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The Li-adsorbed C(100)-(1x1):O Diamond Surface

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ABSTRACT

This paper presents density functional theory results for the Li-adsorbed C(100)-(1x1):O system. Previously it has been shown that at a single monolayer coverage, the binding energy for Li on oxygenated C(100) diamond is substantially higher than that of heavier alkali metals, while at the same time, the presence of the lithium generates a large shift in the diamond workfunction. The system is therefore promising for electronics applications involving diamond. Here, further calculations are presented showing that additional Li atoms above 1ML coverage are far less strongly bound, suggesting the 1ML surface is the most useful for vacuum microelectronic applications.

INTRODUCTION

The surface of diamond has proven to be highly flexible from the point of view of modification and functionalization. The covalent bonding structure of diamond leads to surfaces with oriented dangling bonds that have been used for a variety of chemical, biological and electronic applications. For example, amination of the diamond surface allows for the chemical attachment and preservation of DNA [1]. A hydrogen termination allows for a form of surface transfer doping, giving surface p-type conductivity [2, 3]. Such surfaces have been used to create surface transistors on diamond [4]. Several diamond surfaces exhibit a negative electron affinity (NEA) when hydrogen-terminated [5] or coated in thin layers of metals such as cobalt [6] and barium [7]. The negative electron affinity of diamond, where the conduction band minimum is higher in energy than the vacuum level, is useful for vacuum microelectronic applications such as photodetection and field emission, and possibly also for the tuning of the interface between diamond and other materials.

The NEA of hydrogenated diamond has been extensively studied and can be reproducibly induced on the C(100), C(111) and C(110) surfaces, at least [8], via exposure to a hydrogen plasma. Although the calculated electron affinity of a monohydride-terminated diamond C(100) surface is approximately -2 eV [9, 10, 11], the experimentally measured value is closer to -1.3 eV [12] and is hence a relatively weak NEA. Alternatives to hydrogen for inducing a diamond NEA have been investigated by a number of groups. Metals such as zirconium and cobalt are known to induce a small NEA [13]. Caesium oxide coatings are often used [14] however the caesium is weakly bound, with degradation evident above several hundred degrees centrigrade. Since high temperature operation is one of the possible advantages of using diamond as an electronic material, surface resilience above 500°C is desired for any practical NEA coating.

Recently, theoretical calculations for the adsorption of lithium on clean and oxygenated C(100) diamond surfaces have been reported [11]. The motivation for studying lithium was that the alkali metals generally are known to reduce the workfunction of many metallic and semiconducting surfaces. For diamond-structure semiconductors such as diamond, silicon and germanium, a size effect is apparent, whereby the smaller the alkali, the more strongly bound the species is to the surface but the smaller the reduction in workfunction [15, 16]. As a result, it would be expected that lithium should be the most strongly bound but have a smaller effect on the electron affinity. While such a trend is apparent for lithium on the clean C(100) surface, if the surface is pre-oxygenated the workfunction shift is large, comparable to that induced by caesium, whilst retaining the property of being strongly bound to the surface. The Li-adsorbed C(100)-(1x1):O surface is therefore of interest not only from a theoretical point of view but also as a practical surface for device fabrication.

In this paper, the previous theoretical results are extended to show the effect of increasing the coverage beyond one monolayer by just half an atom per unit cell. The key finding is that the binding energy of each adatom beyond one monolayer drops very rapidly, leading to the hypothesis (recently validated as reported elsewhere in these proceedings) that the Li-adsorbed C(100)-(1x1):O surface can be prepared and handled in a simple manner without the need for carefully calibrated evaporation sources or constant storage under UHV conditions.

THEORY

Calculations were performed using the plane-wave density functional theory package CASTEP on the BlueCrystal Phase 2 high-performance computing cluster at the University of Bristol. Ultrasoft [17] on-the-fly pseudopotentials were used for all calculations. The simulation cell was of dimension 5.05x5.05x35.70 Å consisting of a thin double-sided slab with 14 layers of diamond and approximately 12 Å of vacuum gap on either side. The surface section of each face comprised two (2x1) unit cells, allowing for 0.25 ML increments in coverage by adding a single adsorbate to each side of the slab. It should be noted that here, as elsewhere, one monolayer is defined to be the coverage corresponding to one adsorbate per surface atom, rather than per unit cell. The lattice parameters were determined by optimizing a smaller 8-atom diamond conventional unit cell. Calculations were converged with respect to the cutoff energy, number of diamond layers and vacuum thickness, and geometry optimization was carried out with a force tolerance of 0.02 eV/Å and allowing all atoms in the simulation cell to relax.

The exchange/correlation functional of Perdew and Wang [18] and a cutoff energy of 700 eV were used for all calculations. For the coverage calculations, a Monkhorst-Pack [19] grid of 3x6x1 k-points was used for Brilluoin zone sampling. For density of states calculations, 8x8x1 k-points were used. Workfunctions were calculated with the method of Fall, Binggeli and Baldereschi [20], whereby the energy width between the plane-averaged electrostatic potential energy $V_{es,b}$ and the Fermi level in bulk diamond $E_{f,b}$ is calculated separately and then added to the plane-averaged electrostatic potential energy of the slab $V_{es,s}$ to give the bulk Fermi level of the slab $E_{f,s}$. The workfunction is then the difference between the vacuum level E_{vac} and $E_{f,s}$:

$$\phi = E_{vac} - E_{f,s} = E_{vac} - V_{es,s} + E_{f,b} - V_{es,b} \qquad (1)$$

Average binding energies per adsorbate are calculated as:

$$E_B = (E_t - E_s - NE_a)/N \qquad (2)$$

where E_t is the total energy of the combined slab + adsorbate system, E_s is the total energy of the bare slab, N is the number of adsorbates and E_a is the energy of an isolated adsorbate. The binding energy for *each* adsorbate pair is calculated by:

$$E_B = (E_i - E_{i-2} - 2E_a)/2 \tag{3}$$

where E_i is the energy of the system with i adsorbates.

DISCUSSION

Figure 1 shows the 1.25 ML coverage Li-adsorbed C(100)-(1x1):O surface in comparison to the previously reported optimal 1 ML surface consisting of two Li atoms per unit cell, one over the hexagonal hole site (HH) and the other on top of the 3rd-layer carbon (T3). The (2x1) carbon atom dimer reconstruction remains in place upon further Li adsorption, accompanied by single C-O bonds between the top layer carbons and the oxygen termination. The presence of an extra Li atom over the T3 lithium per two surface unit cells induces a distortion in the overlayer but otherwise does not significantly distort the underlying lattice, as would be expected for diamond. Although the structure distortion appears small, it appears that the repositioning of the positively charged T3 lithium in the first monolayer has a significant effect on the surface charge distribution and hence the workfunction of the material.

The workfunction shift calculated as a function of Li coverage appears in Figure 2. For a fixed coverage, the workfunction shift depends slightly on the adsorption site and for Figure 2 the site(s) leading to a maximal workfunction shift for each coverage have been used. For coverages up to and including 1 ML the preferred sites are detailed in [11]. For 1.25 ML the preferred site is displaced asymmetrically above the T4 carbon site but well above the underlying Li monolayer as shown in Figure 1. The uptake curve shows that once a second monolayer starts to form, the large workfunction shift is rapidly reduced. The shape of the curve is similar to that presented by Nie, et al for Na, K and Rb [15], though with a higher critical coverage since Li is a smaller species. It is interesting and technologically useful that the workfunction shift is essentially linear up to 1 ML coverage. Stable geometries at coverages greater than 1.25 ML were not found, suggesting that layer-by-layer growth above 1 ML is not energetically favourable within the size of the surface unit cell considered. Since diamond is a two-atom FCC lattice and metallic lithium is a one-atom BCC lattice, the Li-Li bond length is significantly larger at 3.04 Å versus 1.54 Å for diamond and one would expect several disordered layers before BCC Li would form. For the 1.25 ML surface the Li-Li bond length between the first and second monolayers is approximately 2.73 Å. It is unclear what growth mode would follow with increasing Li deposition as there have been no studies of Li adsorption on diamond. Stranski-Krastanov growth is observed for the Na on Si(100)-(2x1) system, and a size argument would suggest a similar growth mode for Li on C(100)-(2x1). When an oxygen surface layer is present, the binding energy of the first monolayer is much higher; hence an alternative scheme may be that the first monolayer lithium should be considered independently from subsequent overlayers.

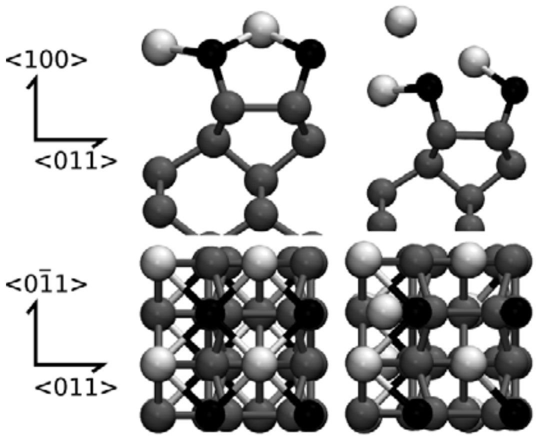

Figure 1: (Left) Top and side views of the 1 ML Li-adsorbed C(100)-(1x1):O surface. (Right) Top and side views of the 1.25 ML Li-adsorbed C(100)-(1x1):O surface, showing the distorted T3 Li position in the first monolayer.

Table 1 shows the calculated energy per adsorbed lithium and the calculated binding energy per additional lithium. Above 1 ML coverage, the binding energy per additional adsorbate drops rapidly, consistent with the nature of the binding for each of the species on the diamond surface. The Mullikan populations for the first monolayer Li atoms show significant charge transfer such that each Li is ionically bound to the four O atoms that surround it. The net effect is that each Li atom in the first monolayer is positively charged to between 0.7e and 0.9e and sits in a net of negative charges sited on the O atoms. In contrast, the next Li adsorbate only gains a positive charge of 0.05e, leading to a much weaker Li-Li bond and a lower binding energy.

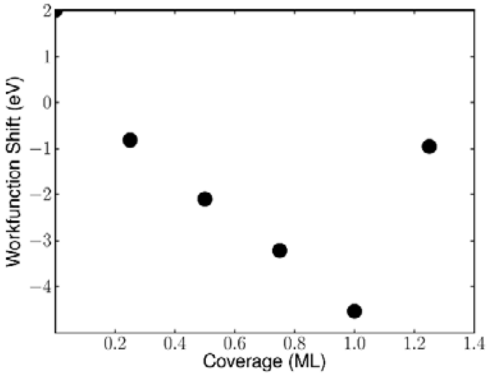

Figure 2: Calculated workfunction shift as a function of lithium coverage for the C(100)-(1x1):O surface, relative to the clean reconstructed C(100)-(2x1) surface, workfunction 6.1 eV [11]. The bare oxygenated surface (0 ML) has a higher workfunction than the clean surface, yielding a positive shift.

Coverage (ML)	E_B per adsorbed Li (eV)	E_B per additional Li (eV)
0.25	5.32	5.32
0.5	4.25	3.17
0.75	4.73	5.69
1.0	4.69	4.59
1.25	3.96	1.01

Table 1: Average energy per adsorbed lithium and energy per additional lithium atom as a function of coverage. At 1.25 ML, the binding energy for the additional lithium drops significantly.

The coordination on the surface is of interest in light of the results in Table 1. Solvation models of Li ions in water suggest that the coordination number ranges between 4-6. Intuitively one would therefore expect that the energy of solvation for a single Li ion in water is not significantly different from the binding energy of the first monolayer Li atoms. On the other hand, further adsorbed Li atoms have a much lower binding energy. The large difference between the two states and the high solubility of many Li compounds suggests that it should be possible to construct an ultrathin lithium layer simply by depositing a thick layer of lithium on oxygenated diamond and water-washing the excess material away. The stability of CsO-terminated diamond surfaces in air is promising as it suggests that the single monolayer surface of Li on oxygenated diamond should also be stable in air, making device fabrication and characterization much simpler. Further calculations are underway to determine any possible reaction modes of the single monolayer surface with common atmospheric species such as N_2, O_2 and H_2O.

CONCLUSIONS

This paper presents calculations showing that above a single monolayer of lithium on the oxygenated C(100) surface, the energy per additional lithium atom drops rapidly due to a weaker bonding between lithium atoms, in contrast to the strong ionic bonding between lithium and oxygen at the diamond interface. Since the single monolayer surface has simultaneously a large negative electron affinity and a strong binding energy per adsorbate, it is potentially useful that subsequent layers are less strongly bound. Recent experiments, reported elsewhere in these proceedings, show that the difference in binding energies can be used to create thin lithium films.

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