First Principles Study of the Binding of 4d and 5d Transition Metals to Graphene

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We study the strength of the binding of 4d and 5d transition metals on a graphene sheet in the limit of high-coverage using first principles density functional theory. A database of the binding energies is presented. Our results show that the elements with low or near-half occupation of the d shell bind strongest to the graphene sheet. We find a transfer of electrons from the transition metal to the graphene sheet; the charge transfer decreases with increasing d shell occupation. Motivated by the strong binding to Hf we also study the binding of graphene to the Hf rich surface of HfO₂. The predicted binding energy of −0.18 eV per C atom when coupled with the existing integration of HfO₂ into Si-based CMOS devices suggests a new route to integrating graphene with silicon, allowing for an integration of graphene-based nanoelectronic components into existing silicon-based technology.

Introduction

Carbon nanostructures such as fullerenes and carbon nanotubes have been at the forefront of materials science for over two decades. Graphene¹ with its two-dimensional honeycomb structure and linear low-energy electron dispersion exhibits a host of interesting chemical and physical properties such as the quantum Hall effect and Klein tunneling, combined with a variety of possible applications ranging from single molecule sensing² to high electron mobility transistors.³ The chemical modification of graphene through the addition of functional groups can lead to graphene derivatives such as graphane⁴ with large application potential. In this work, we focus on a new class of graphene derivatives, obtained by functionalizing graphene with transition metal atoms.

Our aim is to present a first-principles theoretical study of the binding energies of transition metals spanning the 4d and 5d series in the limit of high-coverage. Transition metals are widely used as substrates and contacts for graphene and carbon nanotubes. Au contacts are often used, but other metals have been used and studied as well, such as Pt and Pd.⁵ As a guide to choosing the optimal contacts in, for example, electrochemistry or electronic transport measurements, it is therefore of interest to understand which metals bind most strongly. Furthermore, it has been shown that electronic transport through graphene nanoribbons can be used for single-molecule sensing.² Knowledge of binding energies could allow such measurements to discriminate between analyte atoms or molecules.

Another reason why the study of the binding energies is timely is because recently it was demonstrated that few-atom mass sensing is possible with the help of carbon nanotube and graphene resonators.⁶⁻⁸ The device uses a carbon nanotube or a graphene ribbon as a mechanical resonator. When atoms bind to the nanotube or graphene ribbon, the resonance frequency changes, thereby allowing the detection of small clusters of atoms. In principle, this device could be used to measure not only atomic mass, but also the binding energies of atoms to the resonator, since the shift in the resonance frequency is sensitive to both mass and binding energy. Furthermore, an increase in temperature would preferentially remove weakly bound atoms, whose loss would be detected via a resonance shift. A database of theoretical binding energies would be of tremendous use for interpreting the frequency shifts of such a resonator.

The transition metals studied here are also interesting because (with the exceptions of Au, Ag, Pd, Pt, and Rh) they are all superconducting in their bulk phase at sufficiently low temperature. Three of these, Ta, Tc, and Nb have relatively high critical temperatures of 4.47, 7.8, and 9.25 K, respectively. Hence these three should be desirable candidates for use as superconductor contacts to graphene in superconductor-graphene devices.

One of the metals that we study, Hf, has a further significance, because very recently, a carbon nanotube-based extremely high speed NVRAM using HfO₂ as the insulating layer instead of SiO₂ was constructed.⁹ For this reason, the study of the binding of graphene to Hf is important, since strong binding of graphene to Hf would mean favorable binding to the Hf rich surfaces of HfO₂. If HfO₂ is destined to replace SiO₂ in silicon-based electronics, successful binding of graphene to HfO₂ could allow the integration of novel carbon-based nanoelectronic devices into silicon-based devices.

In the following, we present the results of our first-principles calculations, which were performed using density functional theory (DFT) at the generalized gradient approximation (GGA) level. We study the strength of the binding of 4d and 5d transition metals on graphene in the limit of high-coverage and present a database of binding energies. The magnetization of the functionalized material is also discussed, as well as charge redistribution based on a Bader charge analysis. Finally, we present our results on the strength of the binding of a single graphene sheet on the Hf rich surface of HfO₂.
Results and Discussion

We have performed first-principles DFT calculations on the binding of transition metals to graphene using the Perdew–Burke–Ernzerhof (PBE) functional. The details of the applied method are described at the end of the paper. The calculations were performed with a six carbon atom supercell (in which case the supercell is a hexagon of carbon atoms, see left panel of Figure 1). During the calculations of the functionalized material, a single transition metal atom was placed in the supercell at high symmetry positions: over a carbon atom (atop site), over a single transition metal atom was placed in the supercell at the middle of a carbon–carbon bond (bridge site), or over the middle of a hexagon (hollow site). The distance from the sheet was optimized, while the graphene was considered rigid. For comparison, calculations were also performed on a special kind of supercell in which a $2 \times 2$ triangular lattice of transition metal atoms is attached to a $3 \times 3$ graphene supercell (see right panel of Figure 1). In this arrangement, one of the transition metals is docked at a hollow site, while the rest at bridge sites. This supercell geometry was used in the hafnia surface calculations as well (see below).

Figure 2 shows the results of our PBE calculations for the binding energy of 4d and 5d transition metals to graphene in the limit of high-coverage. A similar trend is found in the case of both series. The binding energy is rather strong for the elements at the start of the series and it starts decreasing as the occupation of the d shell increases. However, the binding energy increases abruptly at the middle of the series, and then starts decreasing again until we reach the noble metals at the end of the series. Qualitatively this means that the binding is strongest when the d shell is nearly empty or half-filled. A complete database of the binding energies can be found in the Supporting Information, along with the binding distances from the graphene sheet.

In addition to this trend, it can be seen that for most elements, the hollow site is the most favorable. Notable exceptions include the last element of both series, Ag and Au. For these elements, we have found that the three sites are energetically roughly equivalent (although it is worth noting that the binding is also extremely weak, especially in the case of Ag). This result contrasts previous studies in the low-coverage limit that found that the atop site is the most favorable, followed by the bridge and finally the hollow site (see refs 10 and 11). We performed test calculations with the local density approximation (LDA) for Ag and Au in the low-coverage limit using a $6 \times 6$ graphene supercell (72 carbon atoms) to ensure that neighboring transition metal atoms are far enough apart to be considered isolated. Our results agree with previous works in the literature, for example, the low-coverage LDA binding energies for Au at the atop, bridge, and hollow sites in our calculations are $-0.70$, $-0.68$, and $-0.53$ eV, respectively, which agree well with the results in ref 11. Thus we conclude that the high-coverage is responsible for the equivalence of the different sites for Ag and Au.

Since the calculations were performed by taking possible spin-polarization into account, we have also obtained the magnetizations for each calculation. These are shown in Figure 3. It can be seen that the magnetization follows a trend set by the occupation of the d shell: spin-polarization is largest at the middle of the series, and smallest at the two ends. The noble metals are completely nonspin-polarized, as expected.

It is worth noting that the presence of spin-polarization has a significant effect on the trends in the binding energy. If we perform these calculations without taking spin-polarization into account, we obtain a somewhat different trend in the middle of the 4d and 5d series; in a nonmagnetic calculation, the binding energy decreases approximately monotonically as the occupation of the d shell increases. In other words, the binding energy can be significantly decreased in the cases when magnetization is very large.

So far we have examined a scenario where transition metal atoms sit atop graphene at high symmetry sites. In such a calculation, the transition metals essentially form a triangular lattice above the graphene substrate, which immediately raises the question of commensurability. In the calculation, the graphene and the transition metal lattice must be commensurate, while in a real experiment this is not necessarily so. Consequently the triangular metal lattice must be scaled to fit onto the graphene commensurately. In the rigid graphene approximation, using the above-mentioned six-atom graphene supercell, the lattice constant of this triangular lattice is three times the carbon–carbon bond length (4.28 Å). We have calculated the
optimized lattice constant for the isolated two-dimensional triangular lattice of each of the studied transition metals to see if this distance is a good approximation. Our results have shown that these lattice constants are in the range of $\sim 2.5 - 3$ Å. This means that our approximation corresponds to an expanded transition metal lattice. Given that the interaction between the transition metals and the graphene will weaken the bonds within the transition metal lattice and therefore the bonds will expand, this is an acceptable model of commensurate full coverage. Still, this raises the question whether an even higher level of coverage is possible.

To test this, we have looked at two additional geometries. First, we examined what happens if instead of having a single transition metal atom in the six-atom graphene supercell, we have three adatoms occupying either three atop sites or three hollow sites. Both cases correspond to a geometry where the transition metals form a triangular lattice with a lattice constant which is smaller than it would be in an isolated monolayer. Because of this one would expect that binding would be weak or unfavorable. Indeed, we have found that in many cases the binding is energetically unfavorable with such a geometry, and even in cases when it is favorable the binding energy is very small. Therefore, it is unlikely that such a high level of coverage can be achieved.

We have also looked at a different kind of supercell, which consists of a $3 \times 3$ graphene supercell and a $2 \times 2$ triangular lattice of transition metal atoms. In this case, it is impossible to dock all the adatoms at the same kind of adsorption site, but it is still possible to attach all of them to high symmetry sites. In the particular setup we used, one adatom is at a hollow site while the other three are at bridge sites (see right panel of Figure 1). In this setup, the lattice constant of the triangular lattice is 3.7 Å, which is much closer to the monolayer values than the 4.28 Å in the original supercell. The binding energies and magnetizations per adatom are shown in Figures 4 and 5, respectively. We have found that in this geometry, most metals bind favorably to the graphene, although the binding energy per adatom is smaller than in the previous case. Furthermore, binding is unfavorable for Ag in this setup. Interestingly, in this geometry the binding energy does not follow the same kind of trend as before. However, one thing that has not changed is that the elements with low d shell occupation bind strongly to the graphene sheet. Thus we can conclude that these elements should be useful in any application where strong binding to graphene is required.

For the sake of completeness, we have also looked more closely at the binding for two examples, Hf and Ta adsorbed at hollow sites. These are worth looking at in detail since strong binding of Hf suggests that graphene may bind favorably to a Hf-rich surface of HfO$_2$, which may facilitate the integration of silicon-based and carbon-based nanoelectronics, while strong binding of Ta is also an interesting result since Ta is a superconductor below 4.47 K and therefore it could be used as a low resistance superconductor contact in superconductor-graphene devices. For these two transition metals, we have performed a full optimization of the functionalized graphene in the supercell geometry of Figure 1a in order to determine whether the interactions distort the graphene lattice significantly. We found that after optimization the distance of the transition metal atom from the graphene sheet changes very little, and the graphene sheet is only slightly distorted with the carbon–carbon bondlengths changing by at most 0.02 Å, which suggests that the distortion can be safely neglected with regards to the study of the binding energy. The change in binding energies is on the order of 0.01 eV (see Table 1).
In addition to the slight distortion of the graphene sheet, the transition metal atoms donate electrons on the order of 1.5–1.8 electrons each to the graphene, based on the Bader charges of the atoms. For the coverage used here, this corresponds to a small carrier density of ~0.27 electrons per carbon atom, which will shift the Fermi level of graphene up from the Dirac point. A similar change in the electronic structure occurs in the presence of a low-coverage of Au atoms. We have calculated this charge transfer (CT) between the adsorbed atoms and the graphene for all elements studied at all three high symmetry sites. What we found is that with the exception of Re all transition metal atoms follow a simple trend: the CT monotonically increases with decreasing d shell occupation. The largest CT is on the order of 1–2 e\(^{-}\) per adsorbed atom (the largest value is 2.54 in the case of Hf docked at the bridge site). The transition metals donate electrons to the graphene, thus shifting the Fermi level up from the Dirac point into the conduction band. In the case of the noble metals, the charge transfer is of opposite sign but since its magnitude is so small (on the order of 0.01 e\(^{-}\)) it is negligible. Re is the only metal that deviates from the aforementioned generic trend: the CT is less than 0.1 e\(^{-}\) whereas in the case of W and Os, its neighbors in the 5d series, the CT is on the order of 0.7–1.2 and 0.3–0.6 e\(^{-}\), respectively. The exact values of the charge transfer for each element can be found in the Supporting Information.

It is worth noting that while the distortion of the sheet is minimal and does not influence the strength of binding, there may be an important influence on the properties of the functionalized material by the edge states in a graphene nanoribbon. Edge states influence the electronic structure of pristine nanoribbons and are also likely to affect properties of the functionalized material. Hence, it is important to keep in mind that the binding energy is likely to be different near the edge of a nanoribbon.

For the future, it may also be of interest to compare graphene with multilayers of graphene and indeed with graphite, since the additional carbon layers beneath the functionalized layer will influence the strength of the binding and may even change the trends reported here. However, we expect the order of magnitude of the binding energies to remain unchanged, since the interaction between neighboring layers of graphite is a weak van der Waals type interaction. For example, the binding of Au on graphite does not differ much from the binding of Au on graphene; the binding energy for the former case is 0.45 eV/atom according to LDA, which compares well with our data and the aforementioned results in ref 11.

Finally, motivated by the strong binding of Hf to graphene, we have also studied the strength of binding between graphene and the Hf rich surface of HfO\(_2\). For this calculation, we used the high-temperature cubic phase of HfO\(_2\) due to the need to select a commensurate supercell. (The structure of HfO\(_2\) at room temperature is monoclinic, but since the composition of elements is the same, we expect that the binding energy of graphene on a Hf rich surface will not change much between different crystal structures of HfO\(_2\).) We used the close-packed (111) surface of cubic HfO\(_2\) that has a triangular lattice of Hf atoms at the top layer. The supercell consisted of a symmetric HfO\(_2\) slab of 28 atomic layers (26 Å wide) and a single layer of graphene attached to one side of it. To overcome the large mismatch in lattice constants (3.58 Å for the triangular Hf lattice on the (111) surface of HfO\(_2\)), a 2 × 2 supercell was used within the surface plane for HfO\(_2\) and a 3 × 3 supercell for graphene, as depicted in Figure 1b. The HfO\(_2\) slab itself was fully optimized prior to the binding energy calculation. The distances of the carbon atoms from the slab were also optimized. The carbon–carbon bond length was scaled down to 1.38 Å to commensurately fit the graphene on the HfO\(_2\) slab.

We have found that the graphene sheet is not repulsed by the HfO\(_2\) slab, rather, it binds there with a binding energy of ~0.18 eV per carbon atom. This compares well with the results obtained for the binding of pure Hf to graphene in the high-coverage limit. The binding energy per carbon atom at the hollow site is ~0.38 eV (obtained from the ~2.26 eV per Hf atom binding energy value in Figure 2), while the binding energy per carbon at the bridge site is ~0.22 eV. The weighted average of these values for one hollow site bound atom and three bridge site bound atoms is ~0.26 eV, which is only ~50% larger than the binding energy per carbon atom on the HfO\(_2\) surface. This result suggests that the binding between graphene and Hf atoms on a Hf rich surface of HfO\(_2\) is weaker but still almost as strong as the binding of pure Hf to graphene. Note however that the distortion of the graphene sheet in this geometry is more significant than before: atoms move out of the original graphene plane by at most ±0.1 Å, which is much larger than what we

![Figure 5](image_url)

**Figure 5.** The PBE magnetizations of 4d and 5d transition metals in the supercell geometry of Figure 1b.

<table>
<thead>
<tr>
<th>Element</th>
<th>(\Delta E_A) (eV)</th>
<th>(\Delta E_B) (eV)</th>
<th>(d_A) (Å)</th>
<th>(d_B) (Å)</th>
<th>CT(_A)</th>
<th>CT(_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>-2.26</td>
<td>-2.28</td>
<td>1.94</td>
<td>2.04</td>
<td>1.77</td>
<td>1.80</td>
</tr>
<tr>
<td>Ta</td>
<td>-2.13</td>
<td>-2.15</td>
<td>1.83</td>
<td>1.96</td>
<td>1.57</td>
<td>1.53</td>
</tr>
</tbody>
</table>

\(^a\) \(\Delta E_i\) (eV): binding energy per transition metal atom. \(d_i\) (Å): distance of the transition metal atom from the sheet. CT\(_i\) (\(\sim\) e\(^{-}\)): charge transfer, i.e., number of electrons removed from the transition metal and transferred to graphene. \(i = A\) in these parameters corresponds to the case of the approximation of a rigid graphene sheet, while \(i = B\) corresponds to the results obtained after the full optimization of the graphene sheet.
found for the high-coverage adsorption of Hf on an isolated graphene sheet. This may be related to the compression of the graphene lattice as enforced by the use of the supercell geometry, and the fact that the Hf atoms on the surface are at different kinds of high symmetry sites of the deposited graphene sheet. In an incommensurate geometry that is likely realized in a real experiment, we expect the distortion to be somewhere in between the two scenarios studied in this work.

Method

During the calculations we used the Vienna ab initio simulation package (VASP)\textsuperscript{14–16} with a plane-wave basis set employed within the framework of the projector augmented-wave method.\textsuperscript{17,18} The plane-wave cutoff energy was set to a high value of 500 eV, ensuring that there would be no basis set superposition errors. A \(6 \times 6\) Monkhorst-Pack \(k\)-point grid was used in the \(k\)-space of the graphene supercell, which is sufficient to reach convergence for the total energy. Charge transfer results were obtained from the analysis of the Bader atomic charges\textsuperscript{19} using an external utility.\textsuperscript{20} The binding energy calculations were performed using the PBE GGA. To check the sensitivity of our results to this approximation, some of the calculations were also conducted using the Ceperley–Alder LDA. For isolated graphene, LDA is known to provide better results. However, for the transition metals it is imperative that the d orbitals are properly described, so it is preferential to instead use a GGA functional, which describes transition metals better than LDA (see, e.g., the surface relaxation of transition metals\textsuperscript{21}). Therefore we focused on the PBE results in this work.

The HfO\(_2\) slab calculations were performed on the close-packed (111) surface using a \(15 \times 15\) Monkhorst-Pack \(k\)-point grid. The geometry was a 26 Å wide slab with Hf layers on both sides and a single sheet of graphene resting on the surface of the slab. For sake of commensurability, a \(2 \times 2\) slab supercell was used and a \(3 \times 3\) graphene supercell was attached to the surface (Figure 1b).

Conclusion

In conclusion, we have obtained a first-principles database of the binding energies of the 4d and 5d transition metals on a graphene sheet in the limit of high-coverage. We found that the metals at the end of the series such as Au and Ag bind weakest, while metals near the start of the series bind strongly, and the binding is strongest at the hollow sites. We have shown that there is a minimal distortion of the graphene sheet and the functionalization is accompanied by a charge transfer from the transition metal to the graphene sheet; the charge transfer can be quite significant in the case of low occupation of the d shell. The strong binding of Ta suggests that Ta may be a good choice as a superconductor contact to graphene. The strong binding of graphene to Hf is retained even when graphene is deposited on the Hf rich (111) surface of cubic HfO\(_2\), which opens up the possibility of interfacing graphene-based nanoelectronic components with silicon-based ones.

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Supporting Information Available: A complete database of the binding energies along with the binding distances from the graphene sheet and charge transfer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes