

Ab initio calculation of electron affinities of diamond surfaces

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(Received 11 August 1997)

The electron affinity (EA) of various terminations of diamond surfaces has been calculated by the *ab initio* pseudopotential method. The bare, reconstructed (100) and (111) surfaces are found to have positive EA's of 0.5 and 0.35 eV, respectively. The hydrogen-terminated surfaces $1 \times 1(100):2\text{H}$, $2 \times 1(100):\text{H}$, and (111):H have sizable negative EA's of order -2.4 , -2.0 , and -2.0 eV, respectively. A symmetrical canting was found to be the most stable geometry for the $1 \times 1(100):2\text{H}$ surface. The oxygen-terminated surfaces have positive affinities of $+2.6$ eV for the more stable ether configuration, while the OH termination has a negative EA. The various values can be understood in terms of the surface dipole of the terminating bond. [S0163-1829(98)04412-9]

I. INTRODUCTION

There is considerable interest in diamond, as it can exhibit a negative electron affinity (NEA). A NEA means that the energy of the bulk conduction-band minimum lies above the vacuum level, so that an electron excited into the conduction band can be emitted into the vacuum with little or no barrier. The NEA property combined with its chemical and physical inertness would allow the use of diamond as a cold cathode for vacuum microelectronics and in field-emission displays.

A NEA is a relatively rare property in semiconductors. A NEA can be obtained by coating some semiconductors with caesium or caesium oxide to create a downward band bending at the surface, but these surfaces have poor stability.¹ The diamond (111) and (100) surfaces are known to possess a NEA when terminated with hydrogen, a termination which is chemically inert. Experimental evidence of the NEA for the (111) surface has been known for almost two decades,^{2,3} and more recently the (100) surface was found to have a NEA.^{4,5} It is therefore of interest to understand the origin of this property, and how it depends on the surface properties.

This paper uses *ab initio* electronic structure calculations to predict the electron affinities for various diamond surfaces. The chemical termination of the surface is found to have a pronounced effect on the affinity, over a range of 6 eV. This effect arises from the presence of a surface dipole created by the polar bonding of the terminations. Consequently, the dipole and hence the affinity depend sensitively on the geometry of the terminating group, and a key role of the calculations is to find this equilibrium geometry for each case.

II. METHOD

Ab initio methods have been used to calculate a variety of properties over the last two decades. The calculation of electron affinities presents some interesting problems. First, the use of density-functional theory precludes the calculation of excited states,⁶ and hence the conduction-band energy. Second, systems studied with plane-wave codes such as used

here must be both small and periodic. Although a surface is readily modelled by an infinite periodic sandwich of substrate and vacuum regions, care must be taken to ensure that bulk properties can be estimated from as little bulk and vacuum as possible.

The scheme that was used to calculate electron affinities is similar to that used in Ref. 7. First, the average Kohn-Sham potential and the energy of the highest occupied electronic level, the valence band maximum, are calculated for bulk diamond. The experimental value of the band gap is then added to the valence-band maximum to give the conduction-band minimum. This gives the energy of the lowest unoccupied bulk level with respect to the bulk potential.

A calculation is performed on a cell containing a bulk region, a vacuum region, and the surface of interest. The average potential in the center of the vacuum and at the center of the bulk are taken, and from this is found the energy of the vacuum level with respect to the average bulk potential. The energy of the lowest unoccupied level with respect to this reference is already known, so the difference between the vacuum level and the conduction band minimum, that is the electron affinity, follows. This scheme is shown in Fig. 1 for two systems, one with a positive electron affinity and one with a negative electron affinity. The bulk potentials have been aligned so that the conduction-band minimum occurs at 0 V.

Finding the average potential in the center of the vacuum is straightforward. The potential in the vacuum decays rapidly to a constant, the only slowly decaying term is the exchange-correlation potential. However, sufficiently far into the vacuum the charge density should fall to zero, at which point the exchange-correlation potential will also be zero, at least in the local-density approximation (LDA) or generalized-gradient approximation (GGA). Thus the contribution of the exchange-correlation potential to the potential in the center of the vacuum region can be taken to be zero, rather than using the small nonzero value arising from the residual charge density in the vacuum region. This treatment will change the absolute value of the electron affinity significantly (increasing it by between 0.3 and 0.5 eV in the case of

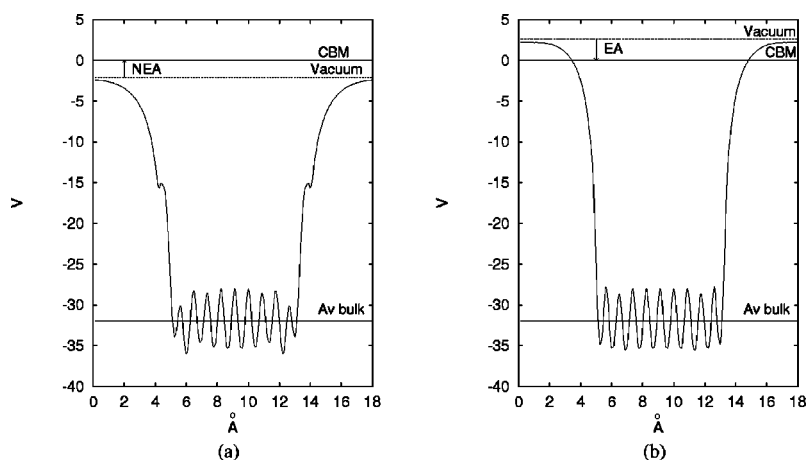


FIG. 1. Potentials across a diamond slab. In (a) is shown $(100)2 \times 1:H$ which has a NEA, and in (b) $(100)1 \times 1:O$, with a positive EA. The average bulk potentials have been aligned to place the conduction-band minimum at zero volts.

the calculations presented here), but will have much less of an effect on the relative values of the electron affinities. Explicitly removing this slowly decaying term from the calculations enhances the convergence of these results with respect to the slab separation.

Averaging the potential in the slab is more difficult, as it tends to be an oscillatory function rather than constant. The scheme used here was to average in the two directions perpendicular to the surface and then to average between successive maxima and successive minima in the bulk region. This ensures an unbiased average over exactly one period which can be seen to converge to a constant value as the bulk is entered. The average cannot be performed on the coarse real-space grid for the potential and charge density in the plane-wave code, but it can be found on the corresponding reciprocal-space grid. This technique is thus similar to the running average technique of Ref. 8, and it adjusts automatically to the lattice constant.

The calculations were carried out using the CASTEP/CETEP code,⁹ which is a plane-wave LDA code with conjugate gradient electronic minimisation and Broyden-Fletcher-Goldfarb-Shanno atomic relaxation. Projector-reduced¹⁰ norm-conserving¹¹ real-space¹² pseudopotentials in the Kleinman-Bylander form¹³ were used, with just an s projector for both carbon and oxygen, and the cutoff was 600 eV for all calculations. The carbon pseudopotential accurately describes single, double, and triple bonds, with the C—C bond length in a range of organic molecules (ethane, ethylene, acetylene) all underestimated by between 1 and 1.2%. The local-density approximation^{14,15} for the exchange-correlation energy was used throughout. A brief test was made of a GGA approximation,¹⁶ but the results were not significantly changed.

The k -point meshes used were Monkhorst-Pack¹⁷ sets with first failure stars greater than 15 Å. The vacuum layer

varied between 8 and 10 Å thick. Eight layers of diamond were used for the 1×1 reconstructions, and ten for the 2×1 reconstructions. The extra layer on each surface for the 2×1 reconstructions was thought necessary as the carbon atoms at the surface are significantly removed from their bulk positions, unlike the case for the 1×1 reconstructions.

It is necessary to ensure that the electron affinity is converged with respect to slab thickness. Care must also be taken to account for the strong dependence of band energies on the lattice constant. Considering first bulk diamond, the energy of the valence-band maximum with respect to the average bulk potential was found to be 26.19 eV at the experimental lattice constant of 3.567 Å. Reducing the lattice constant by just 1.5% lowered the energy to 27.20 eV. This strong dependence of the band energies with lattice constant is not surprising: the kinetic term of the electron energy will scale as the inverse square of the lattice constant, and the exchange-correlation term is also highly dependent on the electron density.¹⁸ In the surface calculations, a and b were held fixed, and free relaxation was permitted along c . This corresponding freedom was given to the bulk material, yielding an energy for the valence-band maximum of 26.47 eV. The addition of the experimental band gap of 5.48 eV (Ref. 19) yields a conduction-band minimum of 31.953 eV.

III. GEOMETRIES

Before discussing the electron affinities, we give the equilibrium geometries. There has been much work published on the reconstructions of the (100) and (111) faces of diamond, with many configurations possible.

The geometries of the $2 \times 1(100)$ and $2 \times 1(100):H$ surface reconstructions are generally agreed upon, as is that of the $1 \times 1(111):H$ termination. For the bare (111) surface, the symmetric Pandey chain reconstruction was used.²⁰ Al-

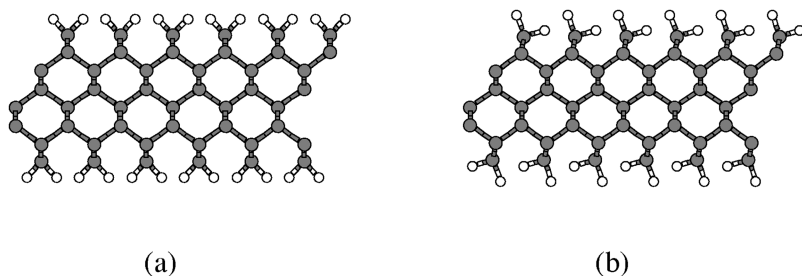


FIG. 2. Two possible configurations for the 2H termination of the (100) surface. In (a) is shown the symmetric configuration, and in (b) the canted structure, with a greater distance between adjacent hydrogens.

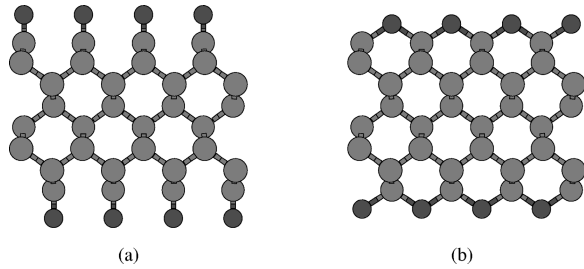


FIG. 3. Two possible configurations for the O termination of the (100) surface. In (a) is shown the “ether” or “bridge” configuration, and in (b) the “ketone” structure.

though other LDA calculations have found a very slight dimerization,²¹ we found none.

The geometry of the 1×1 dihydrogen termination of the (100) surface merits more discussion. Placing the hydrogens symmetrically about the carbon atom, that is at the same height above the surface and in line with the crystallographic axis as shown in Fig. 2(a), gives a rather small H-H distance of just 1.10 Å between hydrogens bonded to adjacent carbons. This is unfavorable, and the hydrogens, when given complete freedom, become canted as shown in Fig. 2(b), increasing their separation to 1.38 Å, and lowering the surface energy by 0.42 eV per surface carbon atom. The option of the hydrogens simply twisting but remaining at the height was also considered, but it was found to produce a much more marginal energy lowering of just 7 meV with respect to the symmetric structure with a twist angle of 14°. Other authors^{22,23} considered only this twisted structure, but we find the canted arrangement to be significantly lower in energy. A 2×1 reconstruction with the hydrogens on neighboring atoms canted in opposite directions, proposed in Ref. 7, was also studied. This reconstruction appears to be very marginally energetically unfavorable by 0.01 eV per surface carbon atom, when compared to the canted unreconstructed surface. The dihydride surface was argued to be barely stable to the loss of hydrogen,²⁴ but thought to be observed experimentally below 1300 K by Hamza, Kubiak, and Stulen,²⁵ although Thoms and Butler²⁶ disagreed. Previous theoretical calculations favored both the symmetric²⁷ and 2×1 -reconstructed canted geometries,⁷ and most recently the 1×1 canted geometry.²⁸ While our results say nothing about the surface’s stability to losing hydrogen, they do suggest that the unreconstructed canted geometry is the more stable, significantly more stable than uncanted geometries.

There exist two possible configurations for oxygen termination; the oxygen could be placed above a surface carbon atom and be double bonded to it in a ketonelike arrangement, or it could lie between two carbons single bonded to each and forming an etherlike bridge. These two possibilities are shown in Fig. 3. The calculations presented here find the bridge configuration to be the more stable by about 0.5 eV per surface carbon atom. This is contrary to the theoretical studies of Whitten *et al.*,²⁹ who found the ketone position to be lower in energy by 0.18 eV, and also to the predictions of chemical bond energies which give a C=O double bond a higher energy than two C—O single bonds. However, we do not believe that there is any error in our calculations of sufficient magnitude to alter this unexpected ordering. The en-

TABLE I. Electron affinities of diamond surfaces.

Surface	Reconstruction	Termination	Number of layers	EA (eV)
(100)	2×1	None	8	0.51
			10	0.69
	1×1	2H (sym)	8	-3.19
		2H (twist)	8	-3.00
	1×1	2H (canted)	8	-2.36
		2H (canted)	8	-2.47
	2×1	H	8	-2.03
			10	-2.05
			12	-2.07
	2×1	OH	10	-2.13
	1×1	O (ketone)	8	3.64
O (ether)		8	2.61	
		10	2.70	
(111)	2×1	None	10	0.35
(111)	1×1	H	8	-2.03

ergy difference was hardly changed on increasing the cutoff to 700 eV. The interoxygen distance of 2.52 Å in these structures could make steric repulsion effects important, for oxygen’s van der Waal’s radius is 1.4 Å. In both geometries the lone pairs on adjacent oxygens are forced to point at each other, but the ideal angle for their orientation on the sp^2 -bonded oxygen is 60° from the surface normal, whereas for the sp^3 -bonded oxygen it is only 54.7°. The experimental analysis of Ando *et al.*³⁰ found both single and double CO bonds, as well as carboxylic anhydride groups.

IV. ELECTRON AFFINITIES

The affinity was calculated for the various surface configurations by finding the vacuum levels and average potentials in the center of the bulk. The results are given in Table I.

The bare reconstructed surfaces are found to have small positive EA’s, 0.5 eV for the $2 \times 1(100)$ surface and 0.35 eV for the $2 \times 1(111)$ surface. These are consistent with the experimental observations of Pate.³¹

The hydrogen-terminated (111) surface is found to have a sizable NEA of -2.0 eV. The EA’s of the hydrogen-terminated (100) surface are interesting. The monohydride $1 \times 1(100):H$ surface has a NEA of -2.0 eV, while the symmetric, uncanted dihydride $1 \times 1(100):2H$ surface is found to be -3.2 eV. The NEA for the symmetrically canted structure, $1 \times 1(100):2H$, reduces to -2.4 eV, and that for the antisymmetric canting to -2.5 eV. Although this magnitude of NEA is greater than that observed experimentally, the difference of 2.5 eV between the bare and monohydride surfaces is similar to the 2.2-eV difference observed experimentally by Humphreys *et al.*⁵ Other self-consistent LDA calculations produce similar results for the monohydride NEA.^{7,32}

The creation of the negative electron affinity can be attributed to the presence of a relatively small dipole on the C—H bond, $C^{\delta-}-H^{\delta+}$, as demonstrated in detail below. The potential drop across the dipole raises the band energies inside the surface with respect to the fixed vacuum level, so

that the bulk conduction band minimum now lies above the vacuum level, as was previously proposed for surfaces³³ and for Schottky barriers.³⁴ The reduction in NEA for the canted (100):2H structure arises because one of the two C—H bonds now lies almost parallel to the surface, so it no longer contributes much to the overall dipole.

The EA of the oxygen-terminated (100) surface is found to be strongly positive, +2.6 eV for the ether configuration and +3.6 eV for the metastable ketone configuration.

V. DISCUSSION

The sequence of calculated electron affinities is consistent with the expected polarizations of surface groups. From electronegativities, hydrogen is expected to be positive when bonded to carbon, and will set up a dipole moment and hence a potential step favoring the escape of electrons. Conversely, oxygen is expected to be negative when bonded to carbon, and this dipole will tend to increase the barrier. The total variation, from 3.6 to -3.19 eV, is quite large. However, this change is consistent with a simple electrostatic dipole model.

Considering an infinite sheet of area A and dipole moment p , the change in potential in crossing from one side of the sheet to the other is given by

$$\Delta\phi = \frac{p}{\epsilon_0 A}. \quad (1)$$

For the case of changes in electron affinities, this reduces to

$$\Delta E = \frac{181\Delta p}{A}, \quad (2)$$

where Δp is the change dipole moment per unit cell, and A the unit cell area, all lengths being in Å, and the unit of charge being the electron. The change $\Delta E = 7$ eV corresponds to a change in the surface dipole moment per unit cell of just 0.25 eÅ, for a unit cell area of $A = 6.4$ Å². This represents quite a small polarization of the surface CO and CH bonds, although the natural polarization of the bonds would be expected to be reduced due to the proximity of the neighboring bonds in the same orientation.

This model of relating electron affinity changes to dipole barriers at the surface extends to the symmetric and canted dihydride surfaces. In the symmetric case the axis of the CH₂ unit is normal to the surface; in the canted case this unit is inclined at 27.5° to the normal, and thus its contribution to the NEA is reduced. In the same way the effect of oxygen would be expected to be greater in the structure which places the oxygen at the greater height above the surface carbon atoms, and hence enhances the dipole it creates. This is the case, with the ketone structure placing the oxygens 1.2 Å above the surface compared with only 0.8 Å for the ether configuration. The change in the EA of these two oxygen-terminated surfaces with respect to the bare surface is also in an approximately 3:2 ratio.

This analysis suggests an alternative way of calculating the relative electron affinities of surfaces. As the relative changes are governed by dipole moments set up at the surface, simply calculating the dipole moment for a region from deep inside the slab to a point in the vacuum would enable the change in EA to be calculated from Eq. (2). Care needs to be taken to choose equivalent points in the bulk from which to calculate the dipole moments—bond centers or atomic positions are good choices—and good agreement with the average potential method presented above is achieved. Such a calculation does not refer to the lattice-constant-dependent position of the valence-band maximum, and stresses that the differences in EA's presented here should be more accurate than the absolute EA's, as they have fewer possible sources of error.

The large NEA for the OH-terminated surface may seem surprising, as the oxygen might be expected to reduce the NEA. However, we note that while the CO bond produces a dipole increasing the positive EA, so the OH bond will produce a dipole opposing this and enhancing the NEA more than a simple CH bond. The effect of oxygen tends to cancel out, and it leaves the COH group as if it were simply a long CH bond. Of course, the C-O-H bond angle complicates the analysis somewhat. This is a similar situation to that of both caesium and caesium oxide producing similar NEA's.¹

Naturally the surface dipole moment does not arise entirely from the placing of ionic cores in a negative background of valence electrons, but will also be affected by the precise distribution of the electrons near the surface. Thus rearrangements which mainly alter the electronic configuration at the surface, for instance by changing between orbitals extending out into the vacuum and orbitals bonded across close to the surface, as would occur during a reconstruction, would be expected to alter the EA too.

VI. CONCLUSIONS

The results of *ab initio* calculations of the geometries and electron affinities of a range of diamond surfaces have been presented, and are seen to be in accord with experiment. The calculated values of electron affinities are convergent for quite modest cell sizes. A clear negative electron affinity has been found for the monohydride (111) and the monohydride and dihydride (100) surfaces, in agreement with experiment. The affinities can be explained in terms of a model in which the terminating groups give rise to a surface dipole, as expected from their atomic electronegativities.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Mike Payne for providing access to computing facilities. The major calculations were performed on 16 nodes of the Hitachi SR2201 located at the University of Cambridge High Performance Computing Facility. Cambridge University is the recipient of a Motorola Corporated Research Laboratory research grant.

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