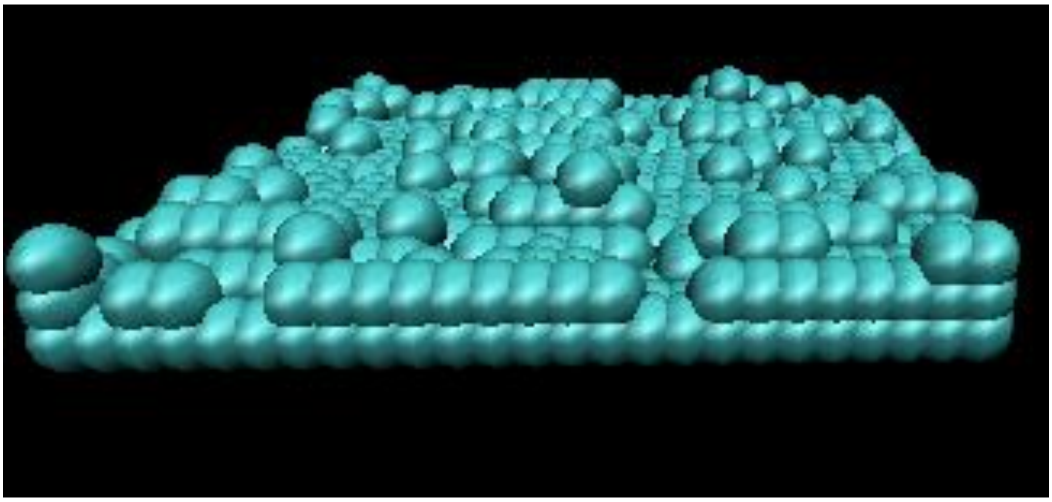
Kinetic Monte Carlo and Molecular Mechanics Simulations on Chemical Vapour Deposition Diamond



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Abstract

Diamond is a compound known since ancient times, always has been related with wealth but during the last century, diamond started to find place in the market for technological applications due to its exceptional physical properties. Nowadays diamond is made artificially at industrial scale as a thin layer in order to exploit better all the properties. This synthetic process is called Chemical Vapour Deposition (CVD), and consists on the one by one addition of carbon atoms to the lattice. In this work, CVD diamond growth is studied by means of computational chemistry. Kinetic Monte Carlo simulations are used to check the growth mechanism and to predict some features of the growth as growth rate and roughness, depending on the starting conditions. The work done in this part was change the starting conditions in order to find relationships. The starting conditions changed were those which can be modified in the laboratory: substrate temperature, gas temperature and concentration of different species near the surfaces. In order to check the importance of some processes in the growth were one by one deactivated and checked the change in the resultant layer. Some interesting relationships were found in very good agreement with the experiments made by other research groups. Also Molecular Mechanics methods were used to optimise some kinds of diamond 2x1 (100) surface, the aim was to calculate surface energies for every surface using the program GULP to carry out these simulations. Hydrogen terminated surface resulted to be more stable than the reconstructed surface. Also energies for the growth steps were calculated.

Acknowledgments

I would like to acknowledge Neil L. Allan for supervise and drive me along the work done during this year. Also I want to acknowledge the rest of Neil Allan´s research group, especially Jeff Rodgers for helping me when I needed and teaching some important and useful things about computational chemistry.

Contents

CCC Induction Course

As part of the Library part of the project, during the first 9 weeks of the course, computational chemistry students did this course, in order to learn different levels of theory, software packages, as well as the operating and queuing systems and basic programming/data extraction. We have spent part of each week solving these exercises and discussing them with the other students in a debrief session. As student on the BSc programme, this course form part of my library project alongside the literature searches during the first term. The time spent in this part of the project was roughly from 6 to 8 hours per week. I will describe briefly the work done each week and, afterwards, I will describe more deeply the exercise done during the sixth week about Solid State Simulations.[33]

1. Summary of the course

- Week 1

  The first week´s work was an introduction to the Unix/Linux operating system. We learned the basic commands to use Unix. We learned as well how to work with VI and the queuing systems.

- Week 2

  We learned different ways of using scripts and programs to manipulate files and to extract data. Bash scripting was the subject of the second week´s exercises. Other programming languages used were Pearl, Fortran and Python.[34]

- Week 3

  This exercise was an introduction to electronic structure methods and how they can be used to explore structure, reactivity and spectroscopy. The computational methods used are based on obtaining approximate solutions to the Schrödinger equation describing the motion of electrons within the molecule. The focus here is not on how these methods work, the calculations use a program called Gaussian, with input and output going through a Graphical Interface, GaussView.

We were asked to calculate the structure of some molecules using ab initio methods; we calculated the vibrational Raman and IR frequencies, the chemical reactivity and optical spectroscopy of different molecules, all using computational methods, afterwards we contrasted the values obtained in the program with the experimental values measured.[35]

- Week 4

The aim of the week 4 exercise was to write a Hartree Fock program using Fortran, using existing bits and pieces, and learn about Hartree Fock theory.[36]

- Week 5

In this week, we ran and modified a Fortran program in order to simulate monoatomic particles that interact with Lennard-Jones potential. The method used was Molecular Dynamics with periodic boundary conditions and the nearest image aproximation. The aim was to calculate the radial distribution function g(r) and the self-diffusion coefficient D. The file was visualised using VMD.[37]

- Week 6

This week was about simulating solids, liquids and gas phase changes. The chief objective of this practical session was to introduce the modelling of solids and liquids, which is playing an ever more important role in the design of new materials and in increasing our understanding of solids and surfaces at the atomistic level. The aims of the experiment were Simulate an oxide and solid state defects, and to model phase changes, to get that were used static lattice, molecular mechanics optimisations and molecular dynamics methods.

There were two exercises to do this week. The first was about study the structure of solid oxides, using computational techniques specifically developed for solid phase chemistry (use of these techniques to investigate solid-solid phase changes, and to examine the role of defects), I will describe this exercise deeply in the next section. In the second part of this practical we studied the structure of liquids, using computational methods that have revolutionised our understanding of the liquid phase.

Systems studied were calcium oxide solid state structures as a function of pressure in the first part and liquid neon as a function of temperature and pressure.

Techniques used: MSYS command line, GULP (to calculate the properties of infinite solids), VMD (molecular viewer program that you can use to display 3D models of molecules) and NAMD (molecular dynamics program that can be used to model molecules in the condensed phase).[38]

- Week 7 & 8

To finish the course we learned the basis to do a good presentation and how to write a project report. We did an oral presentation on our current work supervised by Professor Natalie May.

2. Exercise. Solid State Simulations

The challenge of modelling solids is the large amount of atoms or molecules. Due to this, is not possible to run quantum mechanics solutions because these would require too much time and memory. The perfect solids have translational symmetry, that is, the properties of the unit cell are the properties of the entire solid; molecular mechanics method exploits this symmetry. The solid is considered a group of spheres interacting via springs. The nuclear motion is considered but the electron distribution is considered fixed. Motion is described by classical physics laws, with particles interacting via simple potential energy functions, for instance Lennard Jones potential.

The aim of the exercise is to simulate an oxide and solid state defects produced by missing or extra atoms. The methods used are static lattice, molecular mechanics optimisations and molecular dynamics. The system studied is Calcium Oxide (CaO) solid state structure as a function of pressure. To do this work has been used the program GULP to simulate the properties of infinite (periodic) solids as well as defects in bulk material; use of boundary conditions. Also VMD was needed in order to display the models of the solids in 3D. Typing has been done in MSYS command line, which is similar to UNIX.

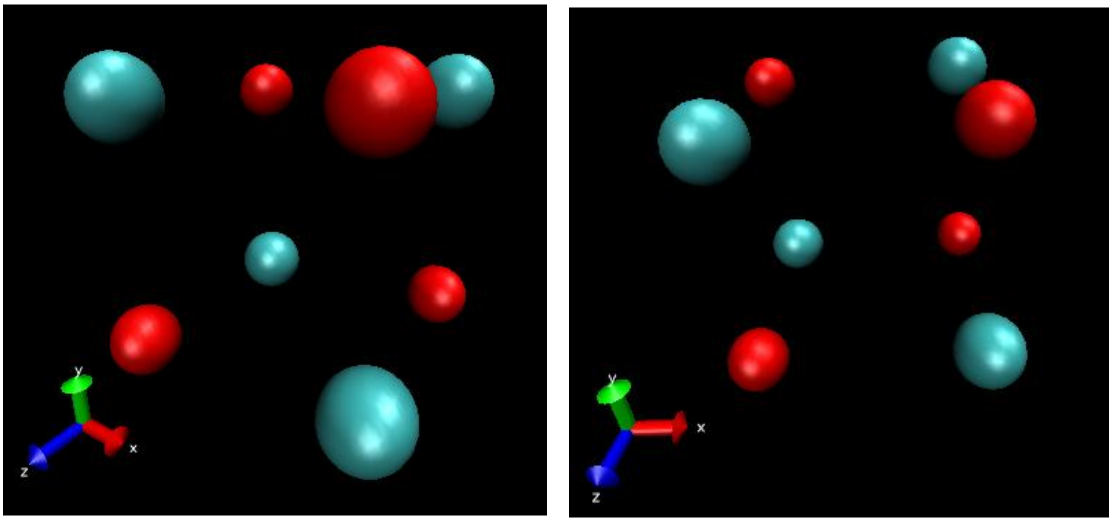
The starting file has the unit cell parameters and interatomic potentials, in this case Buckingham potential

$$V = A\, e^{-r/B} - C / r^6$$

Now a set of exercises has to be solved.

Exercise 1 Optimising the structure

a) Visualise the optimised geometry using VMD. How does this compare to the initial structure before optimisation?



The left image is the CaO cell unit before the optimisation and the right hand image after the optimisation. The structure of the unit cell does not vary, but the distances between ions do.

The structure is the same as NaCl. The coordination number of Ca is 6. There are in the lattice 4 Ca^{2+} ions and 4 O^{2-} ions

b) What is the lattice energy of the input (initial) structure?

E_{L0} = -139.4436 eV = -13454.18 KJ/mole[1]

Cell length = 4.412 Angstrom

c) What is the lattice energy of the final (optimised) structure, and what are the lattice parameters and basis atom positions of the optimised structure? What is the **lattice energy per formula unit**?

E_{Lf} = -143.5620 eV = -13851.54 KJ/mole

Lattice energy after optimisation is more negative, the energy was dropped.

Cell length = 4.825 Angstrom

Increase of the lattice length, only one is needed because all the lattice vectors are equal to each other (cubic unit cell).

To calculate the lattice energy per formula unit, is needed to divide the energy per mole of lattice cell for the number of CaO pairs in the cell, that is 4.

E_{Lf} = - 35.8905 eV = - 3462.89 KJ/mole[2]

d) Calculate the density of the optimised structure and so confirm the value printed out at the end of the output file.

Density of the solid is the mass divided by the volume, in that case mass of the atoms in the unit cell (4 Ca, 4 O) divided by the volume of the unit cell (cell length to the power of 3)

Calcium atomic mass Ca = 40.08 g/mole

Oxygen atomic mass O = 16.00 g/mole

Cell length = 4.825 Angstrom

Density (calculated) = 3.316 g/cm^3

Density (experimental) = 3.35 g/cm^3

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[1] Note that lattice energy is given in kilo Joules per mole of unit cells.

[2] Here, lattice energy is given in Kilo Joules per mole of CaO.

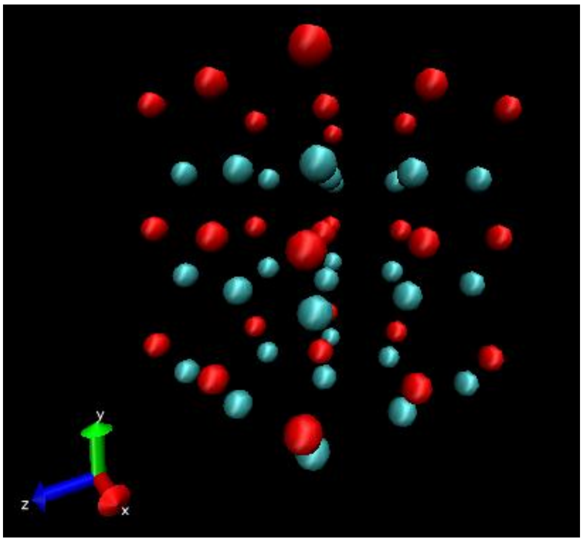
The error in the density calculation is only 1% respect the original value, which is a good result.

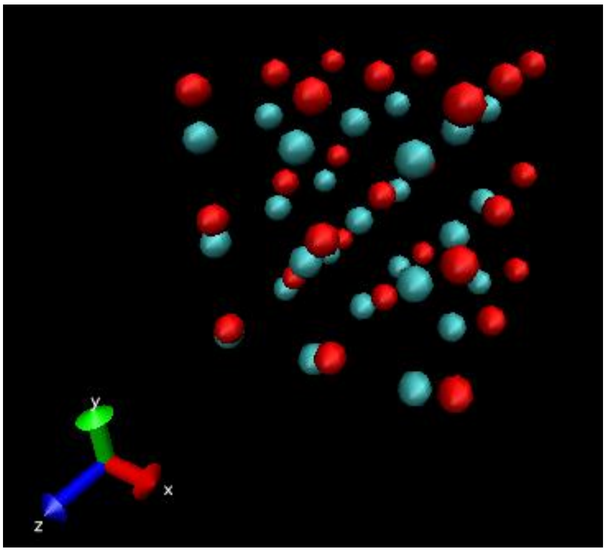
<u>Exercise 2</u> High pressure chemistry

High pressure chemistry is very important in geology; due to large number of processes in the earth occur at high pressures. The purpose of this exercise is to examine if CaO undergo a phase transition state at high pressure. To calculate this, there is a file with a possible structure of CaO at high pressure.

a) Create a PDB file from **cao_p** and visualise it in VDM

b) Run this input file. Extract the PDB and visualise it using VMD. How does this compare to the initial structure? What are the optimised lattice parameters, lattice energy and density? Is the density smaller or larger than that of the structure considered in Exercise 1, and so is it reasonable, that this is a candidate high pressure structure?





The left image corresponds to the CaO structure under P before optimisation ((a) question), and the right one after optimisation

The coordination number of the calcium ion is 8. The unit cell has one calcium ion and one oxygen ion.

Parameters of the initial structure

Cell length = 2.5 Angstrom

Lattice energy = - 30.870 eV = - 2978.5 KJ/mole[3]

Parameters of the optimised structure

Cell length = 2.929 Angstrom

Lattice energy = - 34.700 eV = - 3347.0 KJ/mole

Density = 3.705 g/cm^3

Is a good candidate to be a model for CaO under high pressure because has higher density as the model in exercise 1.

The lowest energy structure at any pressure is that with the lowest enthalpy H (ignoring any entropy considerations). We can optimise a structure at any pressure by changing one line at the end of the input file. Change the line at the end of **cao_p** using write. Note that when this line is changed the program outputs enthalpies rather than energies.

c) Run your modified **cao_p** at 10 GPa, write down the enthalpy per formula unit and work out the internal energy at this pressure. Note that you should write the output to another file.

$$\Delta H = - 33.17 \text{ eV} = 3201 \text{ KJ/mole (per formula unit)}$$

$$\Delta U = \Delta H - pV$$

$$\Delta U = - 3344 \text{ KJ/mole}$$

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[3] This time, as unit cell has one Ca^{2+} and one O^{2-} energy per mole of unit cells and energy per formula unit are equal numerically (but the definition is not equal).

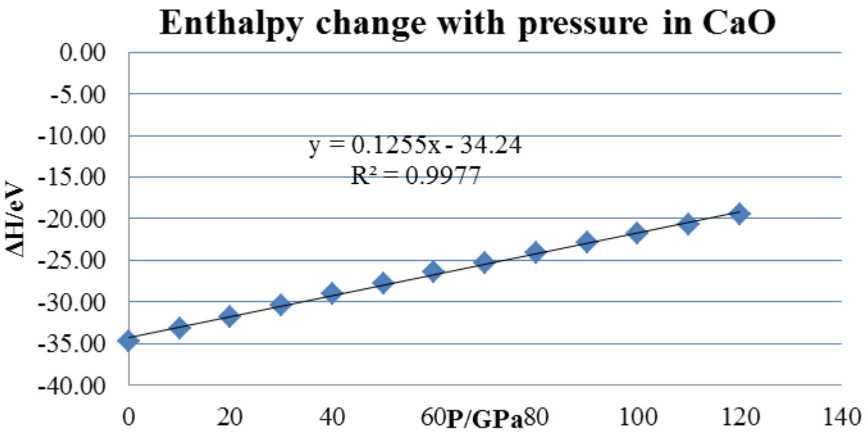


Figure 1. Change in entalphy with pressure in the CaO phase under pressure has a linear dependence of the pressure as seen in the high correlation.

d) By plotting suitable graphs of H vs. P for both structures, investigate whether CaO will undergo a phase transition to the high pressure form over the range of pressures 0-120 GPa (NB you need to plot H per formula unit). Remember to take care with the units!

To solve this problem is needed to look for the pressure which the second conformation has lower entropy than the first, then is more stable and the phase change occurs.

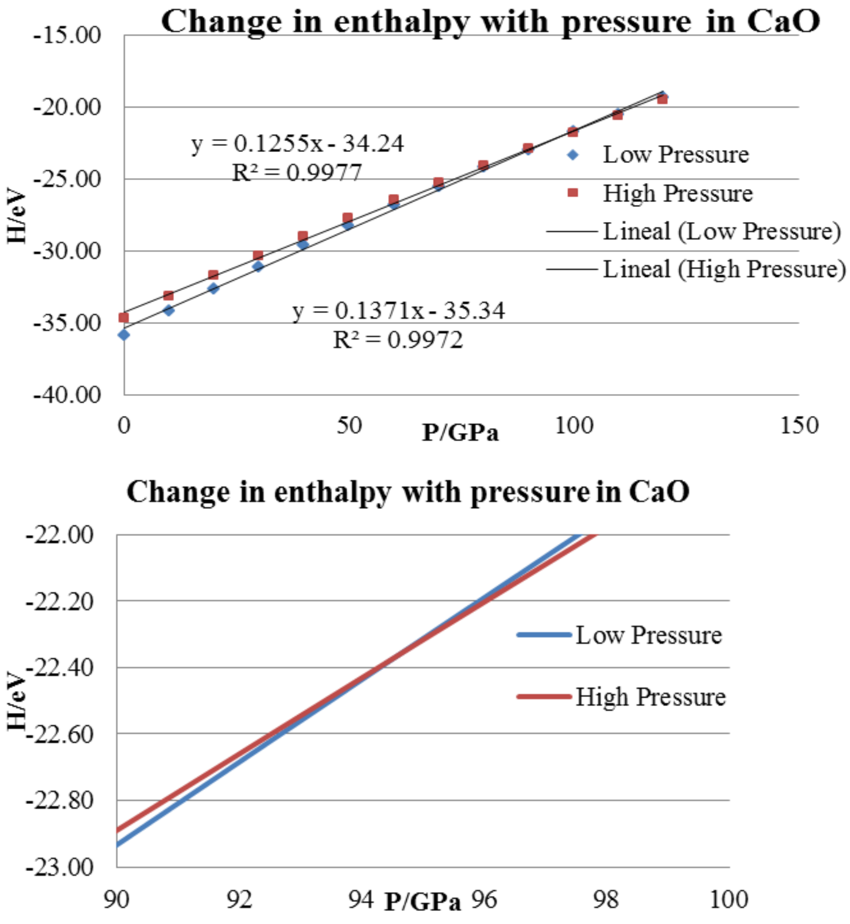


Figure 2. Up) Change in enthalpy with pressure in both conformations of CaO. The crossing point of the lines gives the pressure of phase change, because the high pressure conformation becomes more stable than low pressure conformation.

Down) Zoom in the zone of the phase change

Phase change pressure is calculated solving the equation system of the two regression lines or simply watching where they cross.

Phase change pressure = 95 GPa

Exercise 3 – Defects

Defects are one of the most important features of solid state chemistry. There are four types of defects: Vacancies (missing atoms), interstitial (extra atoms). impurity atoms or extended defects (grain boundaries, dislocations and surfaces).

This exercise consists in modelling defects in CaO working out the energy associated with removing or adding a Ca^{2+} or O^{2-} ion from the lattice. Then the surrounded ions change its conformation (relaxation). To do this is needed to specify the ion removed or added, centre of the sphere of ion relaxation. There are two radii fixed for the two spheres centred in the defect, in each sphere different approximations for relaxation are used (in that case 5 and 11 angstrom). Then specify the ion adding or missing.

a) Run **cavac** and see how the last part of the output differs. Write out the initial (unrelaxed) defect energy and the final (relaxed) defect energy at convergence. How large is the relaxation energy (the difference between these two) as a percentage of the final answer? Can the relaxation energy be neglected?

Initial defect energy (unrelaxed) = 30.60 eV

Final defect energy (relaxed) = 21.80 eV

Percentage of relaxation energy = 40.33%

Relaxation energy cannot be neglected; the percentage of relaxation energy is large enough to be taken in account.

b) Edit the file ovac (using write ovac) so as to work out the defect energy associated with an oxide ion vacancy, rather than a calcium vacancy. Repeat part (a) of this question, but for the oxide ion vacancy.

Unrelaxed defect energy = 30.77 eV

Relaxed defect energy = 22.03 eV

Percentage of relaxation energy = 39.69%

Again, relaxation energy cannot be neglected.

c) An important principle in the chemistry of ionic solids is that any solid must always remain **electrically neutral**. The consequence of this is that neither an O^{2-} vacancy or a Ca^{2+} vacancy can exist by itself, but in a solid containing no impurities, the two can only exist together as a pair. The overall energy to create this pair of defects (known collectively as a *Schottky defect* is given by,

$$\text{D.E.}(\text{Ca}^{2+}\text{ vacancy}) + \text{D.E.}(\text{O}^{2-}\text{ vacancy}) + E_{latt}(\text{CaO}).$$

Where D.E. denotes the defect energy and E_{latt} the (optimised) lattice energy of CaO (per formula unit), which you worked out in exercise 1. This last term arises because the ions removed must go somewhere else such as the surface; they cannot just vanish! Note E_{latt} is negative (GULP defines it as the energy released when the ions come together to form the crystal). Work out the Schottky defect energy in CaO.

Schottky defect energy = 21.80 eV + 22.03 eV – 139.44/4 eV

Schottky defect energy = 8.97 eV

d) Another defect is an ion occupying a position not usually occupied in the solid (an interstitial defect). Calculate the defect energy associated with the interstitial Ca^{2+}. Run this file, write out the initial and final defect energies associated with this interstitial and also express the relaxation energy as a function of the final value.

Initial defect energy = 4.99 eV

Final defect energy = - 8.75 eV

Relaxation energy = - 13.74 eV (57% of final defect energy)

e) Repeat part (d) for an oxide ion interstitial at the same position, using the file **oint**.

Initial defect energy = 4.00 eV

Final defect energy = - 9.21 eV

Relaxation energy = - 13.21 eV (43% of final defect energy)

f) A Frenkel defect is another "compound defect" comprising an ion moving from a lattice site to a non-lattice, interstitial position. The energy for a cation Frenkel defect is the sum of the individual energies for a Ca^{2+} vacancy and a Ca^{2+} interstitial. The energy for the anion Frenkel defect is the sum of the individual energies for an O^{2-} vacancy and an O^{2-}interstitial. Work out the energies of a calcium Frenkel defect and an oxygen Frenkel defect. Which defect - cation Frenkel, anion Frenkel or Schottky - will dominate the defect chemistry of CaO?

Cation (Ca^{2+}) Frenkel = 21.80 eV – 8.75 eV = 13.05 eV

Anion (O^{2-}) Frenkel = 22.03 eV – 9.21 eV = 12.82 eV

Schottky defect dominate the chemistry of CaO because is smaller than the rest. 8.97 eV vs. 13.05 and 12.82 eV.

<u>Exercise 4</u> – Understanding unit cells

a) Draw a clear diagram of the low pressure structure of CaO, showing clearly the atoms in the unit cell and the lattice vectors. What are the coordination numbers of Ca and O? Do the Ca ions form a face-centered cubic, a body-centered cubic, or a simple cubic lattice? How many calcium ions and how many oxygen ions are there in the unit cell?

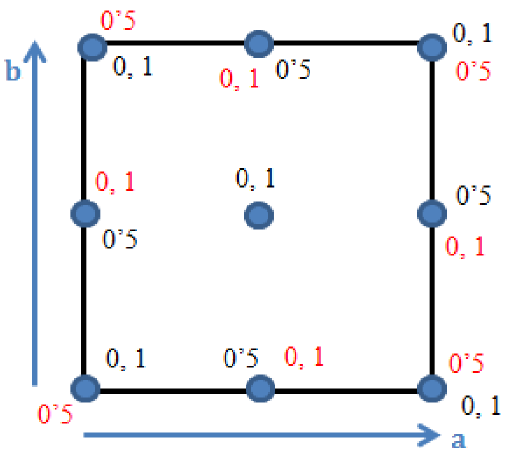


Figure 3. Diagram of the low pressure structure of CaO. The dots are the places where ions are, and the numbers represent the positions of the atoms along z axis in the unit cell.

Black font indicates Ca^{2+} ions position

Red font indicates O^{2-} ions position

Coordination numbers: Ca^{2+} 6 O^{2-} 6

Ca^{2+} ions form a face centred structure

Number of ions in cell: Ca^{2+} 4 O^{2-} 4

b) Draw a clear diagram of the high pressure structure of CaO, showing clearly the atoms in the unit cell and the lattice vectors. What are the coordination numbers of Ca and O? Do the Ca ions form a face-centered cubic, a body-centered cubic or a simple cubic lattice? How many calcium ions and how many oxygen ions are there in the unit cell? What ionic compound adopts this structure at zero pressure?

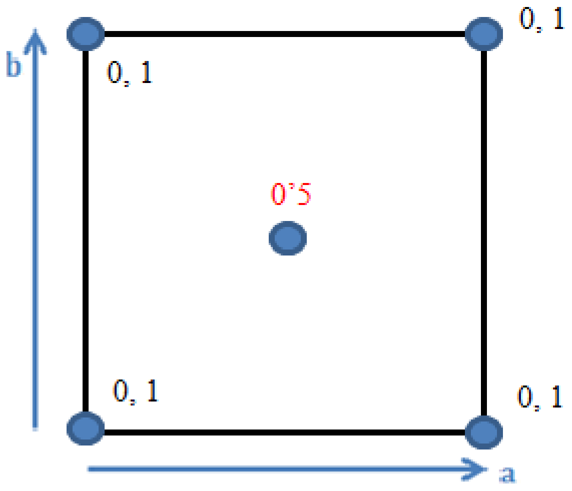


Figure 4. Diagram of the low pressure structure of CaO. The dots are the places where ions are, and the numbers represent the positions of the atoms along z axis in the unit cell.

Black font indicates Ca^{2+} ions position

Red font indicates O^{2-} ions position

Coordination numbers: Ca^{2+} 8 O^{2-} 8

Ca^{2+} ions form a simple lattice (cubic) structure

Number of ions in cell: Ca^{2+} 1 O^{2-} 1

Caesium chloride is an example of two interpenetrating simple cubic lattices.

c) Plot a graph of V vs. r for the short-range potential acting between any pair of oxygen ions over the range 1-3 Å. What is the physical origin of the A exp(-r / B) term and the -C / r^6 term on the right of equation 1?

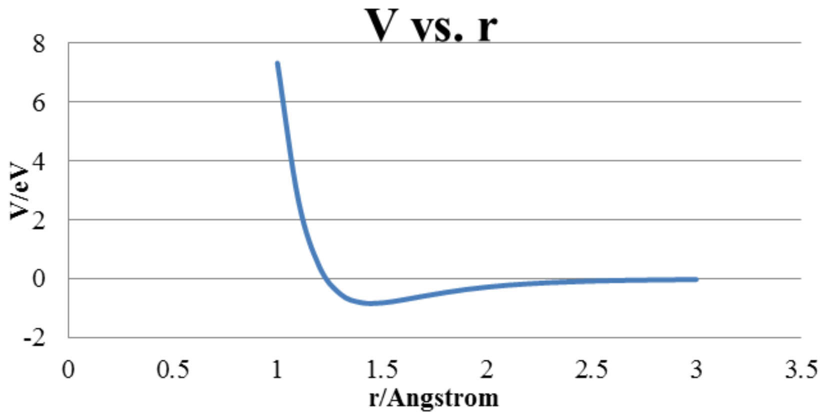


Figure 6. V vs. r according to Buckingham potential with values A = 22764 eV, B = 0.149 Angstrom and C = 20.37 eV A^6

A exp(-r / B) term is always positive, so is the repulsive term, while -C / r^6 is negative and account for the attractions of the particles. The attractive term, corresponds to the van der Waals forces and the repulsive term is the electrostatic repulsion.

Library part

1. Introduction

Diamond is a well-known compound, extracted and traded for more than 4000 years. It is a symbol of wealth and prestige, diamond is also valuable for its superlative physical properties, such as hardness or thermal conductivity. Diamond has a wide range of applications where can be used. This explains the increase in demand for technology applications. The scientific community has been forced to develop methods in order to synthesize artificial diamond with the same properties as the natural one.

Diamond is not the thermodynamically phase of carbon at standard conditions, but is a metastable phase, that is, thermodynamically unstable (the stable carbon form at room temperature and pressure is graphite, Diamond – Graphite $\Delta G^0(298K) = -2.9\ kJmol^{-1}$), but is kinetically stable, that is the reason for not decomposing to graphite (at least for millions of years). This is because the activation energy gap is very large.[1] Carbon atoms are arranged in a very rigid crystal lattice, each carbon atom is tetrahedrally surrounded by 4 equidistant neighbours at 154.45pm. The tetrahedra are arranged to give a unit cell[2] with $a_0 = 356.68$ pm as shown in Fig 1.

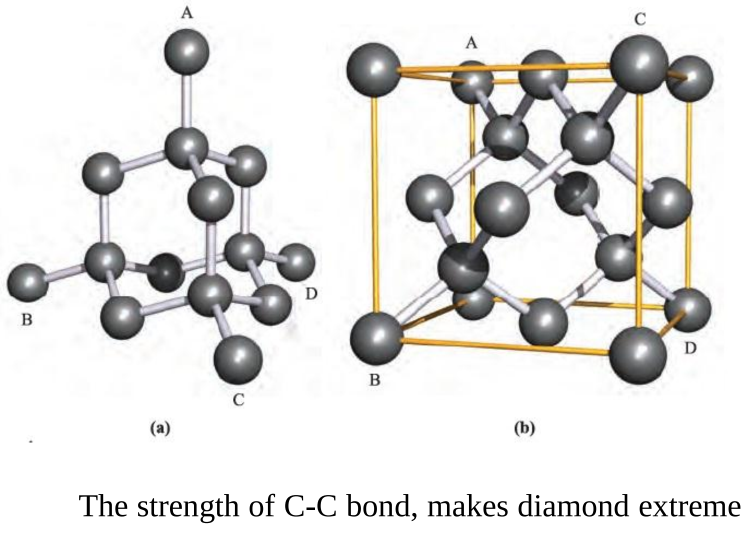


Figure 7.[1] a) Atomic arrangement of carbon atoms in diamond b) Diamond unit cell.

*Catherine E. Housecroft, Alan G. Sharpe, *Inorganic Chemistry*, 2nd edn, Pearson Prentice Hall, 2005

The strength of C-C bond, makes diamond extremely hard and involatile.[2] Some of diamond physical properties are summarised in Table 1.

Table 1. Some properties of Diamond[2, 3]

Density	3.514 g cm^{-3}

Hardness	10 Mohs
Melting Point	4100 ± 200 K (at 125 kbar)
ΔH_{subl}	710 kJ mol^{-1} (to monoatomic C(g))
Refractive index	2.41 (at 546 nm)
Band gap	580 kJ mol^{-1}
Resistivity ρ	$10^{14} – 10^{16}$ ohm cm
$\Delta H_{combustion}$	395.41 kJ mol^{-1}
ΔH_f^o	1.90 kJ mol^{-1}

Extreme mechanical hardness (ca. 90 GPa) and wear resistance

Bulk modulus	(1.2×10^{12} N m^{-2})
Compressibility	(8.3×10^{-13} m^2 N^{-1})

Has the highest room temperature thermal conductivity (2×10^3 W m^{-1} K^{-1})

Thermal expansion coefficient at room temperature very low (1×10^{-6} K)

Broad optical transparency from the deep ultraviolet to the far infrared

Highest sound propagation velocity (17.5 km s^{-1})

Very good electrical insulator (room temperature resistivity is *ca.* 1013 Ω cm)

Diamond can be doped, becoming a semiconductor with a wide bad gap of 5.4eV

Very resistant to chemical corrosion

Biologically compatible

Some surfaces exhibit very low or ‘negative’ electron affinity

Diamond is extracted in mines from all around the world. Diamond mines were first discovered in India and Borneo, since 18th century mines have been located in South Africa, Brazil, Russia, etc. Nowadays the greatest sources are mainly in Botswana, Russia, Canada and South Africa.[4] Due to its outstanding properties mentioned before, diamond has a lot of possible applications, but because of its scarcity and high price, natural diamond cannot be used in all the applications wanted. For this reason, researchers’ aim is to synthesize cheap diamond on an industrial scale.

The main difficulty of synthesize diamond is its thermodynamic metastability under low pressures, and for this reason, diamond was first synthesized under conditions where it is the more stable thermodynamic allotrope.[9] General Electric was the first company to obtain synthetic diamond in 1955. As diamond is the densest carbon form, it is therefore the most stable allotrope under high pressure. This was the basis for the method used by Robert Wentorf's group. They mimicked the way in which diamond is made in nature; using High Pressure and High Temperature (HPHT process). During several years this has been the unique way to produce diamond, but has remarkable disadvantages; it is a very expensive process to carry out due to the large amount of energy needed to reach high pressures and temperatures.[5]

Is very difficult to exploit the properties of the both natural and HPHT synthesized diamond, this is because yield stones or grit. A diamond thin film was needed to exploit its properties. In the late 1960s a new method to synthesize diamond was developed: Chemical Vapour Deposition (CVD).[3]

2. Chemical Vapour Deposition

Chemical Vapour Deposition is a chemical process which involves a gas phase chemical reaction on a solid and hot surface, with deposition onto this surface. The substrate is exposed in a close chamber to the activated gas mixture and the diamond layer is formed. The resultant products of this process are high-quality films (with high purity). The solid layer properties vary depending on the conditions. Different parameters lead to different solid forms; single crystal, polycrystalline and epitaxial growth are possible. Reactor type plays a very important role in the deposition, as do temperature, pressure and mixture composition. In order to increase the growth rate, enhanced processes have been developed; plasmas, ions, photons, lasers, hot filaments, combustion reactions, etc. Despite of the large amount of applications and the advantages of the method, cannot be used in all applications wanted for different reasons: the reaction cannot be carried out either because the substrate cannot withstand the high temperatures in solid phase, has a high thermal expansion coefficient with the consequent break stresses when is cooled down again or the reaction produces hazardous by-products. The precursor has to be volatile (and better if not dangerous or explosive). The semiconductor industry has been using CVD for years (in silicon-based microelectronics) being the main field where CVD is used, but also CVD has applications in coating for wear and corrosion resistance in tools, more recent applications have been found in optoelectronics (solid state lightning using light emitting diodes, LEDs), microelectromecanic structures (MEMS) and of course in nanotechnology, what started recently to have great interest.[8] Another application being developed (with some market applications already) is diamond synthesized by CVD, and it is the main subject of this work.

3. CVD Diamond

Instead of duplicating nature's method of diamond formation, in diamond made by CVD, carbon atoms are added one at a time to an initial surface. Lower temperatures and much lower pressures are needed and, consequently, CVD has advantages over HPHT in terms of equipment and energy costs. Another advantage is the possibility of growth good quality diamond onto non diamond surfaces, very useful for several applications.[6] Under CVD conditions, diamond is not the most stable allotrope of carbon. To obtain diamond instead of graphite (most stable allotrope of carbon under these conditions), etching-deposition rate control is necessary. That is, etching rate for non-diamond species has to be higher than the deposition rate and the opposite for diamond; for which etching rate has to be lower than deposition rate. To get this, oxidant reagents can be added to the mixture, since graphite and other non-diamond species are easily oxidised while diamond is chemically very stable and non-reactive. Hydrogen atoms are also useful as purifying component in the "cleaning" process. The latter is the most used because the selectivity of hydrogen atoms etching on graphite.[9]

3.1. Procedure

There are different types of processes to obtain a diamond thin film by chemical vapour deposition, but all of them have some similarities and elements in common;

i. Substrate, can be metallic, ionic or covalent solid but have to stand the high process temperatures without melting (1000-1400K), must have a low thermal expansion coefficient since diamond has one of the lowest (Table 1). If the substrate contracts much more than diamond, when it is cooled down, the diamond layer can break or bow the sample. Also is helpful that the substrate is able of forming a carbide layer to act as "glue", it not if the carbon reacts very favourably with the substrate (e.g. iron, cobalt, etc.) and dissolves in it.

According to carbon-substrate interactions, substrates can be divided into three main groups:

  a) Little or no solubility or reaction with C. Diamond does not adhere well to the substrate surface and is usually flaked. Examples are Cu, Pb, Ag and sapphire.
  b) Substantial mutual solubility with C. Often Diamond growth starts after substrate is saturated with carbon. Examples are Pt, Fe, Ti.
  c) Substrate forms a carbide layer. This is the ideal case. The carbide layer is thin and helps diamond to growth and to stay “stuck” to the substrate. Examples are Si, W, SiC, etc.

The most used substrates are single crystal silicon wafer and tungsten.[3, 6]

ii. Gas precursor chemical reagent, a rich carbon gas, typically methane, but also acetylene has been proved to be effective.[7] This gas is in low concentration (1%) mixed with hydrogen. Sometimes other compounds are added to the mixture, nitrogen even in small quantities to help the nucleation process and oxidizing reagents to help in graphite etching.

iii. Activation source. The gas containing precursor molecules are activated in order to react with the substrate. There are several means of transmitting the energy needed in order to activate the gas; thermal (hot filament), electric discharges (DC, RF or microwave) or combustion flame (oxyacetylene torch).[11] Plasma and microwave plasma activation has now become the most utilized activation method (thermal activation used to be the more popular).[10]

At the end of the process, a diamond thin film is obtained. Growth rate, surface morphology (roughness) and quality can be evaluated and are dependent on the process’ conditions. The quality, which is a subjective concept, can be evaluated by measuring properties as crystallinity, sp^3-sp^2 ratio and C-H vs. C-C. Quality of the film and growth rate is usually inversely proportional related variables. When growth rate is increased normally at the expense of lose quality.[6]

The process can be summarised as follows; a gas mixture with the precursor gas in a mixture with hydrogen is introduced into the reactor chamber, then activated by the activation source, transported through the reactor by convection and diffusion and finally is deposited onto the substrate surface (which is heated). With these bases, different reactor types have been developed;

3.2. Hot Filament

Hot Filament CVD (HFCVD) is the simplest method and one of the most popular. This belongs to the group of methods where thermal activation of the precursor molecules is carried out by a hot filament.

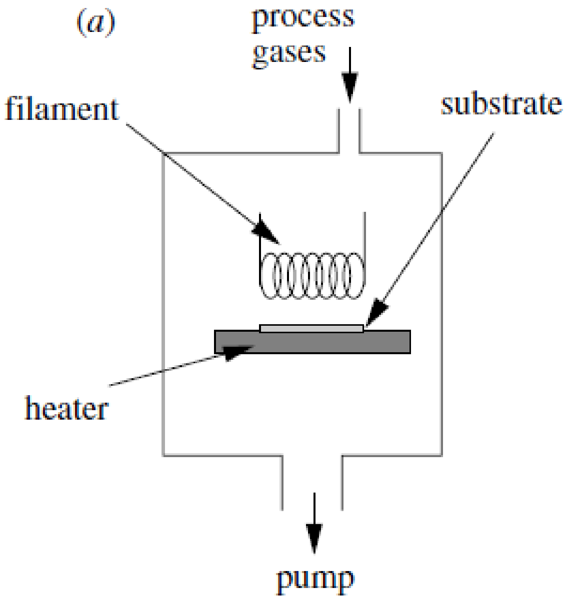


Figure 8. Scheme of a hot filament chemical vapour deposition reactor.[3]

Gas mixture is pumped in the reactor chamber with a continuous flow, maintaining 20-30 torr pressure; the heater keeps the substrate between 700-900ºC. The hot filament is electrically heated up to temperatures of 2200ºC. The hot filament has to resist these temperatures and be unreactive towards the components of the gas mixture. Tungsten is usually the material with the filament is made of; sometimes it reacts with the carbon compounds and forms tungsten carbide, this reaction is unwanted because it leads to short lifetimes of the filament and makes it brittle.

HFCVD is cheap and easy to carry out and yields good quality polycrystalline diamond with a growth rate between 1 and 10 micrometres per hour. However, has some disadvantages; the tungsten carbide formation mentioned before, diamond crystal can be contaminated with particles of the hot filament metal, making diamond obtained by this method, unable for electronic applications, which cannot be used with oxidising reagents due to hot filament is highly sensitive to oxidation.[3]

3.3. Microwave Plasma enhanced

Microwave plasma enhanced CVD (MWCVD) has become the most popular techniques for diamond growing. The conditions are similar to that of HFCVD, and the pressure is low as well. The activation of the precursor molecule is produced by electric discharges. Microwave power source is coupled to the reactor. Microwave discharge of 2.45 GHz produces electron collision with the gas, heating and dissociating it and therefore active molecules are generated to deposit onto the surface.

NIRIM and ASTEX type reactors are two of the most popular reactors. The power of the source is around 5 kilowatts. MWCVD methods are cleaner than HFCVD and gas mixture can contain oxidising molecules such as oxygen, fluorine or chlorine. Growth rates given by these methods exceed 10 µm h^{-1}.

Plasma jet, arc jet or plasma torch methods have been suggested as methods to substitute low pressure methods, allowing much higher growth rates. Pressure varies from 100 torr to 1 atmosphere.[3]

3.4. Oxyacetylene torch CVD

In this system, acetylene is mixed with oxygen in higher concentration in order to have a rich carbon compounds concentration in a region when the substrate is placed. Oxyacetylene CVD is simple in terms of equipment, is carried out at atmospheric pressure, and cheap. Growth rates of 200 µm h^{-1} are achieved. Disadvantages of the method are the production of non-diamond concentration in layers and the limited substrate area which can be coated, this is the reason for the low popularity of this method.[3]

4. CVD Diamond types

Different types of diamond crystals are obtained depending on some parameters. To predict the different morphology, electronic properties and mechanical properties of diamond crystals, the understood of growth mechanism is needed. The parameters which govern the formation of one type of diamond or another are mainly three: substrate temperature, gas mixture and process pressure.

Substrate temperature is usually above 700ºC. Methane concentration in the gas mixture is ~1% vol. Increasing the methane concentration leads to faster growth but with smaller grain size and quality, and vice versa. Also the presence of molecules like nitrogen or oxygen in the mixture, even in parts per million, increases the growth rate as a result of a better nucleation process. Process pressure depending on the method can vary from 20 torr to one atmosphere. Another parameter which affects the diamond is the reactor used to carry out the reaction.[12]

The different types of CVD diamond that can be synthetized can be categorised by the morphology and grain size of the crystal. The grain size varies from a few nanometres to millimetres. Four main groups are used to classify diamond thin films based on the grain size: ultrananocrystalline (UNCD) 2-10 nm, nanocrystalline (NCD) 10-1000 nm, microcrystalline or polycrystalline (MCD or PCD) 1-100 µm and single crystal diamond (SCD) > 0.1 mm. Each, requires different reaction conditions.[11]

UNCD has a grain size smaller than 10 nm; Due to the small grain size, roughly 10% of the carbon atoms are at the grain boundaries. It is synthesized using gas mixtures of 1% methane in argon adding a small quantity of hydrogen ~1-3%. Process pressure used in this process is higher than for the microcrystalline diamond; 100-200 torr in a hot filament reactor. The thermal conductivity of Argon is much lower than that of hydrogen. For that reason plasma is formed easily, allowing the CVD growth at lower temperatures down to 400ºC.[11] UNCD growth is dominated by C atoms adding to monoradical sites (they keep reacting on the surface forming defects).

Nanocrystalline diamond is synthesized in similar conditions as MCD but with higher methane concentration up to 5% vol. exhibit a columnar growth. The roughness and grain size increase with layer thickness. Growth is dominated by CH_3 addition to biradical sites, and it is higher than for UNCD

Microcrystalline diamond was the first type of diamond synthesized by CVD. It is synthesized by mixtures with methane concentration of 1% in hydrogen with low pressures. Growth is mainly dominated by reaction of CH_3 onto both biradical and monoradical sites.

Single crystal diamond is synthesized in order to avoid worsening of properties that appear in diamond with smaller grain size due to grain boundaries. It can be used for jewellery as well with a lower price. SCD can be grown in high power MW plasma enhanced CVD reactor with a mixture of 1-12& CH_4/H_2, sometimes with small additions of N_2 or O_2. Growth is “only” dominated by CH_3 reactions with monoradical sites due to the high hydrogen atoms concentration.

4.1. Characterisation

Raman spectroscopy is one of the most popular methods of studying diamond and in general any carbon-based material. The diamond structure has high symmetry and has a single peak in Raman spectroscopy in Brillouin zone at 1332 cm^{-1} Raman shift. This peak is corresponds to the T_{2g} mode due to Carbon-Carbon stretching.[13]

In nanocrystalline diamond more peaks have been observed but are not well assigned. The peak close to 1150 cm^{-1} is likely due to polyacetylene type structures located at grain boundaries and interfaces. A broad peak at 500 cm^{-1} has been also measured; this peak is probably due to defects or surface reconstructions which increase as the surface-to-bulk carbon ratio increases. An ab initio study of nanocrystalline diamond particles with T_d symmetry up to 1 nm size was made in order to explain changes in the Raman active optical phonon frequency with particle size.[12] Hartree Fock and B3LYP were the theories utilised. The study showed three parts in the spectra: A breathing mode/cage deformation with frequency up to 500 cm^{-1}, a broad mixed C-C stretch and C-H bending modes between 1000-1400 cm^{-1} and a high wave number C-H stretch region. D and G peaks at 1370 and 1550 cm^{-1} are due to sp^2 carbon atoms, and becomes more prominent as the particle size decreases.[11] Raman spectra of hydrogen terminated diamond nanoparticles are very different from crystallites confined within a matrix of amorphous carbon. However no relationship was found between the 500 cm^{-1} and 1150 cm^{-1} peaks and nanocrystalline diamond structure, and therefore, it was suggested that these peaks are due to defects, surface structures or non-diamond material.[13]

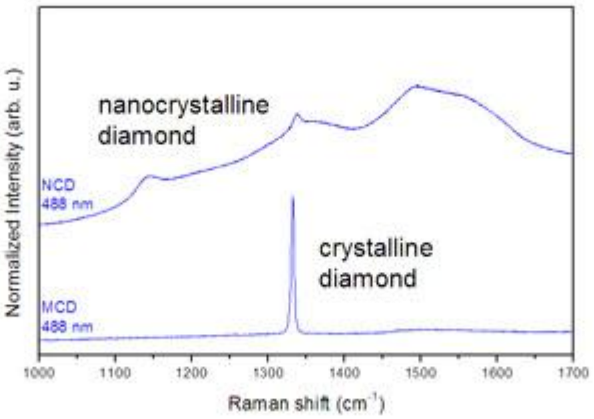


Figure 9. Raman spectra of crystalline diamond with a single peak at 1332 cm-1 and nanocrystalline diamond. Keeps the diamond peak (attenuated) and shows new peaks due to defects and sp^2 carbon atoms.[29]

5. Applications of CVD Diamond

Due to diamond's superlative properties and the improvement of the CVD techniques (higher growth rates and better qualities are being achieved) CVD diamond has already market applications; CVD Diamond is now relatively cheap, and much cheaper than natural diamond.

One application for diamond is obviously in jewelry as substitute of natural diamond; CVD diamond is indistinguishable from and has the same properties as natural diamond. It is much cheaper and can be synthesized colored for example yellow by adding nitrogen atoms or blue by boron atoms.[30]

Due to its hardness, diamond can be used for example in cutting tools, by coating the diamond onto the surface of tungsten carbide tools. Tools coated with diamond have long life, cut fast and with good finish. The problem for some applications is the reactivity of diamond with ferrous materials, so diamond cannot be used to cut iron or steel. It has been used also to coat tungsten wires and tubes making them stiffer and stronger than the uncoated ones. Hollow diamond tubes can be made by dissolving chemically the metal (diamond is stable to the reaction with oxidizers) after the deposition.[27]

An optical application for CVD diamond is its use as antireflecting coatings due to the low coefficient of absorption in the IR spectrum and to erosion and corrosion resistant coatings for infrared optics.[9]

Due to its high thermal conductivity, CVD Diamond is used in devices to spread the heat flux by placing a layer of diamond between the device and the cooling system.

As a result higher speed operation devices can be made and can be more tightly packed without overheating.[3]

Diamond doped with boron can be used to make p-type semiconductors.[28] However is very difficult to make n-type semiconductors due to close packing of diamond, P or As which are the usual dopants for silicon devices, are too big to dope diamond. Research is being done to dope with Li to obtain n-type semiconductors.

Due to its properties, CVD diamond is thought to have many future applications. For example in electronics, by doping the diamond can be changed from an electrical insulator to a semiconductor. However there are some problems such as the large amount of defects in polycrystalline diamond, and the close packing and rigidity of the diamond lattice makes doping with big atoms like Silicon, Phosphor or Arsenic very difficult.

Further potential applications of CVD Diamond can be found in quantum computing, biosensing, thermo ionic solar cells and others. But they are not expected on a short timescale.

6. Growth mechanism

The exact growth mechanism of CVD Diamond is not well known at the moment. Several studies have been made in order to understand the diamond growth and then, control the parameters to get higher growth rates with better film quality. To study the diamond growth, spectroscopic, kinetic and computational methods are used together. When a mechanism is proposed, simulations are made in order to probe the growth model. If it is valid, then the program will reproduce accurately the features of diamond layer (growth and morphology) under the same conditions as the experiment.

6.1. Standard Growth Mechanism

One of the most accepted mechanisms is the Standard Growth Mechanism (SGM) and it was developed in the early 90’s by Butler, Woodwin et al.[14] SGM is a robust description of the CVD process.

First of all, the gas mixture is pumped into the reactor and is activated. Then it is ready to react onto the surface's substrate. The hydrocarbon compound (typically methane) is mixed in 1% with excess hydrogen as mentioned before. Mixture activation (either thermal or plasma activation) consists in dissociation of hydrogen molecules into hydrogen atoms (1-40%). Hydrogen atoms are precisely the driving force for the process according to SGM theory; they are responsible for hydrogen abstraction on the diamond surface (it is this reaction which dominates the mechanism and the kinetics of the reaction) letting CH_3 radicals to adding to the surface. The hydrogen atoms also etch back into the gas phase any non-diamond species adsorbed onto the surface, for example graphitic carbon. CH_3 radicals are believed to be the main growth species, adding to the diamond surface. The main reactions are:

$$H_2 \rightarrow 2H\cdot$$

$$H\cdot + CH_4 \rightarrow CH_3 + H_2$$

$$C_d\text{-}H + H\cdot \rightarrow C_d\cdot + H_2$$

$$Cd\cdot + CH_3 \rightarrow C_d\text{-}C_dH_3 \quad \text{(following H abstraction by H}\cdot\text{)}$$

Here we see the importance of hydrogen atoms in the CVD process, and the methane radical as the growth species. Other CH_y species (with $y = 0 - 2$) can contribute to the diamond growth but are not as important as CH_3 and therefore are not taken in account in this method.[14]

Reactions between monocarbon species to form dicarbon species are not very common due to the low concentration of hydrocarbon molecules into the gas phase. Actually, when acetylene is used as carbon containing compound instead of methane, CH_3 radical concentration near to the substrate surface has been measured to be similar to that when methane is used as the precursor molecule. This CH_3 formation is dominated by gas phase chemistry.[15]

$$C_2H_2 + H \rightarrow C_2H + H_2$$

The SGM generic model demonstrates that the fraction of radical sites is only a function of temperature. The growth of adsorbed hydrocarbons into the lattice depends on the atomic hydrogen flux, and diamond growth is limited by H abstraction at low temperatures and by thermal desorption at higher temperatures. Finally it says that the film quality is proportional to the hydrogen flux and inversely proportional to the reactive hydrocarbon flux as was stated before. This model does not take in account the stereochemistry of the surface.[14]

This theory successful predicts some of the general features of morphology, as well as predicting growth rates to within an order of magnitude. But on the other hand SGM cannot predict the crystallite size for a given conditions and does not incorporate mechanism for nucleation of a new layer. New mechanisms based in SGM have been proposed in order to solve these limitations.

6.2. University of Bristol Growth Mechanism

Paul May's group at University of Bristol developed a modified mechanism of SGM for CVD diamond.[12] Reaction of all hydrocarbon radical species with one carbon atom are considered CH_y ($y = 0$-3) on monoradical and biradical sites. Only mono-carbon radical species are considered, since it has been proved that C_x, $x > 1$ species are not important in the diamond growth.[17] The growth model also relies upon surface migration of CH_2 groups along and across the reconstructed dimer rows. The growth depends on hydrogen atoms and radical (CH_y) concentrations; they compete for reaction at the diamond surface. The UoB growth model is able to predict growth rates to within a factor of two of experimental observations and also the crystal size predicted by the model is in very good agreement with the experimental observations. From this model are derived expressions for the fraction of surface radical sites based upon the substrate temperature, T_S, and the concentrations of H and H_2 above the surface.

The mechanism of diamond growth is not a simple one-step mechanism; there are several steps, constituent parts which together can explain the growth. The following are the most important events in the diamond growth:

- **Growth from CH_3**. In CVD Diamond growth, all radical C_1 species compete for reacting with the substrate surface. Under regular conditions, CH_3 radical is the most abundant species. CH_3 can add either to monoradical or biradical sites (biradical sites are ten times less abundant than monoradical under normal conditions, 12% and 1.4%[18]). When it adds to a biradical site, the growth rate is proportional to the flux of diamond precursor at the substrate, and reaction to form a bridging CH_2 group occur before desorption. When CH_3 is added to a monoradical site, CH_3 desorption rate is comparable with H abstraction rate. High [H] will favour monoradical pathway, and therefore single crystal diamond, while biradical way favours the renucleation and therefore yields small grain size diamond.[16]

- **Growth from CH_y (y = 0**-2). Under high filament temperatures and in MW PECVD reactors (at 700K), carbon atom concentrations can be even higher than CH_3 concentration near the surface. These radicals can react via both monoradical and biradical sites, the adduct remain active once react onto the surface and can react again with the surface producing surface defects by cross-linking which can act as a renucleation point.[16]
- **Renucleation of a new layer**. CH_2 can migrate along and across the dimer chains and a new nucleation point for the layer is produced when surface hydrogen react with another migrating CH_2 group.[16]
- **β scission**. This process avoids the building of polymer chains on the surface. It takes its name because the bond is broken in the second carbon atom of the chain (carbon β). Ethylene molecule is etched back into the gas phase after β scission, and a radical is formed in the surface carbon atom. This process is highly efficient, rapid and costs low energy.

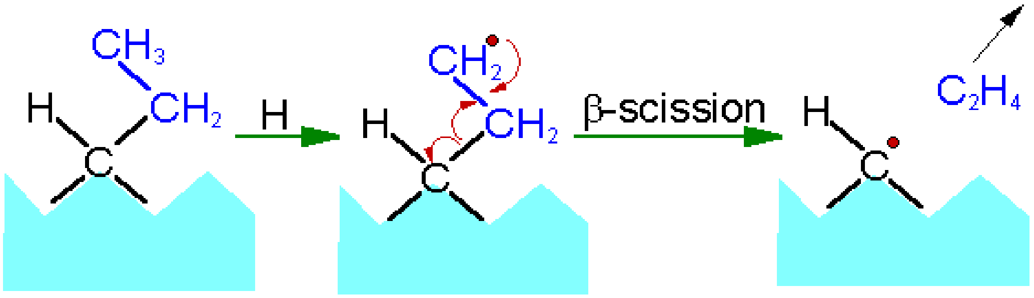


Figure 10. β scission reaction removes long chain atoms C_xH_y ($x \geq 2$) from the diamond surface.

Recent study has evidenced the low impact of β scission in the diamond growth.[12]

Larger grain sizes are obtained at higher [H]/[CH_y] rates. We can conclude that grain size < d > and morphology of the film are function of H, H_2, CH_y concentrations, the probability of renucleation and deposition conditions. In addition to this, diamond growth is affected also by other external reagents present in the initial mixture.

- **Nitrogen**. The presence of Nitrogen in the gas mixture (C:N 1:1) increases the film quality and larger growth rates, however, Nitrogen doping is very ineffective; there are only very small amount of nitrogen in the resultant diamond film after the reaction. This suggests a mechanism based on deposition and successive etching of nitrogen. At high temperatures, nitrogen addition leads to higher growth rate but with worse film quality. This is because to N_2 can catalyse the reaction of hydrogen molecules decomposition and, therefore, the etching of non-diamond substrates on the surface is not so effective.[19]
- **Phospine**. Like nitrogen, phosphine added to the gas mixture increases the growth rate (2 or 3 times with a concentration of 2000ppm PH_3). PH_3 changes the crystal morphology in favour of (100) and at higher concentrations it changes again to (111) faceted crystals. Phosphorous currently is too big to introduce into the tightly packaged diamond lattice, so cannot be used as a dopant in semiconductor industry.[20]

7. Modelling

No direct experimental evidence of the growth mechanism can be obtained; a mechanism can be accepted because it explains and predicts growth features well or can be rejected if it does not. Computational methods are typically the best to study the mechanisms of CVD diamond growth. Several studies made by the University of Bristol group or others use computational simulations in order to explain and understand better the growth.

The most popular computational methods to study the CVD diamond growth are Molecular Dynamics (MD), Monte Carlo (MC) and Kinetic Monte Carlo (KMC). These methods are explained in the next pages.

7.1. Molecular Dynamics[25]

Molecular Dynamics (MD) methods are based in the generation of a trajectory in the space. The trajectory generated depends on the initial state of the system, both coordinates and velocities according to Newton’s second law by a series of finite time steps. A typical time step is ~10^{-15} s and a simulation involving 10^6 steps thus “only” covers ~10^{-9} s. This is substantially shorter than many important phenomena, like the considered in this work and MD methods, in analogy with MC, tend to only sample the region in phase space close to the starting condition. Furthermore, MD methods simulate the physical evolution of configurations and can easily become trapped in energy wells.

7.2. Monte Carlo[25]

The analysis of potential energy surface by locating the minima and saddle points corresponds to modelling the system at a temperature of 0 K. In this point all the vibrational, rotational and electronic levels are in the ground state. This can be a good method to evaluate the energy of some systems, for instance ideal gases, taking in account the rotational partition function for a single molecule. Crystalline solids can be very well described because the properties of the unit cell are the same in the entire solid (translational principle). The electronic structure methods do this task by solving the Schrodinger equation. On the other hand, most of the real systems in chemistry and biology are liquids and solutions, their behaviour cannot be described as them in the ground state, in such systems, interactions between particles and solvent that cannot be ignored. Macroscopic properties must be estimated from a representative sampling of the phase space. Simulations methods try to obtain a representative sampling of a system at a finite temperature. The Monte Carlo method is useful to describe the interactions between solute and solvent.[22]

The two main techniques to generate an ensemble are Molecular Dynamics (MD) and Monte Carlo (MC) methods, the latter being the most important in this work. Monte Carlo methods[23] are based on the random change of configuration of a molecule. Then the energy of the resultant configuration is evaluated, two different things can happen;

- The energy of the modified conformation is lower than the energy of the starting conformation. In that case this conformation is chosen as starting point for the next step
- The energy of the modified conformation is higher than the energy of starting conformation, then a random number ‘P’ between 0 and 1 is generated and

compared with the Boltzmann energy $e^{-\Delta E/RT}$, another two possibilities spring up here

- If $P < e^{-\Delta E/RT}$, the new structure is accepted and is the starting point for the next calculation
- If $P > e^{-\Delta E/RT}$, the original molecule is the starting point for the following calculation

The configurations obtained by this Metropolis procedure[24] obey a Boltzmann distribution. Atoms are spherical particles, so in a system of atoms, centre of mass of each particle are the only variables.

A simulation can be characterized by properties such as Pressure (P), Volume (V), total Energy (E), Temperature (T), Number of particles (N), chemical potential (μ), etc. but not all of them are independent. Monte Carlo simulations are NVT type, that is, number of particles, volume and temperature are constant. This is called “canonical”, and in the equilibrium state, the Helmholtz free energy is at a minimum.

Hybrid MC/MD methods have been developed in order to exploit the best of each method. These typically perform a MD simulation with an occasional MC step.[31,32]

7.3. Kinetic Monte Carlo[26]

KMC is a simulation method, again using random numbers.

Metropolis algorithm was developed in 1950s in Los Alamos laboratory when the first computers appeared. This method is based in calculate geometries energy by moving one atom at a time (see above).

KMC simulations were used for the first time in radiation damage annealing. It can be used as well in surface absorption, diffusion and growth of atomistic systems but also in statistical physics. KMC is a powerful method which can give sometimes, under certain conditions the exact dynamical evolution of a system (know all possible reactions and their rate constants is needed).

MD simulations have the “time-scale” problem. That is, accurate integration requires time steps of 10^{-15} s, short enough to solve atomic vibrations. That make the overall time of a MD simulation not longer than one microsecond. Some studies have focused on processes which take place on much longer time scales than 1 microsecond; in these kinds of processes KMC simulations are used: KMC does not follow particles' trajectories, but treat directly step to step jumps (long time dynamics). That led to time steps even longer than one second. Infrequent events studied are occasional transitions and take a long time usually, relative to the time of a vibrational period (amount of time taken in a MD time step).

Solid state systems can be described as systems in which each state has a single energy basin. It takes a long time between transitions because system has to surmount the energy barrier among states. In these systems all the entire state is moved to a new state (not individual particles).

For each escape pathway from one system i to another j, exists a probability per unit of time given by the constant k_{ij}, the value of this constant is depends on the potential energies of the systems i and j and on the energy of the activation barrier. Transitions to one step to another only depend on the rate, k_{ij}. When a system is in one state, it does not matter in what state was before (the way it reached the state).

For each pathway to go from one state to another exist an exponential first-escape time distribution.

$$p_{ij}(t) = k_{ij}\exp(-k_{ij}\,t)$$

The overall rate of a system to scape to another state is given by the sum of every single constant.

$$k_{ij} = \Sigma k_{tot}$$

KMC needs a random number generator to work. The interval of the numbers generated have to be (0,1).

To design a KMC program, (stochastic algorithm from state to state) all rate constants for each process have to be known. The procedure is the following: the rate constants for each process are summed and ordered in a array $s(j) = k_{1,}\ k_1 + k_2,\ k_1 + k_2 + k_{3,\ldots,}\ k_{tot}$ $s(j) = \Sigma_q^j k_{iq}$. The total rate constant is obtained k_{tot}, then, a random number r is generated in the interval (0,1) and multiplied by k_{tot}, rk_{tot} is contrasted with the list of rate constants sums, the process stops at the first element for which $s(j) < rk_{tot}$, and this process j is carried out. If rk_{tot} is for instance, bigger than k_1 and smaller than $k_1 + k_2 + k_3$, then the process 2 will occur.

Rate constants can be calculated by different theories as Transition State Theory, Harmonic Transition State Theory or Arrhenius equation.

To summarize, Kinetic Monte Carlo simulations are very powerful; given a set of constant rates, KMC model can develop the system dynamically throughout the state space; the system will do first order arbitrary transitions between the different states. In solid state simulations, the states correspond to basins in the potential energy surface. KMC can give the exact evolution of a system state to state.

7.4. KMC model of University of Bristol

The procedure for the KMC program is first the creation of a diamond surface, then, the relevant processes and mechanisms are constructed. Ref. 12 proceeds as follows:

Carbon species (CH_3, CH_2, C_2H_2, etc.) were supposed to strike the surface randomly with a certain impact rate (given by temperature at surface, concentration and molecular mass). Some of the species adsorb to the surface with a probability known from experiment or other calculations.

This KMC simulation shows that migration is possible. The probability of Carbon species to jumping to a neighbour site depends on activation barrier and surface temperature, while the probability of carbon species bonding to the step edge propagating lattice depend on results of detailed calculation based upon: Modelling geometry, steric effects and kinetic data.

There are three different possibilities for the migration down a step-edge; i) species drops down to the bottom of the step edge and adds to the lattice (“lemmings”), the specie desorbs back into gas phase with bonds rupture (“eagles”) and the species stay where is and migrates back away from the edge (“Cowards”). These three reactions are governed by the Enrlich-Schowoebel potential (ESP). This is the barrier which the species in the edge must overcome to fall down a step-edge. To know which of these processes is the lowest in activation energy in the Diamond growth, ab initio calculations are carried out. In ref (12) argue that “cowards” is the best option for this migration, however in recent studies, better ab initio calculations were made and determined that “lemmings” are the best choice.[21]

For the nucleation of a new layer, an isolated CH_3 radical group adsorb onto a diamond surface without step-edges. This group has some possible fates. It can migrate across the surface, it can hop along and across dimer rows (CH_2 bridging group), and a migrating group can encounter a second carbon migrating randomly across the surface. This is the Langmuir-Hinshelwood mechanism (LH). If the second carbon species adsorb on a site adjacent to occupied by the first C and reacts with its neighbour the result is a C_2, in this case, we have an Eley-Rideal (ER) process. The latter C_2 is the seed for the nucleation of a new layer. According to this method, the minimum number of blocks to become unetchable and immobile is 4. A LH nucleation rate depends on the migration rate which depends on surface temperature, while the ER nucleation rate depends on the surface temperature as well but also on rate of CH_3 adsorption (sensitive to gas conditions near the surface).

Migrating carbon species can form an immobile surface defect if bond breaking and reforming during migration steps go awry. Some surface defects are etched back into the gas phase but others stay long enough to act as a nucleus for a new layer that is not likely to follow the orientation of the rest of layers. Other surface defects can be produced by adsorption of C atoms or CH radicals.

Several improvements of this method have been done in order to calculate better the growth rates and morphologies varying the conditions. The requirements for a good KMC model are:

- Not too long computational time. A very detailed model can spend most of the time calculating unimportant events.
- The essential kinetic parameters have to be known with precision (from experiments or other calculation). Activation barriers for migration, pre exponential factors for the Arrhenius equation.
- Knowledge of concentration of species near the surface (measured by spectroscopy)

Experimental part

Here the library part ends and starts the experimental part of the project. Experiments done and results are described in the next pages.

The computational work done is divided into two main parts, the first one corresponds to the simulation of CVD diamond growth using Kinetic Monte Carlo simulations and the second one involves energy calculations of diamond surfaces using Molecular Mechanics.

1. Kinetic Monte Carlo

CVD diamond growth has been simulated using Kinetic Monte Carlo program. A mechanism cannot be proved experimentally, that is the reason why computational chemistry is so important, a mechanism is accepted if can reproduce and predict the results of experiment for a given starting conditions, otherwise is rejected. In this program, variables are changed one by one in order to know how every variable affect to the growth. The most important results of the simulation are growth rate and roughness because are measurable in the experiments.

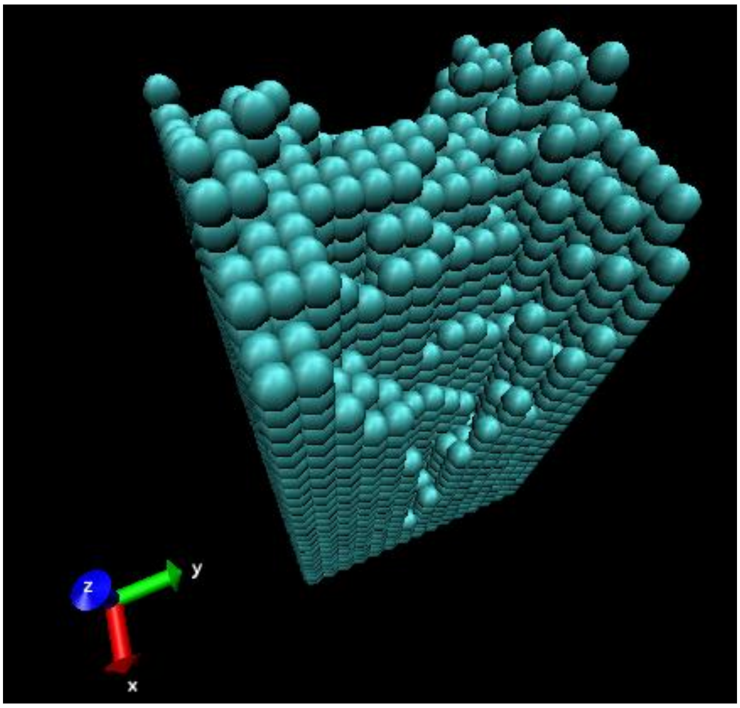


Figure 11 Visualisation of the diamond growth simulation. The initial state is a perfect planar surface, and is responsible of the time needed for growth rate and roughness to converge (higher for roughness).

1.1 The program

This KMC program was written mainly in Fortran language (also some parts in Bash and Phyton) by PhD student Jeff Rodgers.

The program contains one input file, input.txt, in which starting conditions are included:

- Activation or deactivation of 8 processes:
    - Surface activation, Surface deactivation, Addition, Etching, Adsorption activation, Adsorption deactivation, Migration, Beta scission
- Substrate temperature
- Gas temperature
- Concentration of different species near the surface:
    - [H], [H_2], [CH_3], [CH_2], [CH], [C]
- Steric and sticking factors of each species
- Grid size
- End time
- Step time

These conditions are fixed and the program is run, then output files are generated containing information of the simulation, visual images and the results. The main results of the program are saved in an output file, in that program are stored simulation data such as rates and times that every process happened (etching, migration, surface activation, Langmuir-Hinselwood process, Eley-Rideal process, etc.), also growth rate, total simulation time, average height, minimum and maximum height, and roughness. Only growth rate and roughness are taken in account due to they are the only parameters which can be measured experimentally.

1.2 Work done and results

The work done in this part of the project involves change one by one all parameters of the input file and check how each one affect to the two measurable parameters of the resultant diamond film, also find relationships of this experiment with the experiments described in the literature.

Description and result of each of these experiments are described in the following pages along with explanation of what each process means.

1.2.1 Substrate temperature

The first experiment made was change substrate temperature from 600 to 2000K with an increment of 100K. Every simulation was repeated three times for each starting conditions, and the values obtained averaged in order to get a statistically good value.

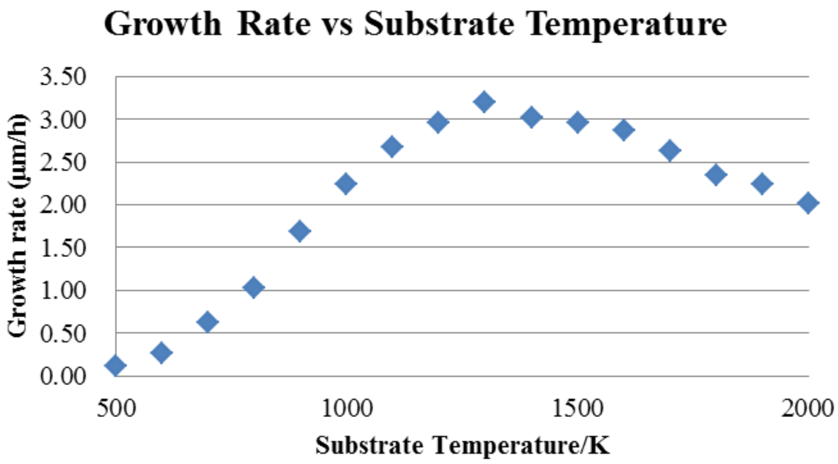


Figure 12 Change in growth rate with substrate temperature. The other variables are kept constant.

A maximum in substrate temperature is found around 1300K, the different processes which affect growth are arranged to make the growth the fastest possible at this temperature. This value despite depends in several more parameters, is in very good agreement with the experimental values obtained by other research groups:

1100-1300 K Chang et al.[39]

1370 K Baldwin et al.[40]

However, roughness stays more or less constant with substrate temperature,

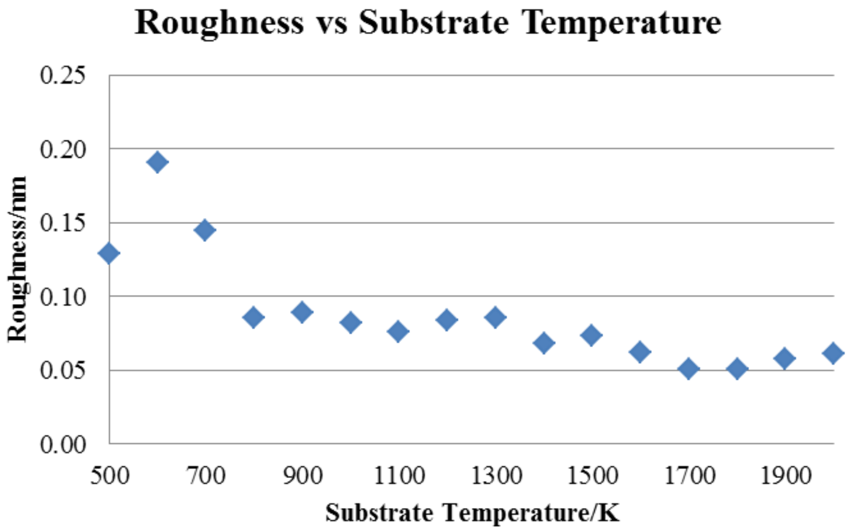


Figure 13 Change in roughness with Substrate temperature variation.

As can be seen, roughness is constant with substrate temperatures for temperatures higher than 800 K, for temperatures lower than 800 K there is no growth.

1.2.2 Gas temperature

The temperature of the gas where increased from 600 to 3500 K with 100 K steps,

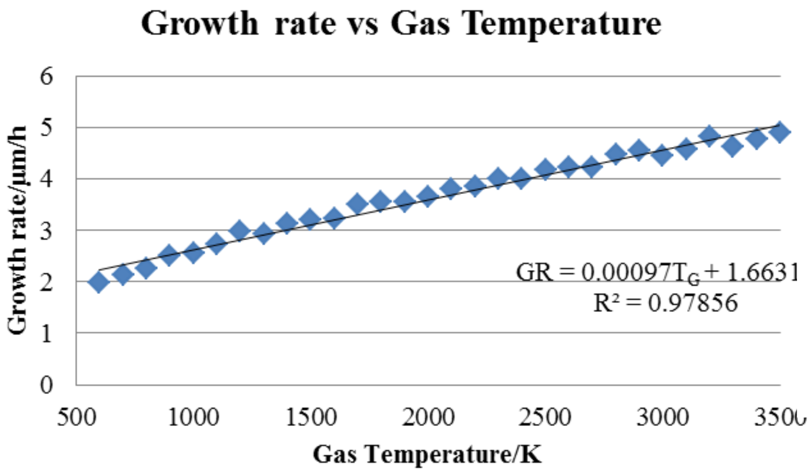


Figure 14 Change in growth rate when changing gas temperature, keeping the other variables constant. (substrate temperature 1173 K)

Growth rate increases linearly with gas temperature, probably due to higher impact rate of the gas against the surface, if the gas is hotter, moves at higher speed, and therefore collides more times per unit time onto the surface.

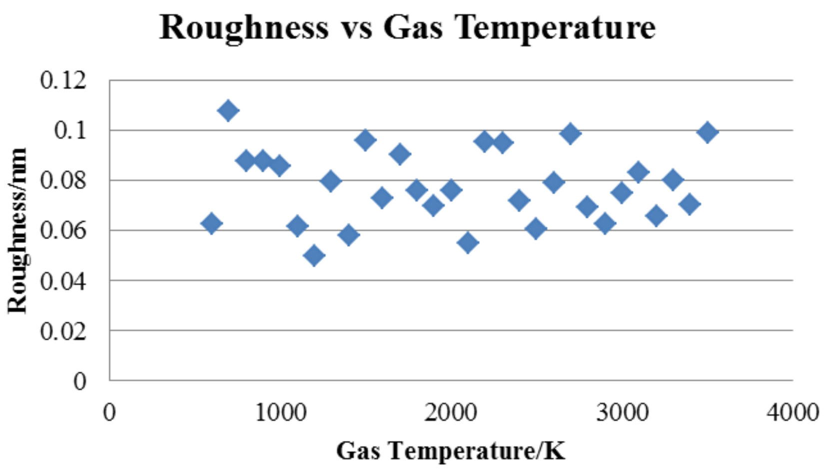


Figure 15 Change in roughness with gas temperature change.

On the other hand, roughness is random for gas temperature change, but is always kept among 0.5 and 0.11.

1.2.3 Deactivation of the 8 processes

Now the eight processes are deactivated one by one and gas temperature and substrate temperature are changed as in the last experiments to check the importance of these processes in the growth.

Surface activation and addition are essential for the process, if they are deactivated, any atom can join to the layer and therefore there is no growth. Deactivation of the other processes affect in different ways to the growth but they are not completely vital.

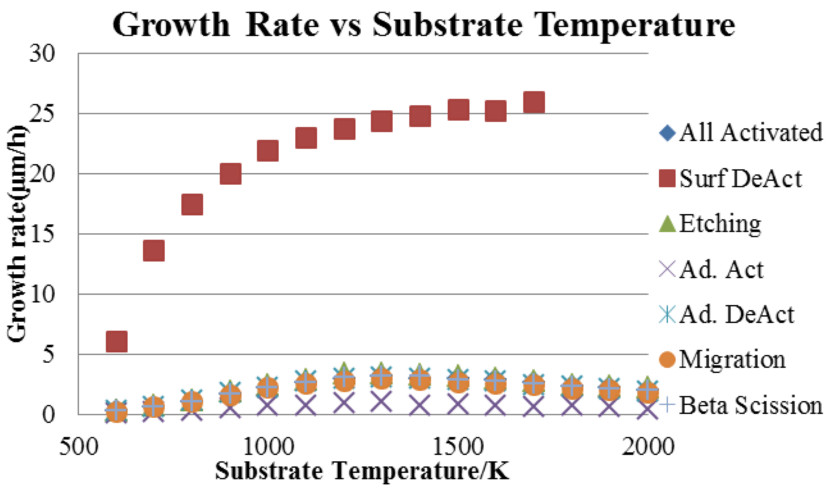


Figure 16 Change in growth rate when substrate temperature is changed for deactivation of different processes.

Surface deactivation plays a very important role in the growth as can be seen in the graph. Diamond growth is around 10 times bigger if there is no surface deactivation. Sites activated remain activated, do not react with hydrogen atoms any more. The growth when surface deactivation is deactivated has no minimum around 1300 K as in all the other cases, for that reason, can be declared that surface deactivation is the responsible of the lower growth rate for temperatures higher than 1300 K.

Adsorption activation is the other process which affects more to the growth rate, if is deactivated, growth rate decreases roughly to the third part.

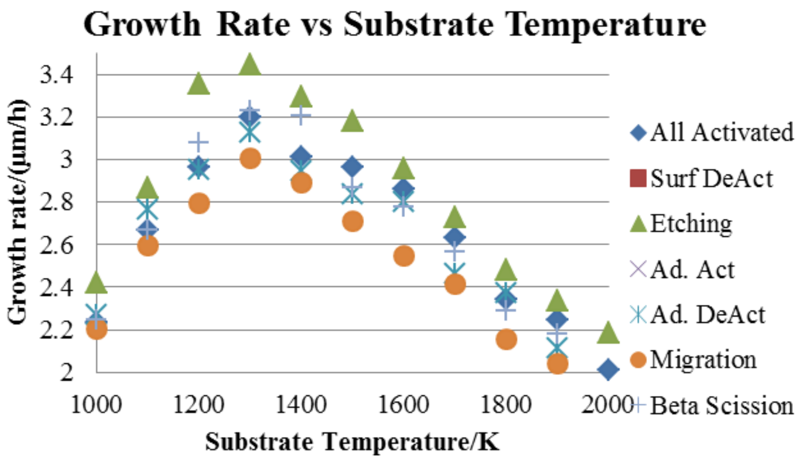


Figure 17 Change in growth rate when substrate temperature is changed for deactivation of different processes.

The other processes do not influence so much to the growth rate, but are still influent in it. For example deactivating etching, obviously growth rate increases, since all atoms added to the lattice remain joined to it.

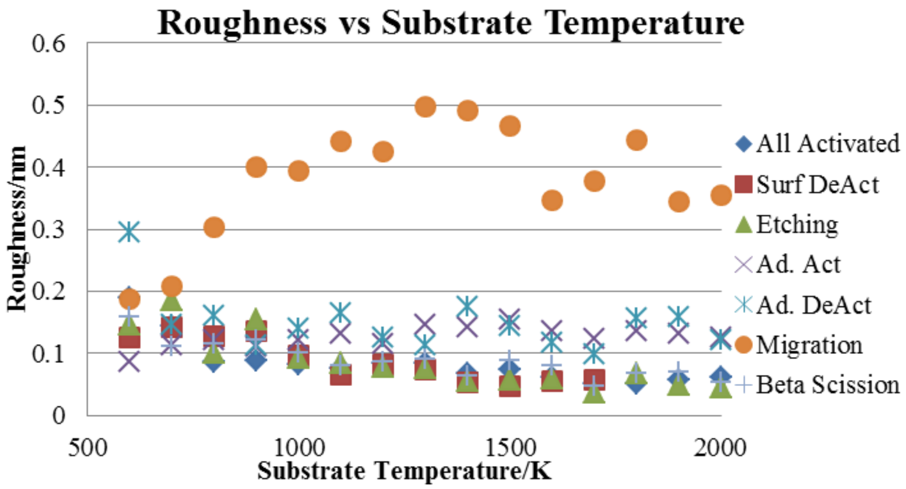
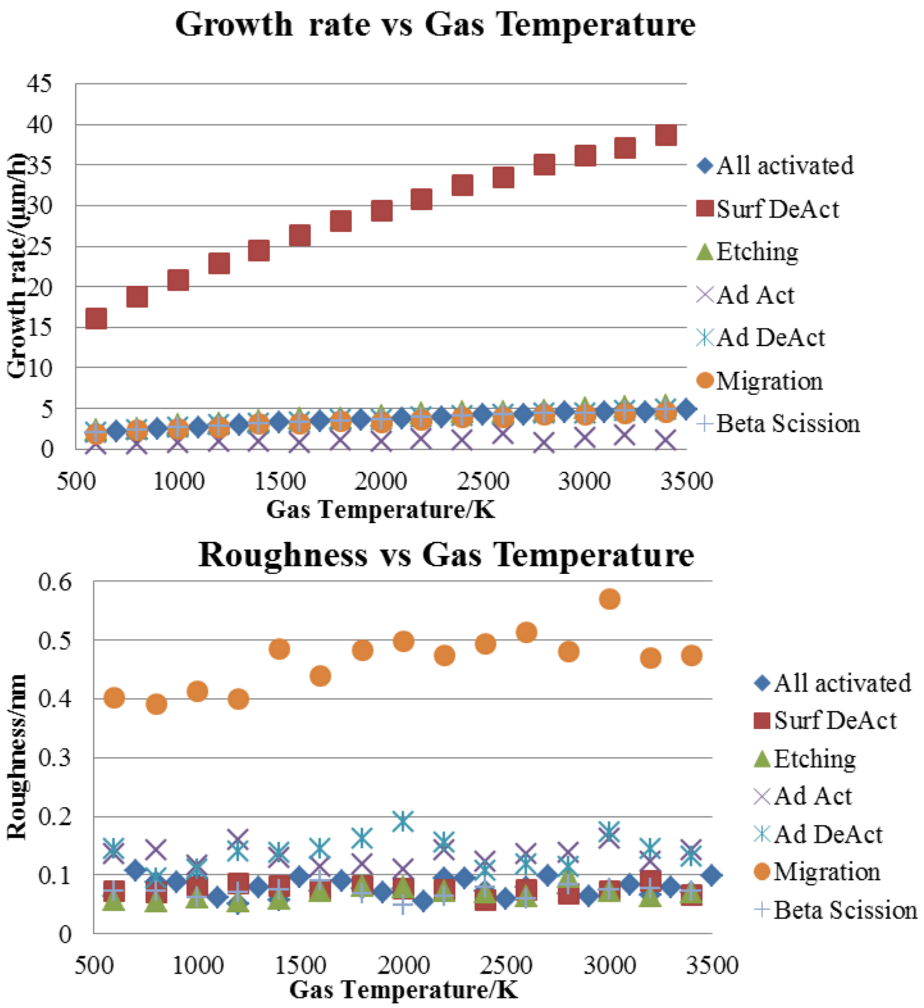


Figure 18 Change in growth rate when substrate temperature is changed for deactivation of different processes.

Roughness is more or less constant for all temperatures and for all deactivated processes except for migration. Roughness is around five times higher when migration is deactivated. The reason for that behaviour is the impossibility for the carbon units on the surface to migrate along the surface till they find another unit to join and to form an unetchable and immobile unit. In the case where migration is deactivated, then there are scattered units on the surface and each one is a nucleation point, the more nucleation points the more chances to produce defects and therefore, roughness increases.

Similar behaviour of growth rate is seen when gas temperature is changed.



<u>Figure 19 & 20</u> Change in growth rate and roughness when gas temperature is changed for deactivation of different processes.

Again, growth rate increases when surface deactivation is deactivated and roughness increases when migration is deactivated.

1.2.4 Concentration of species near the surface

The KMC program has the option to change some radical species near the surface, such as all monocarbon radical species, hydrogen atoms and hydrogen molecules. Variation in those concentrations affects the growth rate and roughness. Experiments were made for all monocarbon radical species and all results were similar, here only results for CH_3 radical concentration are showed.

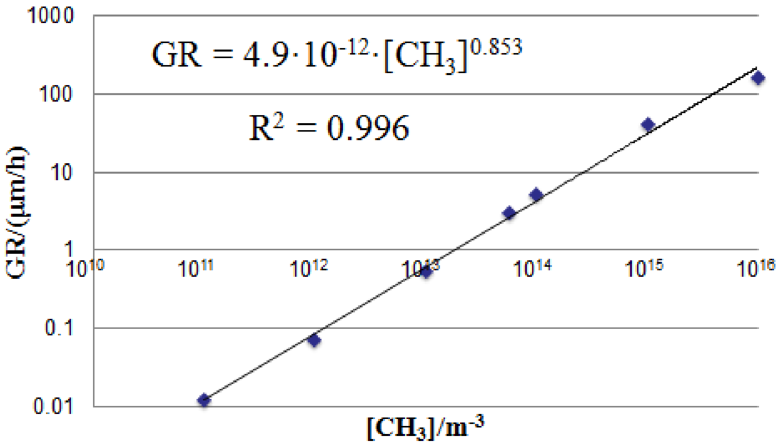


Figure 21 Change in growth rate with CH_3 radical species above the diamond surface.

Growth rate increases with radical concentration near the surface, the higher the radical concentration, the more the collisions against the surface and the faster the growth. Growth rate fit to this potential equation very well.

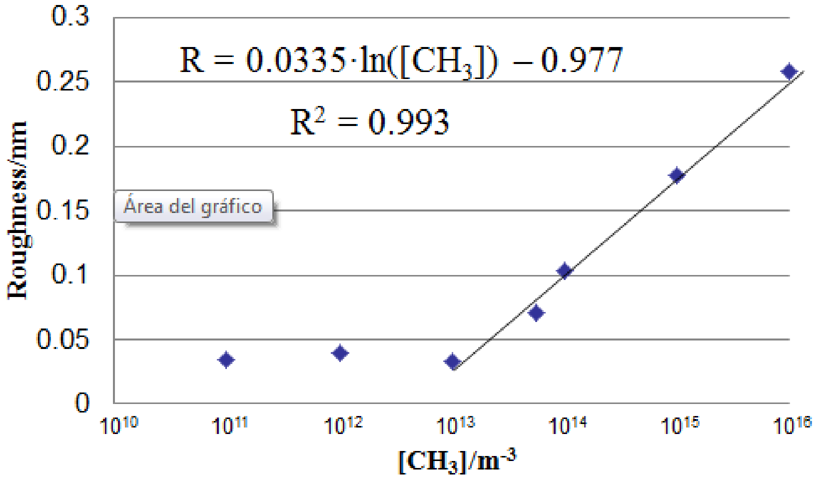


Figure 22 Change in roughness with CH_3 radical species above the diamond surface.

Similarly, roughness also increases when radical concentration near the surface increases. This time, roughness increment is logarithmic. Roughness is a measure of the deviations of our actual surface from a perfect flat surface, therefore can be said that quality of the film is inversely proportional to the rate of growth.

Parallel calculations were made for CH_2, CH and C radical. And the results were similar.

Hydrogen atoms and molecules concentrations were changed as well

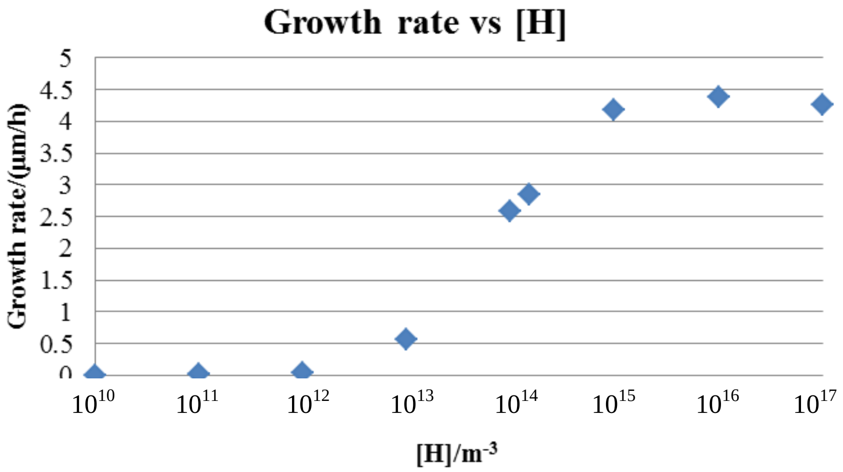


Figure 23 Change in growth rate with hydrogen radical species above the diamond surface.

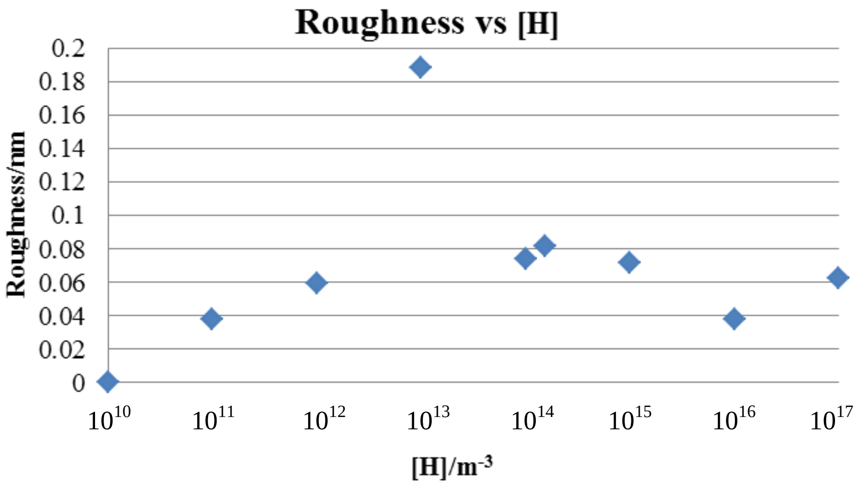


Figure 24 Change in roughness with H radical species above the diamond surface.

Growth is faster when hydrogen atom concentrations over the surface increases but stays constant for concentrations higher than 10^{15}. However, roughness is more or less constant except for the data of 10^{13} which is probably wrong.

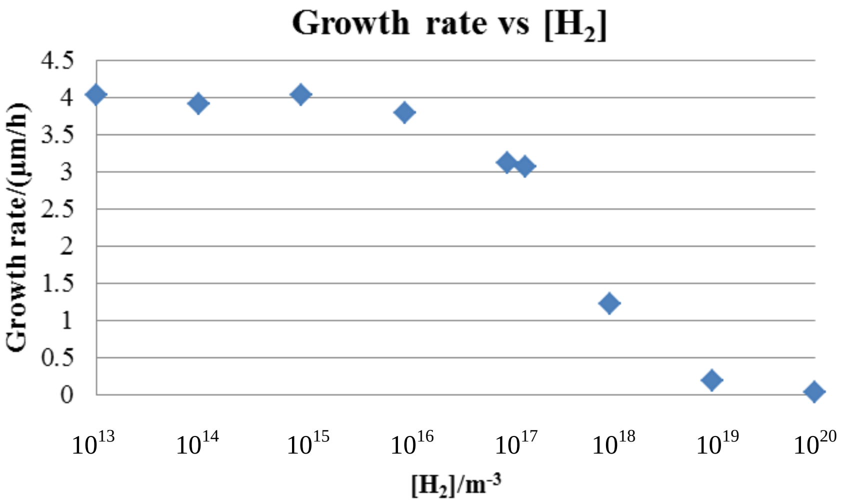


Figure 25 Change in growth rate with hydrogen molecule concentration above the diamond surface.

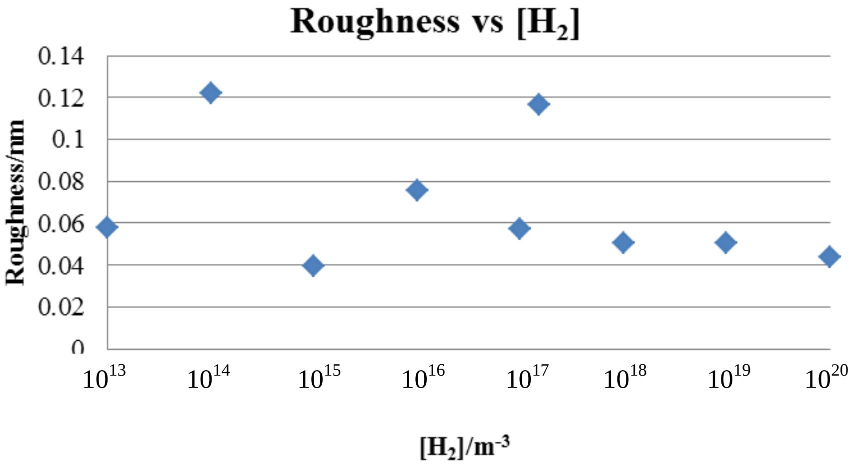


Figure 26 Change in roughness with H_2 concentration above the diamond surface.

Growth rate behaviour with hydrogen concentration change is completely opposite than for hydrogen atoms change. It decreases for higher hydrogen concentration near the surface. Roughness is also similar.

Steric and sticking factors represent the probability of a radical to join a surface, are numbers from 0 to 1. These numbers cannot be modified experimentally but are interesting because can be adjusted to the optimum value. Each species has different steric and sticking factors; for example, for CH_3 are lower than for C atoms.

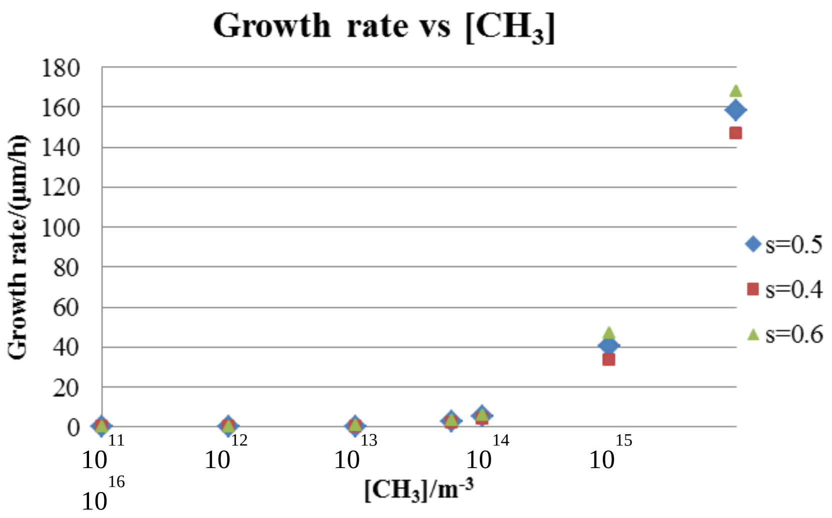


Figure 27 Change in growth rate with CH_3 radical species above the diamond surface. Steric factors from 0.4 to 0.6.

There is a slightly increment of growth rate for higher values of the steric factors (the radical is more likely to join the surface), similar trend is observed varying the sticking factors for CH_3 and all the other radical species.

2. Molecular Mechanics

This part of the work involves energy calculation of different diamond surfaces using GULP, a program which carries out molecular mechanics simulations.

Molecular mechanics is a computational method which uses simple empirical force fields between atoms, bonds are treated as springs and atoms as charged points. All potentials come from classical physics. Molecular mechanics methods do not model electrons, that is the reason why calculations are faster than quantum mechanics methods, but are less accurate as well. Data used in these calculations come from quantum mechanics calculations or are experimental data.[25]

Molecular mechanics is a good mechanism to calculate the minimum energy of stable systems such as surfaces or structures, but is not valid to calculate reaction energies.

In the program were used periodic boundary conditions. The periodic boundary conditions are normally employed for the study of infinite systems, as infinite solids or liquids. The basis for this method is to replicate the unit in all directions of the space. For this particular case, 2 regions are created; the region 1 corresponds to the diamond surface and is the region which is going to be changed for the different cases. It is replicated in X and Y directions to obtain an “infinite” surface. Region 2 is the bulk, does not change form experiment to experiment, is replicated in the X and Y directions as well, but also in the –Z direction. Doing this “trick” a pseudo-infinite lattice is obtained.

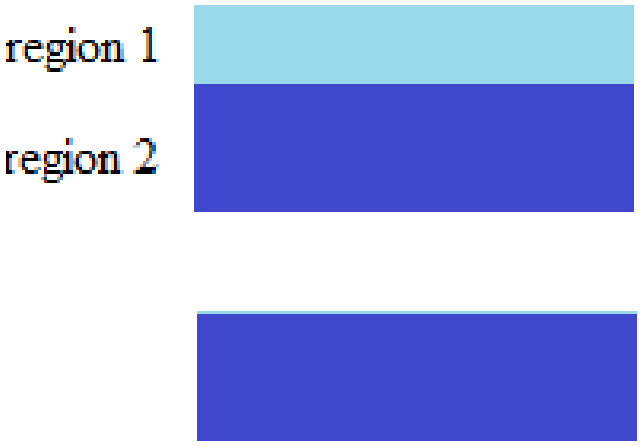


Figure 28 Scheme of the periodic boundary conditions used in the program, region 1 is the surface and region 2 is the bulk.

Brenner potential was the potential function utilised for optimise the diamond surfaces. This potential has been largely used for the calculation of all kind of hydrocarbon species. Brenner potential is a bond order potential, is based on the Linus Pauling concept of bond order. It can describe different bonding states of an atom. The strength of a bond depends on the bond order.[41, 42]

2.1 Work done and results

The work done with the program was calculate the minimum energy of structures and surfaces of diamond, in particular 2x1 (100) diamond surface under different conditions.

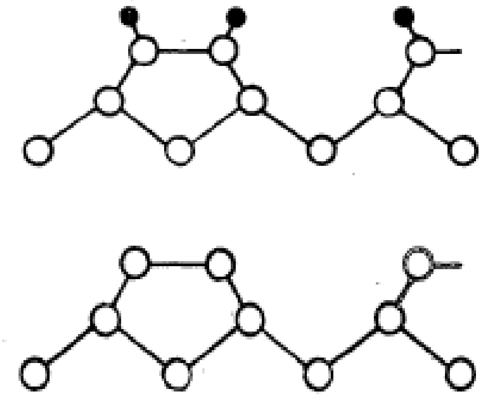


Figure 29 Up) Scheme of diamond 2x1 (100) hydrogen-terminated surface, that is, carbon atoms on the surface are joined to hydrogen atoms. Down) Scheme of diamond 2x1 (100) reconstructed surface, or clean surface, in that case, the surface is composed by carbon atoms in a 100% there is no hydrogen atoms. Carbon atoms on the surface are joined to each other by a double bond. (Just the two surface atoms)

Hydrogen terminated and reconstructed surface were optimised but also were optimised other surfaces corresponding to different steps of the diamond growth such as activated surface, addition of CH_3, activation of this latter surface and formation of a CH_2 bridge.

First of all, diamond unit cell was optimised to check the reliability of the Brenner potential, the results were in very good agreement with the experimental data; the calculated unit cell length difference with the experimental one was less than 0.1% so Brenner potential can be used for the study of diamond surfaces. Then, hydrogen terminated and reconstructed surface were optimised.

Figure 30 surface energies of the reconstructed and hydrogen terminated surface of 2x1 (100) diamond.

The main result of the optimisation is the energy of every surface, hydrogen terminated surface is 11 Jm^{-2} lower in energy than the reconstructed surface. That is, hydrogen terminated surface is more stable than reconstructed surface. This is due to double bonds in the reconstructed surface are not in a plane but bent.

After that, different steps; the surface energies for each step are the in the growth were optimised as well as the CH_2 bridge formation following:

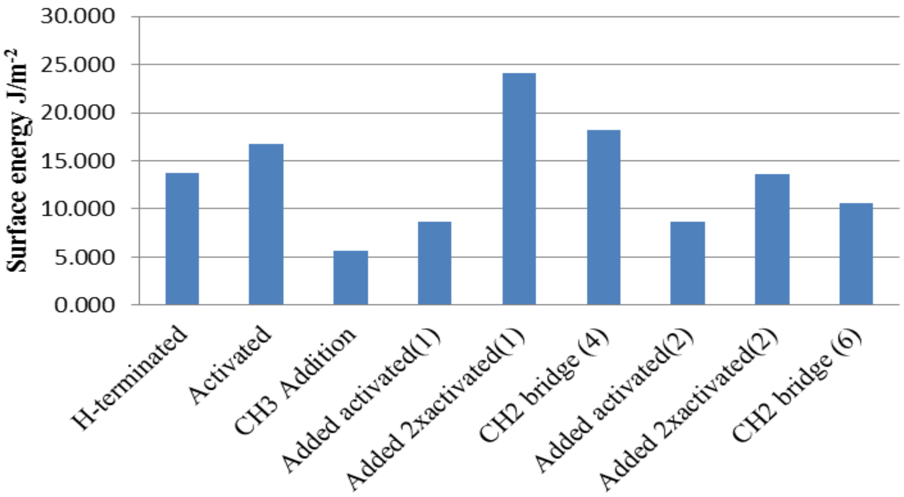


Figure 31 Surface energies of different steps of the diamond growth. (1) leads to the formation of the 4 membered bridge and (2) the 6 membered bridge.

As seen the activation of a surface always leads to higher surface energies, and the bridge formation to lower surface energies. 6 membered bridges are more stable than the 4 membered bridges.

Conclusions

Now, the main results of this work are going to be summarized.

Kinetic Monte Carlo

In the KMC simulations, are several results extracted from the calculations:

- A maximum in the growth rate was found with a substrate temperature around 1300 K; this temperature of course depends on several variables, but is in very good agreement with the experimental results of other research groups showed in ref 39 and 40.
- Growth rate increases linearly with gas temperature; this behaviour is due to the higher rate of impacts against the surface.
- Roughness is stable for the change in gas temperature and substrate temperature in the range where there is an actual growth and is among 0.05 nm and 0.10 nm.
- Surface deactivation and addition deactivation are the two most important processes in the diamond growth because deactivating them, growth rate increases by a factor of ten in the first case and decreases by a factor of three in the second case. Addition and surface activation are vital; deactivating them there is no growth. The rest of the processes are not so influent for the growth rate, for example deactivating etching, growth rate increases slightly. Surface deactivation is the process responsible of the maximum in growth rate with substrate temperatures around 1300 K, otherwise growth rate would increase with substrate temperature increment
- As a result of deactivate migration, roughness increases significantly. The reason for that behaviour is the impossibility for the carbon units on the surface to migrate along the surface till they find another unit to join and to form an unetchable and immobile unit, then there are scattered units on the surface and each one is a nucleation point, the more nucleation points the more chances to produce defects and therefore, roughness is increased.
- When radical concentrations near the surface are increased, growth rate increases potentially, and roughness increases as well, but logarithmically. Since roughness is related with the quality of the film, can be said that increasing

radical concentrations over the surface, growth rate increases but at the expense of film quality.

- The result of increase hydrogen atom concentration near the surface is the increment in growth rate but stays stable at concentrations higher than 10^{15} m^{-3}. On the other hand, with hydrogen molecule concentration change, growth rate decreases and stays unchangeable for concentrations higher to 10^{19} m^{-3}. Roughness remains stable between 0.05 nm and 0.10 nm.

Molecular Mechanics

- Brenner potential is able to be used for molecular mechanics optimisation of more diamond surfaces.
- Hydrogen terminated surface is more stable than the reconstructed or clean surface, surface energy is lower for hydrogen terminated surface and this is due to the more favourable disposition of the atoms bound to the carbon atom on the surface, however for the reconstructed surface the most stable conformation would be planar and the atoms are not in a plane but bent as an umbrella.
- Activation of any surface increases surface energy.
- Bridges formation decreases surface energy, because a bond is more stable than two dangling bonds.
- 6 membered bridges are more stable than 4 membered bridge;, that is the reason why 6 member bridge formations is the path for diamond growth.

Future work

Further work can be made using this work as basis. There are several open ways of research in both Kinetic Monte Carlo and Molecular Mechanics simulations.

Kinetic Monte Carlo

- One possible field of research can be adjust the steric and sticking factors in order to obtain better results according to the experiments.
- Also could be interesting to find a way to predict grain size for a given starting conditions, one possible way can be find a relationship between grain size and roughness.

Molecular Mechanics

- Calculate the transition state energies for the growth steps such as migration, beta scission or bridge formation and from this data, predict the probability of them to occur.
- Optimise more structures than 2x1 (100) surface and calculate differences among them.
- Another very interesting research field would be modelling surface defects for the diamond, since are an important feature for diamond growth.

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