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Foreign atoms on the three low index diamond surfaces

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Abstract

The topmost atom layers of any surface often play very crucial roles regarding the surface properties, in addition to facilitating the interaction of materials with their external environment. They form substrates for both homo and hetero-epitaxial growth of thin films used in semiconducting device fabrication and in other cases act as heterogeneous catalysts used to induce and steer a given chemical reaction. They are the key players in many surface processes such as bonding, wettability, surface conductivity, lubrication, optical absorption and corrosion among many others.

Some of these processes can be affected quite significantly by the foreign atoms residing on the surfaces, which may be introduced onto the surfaces either intentionally or through alien means. It is therefore extremely important when studying surface properties to pay keen interest towards their nature and where necessary the foreign atoms residing on them, their bonding sites and also the bonds that they form, as well as their proportions.

Foreign atoms on diamond surfaces have already been shown to alter its surface properties in a way that makes it quite useful in various technological applications and in other cases less attractive. Among the many foreign atoms that may bond onto polished diamond surfaces, oxygen has so far been shown to be among the main adsorbate on diamond surfaces prepared through mechanical polishing and then cleaned in an acid mixture, followed by rinsing in deionised water.

This was confirmed by our XPS studies which further established that the optimum oxygen coverage on clean diamond surfaces was 0.5monolayers on the (100) surface, and 0.3monolayers on both the (110) and (111) surfaces. The oxygen atoms were further bonded in various oxidation states, sometimes forming C-O or C=O bonds and in other cases C-OH bonds. The C=O bond

was found to be the most stable configuration on the (111) surfaces, while the C-O-C and C-OH dominated on the (100) surfaces. The (110) surface had four major functional groups, which included the C-OH, C-O-C, C=O and COOH groups, with none of them showing any outright dominance. Few cases were nonetheless considered on this surface, and the absence of any specific group being the most stable was attributed to the nature of the surface. Some minor groups such as O-C-O, O-C=O, C-O-C=O and H-C=O were also observed occasionally on the three surfaces, and these were believed to reside at suitable sites with more dangling bonds such as steps, edges etc.

This study also investigated quite extensively the transfer of ^{13}C atoms onto polished diamond surfaces. The source of the ^{13}C atoms was the polishing olive oil (principally olein), labelled with 99% ^{13}C atoms, since olive oil is normally used to polish diamond surfaces. It therefore doubles as a lubricant and in other cases as a source of the hydrogen atoms that terminate the polished diamond surfaces. By using nuclear reaction analysis and the 550keV ^{13}C(p,γ)^{14}N resonant nuclear reaction, it was found that when diamond surfaces were polished with this labelled oil, a full monolayer of ^{13}C atoms was always found bonded on to each of the three diamond surfaces. This was quite a high coverage, and at the same time also an interesting result, because the possibility of being able to transfer atoms from the polishing lubricant to the surface had key implications. Among them, novel surfaces could perhaps be prepared in the manner suggested in this work, while labelling of surfaces for identification could also be a possible application.

By analyzing the gamma rays emitted from the nuclear reaction as a function of the exciting proton's energy, the nuclear reaction's width was found to be 25$\pm$1keV, which was in excellent agreement with other studies. This value of the width was nonetheless narrower than the most recently quoted value of 32.5keV, which is composed of both s and p-waves. Due to the geometry of our detector, the value of 25keV was believed to be due to contributions from the isotropic s-wave only. Our results further showed that it was unlikely that clumping would occur on strongly covalent surfaces, while previous works indicated that there was no exchange of labelled carbon atoms at a diamond surface. As such, a distribution in depth was clearly ruled out. The narrow

width of the nuclear reaction confirmed that the ^{13}C surface layer was indeed very thin, and possibly the thinnest layer that can be formed, thereby being better than most supported thin targets. This was yet another way of preparing thin targets for nuclear reaction applications.

This work was based primarily on the study of diamond surfaces that are polished mechanically. Mechanical polishing is the earliest and also the most well developed method for preparing well characterised diamond surfaces. Diamond surfaces prepared through mechanical polishing are known to be bulk-like, and also terminated with a layer of hydrogen. Exposure of these to air adds a monolayer of oxygen and/or hydroxyl groups as observed in the XPS studies. When given an extra 30 or more minutes of manual polishing, these surfaces are believed to be very flat, but their degree of roughness has not been investigated directly up until now. The manual polishing exposes a new surface, which is probably different from that achieved after the mechanical polishing. By using atomic force microscopy and optical microscopy within the Nomarski interference mode, it was found that both the mechanically and manually polished diamond surfaces were composed of a series of parallel polishing lines. They all had very small roughnesses, with the manually polished surfaces being smoother. Some of the polishing grooves were wider and also deeper, while others were shallower and much smaller and these were found to be residing inside the larger ones. The AFM results in particular revealed that the amount of surface roughness on the three low index polished diamond surfaces was varied, albeit in a small way, and also depending on whether the surfaces were polished only mechanically, or if they were given the extra manual polishing. Details of the actual roughnesses on each face after the mechanical and manual polishing stages are given in the thesis.

Annealing these surfaces under vacuum conditions of better than 10^{-6} Torr, up to temperatures of 250 and 750°C, revealed that the 250°C anneal did not change the surface roughness much from what it was before the annealing. It was thus believed that if any changes occurred, these resulted only in the desorption of the physisorbed species. However, annealing the surfaces to 750°C under vacuum resulted in some changes in the overall surface roughness of all the the three low index faces, which were not observed at the 250°C anneal.

This was therefore believed to lead to surface etching and in some instances smoothing of the surfaces, as the surface-bonded species got desorbed as C-O groups. Lack of severe etching was attributed to the fact that not all the adsorbates got desorbed by the 750°C anneal.

The role of oxygen atoms and hydroxyl groups on diamond surfaces has been a subject of debate for a while now. Their stable sites, how they are bonded and their proportions (i.e. monolayers) under various conditions are issues that are yet to be fully resolved. Using density functional theory, this study sought to establish the preferred bonding sites and configurations of the oxygen atoms and the hydroxyl groups on the single-dangling-bond (111) (1×1) and (2×1) diamond surfaces. This was intended to complement the experimental work done in the XPS studies, and also other works reported in literature. It was realized by computing the adsorption energies of oxygen atoms and hydroxyl groups from first principles at various sites and for varying monolayer coverages. Among the sites investigated were the ONTOP, bridge, hexagonal close packed (HCP) and the face centred cubic (FCC) sites. The coverages were varied between the full, half, third and quarter monolayers. By comparing the adsorption energies as well as the total minimum energies of the different systems, it was found that the ONTOP site was overall the most stable bonding site on diamond (111)-(1×1) surfaces, while the third monolayer coverage was the most preferred one. The half monolayer bridge site bonded with oxygen atoms was found to be the most stable site and coverage on the (2×1) reconstructed surface.

In addition, while the bond lengths and angles were preserved close to the experimental values of 1.54Å for the C-C bonds and 109.4° respectively within the bulk, those in the topmost bilayer of carbon atoms were not. They were found to elongate by as much as 10% and others contracted by as much as -6%. The bond angles varied predominantly between 101 and 112°. Some of the surface bond length changes were attributed to the presence of the adsorbates, while others were due to the strong rehybridization within these layers, especially between the 2nd and 3rd carbon atom layers of the C(111)-(1×1) surfaces. Bond lengths within the bulk regions varied by less than ±1% of the bulk bond length for both the (1×1) and (2×1) surfaces. Very small buckling and no dimerization of the surface bonds was observed on the clean (2×1) reconstructed

C(111) surfaces, but some considerable buckling of the upper π-bonded surface layer was observed after the adsorption of oxygen atoms or hydroxyl groups.

The computed bulk properties of diamond such as the bulk modulus (4.16Mbar), the cohesive energy (7.89eV/atom) and the lattice constant of 3.563Å were all well within the expected theoretical and experimental ranges. The same applied to the bulk properties of the free oxygen molecule and the hydroxyl group. Their bond lengths were 1.21 and 0.978Å for the oxygen molecule and the hydroxyl group respectively, while the binding energy and vibrational frequency of the free oxygen molecule were 3.31eV/atom and 1550cm^{-1} respectively.

Both the O atoms and OH groups were also found to affect not only the electronic density of states of diamond, but also the work function. Oxygen atoms led to an increase of the work function, while the hydroxyl group's adsorption resulted in decreasing of the work function, owing to the resulting surface dipoles, which in turn makes the surfaces to posses negative electron affinity. An average valence band width for bulk diamond of $\sim$21eV was obtained and both surface states due to the oxygen atoms and the carbon atoms were established at different energies.

The half monolayer coverages of oxygen atoms at the ONTOP and bridge sites were found to be insufficient for lifting the (2×1) surface reconstruction, while all the full monolayer coverages and the hydroxyl terminations resulted in the lifting of the surface reconstruction to the unreconstructed (1×1) surface. The inability of the half monolayers coverages with oxygen atoms to break the (2×1) surface reconstruction was attributed to an activation barrier of going from oxygen on a (2×1) to oxygen on a (1×1) surface. It was further found that on the C(111)-(1×1) surface, repulsion between the oxygen adsorbates started at coverages greater than 0.33monolayers, while for the hydroxyl termination, it was not until coverages greater than 0.5monolayers that the systems got less stable due to the OH-OH repulsions.

Much of this work has been published in various journal, and also presented in both international and local conferences as shown in Appendix A. Some more publications and conference presentations are also planned for.