Surface functionalization of H-terminated diamond with NH and NH$_2$ on the (1 0 0), (1 1 0) and (1 1 1) surface planes using Density Functional Theory

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Abstract

The adsorption energy of aminated diamond surfaces on the (1 1 1), (1 1 0) and (1 0 0) diamond surfaces have been calculated with density functional theory (DFT). The resulting values show that bridging is favoured before on-top nitrogen at low coverage for all the low index planes. The trend is even more pronounced as the coverage increases, most likely due to sterical hindrance. As expected, the imidogen (NH) and amidogen (NH$_2$) groups are bonded to the surface planes in the order (1 0 0)>(1 1 1)>(1 1 0) as decrease in energy is the highest on the (1 0 0) plane and lowest on the (1 010) plane. The effect of sterical hindrance is largest at the (1 1 0) surface while the (1 0 0) surface is almost unaffected by neighbouring functional groups. Also, double bonded on-top imidogen (NH) is the least stable group at the (1 0 0) surface at low coverage while it is almost as stable as bridging NH when having a full mono-layer. Moreover, on-top imidogen (NH) was highly distorted and forced a change in surface geometry

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1 Goal

The goal of this study was firstly to find out which one of amidogen (NH_2) and imidogen (NH, on-top or bridge) is theoretically most strongly bonded to a diamond surface. Secondly to find out whether NH_2 or NH (on-top or bridge) is theoretically best attached to a (1 0 0), (1 1 0) or (1 1 1) oriented diamond surface.

2 Introduction

2.1 Background

Diamond, and in particular nanodiamond, has become a promising candidate for several fields of application. One of those applications is to use it in medical and biological sciences as it possess biocompatibility as well as good chemical and electrical properties. It also has a large electro-potential window, which may be further enhanced or inhibited by modifying the surface. Furthermore, even though diamonds show good physical/chemical stability, the surfaces are still easily modified or functionalized by photochemical reactions [1].

To use diamond for medical purposes such as the growing of bones, proteins and DNA must first be successfully attached to the diamond surface. One way to enhance the attachment of these types of molecules is functionalizing surfaces with various biologically common functional groups before trying to bind the specific molecule to the surface. Amine-based groups in particular may be a good step on the way to so this since both imidogen (NH-) and amidogen (NH_2) are part of many well known biochemical and organical reactions. This has already been done as preliminary step in binding DNA to a diamond surface. Aminating the surface by UV-radiation will also make the surface pH sensitive depending on the amount of UV-radiation. Furthermore, amidogen (NH_2, on-top) groups produced by long-term UV-radiation have proven to be stable under exposure to air. [2]. It has also been reported that diamond has high stability and sensibility as well as compatibility with microelectronic processing technology. All of these properties also make diamond a promising candidate for biological integration of microelectronics as well as biological modification [3].

There are also several well established ways to produce diamond in industrial and laboratory settings aside from CVD (Chemical Vapor Deposition). Naturally, the surface chemistry will vary depending on chosen method. Specifically, nano-diamonds can for example be produced using shock waves (so called shock-wave diamond) or explosives

(detonation diamond) on carbon materials. The surface of shock-wave diamond is graphitized and detonation diamond is covered with various oxygen containing groups. The surface of detonation diamond have been successfully homogenised using oxidative (yielding for example mostly keto- and carboxyl-groups) or reductive methods with the latter yielding, for example, an H-terminated or OH-terminated surface. CVD-diamond will, generally, yield an H-terminated surface without further cleaning or homogenisation.[4] Also, several studies have already been made concerning low-index planes of diamonds, mostly practical work, but also some purely computational studies. Some of those cover the adsorption of amines on diamond. One of these are a relatively early study that regarded the full coverage (mono-layer) of NH_2 on the (1 1 1), (1 1 0) and (1 0 0) planes of diamond surfaces. They used MM (Molecular Mechanics). The results showed that full coverage meant great distortion of the structure at the (1 1 0) and (1 1 1) cleavage of the diamond surface. Although the report did not report either enthalpies or adsorption energies, this may indicate that full coverage is unlikely. The (1 0 0) surface did not show any significant distortion. [5]

Another, slightly more recent study has been done regarding adsorption of NH_2 on a reconstructed (1 0 0)-diamond surface using DFT (Density Functinal Theory) with the GGA (General Gradient Approximation) approximation. The resulting energies, while comparing a structure with two nearby NH_2 groups with one with hydrogen instead, showed that the energy levels were lower in the latter case. It is hence unlikely that two amino-groups will form in two nearby reaction sites at the reconstructed (1 0 0) diamond surface. [6]

Amidogen (NH) and Amine (NH_2) adsorption has also been found to be energetically favoured around room temperature on the (1 0 0), (1 1 0), and (1 1 1) planes of nanodiamond using density functional tight binding simulations. [7]

3 Theory

3.1 Surfaces of diamond

3.1.1 General surface theory

The reactivity of a crystal surface is known to be dependent of the surface structure and morphology, which do not only depend on the crystal lattice, but also the orientation of the intersection in relation to the crystal lattice. Both coordination numbers and numbers of possible reaction sites differ depending on plane (orientation of the

Figure 1: A description of the (1 0 0), (1 1 1) and (1 1 0) planes. This picture was picked from an online glossary [10], but the same information can be found in any book pertaining basic solid state chemistry

intersection) and surface morphology. The specific plane is formally described using miller indexes where the numbers represent the intersection through the three mayor crystallographic axes of the lattice. The three most simple surface planes are (1 1 1), (1 1 0) and (1 0 0) but it is possible to use higher indexes. The (1 1 1), (1 1 0) and (1 0 0) planes are demonstrated in figure 1. Naturally, properties that generally leads to larger surface energy such as large surface areas and low coordination numbers on surface atoms generally means a higher reactivity and a stronger binding of an adsorbate. Another property that affect surface energy, and thus its reactivity, is how close-packed the surface atoms are. The direction of free bonds at the radical surface also plays a role in how well an adsorbate can be bonded to the surface [8, 9].

3.1.2 Structure of the low index surfaces of diamond

For simplicity, this study only explores the adsorption of ammonia on diamond at the three low-index surfaces (1 1 1), (1 1 0) and (1 0 0). The overall structure of diamond is a derivative of the zinkblende-structure where all atoms are the same (se figure 2). In other words, all carbon atoms in the bulk have the coordination number 4 meaning sp^3-hybridisation and a tetrahedral symmetry around the atoms (se figure 2). A closer look at the three planes show that the surface atoms has the same coordination number, which is three, but the rest is different. The (1 0 0) plane does not keep perfect tetrahedral symmetry around the carbon atoms at the surface and are less close-packed than the other two planes studied and is therefore expected to have the largest surface energy. One might even speculate that it is possible for a bond to break between two neighbouring surface atoms, creating lower coordination numbers. In comparison, the (1 1 0) and (1 1 1)

HM:F-43M #216
a=5.434Å
b=5.434Å
c=5.434Å
α=90.000°
β=90.000°
γ=90.000°

Figure 2: The general lattice of diamond. This picture was generated on a free, online resource center, but the same information can be obtained in many ways and the diamond structure as well as the that of zinkblende are both to be considered general nowledge.

planes do keep the tetrahedral symmetry around the carbon atoms. One can also see that while the surface of the (1 1 1) plane seem more close-packed than the (1 1 0), the free bonds of the latter is actually closer to each other in the latter case. A schematic illustration displaying the free bonds (refererred to as dangling bonds) of the three planes is shown in figure 3.

3.2   General computional theory

Molecular modelling is a good way to get further understanding of the workings of chemical systems and molecules. Environment can be strictly defined and properties that would otherwise be very hard, impossible or very expensive might be studied. There is however, no perfect model simulating an exact replica of the real world, which gives

(1 1̄ 1)   (1 1̄ 0)   (1 0 0)

Figure 3: Schematic illustration displaing the dangling bonds of the (1 1 1), (1 1 0) and (1 0 0) plane from the side (top) and from above (bottom).

all the answers. It is, specifically, impossible to get an exact and true electron configuration.

There are hence several different approaches and methods developed for modelling chemical systems, each using their own approximations that have their own pros and cons. Those use quantum mechanics, molecular mechanics or a statistical approach. Quantum mechanical methods are, in essence, solving the problem by approximate solutions of the Shcrödinger equation. Molecular mechanics uses classical mechanics and replace the electrons to be a fixed force field. Molecular mechanics might generate properties such as temperature dependence, different kinetical properties and even information about systems that are not in equilibrium. The statistical approach uses the inherent statistical properties that exist within all systems and will therefore only give information about systems in equilibrium, which those methods are very good at. Those two methods are cheap in computational time and requirement, so very large systems can be simulated at a short time. They do not, however, give any information about electron configuration (which is what this study wanted) [11]. Hence the quantum mechanical approach had to be used here.

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