Intercalation of Au Atoms into SiC(0001)/Buffer Interfaces—A First-Principles Density Functional Theory Study

Amirhossein Bayani* and Karin Larsson

ABSTRACT: The process of Au intercalation into a SiC/buffer interface has been theoretically investigated here by using density functional theory (DFT) and the nudged elastic band (NEB) method. Energy barriers were at first calculated (using NEB) for the transfer of an Au atom through a free-standing graphene sheet. The graphene sheet was either of a nondefect character or with a defect in the form of an enlarged hexagonal carbon ring. Defects in the form of single and double vacancies were also considered. Besides giving a qualitative prediction of the relative energy barriers for the corresponding SiC/buffer interfaces, some of the graphene calculations also proved evidence of energy minima close to the graphene sheet. The most stable Au positions within the SiC/buffer interface were, therefore, calculated by performing geometry optimization with Au in the vicinity of the buffer layer. Based on these NEB and DFT calculations, two factors were observed to have a great influence on the Au intercalation process: (i) energy barrier and (ii) preferential bonding of Au to the radical C atoms at the edges of the vacancies. The energy barriers were considerably smaller in the presence of vacancies. However, the Au atoms preferred to bond to the edge atoms of these vacancies when approaching the buffer layer. It can thereby be concluded that the Au intercalation will only occur for a nondefect buffer layer when using high temperature and/or by using high-energy impacts by Au atoms. For this type of Au intercalation, the buffer layer will become completely detached from the SiC surface, forming a single layer of graphene with an intact Dirac point.

RESULTS AND DISCUSSIONS

Au Intercalation through a Buffer Layer. Calculation of the Energy Barriers for a Free-Standing Graphene Sheet. For the Au intercalation process, through the carbon buffer layer and into the SiC(0001)/buffer interface, different types of buffer layers have been considered in the present study (a defect-free buffer layer and layers with single or double

INTRODUCTION

Large-scale production of graphene is very challenging for various types of industrial applications. Intercalation methods based on thermal annealing have been shown to be a promising way to produce graphene sheets in large sizes.\textsuperscript{1–3} It has been experimentally shown that intercalation with different types of elements (such as H,\textsuperscript{4} Li,\textsuperscript{5} Ge,\textsuperscript{6} F,\textsuperscript{7} Au,\textsuperscript{8} Pt,\textsuperscript{9} and Cu\textsuperscript{10}), followed by thermal annealing, is a suitable way to fabricate high-quality single-layer graphene on SiC substrates.

Different theoretical studies have focused on the mechanism of intercalation with either Li\textsuperscript{11} or Cu\textsuperscript{12} into the SiC/buffer interface. It has been shown that the intercalation will take place through defects in the buffer layer. However, to the best of our knowledge, the mechanism of intercalation with Au atoms has not yet been theoretically addressed. Also, previous theoretical studies have only dealt with the energy barrier in the atom intercalation process. However, the complete optimization of the geometrical interface structure (especially after the intercalation process) still needs to be addressed.

In the present study, the intercalation of Au atoms into the interface between a buffer layer and the underlying SiC(0001) substrate has been theoretically considered. In order to estimate the energy barrier for the Au intercalation process, the climbing image nudged elastic band (NEB) has been used in combination with a density functional theory (DFT) method. The preferred position of the intercalated Au atom, in addition to the corresponding bond situation, was obtained by using DFT calculations. The electronic structure of the buffer layer (in the SiC/buffer systems) was also calculated by using a DFT method. For the buffer layer, the influence by various types of defects was especially considered. These defects include single and double vacancies, as well as an enlarged hexagonal C ring. The purpose was to study and gain knowledge about the influence of these defects on (i) the energy barrier of the Au intercalation process and on (ii) the eventual interactions between Au and the buffer layer C atoms.

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waals interactions do take place. However, this type of
interaction is very weak and can only be observed for an energy
barrier for a defect-free graphene sheet is extremely large (56.1
eV). Hence, it is obvious that a larger supercell must be
considered in order to obtain more accurate values of the
energy barriers. All C atoms in graphene will, otherwise, move
during the process of penetration, which is not the favorable
pathway in real systems with just a few metal atoms
penetrating the buffer layer simultaneously. A large enough
supercell will permit the formation of a local nucleation
process that occurs in either the initial or final stage of the
intercalation. After the initial nucleation, the intercalating
material will propagate across the supercell. 13 It is also
important to mention that during Au penetration through
the defect-free graphene sheet (black line in Figure 1), van der
Waals interactions do take place. However, this type of
interaction is very weak and can only be observed for an energy
range of −0.5 to 1 eV (in Figure 1a).

As the next step in the investigation, single and double
vacancies were considered by removing one and two carbon
atoms, respectively, from the center of the graphene sheet (see
Figure 1c). For these models, the Au penetrations were
assumed to take place exactly at the positions of the vacancies.
For the graphene sheet with a single vacancy (SV), an energy
minimum (at −3.98 eV) was observed at a graphene−Au
distance of 1.5 Å, followed by an energy maximum (of 10.7
eV) at the Au interception with graphene (see Figure 1a).
From this result, it is possible to conclude that the Au atom
prefers to bind to graphene SV, with a chemisorption energy of
2.94 eV (283.66 kJ/mol) and at a distance of 1.5 Å from the
graphene sheet (at low temperatures and/or low Au impact
energies). Moreover, an energy maximum of 10.7 eV was
found to be 5 times smaller than that of a graphene sheet
with no defects. On the contrary, a complete lack of energy
maximum was observed when studying a graphene sheet with
double vacancy (DV). Instead, an energy minimum of −8.0 eV
was found at the interception with the graphene sheet. Hence,
for this type of defect, the Au atom prefers to be chemically
captured within the graphene sheet. 14

The penetration by Au has also been studied for a graphene
sheet where one of the six-membered rings has been enlarged
(with C−C distances equal to 1.9 Å; see Figure 1c). The
resulting barrier energy decreased to 4.5 eV (with respect to
the result for a nonperturbed defect-free graphene sheet).
Moreover, a tendency for energy minima was also observed in
the vicinity of the graphene sheet.

Calculation of Stable Geometrical Structures of SiC/
Buffer-Au Systems. The interaction between Au and the SiC/
buffer interface was also studied in the present work. In the
construction of the supercell model, a 4 × 4 graphene sheet
(i.e., with 4 × 4 unit cell size) was initially positioned on top of
the Si surface of SiC(0001), with a matching of
2√3 × 2√3R30° with respect to the SiC structure. As was
the situation with a free-standing graphene sheet, this attached
graphene layer was either defect-free or had a single (or
double) vacancy. The situation with an enlarged hexagonal C
ring was also here considered. These SiC(0001)/graphene
systems were thereafter geometry optimized, whereby
corresponding SiC(0001)/buffer systems were obtained. For
each of these systems, the next step was to position one Au
atom above the center of the hexagonal ring or the vacancy of
the buffer layer. Geometry optimizations were, thereafter,

![Image](image-url)
performed but with fixed Au positions at 0.5, 0.1, 0, −0.1, and −0.2 Å with respect to the buffer layers. The positive and negative values correspond to Au positions above and under the buffer layer, respectively. Moreover, zero indicates the interception with the buffer layer. The purpose with these calculations was to more accurately calculate the most stable geometrical structures (i) at the point of the interception, as well as (ii) just before and (iii) after penetration through the buffer layers. The idea behind these calculations comes from the presented potential energy curves in Figure 1a (for nondefect and defect graphene sheets).

The possibility for intercalation through a defect-free buffer layer was at first studied. The calculations showed that the intercalation cannot take place for this type of the non-perturbed buffer layer structure (i.e., without the addition of extra energy). In fact, when starting the geometry optimization from an Au position 0.5 or 0.1 Å above the buffer layer, the gold atoms were repelled from the buffer layer (see Videos S1 and S2 in Supporting Information). These results are in complete agreement with the corresponding results for a graphene sheet (i.e., the total energy for an Au position of 0.5 or 0.1 Å above the graphene sheet is larger than for any Au position further away from graphene). Moreover, the final SiC/Au/graphene structure was found to be more energetically stable than the initial SiC/buffer/Au structure (by a value of 2.16 eV/supercell). Hence, the intercalation process is thermodynamically possible but kinetically hindered. Next, we assumed that Au overcame the energy barrier by considering gold atom exactly at the middle of and 0.1 Å below the GS. We found that in this situation, intercalation can happen and the graphene sheet detached completely from the SiC substrate (see Videos S3 and S4). Finally, when the Au atom was initially positioned 0.2 Å below the buffer layer, the latter did not only detach from the SiC substrate (as a result of the geometry optimization) but also formed a perfect planer graphene sheet (see Video S5). The optimized geometries of SiC/buffer and SiC/Au/graphene are shown in Figure 2, with the Au atom initially located at 0.1 Å above, at the middle of, and 0.2 Å below the buffer layer.

As the next step, the same procedure was used for single- and double-vacancy buffer layers. It was then observed that the Au intercalation cannot take place. Neither for the Au atom initially above, nor below, the buffer layer (see Videos S6 and S7 files). As an explanation to these observations, dangling bonds (i.e., radical C atoms) were formed at the edges of the vacancies when creating these single and double vacancies. Therefore, the Au atom became trapped in the buffer layer, forming covalent bonds with buffer C atoms. The initial and final geometrical structures of the SiC/Au/buffer system, with single and double vacancies in the buffer layer, are presented in Figure 3. The Au atom, here, has been initially positioned 0.2 Å below the buffer layer. These two structures are further proof of the fact that intercalation with Au atoms cannot take place through a buffer layer with either single or double vacancies.

As a conclusion, vacancies in the buffer layer will reduce the energy barrier for an Au intercalation process. However, the vacancies contain “dangling bonds” (i.e., C atoms with unpaired electrons), which will cause bond formation with the Au atom. The latter of these factors were found to be decisive in the prevention of the Au intercalation process.

Electronic Properties of the Buffer Layer (before and after Au Intercalation). The projected band structure for a nondefect buffer layer, being attached to SiC(0001), has been calculated before and after a successful Au intercalation process. The purpose of these calculations was to confirm that the result of the intercalation process is the formation of a detached graphene sheet. The calculated band structures, for the initial and final geometrical structures, can be seen in Figure 4. As can be seen in this figure, there is no evidence of a Dirac point (DP) of graphene for the initial structure, where
the buffer layer was partially bound to the Si surface of the SiC substrate. However, the DP was completely recovered for the final structure with a free-standing graphene sheet. Moreover, there is a linear dispersion of \( \pi \)-bands for this monolayer of graphene. This result is a strong support for the observation that graphene has become completely detached from the surface of the SiC substrate. Intercalation by Au has, therefore, led to a quasi-free-standing layer of graphene, which has also been observed by experimentalists. Only one Au atom per supercell was responsible for this detachment, which is equivalent to 3.12% of the total number of C atoms in the buffer layer. We can also observe a gap at the DP of graphene, which has its origin in the A B sublattice symmetry breaking of graphene (due to the interaction with Au).

**CONCLUSIONS**

The purpose of the present work was to study the intercalation of Au atoms into SiC(0001)/buffer systems. However, these model systems were too big for calculations using the climbing image NEB method. Hence, more qualitative values of the intercalation energy barriers were instead obtained by examining the penetration of an Au atom through a graphene sheet. Both defect-free sheets, as well as graphene sheets with single and double vacancies, were used in these calculations. The energy barrier for Au penetration through a defect-free graphene sheet was shown to be very high, which will prevent the occurrence of Au penetration (i.e., without the addition of extra energy). On the contrary, the corresponding energy barriers were significantly reduced for single and double vacancies in the graphene sheet. In fact, the energy barrier for a SV was 5 times smaller than for a defect-free graphene sheet. Moreover, a graphene sheet with a DV did not show any energy barrier at all. Another type of defect in graphene has also been created by enlarging one of the hexagonal rings. The calculated energy barrier for this type of defect was almost 12 times smaller than for a defect-free graphene sheet. Other interesting observations were made for these graphene sheets, and that were the energy minima which were observed for the defect-containing sheets. Geometry optimization calculations were, therefore, made (based on DFT) for the larger SiC(0001)/buffer system, where the Au atom was initially positioned right above or below the carbon buffer layer. Even though the graphene layer defects caused smaller energy barriers for the Au penetration, this type of process could not take place on the SiC(0001)/buffer surface. The reason is the radical C atoms that surrounds the defects, which will interact with (and thereby bind to) the approaching Au atom. The only possibility for an Au intercalation is by using a defect-free buffer layer and a large enough energy contribution (either by using a high enough temperature or by using Au bombardment with high velocities).

When deliberately positioning the Au atom within the nondefect SiC(0001)/buffer interface, and thereafter performing a geometry optimization calculation, a graphene sheet was found to be completely detached from the SiC substrate. (It is, thus, here assumed that the intercalation process has taken place). The projected band structures for the SiC(0001)/buffer structure, before and after Au intercalation, were also calculated. As a result, the detached graphene sheet recovered its DP, which is the ultimate proof of a free-standing graphene structure. These results do shed some light on the prerequisites for Au intercalation into a SiC(0001)/buffer interface.

**COMPUTATIONAL METHODS**

NEB calculations, optimization of geometrical structures, and analysis of electronic structures have in the present study been performed by using DFT (as implemented in the Quantum ATK 2019.03 simulation package). The PseudoDojo-High norm-conserving pseudopotential, based on a Perdew, Burke, and Ernzerhof functional, was used for the total energy calculations. Also, the DFT-D2 method, in combination with counterpoise corrections, was considered in describing the long-range van der Waals forces between the buffer layer and the intercalated Au atoms. As a model of the SiC/buffer system, a supercell was initially built which consisted of a \( 8 \times 8 \) graphene sheet on top of a SiC(0001) substrate (on the Si face of SiC). This system was, thereafter, geometry optimized to produce the SiC/buffer system. A free-standing graphene sheet was also modeled in the present study. The graphene model was used to estimate the intercalation energy barrier for an Au atom, and the model of the SiC/buffer system was used in studying the interaction between the intercalating Au atom and the SiC/buffer system. A Monkhorst–Pack sampling of \( 5 \times 5 \times 1 \) and a cutoff energy of 80 ha were considered for both the NEB calculations (for the energy barriers) and the geometry optimizations (for the interactions). Moreover, a periodic boundary condition, with a vacuum size of 25 Å, was used for all calculations in the present study. Also, the image-dependent pair potential method was used as an interpolation method in the climbing image NEB calculations (where also the initial and final steps were geometry optimized).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01985.

Geometry optimization from an Au position 0.5 above the buffer layer (MP4)

Geometry optimization from an Au position 0.1 Å above the buffer layer (MP4)

Detachment of graphene sheet completely from the SiC substrate (MP4)
Intercalation process (MP4)  
Formation of a perfect planar graphene sheet (MP4)  
Intercalation of Au atom initially below the buffer layer with single vacancy (MP4)  
Intercalation of Au atom initially below the buffer layer with double vacancy (MP4)

■ AUTHOR INFORMATION

Corresponding Author
Amirhossein Bayani — Department of Chemistry-Ångström Laboratory, Uppsala University, Uppsala 752 37, Sweden; 
Email: amirhossein.bayani@kemi.uu.se

Author
Karin Larsson — Department of Chemistry-Ångström Laboratory, Uppsala University, Uppsala 752 37, Sweden

Complete contact information is available at:  
https://pubs.acs.org/10.1021/acsomega.0c01985

Notes
The authors declare no competing financial interest.

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