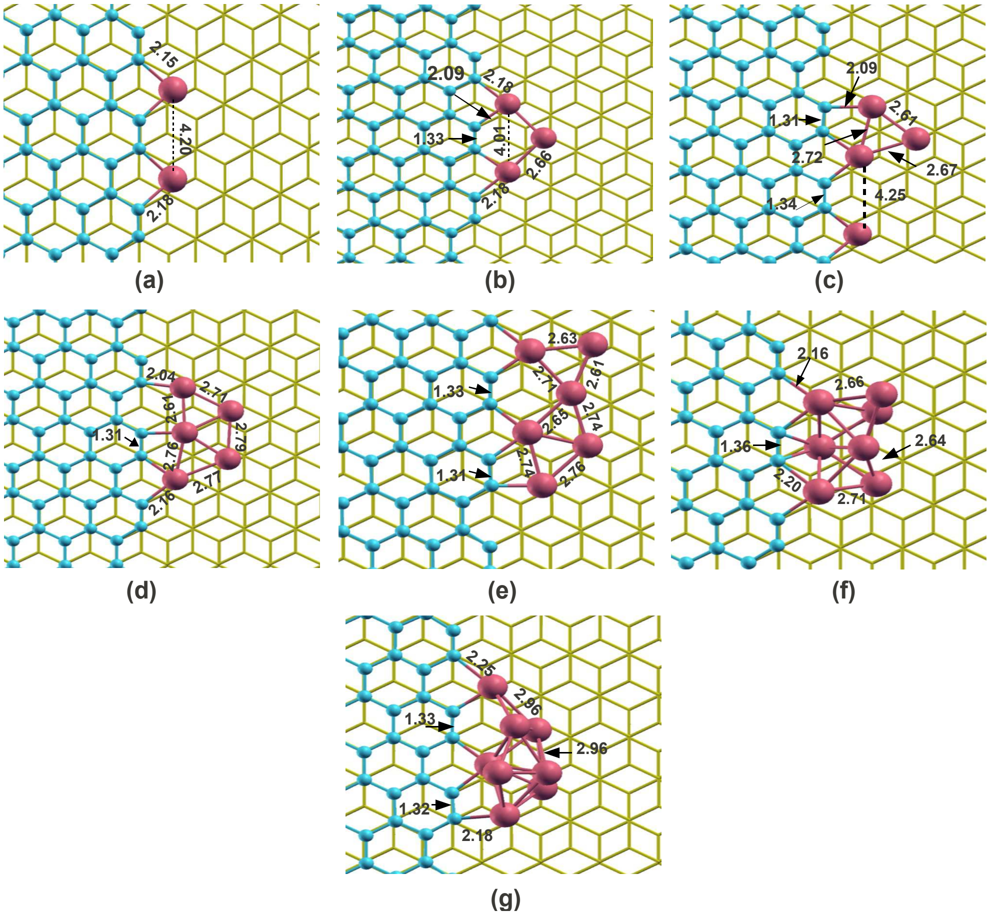
Size	E_a (eV)	M (μ_B)	Q (e)
1	3.20	0.98	0.38
2	4.76	0.00	0.73
3	5.35	0.00	0.39
4	6.15	0.00	0.74
5	6.06	0.99	0.67
6	6.21	0.00	0.70
7	5.32	0.00	1.04
8	5.54	0.00	0.76

As discussed in section 1, experiments indicate that steps act as attractive sinks. We tried to have a quantitative idea about the distance up to which the 'basin of attraction' of a step extends. This would be the location of the maximum of the potential energy surface of an adatom on the surface as one moves away from the step edge. We find this by identifying the maximum distance from where an Ag adatom relaxes to the step edge without any barrier. Interestingly, the basin of attraction is not symmetric on the upper and lower terraces, which is consistent with experimental observations[3,6]. In our L(S)DA calculations, it extends up to ∼ 6.0 Å on the lower terrace while it is only 3.5 Å on the upper terrace. As mentioned earlier, interactions between a clean graphite substrate and Ag atoms are dominated by dispersion forces. Therefore, it becomes important to check that these results are not artifacts of L(S)DA. For this we calculated the extent of the basin of attraction on the lower terrace using the vdW-DF2 functional as well. It turns out that the basin of attraction is exactly of the same size in terms of the number of bond lengths from the step edge.

Before we consider diffusion of clusters, we wanted to have a quantitative estimate of the diffusion barrier of a single adatom along the step edge. For this we considered two consecutive active sites on the step-edge and calculated the diffusion barrier between them using the CINEB method. The barrier turns out to be 0.92 eV. This is much larger than the diffusion barrier of Ag atoms on a clean graphite substrate which is 0.052 eV, both calculated at the L(S)DA level. It should be emphasized that this result is on diffusion of a single Ag atom. It is likely that diffusion of clusters have different paths or mechanisms. We will consider diffusion of larger clusters in the later sections.

Next we studied adsorption of an Ag_2 dimer on graphite step-edge. For initial structures, we considered many orientations of the dimer near the step at both the upper and lower terraces. From all the initial structures we start with, the dimer always moves towards the step and dissociates into two Ag atoms. The two Ag atoms attach to two consecutive active sites of the step as shown Figure 5(a). The adsorption energy turns out to be $E_a = 4.76$ eV. The same behavior is obtained with vdW-DF2 method, except that the adsorption energy is lower in this case (∼ 1 eV). An isolated Ag_2 dimer has a bond length of 2.49 Å (Figure 1(a)), but after deposition the distance between two Ag atoms increase to 4.20 Å. Clearly, the Ag-Ag bond breaks, which implies that gain in Ag-C bonding energy is larger than the cost of Ag-Ag bond breaking. For larger sized clusters, the final structure after deposition near step edge is determined by the competition between Ag-C bond formation and Ag-Ag bond stretching or breaking. As we discuss later, in many cases the cluster is distorted or fragmented after deposition.

An Ag_3 trimer has an isosceles triangular structure in the ground state in which two of the Ag-Ag bond lengths are 2.60 Å, and the third one is 2.61 Å. After deposition near the



(a) (b) (c) (d) (e) (f) (g)

Fig. 5 Lowest energy structures obtained after adsorption of Ag_n ($n = 2-8$) clusters on a stepped graphite surface. Relevant bond lengths are indicated (in Å).

step, one of the Ag-Ag bonds is broken, and the two Ag atoms occupy two neighboring active sites at a separation of 4.01 Å. The third Ag atom remains bonded to these two Ag atoms at bond distances of 2.66 Å (Figure 5(b)). In this structure the adsorption energy is 5.35 eV. We also created a structure by hand in which the Ag_3 is completely broken, and the three Ag atoms occupy three neighboring active sites. This structure is 1.24 eV lower in energy than the previous structure. Obviously, there is a kinetic barrier between these two structures as otherwise all the Ag atoms would have moved to the the active sites. We performed CINEB calculations to get a rough estimate of this barrier, and it turned out to be 0.57 eV.

An Ag_4 cluster has a rhombus structure in its ground state in the gas phase (Figure 1(c)) with Ag-Ag bond lengths of 2.64 Å. Interestingly, after deposition it breaks into two fragments: an Ag_3 cluster and an Ag atom (Figure 5(c)). The minimum distance between these two is 4.25 Å, which is quite large for a chemical bond. The adsorption energy in this structure is 6.15 eV. For Ag_5 cluster the ground state in gas phase is a planar structure with two-fold rotational symmetry (Figure 1(d)). After deposition, unlike the Ag_4 cluster, Ag_5 does not break into fragments. It retains its gas phase shape but with very different bond lengths. Its bond lengths increase significantly to maximize the Ag-C bonding as shown in Figure 5(d). Apart from the Ag adatom, Ag_5 is the only other cluster we found which has a non-zero spin moment (0.67 μ_B) in the lowest energy structure at 0 K. The spin is localized mostly on an edge C atom that is the second neighbor of the Ag atoms, and on two Ag atoms in the cluster. The spin density iso-surface in this case is shown in Figure S3.

Ag_6, Ag_7 and Ag_8 clusters are heavily deformed after deposition from their gas phase structures (Figure 5(e,f,g)). In the gas phase, an Ag_6 cluster has a planar structure with three-fold symmetry, an Ag_7 cluster is a pentagonal bi-pyramid and an Ag_8 cluster is a bicapped-octahedron in their respective ground states (Figure 1(e,f,g)). After deposition, their struc-

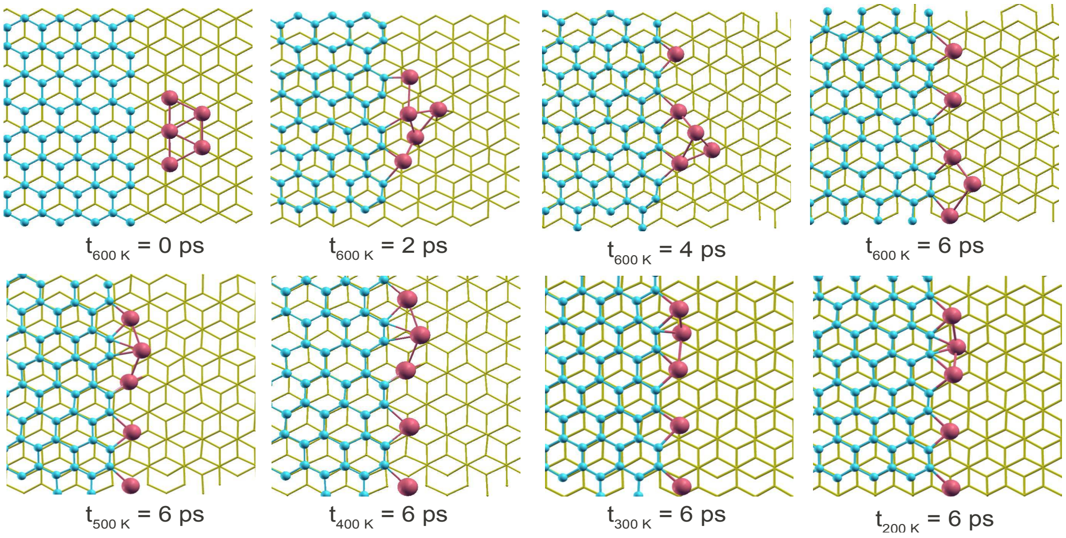


Fig. 6 Top panels: Snapshots from the MD simulation of an Ag_5 cluster on a stepped graphite surface at T= 600 K at specified times. Bottom panels: Snapshots after 6 ps of MD simulation at each temperature.

tures are distorted in ways that they can have maximum Ag-C bonding with the minimum energy cost for stretching of Ag-Ag bonds. One point worth noting here is that unlike Ag_2 or Ag_4, none of the Ag atoms at these sizes ($n = 6-8$) gets completely dissociated from the cluster.

3.0.3 Finite temperature results. From the above discussions it is clear that Ag clusters deposited on a stepped graphite surface try to maximize Ag-C bonds. Ag_2 dimer spontaneously dissociates even at zero temperature. Ag_3 would break into three Ag atoms located at three active sites if it could. The process is kinetically hindered. Ag_4 also dissociates into two fragments. The larger clusters are significantly distorted. As the example of Ag_3 shows, it is possible that the larger clusters would also dissociate near a step edge if they could cross the kinetic barriers hindering this. It is also useful to know how these clusters diffuse on the HOPG substrate after deposition, and after their possible dissociation. In order to explore the behavior of larger clusters on the stepped surface at finite temperatures in more detail, we simulate the annealing of Ag_5 and Ag_8 at 600 K deposited on the lower terrace. In particular, we start MD calculations at 600 K with the clusters in the same initial structure that gave the lowest energy structure in the zero temperature situation. Initial velocities of the atoms are chosen randomly according the Maxwell-Boltzman distribution. We then slowly cool the temperature down to 200 K in steps of 100 K making sure that the system thermalizes at every temperature in the cooling schedule. It takes $\sim$ 0.4 ps for the system to thermalize at a given temperature. But we let it evolve for 6 ps before lowering temperature to the next step. Ideally one should study many MD trajectories at each size to get an idea about the statistical behavior of a number of clusters being deposited on the substrate. However, this is computationally too expensive to be practical. Moreover, since Ag clusters and adatoms tend to move towards the step edge and get adsorbed there even at zero temperature, it is expected that they will diffuse more easily at finite temperatures. Although starting from different initial structures would lead to trajectories differing in their details, the qualitative features would remain the same. Our observations from the MD calculations are as follows.

At 600 K an Ag_5 cluster moves as a single entity on the terrace, and reaches the step within 0.3 ps. Once it reaches the step edge, the cluster atoms start moving independently. Atoms that are close to the active sites are immediately trapped and atoms away from the active sites move until they find vacant active sites. Finally, the Ag atoms arrange themselves into an atomically thin nanowire along the step edge. Since we have only four active sites in our simulation box, only four of the Ag atoms can be trapped at the active sites. The last remaining Ag atom is bonded to two consecutive Ag atoms which are already trapped at active sites or to a C atom at the edge. Between 600 K and 400 K we also occasionally find that an Ag atom at an active site is ‘pushed’ out of its position by another one away from the active site. At 300 K or lower, this process stopped. All the Ag atoms finally take positions along the step edge, either trapped at active sites or bonded to two C atoms of a step-edge dimer and two Ag atoms. After this the atoms only executed thermal vibrations. We do not find any moment on the Ag or edge C atoms in this low temperature structure. A summary of this simulation is presented in Fig 6. Videos of our MD simulations of Ag_5 clusters at all temperatures are provided as Supplementary Information.

Dynamics of of Ag_8 is slightly different from that of Ag_5 because of its larger size, larger number of Ag-Ag bonds, and non-planar structure. Ag_8 takes about 0.6 ps to reach the step edge, and after that the cluster atoms start moving independently. At 2 ps, only three of the cluster atoms get attached to the step edge, while others are still within the cluster environment. At 4 ps, four of the Ag atoms are found near the step edge, three of them are at active sites and one of them is close to a step edge C_2 dimer. At 6 ps they assemble into a nanowire structure. The number of Ag atoms is larger than the number of active sites we have in our simulation cell. Hence not all of them can find an active site individually. What happens is quite interesting. Some of them find active sites, and get trapped there. Others are found close to a step C_2 dimer or close to other Ag atoms that are trapped at active sites. Pushing out of Ag atoms close to the C atoms by those away from them is seen in this case also. The Ag atoms away from the step edge are seen to diffuse along the step direction between 600 K and 400 K. As the temperature is lowered, such diffusion becomes less pronounced. Finally, at 200 K five of the Ag atoms are found close to the step edge C atoms, and the three remaining Ag atoms are found farther away from the step, bonded to the Ag atoms near the step. A summary of this calculation is presented in Figure 7. *

The main conclusions we draw from these finite temperature MD simulations are as follows. Clusters deposited on the surface at $\sim$ 600 K diffuse as a single entity on the terraces but disintegrate at the step edges. The Ag atoms tend to form a nano-wire like structure along the step edges with each Ag atom ideally occupying one active site. If there are not enough active sites nearby, or, if somehow, some of the Ag atoms cannot diffuse to the step edge C atoms (which is more likely to happen for larger clusters and low temperatures), those atoms get attached to the Ag atoms already trapped at the edge. This may produce dumbbell-like shapes in STM images. Our simulations of the Ag_8 cluster show that Ag atoms that get bonded to the step edge C atoms do not diffuse even at 600 K over the time scale we can explore here. It is the Ag atoms away from the step, bonded to other Ag atoms, that diffuse along the step direction. Based on these observations we suggest that by depositing small size-selected Ag clusters on a stepped graphite surface at elevated temperatures ($\sim$ 600 K), and controlling the cluster density to match the available step-edge active sites, it may be possible to fabricate self-assembled atomically thin nano-wires. These observations also show that the assumption in the Gates-Robins model that the clusters trapped at the step edge are completely immobile is simplistic.

3.0.4 Band-structure of 1D monoatomic chain along stepped surface. With this insight into the diffusion of Ag clusters on the terraces and along the steps of a graphite surface, we now try to understand the electronic structure of a system when a nanowire-like structure has been formed along the step edge. First we calculate the band structure of an ideal system: a silver nano-wire formed at the step-edge with each of the active sites being occupied by an Ag adatom. A similar structure at a zig-zag step was studied in some recent works[24,25] without exploring how such a structure can possibly be formed. In contrast to the band structure of the relaxed stepped graphite, there is a band crossing the Fermi level in this nanowire structure (Figure 3(b)). The partial density of states (not shown) of the system shows a finite density of Ag *s* and C *p* states at the Fermi level. Thus a conducting channel is formed not by the Ag atoms alone (which are > 4 Å apart), but by the Ag-C-Ag-C-$\cdots$ chain. We also calculated the band structure for the low temperature structures of Ag_5 and Ag_8 clusters shown in Figs 6 and 7. These were also metallic in nature indicating that a conducting nano-wire can be formed by depositing Ag clusters on this surface under appropriate conditions of temperature and cluster density.

4 Conclusions

It is shown that step edges on a graphite surface act as attractive sinks for silver adatoms and clusters. The microscopic mechanism of the attractive nature of the step edges is clarified for the first time. Due to the existence dangling bonds on the edge C atoms, the grooves at the armchair edge act as active sites of attraction for individual Ag atoms. In fact, some small clusters such as Ag_2 and Ag_4 dissociate to take advantage of the strong Ag-C bonds even at 0 K. A large region extending up to 6 Å from the step-edge on the lower terrace, and 3.5 Å on the upper terrace acts as the basin of attraction for an individual Ag adatom. Finite temperature MD calculations suggest that clusters deposited on HOPG at $\sim$ 600 K diffuse rapidly on the terrace till they reach a step-edge. Once at the step-edge they tend to break up in a way so that each Ag atom tries to occupy an active site. If that is somehow hindered, some of the Ag atoms get trapped at active sites, or get bonded to the edge dimers while the other Ag atoms bond to these Ag atoms. The Ag atoms away from the step edge diffuse significantly along the step direction at elevated temperatures. Therefore, it is clear that what diffuse along step edges are individual atoms of the cluster, and not the cluster as a whole. A linear chain of Ag atoms occupying active sites, and the structures of Ag_5 and Ag_8 clusters obtained after an-

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* File size limitation does not allow us to share videos of MD of Ag_8.

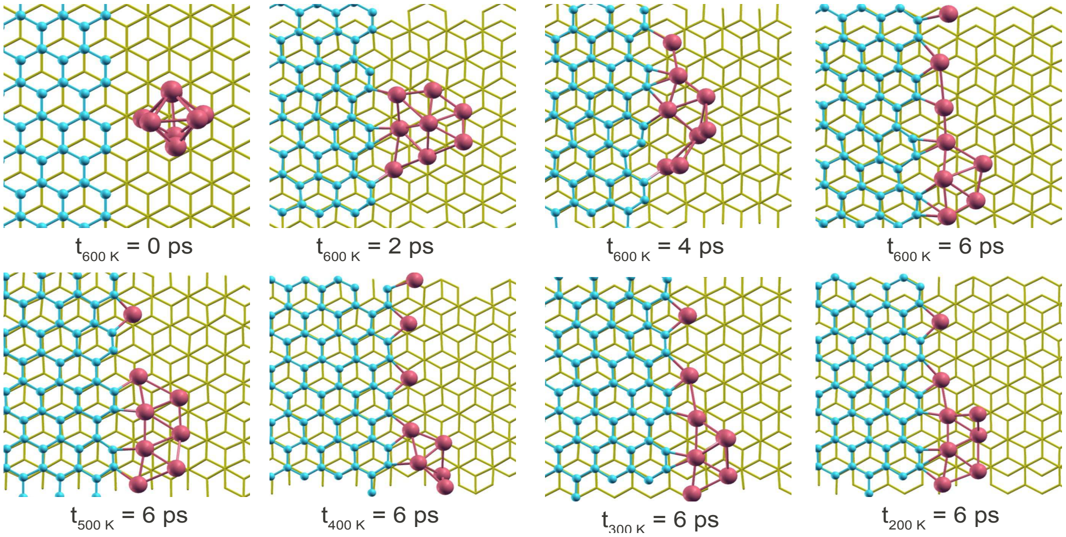

Fig. 7 Top panels: Snapshots from the MD simulation of an Ag_8 cluster on a stepped graphite surface at T= 600 K at specified times. Bottom panels: Snapshots after 6 ps of MD simulation at each temperature.

nealing at 600 K, all turn out to be metallic.

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