

Ab initio structural and electronic study of metals on diamond (111)-(1×1) surface

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Abstract

Metal contacts on clean diamond surfaces have been studied using *ab initio* Density Functional Theory. Five metals, i.e., gold, titanium, tantalum, vanadium and palladium on these surface were studied. Gold and palladium were found to form weak bonds on clean diamond (111) surface compared to the other three metals. The clean diamond surface was found to have surface states which were modified by oxygen but removed by hydrogen. Density of states revealed that on adsorption, these metals removed the band gap on clean diamond surface. A peak that was characteristic of diamond was observed at ≈ -11.8 eV. For the clean diamond surface terminated with Au and Pd, states due to Au-2p orbitals were observed at -2.5 eV and ≈ -1.5 eV, while Pd-5s orbitals were located at ≈ -1.7 eV and -0.5 eV. Ti, Ta and V showed unique states at high binding energies; ≈ -38 eV for V, ≈ -34 eV for Ta and ≈ -32.5 eV for Ti, which may explain their strong bonding.

1 Introduction

Semiconducting diamond has found many applications in the electronics industry. The fabricated diamond electronic devices often connects to metallic conductors in electric circuit. Hewett *et al* [1] argue that contacts formed on diamond must as a primary requirement have a very low contact resistance, they must also be strongly adhesive, be able to withstand the harsh environments for which diamond devices are intended and they should also be compatible with conventional device processing techniques.

Techniques have already been developed to measure ohmic contact characteristics on naturally occurring p-type diamond (type IIb) when adsorbed with some carbide forming metals [3]. Empirically, circular transmission line method (c-TLM) of Reeves [4] together with an end resistance measurement has been used to study the properties of Au, Au/Ti and Al/Ti on hydrogenated CVD diamond [2].

This work provides a theoretical treatment to what is observed experimentally [3] with regard to the formation of ohmic contacts. In doing this, the study examines the atomic monolayer of carbide forming metals; Ti, Ta and V on diamond, and two non-carbide forming metal, Au and Pd.

2 Computational procedure.

Calculations in this work were performed using the *Quantum-ESPRESSO* computer code [5, 6]. It is based on Density Functional Theory (DFT), plane waves and pseudopotentials (both ultrasoft and norm-conserving). Conjugate gradient electronic minimization was used in energy minimization. In this study, electron-ion interactions are described using ultrasoft pseudopotentials. The exchange and correlation energies were calculated with the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [7, 8]. Geometry optimizations were performed by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The structures were relaxed to an accuracy better than 10^{-5} Ry in their total energies. The plane wave cutoff energy was thoroughly tested and an optimized value of 37 Ry used for all calculations done in this work. Optimized \mathbf{k} -points of $4 \times 4 \times 4$ for bulk and $4 \times 4 \times 1$ for surfaces were used. The cell parameters were fixed at the experimental value of the bulk crystal during geometry optimizations while the total energies were minimized with symmetries.

3 Results

Results of calculations for bulk diamond, which were in good agreement with experiment are summarized in Table 1.

The study considered the energetics of relaxed geometries of the C(111)-(1×1) surface with and without the adsorbed atoms. The ground state energies of free H, O, Au, Ti, Ta, Pd and V atoms were calculated since they are required in determination of cohesive energies of these elements on diamond.

Table 1: Calculated DFT-GGA parameters of bulk diamond together with their experimental values and their % deviation with respect to the corresponding experimental values.

Parameter	Calculated. Value	Expt. value[Ref]	% deviation
Lattice constant, a_o , (Å)	3.568	3.567 [9]	0.03
C-C atom distance (Å)	1.540	1.540 [9]	0.00
Bulk Modulus (Mbar)	4.220	4.420 [9]	-4.54
Cohesive energy (eV/atom)	-9.10	-7.37 [10]	23.47

3.1 Structural Changes of Relaxed Diamond (111)-(1×1) Surface

A five bi-layer C-atom slab was taken to represent the diamond surface because it makes the calculations less expensive computationally and was found to be representative of the diamond's bulk and surface properties. Following system relaxation, bond length changes and bond angles for the surface, near surface and bulk regions were obtained using the Xcrysden program [11].

Alternate contraction and expansion of bonds in the surface region in the clean surface as seen in both Table 2 and Figure 1 suggests a bulk symmetry breakdown. This however seems to be stabilized by hydrogen and partly by oxygen termination (see Figure 2).

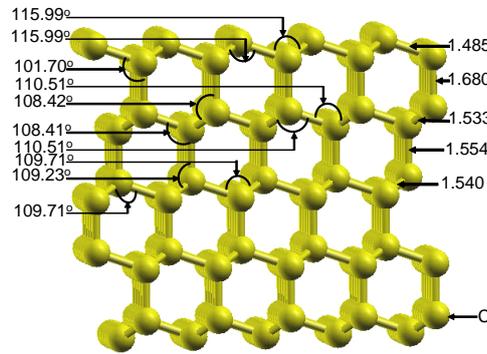


Figure 1: Relaxed clean diamond (111)-(1×1) surface. The bond lengths are in Angstroms.

Table 2: Bond lengths and their % changes in relaxed; clean (1×1), hydrogenated and oxygenated diamond surface. $r_{(C-H)}$ $r_{(C-O)}$ are the C-H and C-O bond lengths while $r_1(C-C)$, $r_2(C-C)$... are the C-C bond lengths between the first and second, second and third atomic layers, etc. The % bond length changes (in brackets) are relative to the experimental C-C bond length of 1.540 Å for C-C, 1.100 Å for C-H and 1.360 Å for C-O.

Bond	Relaxed bond length (Å) Clean surface	Relaxed bond length (Å) Hydrogenated surface	Relaxed bond length (Å) Oxygenated surface
$r_{(C-H)}$		1.100(0.00)	
$r_{(C-O)}$			1.321 (-2.87)
$r_1(C-C)$	1.485 (-3.57)	1.533 (-0.45)	1.561 (+1.36)
$r_2(C-C)$	1.680 (+9.09)	1.545 (+0.32)	1.528 (-0.78)
$r_3(C-C)$	1.533 (-0.45)	1.542 (+0.13)	1.543 (+0.19)
$r_4(C-C)$	1.554 (+0.91)	1.540 (0.00)	1.537 (-0.19)
$r_5(C-C)$	1.540 (0.00)	1.545 (+0.13)	1.542 (+0.13)

3.2 Structural Properties of Diamond-Metal Interfaces.

3.2.1 The C-metal bond lengths

The surfaces were modeled ensuring that each had full monolayer termination of adsorbates (see Figures 3), to avoid any influence of dangling bonds which may otherwise affect the electrical conductivity of the surfaces as well as maintain the bulk-like structure. This keeps the surface from reconstructing as is the case with a clean C (111)-(2×1) [12]. Unavailable bond length values were approximated by the sum of the covalent radii of the atoms forming the bond, using equation (1).

$$r_{cov} = r_a + r_b, \quad (1)$$

where r_{cov} is the interatomic distance of a molecule made up of elements a and b whose covalent radii are r_a and r_b , respectively.

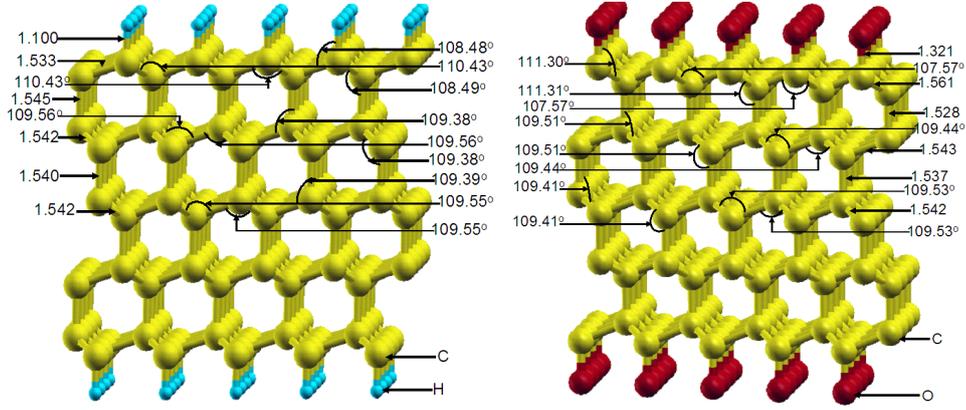


Figure 2: Relaxed hydrogenated and oxygenated diamond (111) surfaces. Hydrogen and oxygen atoms occupy a full ML coverage at the on-top site.

The systems were then allowed to relax, sample structures for the (1×1) surface terminated with a carbide/non-carbide forming metal, (Ta)/Au) are shown in Figure 3 and results recorded in Table 3.

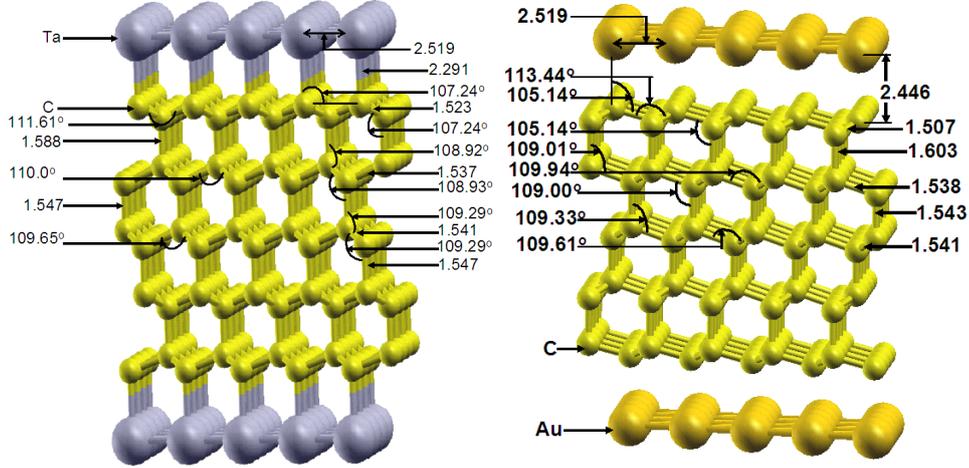


Figure 3: Tantalum and gold on clean diamond (111) surface showing metallization of diamond surface. The bond lengths are in Angstroms.

Table 3: Calculated bond lengths (between bolded atoms) when ohmic contacts form on clean, hydrogenated and oxygenated diamond (111)(1×1) surfaces. The % change in bond lengths are given with respect to the approximated bond lengths, since no experimental or theoretical data was available.

Adsorbing species	Approximated bond length (Å)	Relaxed Bond length (Å)	% change in bond length
C-Au	2.21	2.45	10.86
C-Pd	2.08	2.24	7.69
C-Ta	2.15	2.29	6.51
C-Ti	2.13	2.31	8.45
C-V	2.02	2.21	9.41

C-Metal bonds for all metal atoms showed significant bond elongation with respect to modeled values, the largest increase of $\approx +11\%$ occurring in the C-Au and the shortest of 6.5% in C-Ta. This was, however, not unexpected since gold is basically inert, and hence less reaction was expected at the interface.

In surfaces, cohesive energy is the energy required to remove an adsorbed atom. Cohesive energy therefore gives an indication of whether the adsorbate is chemisorbed or physisorbed. The cohesive energies for adsorbates on clean diamond surface were obtained using equation 2 and results shown in Figure 4.

$$E_{coh}(x) = \frac{1}{N} \left\{ E_{slab}(x) - E_{clean-surf} - N[E_{atom}(x)] \right\} \times 13.6, \quad (2)$$

where $E_{slab}(x)$ is the total energy of the clean diamond slab terminated with an atom of element x , $E_{clean-surf}$ is the total energy of the clean surface. $E_{atom}(x)$ is the total energy of a free atom of ele-

ment x and N is the number of element x atoms per surface unit cell; $N = 2$, since the calculations were for full monolayer coverages, x is the terminating species.

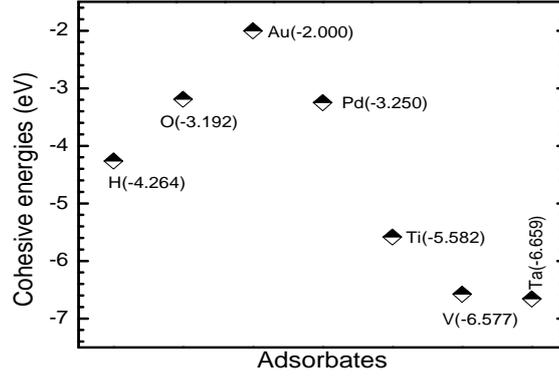


Figure 4: Calculated cohesive energies of the different ohmic contacts (metal adsorbates) on clean diamond surfaces. Cohesive energies of oxygen and hydrogen are also shown though they do not form ohmic contacts on diamond surface.

3.3 Electronic Properties

3.3.1 Density of States (DOS) for Clean Diamond Surface

It was necessary to determine the density of states of the clean surface first, so that the effect of the adsorbates could then be established. Figure 5 shows the DOS and PDOS for a clean diamond surface which are constituted of broad valence bands and a slightly narrow conduction band with some states at the Fermi level i.e., at 0 eV attributed to the presence of dangling bonds on the clean diamond surface. Olguín [13] argues that a surface introduced on an infinite periodic system, makes the system semi-infinite, with the boundary conditions dictating that the wave function has to be zero at the surface. The new boundary conditions manifest themselves in changes in the energy spectrum and in the occurrence of new states. The valence bands had a band width of ≈ 21.5 eV, a slight deviation from that observed by Zheng *et al* [14] of 21.71 eV. This value also compares well with 21.0 ± 1.0 eV obtained by Himpsel *et al* [15]. The empty conduction bands which were narrower than the valence bands had a band width of ≈ 11.5 eV. A band gap of 4.56 eV was obtained, though it was much smaller than the bulk value of 5.5 eV [9]. Hafner *et al* [16], obtained a band gap of 4.25 eV using first principles approach. The deviation observed between our computed value and the experimental one was attributed to the fact that both local density approximation (LDA) and generalized gradient approximations (GGA) tend to underestimate the fundamental gap [17].

A state that is characteristic of diamond was observed at slightly above -11.8 eV, a value not very far from -12.5 eV obtained by Derry *et al* [18] from DFT calculations, and very close to -12.0 eV obtained by Zheng *et al* [14] from first principles, and -13.2 eV obtained by Reinke *et al* [19] from their experiments. There was no evidence of any surface states effect extending into the bulk. This explains the preservation of diamond bulk structure as seen in Figure 1 where there were minimal changes in bulk bond length and bond angles, for deep lying layers.

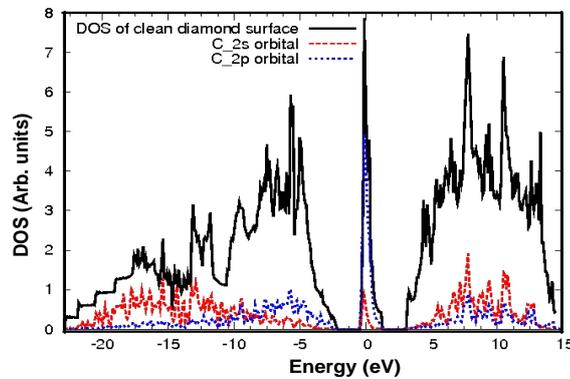


Figure 5: DOS for clean C(111)-(1 \times 1) surface. The surface consists of ten atoms in a five bilayer slab.

3.3.2 Carbide Forming Metals on Clean Diamond Surface

The DOS for these metals (Ti, Ta and V) showed similar characteristics to each other (see Figure 6 for Ti on clean surface). These metals removed the energy band gap completely, hence rendering the diamond surface

to exhibit a metallic character. It was also established that apart from the usual broad valence and narrow conduction bands on clean diamond surface, there were new states at high binding energies occurring at ≈ -37.5 eV for vanadium, ≈ -34 eV for tantalum (not shown here) and ≈ -32 eV for titanium, respectively. In the case of titanium on clean diamond surface, these states were due to Ti-2p orbitals. The d orbitals were observed to have their effect mostly around the Fermi level, resulting in peaks at ≈ -0.4 eV and other peaks which manifest themselves as surface states just above the Fermi level. The states at high binding energies may explain the high cohesive energies observed for these metals. The conduction band was slightly wider as compared to that of the clean diamond surface thereby enhancing conductivity. The surface states observed on clean diamond surface were diminished, implying that the metals facilitate easy flow of charge carriers from the semi-conductor to the metal and vice versa.

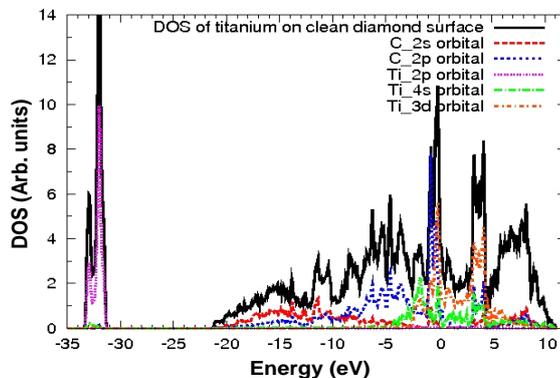


Figure 6: DOS for titanium on clean diamond surface.

3.3.3 Non-Carbide Forming Metals on Clean Diamond Surface

Unlike the carbide forming metals which had states at high binding energies, gold and palladium did not have these states. The absence of these states could explain the low cohesive energies exhibited by the two metals as shown in Figure 7 for Pd.

The valence bandwidth was ≈ 22 eV and a wider conduction band of ≈ 14 eV was observed. The fairly enlarged conduction bands explain why gold forms good contacts on a diamond surface. Though the band gap is not present, there is a clear distinction between the valence and conduction bands which are joined by some diminished states where a band gap existed in the the unterminated surface. Just above the Fermi level in both cases of gold and palladium terminated clean surface there are low lying states dominated by Au 2p and Pd 5s orbitals (see Figure 7).

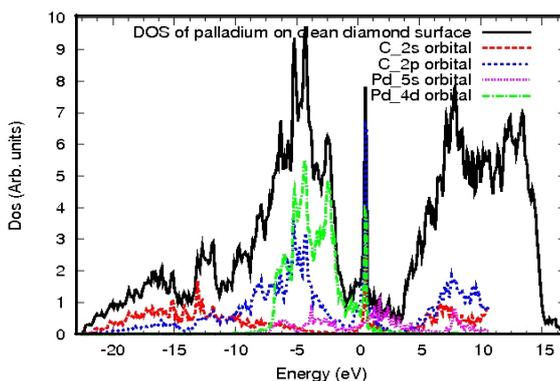


Figure 7: DOS for Palladium on clean diamond surface.

4 Conclusions

The study has revealed a clear correlation between C-metal bond lengths and their respective cohesive energies. A shorter bond length between atoms resulted in stronger bonds, hence a correspondingly high cohesive energy e.g. gold case. The states responsible for the strong bonding in the case of Ti, Ta and V (at high binding energies) were absent in the case of Au and Pd. In spite of this, they still had expanded conduction bands just like the case of Ti, Ta and V. These characteristics fit in well with diamond electronic devices that are often used or are envisaged to be used under harsh environments.

Like gold, palladium also showed a weak bond on diamond surface possibly due to its chemistry of having filled d orbitals. The known carbide forming metals on the other hand had strong bonds formed between them as confirmed by their high cohesive energies.

According to this study, Tantalum, vanadium and titanium are therefore proposed for use as ohmic contacts in diamond-based electronics due to their strong adherence properties.

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