p-type surface doping of diamond: a first-principles study

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Abstract
Surface p-type conduction in diamond has been linked to an aqueous layer on a hydrogenated surface. We have used local density function theory to examine the electronic properties of molecular adsorbates on diamond surfaces. We find that a wide range of adsorbates are able to transfer an electron from the valence band into the molecule, facilitating hole conduction.

1. Introduction

Diamond, with a $\sim$5.5 eV indirect band gap, is a highly resistive material. In order to produce p-type diamond, one usually adds boron, which has an acceptor level at about $E_v + 0.37$ eV [1]. This, although considered to be shallow, is sufficiently high in energy to result in a very low ionization fraction at room temperature. However, strongly p-type material with an activation energy an order of magnitude lower than boron can be generated in the surface region. Sheet concentrations of 10^{13}–10^{14} cm^{-2} have been recorded with mobilities of up to 70 cm^2 V^{-1} s^{-1} [2]. However, the source of the conductivity is not well understood.

It has been established that a prerequisite for conductivity is surface hydrogenation. Hydrogenation generates a surface dipole which can lead to a negative electron affinity [3], and a high concentration of hydrogen in a layer about 20 nm deep [4]. The subsurface hydrogen might be responsible for passivating electrically active defects in this region [5], but it has been suggested that it also acts as a shallow acceptor [6]. The boron acceptor is believed to be an effective-mass acceptor, and hence possess a delocalized acceptor wavefunction. This implies that a wavefunction associated with the shallow surface acceptor must be even more delocalized than that of boron, and it is difficult to reconcile such a wavefunction with a point defect. It is possible that the hydrogen-related acceptor is an extended defect, but to date no detailed model has been put forward in the literature.

Heating to over 200 $^\circ$C increases the resistivity of the sample [7], which can be reversed by exposure to atmosphere for an hour. This has obvious implications for device application of this type of conductivity, such as in field-effect transistors, although devices of commercial quality have been produced [8].

One suggested mechanism is that surface adsorbates, within a surface aqueous layer, are responsible for the surface conductivity [9, 10]. This has been related to the observation of an enhancement in the conductivity when the surface is exposed to NO_2, whereas NH_3 suppresses the effect [11]. Surface adsorbates are expected to be physisorbed rather than chemisorbed, and as a consequence would be expected to have a relatively low thermal stability, as observed.

The aqueous layer model relies on a process such as $2(H_3O^+) \rightarrow H_2 + 2(H_2O) + 2h^+$, where the hydrogen is being lost to the gas phase. This process proceeds in this direction because the molecular hydrogen is lost from solution at the surface due to the very low solubility of H_2 in water, and its negligible atmospheric concentration. This process would then be affected by the partial pressure of hydrogen in the gas phase. The reaction leaves two holes in the valence band, provided that balancing negative ions are present.

However, the picture is still far from clear. Recent experiments show that, although exposure to atmosphere does lower the resistivity, the initial hydrogenation has a much larger effect in lowering the resistivity [12], and it appears that there is some combination of mechanisms giving rise to the conductivity.

In this paper we report the results of local density function calculations examining the electronic structure of molecules close to the surface of diamond.

2. Method

Local density functional calculations using the AIMPRO code [13] have been used to examine the electrical properties of various surface adsorbates. Calculations employed hydrogen-terminated clusters containing around 200 atoms. The atoms are treated using the pseudo-potentials of reference [14], except for hydrogen where the bare Coulomb potential is used. The wavefunction basis consists of independent s- and p-Gaussian orbitals sited on atoms and bond centres. The charge density is fitted with independent s-Gaussian functions with different widths on each type of atom and bond centre.

The surfaces are simulated by taking an approximately spherical cluster and bisecting it along the desired crystallographic plane. The exposed surface is then reconstructed and hydrogenated as appropriate for the surface. The clusters are chosen such that the surface area contains 20–30 surface sites. The adsorbates are then placed above the surface and all atoms except the hydrogen on the back of the clusters are allowed to relax.

3. Results

We have considered a range of adsorbate molecules. The candidate put forward by Ristein *et al* is CO_3H^- [10], which originates from reactions of atmospheric CO_2 in solution. Probably the most important surface for CVD diamond samples is (001), due to the large facets of this orientation in high-quality material. The conventional description of the (001) surface is a (2×1) reconstruction where the surface C atoms pair off in rows. The clean, reconstructed surface is believed to exhibit a positive electron affinity, and this argument has been used to reject oxidized surfaces as candidates for the p-type conductivity, in line with experimental observation [10].

We have relaxed the CO_3H molecule above the clean and hydrogenated (2×1)-reconstructed (001) surfaces. A diagram illustrating the cluster geometry used in the simulations of this particular hydrogenated surface is given in figure 1.

The electronic structure can be understood from the Kohn–Sham eigenvalues as plotted in figure 2. The 'pure' cluster exhibits a band gap between the valence band maximum (VBM) at
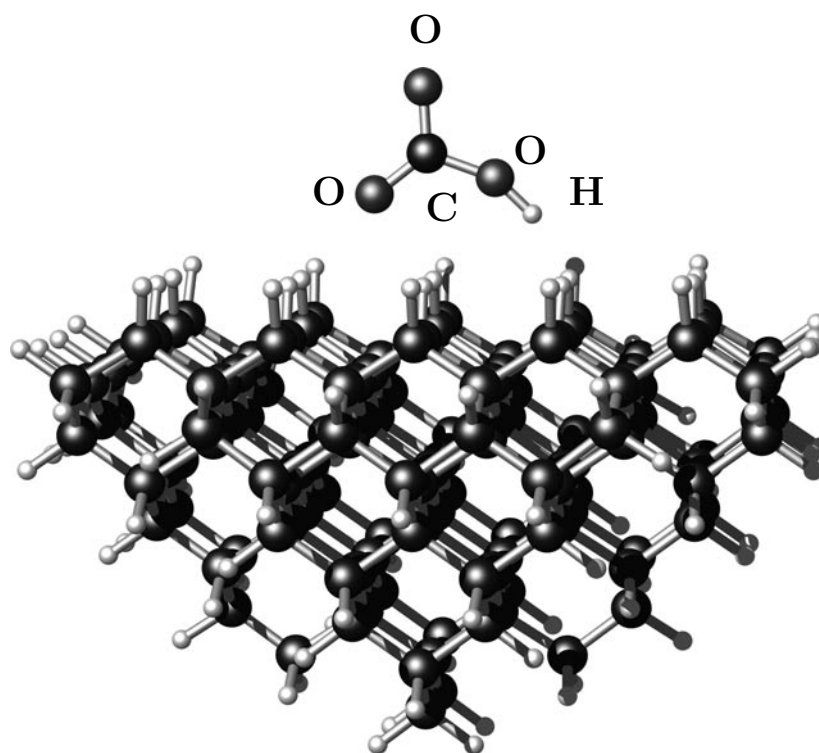
Figure 1. A schematic diagram of the CO$_3$H molecule above the (2×1)-reconstructed, hydrogenated (001) surface. The large atomic cluster shows the C (black) and surface hydrogen (white).
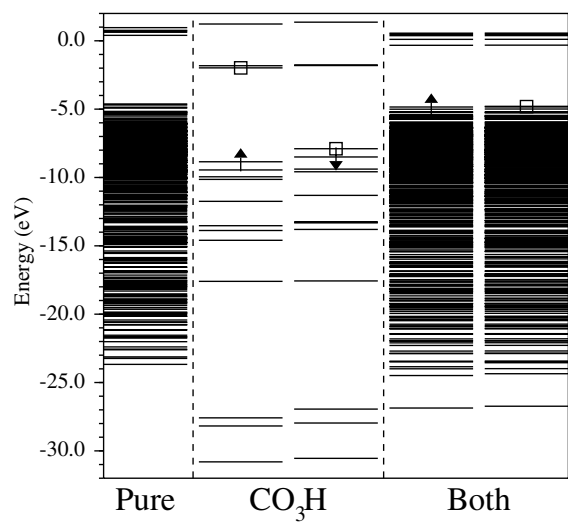

Figure 2. Kohn–Sham eigenvalues for the (2×1)-reconstructed (001) hydrogenated surface, the neutral CO$_3$H molecule and the combined system. For the molecule the HOMOs are indicated by arrows and LUMOs by empty squares. The combined system has a hole in the top of the spin-down spectrum.

around -5 eV and the conduction band minimum just above 0 eV. Since the neutral molecule has an odd number of electrons, the lowest unoccupied molecular orbital (LUMO), taken to be spin down in our calculations, as indicated in the figure, is lower in energy than the VBM of the surface cluster. When the systems are brought together, the wavefunctions mix. In order to achieve a self-consistent charge density it is necessary to fill the Kohn–Sham levels using Fermi statistics, resulting in a number of Kohn–Sham eigenlevels around E_v being partially occupied. However, most of the states are localized in diamond and not the molecule. This confirms that CO_3H would tend to act as a surface acceptor, leaving a hole in the valence band. When the combined system of diamond cluster and surface adsorbate is relaxed in the negative charge state, there is no valence band hole; i.e. the system becomes passive, as one would expect.

We have repeated the calculations for H-terminated (110) and (111) surfaces, obtaining qualitatively similar results. In all cases the presence of a CO_3H molecule on the surface results in charge transfer to the molecule and hence a hole in the VBM.

There is also the possibility that the CO_3H would tend to chemisorb rather than physisorb to the surface. Therefore we relaxed the (110) surface where a single surface H has been replaced by the CO_3H molecule. The initial condition placed one of the O atoms within ~ 1.5 Å of the surface C atom. The molecule relaxed away from the surface, generating a final structure with a physisorbed molecule and a surface dangling bond. We have calculated that CO_3H_2 above a hydrogenated surface where a single H atom has been removed is 2.3 eV higher in energy than CO_3H above a fully hydrogenated surface. Hence, abstraction of hydrogen by CO_3H is very unlikely to occur.

This leads to two conclusions. The first is that one would expect the system to be physisorbed rather than chemisorbed, as in the model of Ristein *et al* [10]. Secondly, the presence of the surface dangling bond generates a deep donor level that compensates the hole generated by the acceptor molecule. This means that the absence of a fraction of the surface H layer would suppress the p-type conductivity.

Experimental studies have established that exposure to NO_2 enhances the p-type conduction whereas NH_3 suppresses it [11]. We have therefore examined the electronic structure of these molecules on the hydrogenated (110) surface. The resulting Kohn–Sham eigenvalues are plotted in figure 3.

It is useful to note the location of the LUMO for these adsorbed molecules relative to the VBM of the hydrogenated surface cluster. The LUMOs for NH_3 and NO_2 are listed in table 1. One observation is that the LUMO for NO_2 is lower than the highest occupied molecular orbital of the diamond surface, and NH_3 possesses only filled levels below the VBM. This conclusion is unaffected for physisorbed species such as NO_3^- (a reaction product of NO_2 in solution).

Table 1. The energy of the lowest unoccupied molecular orbital for various candidate adsorbate molecules (eV), in the neutral charge state. The HOMO of the cluster, which represents the valence band top, is in the vicinity of -5 eV, depending on the surface orientation.

Molecule:	CO_3	NO_3	CO_3H	OH	BO_3H_2	NO_2	C_{60}	CO	H_3O	H_2O	NH_3	H	H_2
LUMO:	-9.1	-8.7	-7.9	-7.7	-7.4	-6.5	-5.2	-2.6	-2.0	-1.0	0.5	1.1	1.4

An interesting result has been found for C_{60}. The LUMO of this molecule is around the same energy as the diamond VBM, and calculations for the combined systems show that a net charge transfer occurs. This is similar the to case of C_{60} on a Si surface [15]. This could have important implications for generating thermally stable surface conductivity.
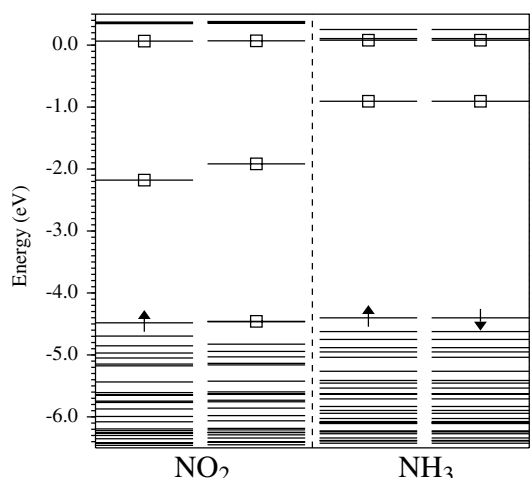
Figure 3. Kohn–Sham eigenvalues for NO_2 and NH_3 above the hydrogenated (110) surface. Filled levels are indicated by arrows and empty levels by empty squares.

We have also examined a range of other surface adsorbates, also listed in table 1. In each case, where the LUMO of the isolated molecule is lower than the VBM, the system made up from the molecule above the hydrogenated surface possesses a hole in the VBM. Conversely, where the LUMO of the isolated molecule is above the VBM, any charge transfer is insufficient to generate a hole.

A significant example of a molecule that induces a hole in the valence band is the hydroxyl ion, which is present in *all* aqueous solutions. [OH^-] depends on several factors, but processes that liberate molecular hydrogen from solution would tend to increase the concentration of hydroxyl ions.

Mass spectroscopy has been used to try to establish the molecules responsible for the surface conductivity [7]. The experiment showed that in the temperature range where the conductivity drops off, a peak is detected in the CO emission. This was interpreted as CO giving rise to the effect. However, as one can see from table 1, one would certainly not expect the molecule to be sufficiently electronegative to extract an electron. Our simulations with CO above the hydrogenated (110) surface confirm that this cannot be the adsorbate responsible for the conductivity.

Extending table 1 to include strong acids such as ($HNO_3 + H_2SO_4$), one might expect the same effect. However, this neglects any reactions with the surface, and in fact this is a solution used to remove the surface hydrogen layer [10]. So, in order for the surface contaminant to produce the desired p-type conductivity, the adsorbate must not react with the surface, but must be sufficiently electronegative to pull an electron out of the VBM.

4. Conclusions

In summary, using *ab initio* cluster calculations, we find that CO_3H and other adsorbates with sufficiently large electron affinities will induce a hole in the top of the valence band, in support of the models presented in the literature [9, 10]. An important result is that C_{60} is a potential surface acceptor.

However, it seems unlikely that this mechanism is the whole picture for p-type surface conductivity, and the precise role of the sub-surface hydrogen has yet to be fully explored.

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