Exploring the Effects of Metal Oxide Termination of Diamond on its Work Function and Electron Affinity

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Abstract

Diamond is very well known for being a wide band gap semiconductor and has numerous applications, including in thermionic energy convertors. The unique quality of diamond is its negative electron affinity when synthesised in a number of ways.

This project considered how the presence of metal oxides, specifically scandium oxide presence on the surface of diamond affects the work function and the electron affinity. Through this the work function can be determined. Experiments involved doping diamond with boron and depositing metals on to the surface. The amount of metal deposited was determined by x-ray photo electron spectroscopy and the work function determined by ultraviolet photoelectron spectroscopy.

Acknowledgements

I would first like to thank Paul May as without him this project wouldn’t have been possible.

I would also like to thank Ramiz Zulkharnay for his time, and his patience in supervising me throughout this project

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1 - Introduction

Since the first synthetic diamond was made in 1926 [1], experiments involving diamond have become increasingly common. Originally, its fluorescent and phosphorescent properties under short wavelengths were studied, but it is now being researched into its uses in thermionic energy converters.
Table 1 shows the general properties of diamond that make it viable in a wide range of applications.

Table 1: Important properties of diamond

Property	Value	Units
Hardness	$1.0 * 10^4$	kg mm$_{-2}$
Tensile Strength	>1.2	GPa
Compressive Strength	>110	GPa
Density	3.52	g m$_{-3}$
Youngs Modulus	1.22	GPa
Thermal conductivity	2.0 x 10$_3$	W m$_{-1}$K$_{-1}$
Thermal expansion coefficient	1.1 x10$_{-6}$	K$_{-1}$
Electron affinity	Negative	On H-terminated surface
Optical transparency	From deep UV to far IR	N/A

This report looks at how synthetic diamond can be made, and how metal oxide surface terminations change the electron emission properties of thin film diamond.

In experiments such as the one presented herein, natural diamond is not preferred due to the randomness of its size and shape, instead synthetic diamond is to ensure experimental repeatability. Two ways of creating synthetic diamond include High Pressure High Temperature (H.P.H.T.) and Chemical Vapour Deposition (CVD).

1.1 - High Pressure High Temperature

The High Pressure High Temperature method of creating diamond was developed in 1955 by Brundy *et al.* at General Electric. It requires pressures of up to 6.5 GPa and temperatures of 1300-1700 °C, depending on the crystal geometry required and the solvent used [2].

1.2 - Chemical Vapour Deposition

Chemical vapour deposition is a process that can create diamonds in a more controlled way compared to H.P.H.T. It involves a gas phase reaction above a solid surface which causes a deposition onto the solid surface itself. CVD generally involves thermal or plasma activation of a carbon-containing process gas.
Chemical growth of diamond normally requires a temperature between 1000-1400 K with varying growth periods. However, the faster the growth of diamond the lower the quality. This is determined by the number of sp$_3$ hybridised carbons in comparison to graphite, sp$_2$ hybridised carbons [3].

1.3 - Diamond Structure

CVD diamond exhibits 3 surfaces which are represented by the Miller indices (100), (110) and (111). The (100) structure seems to be the most chemically significant as it is the slowest growth followed by the (111) structure. The (110) structure is the fastest growing structure and hence grows out. [4]

1.3.1 - (100) structure

An ideal (100) surface should have surface carbon atoms with two dangling bonds. This is energetically unfavourable so the diamond reforms into a (2x1) structure forming double bonds in an unsaturated sp_3-like coordination. This reduces the total energy by reducing the number of dangling bonds. [5] By forming these double bonds, the electrons occupy the π state and leave the π^* state unoccupied. This leaves a 1.3 eV band gap between occupied and unoccupied states causing a semiconducting surface. [6]

1.3.2 - (111) structure

The (111) structure is the lowest surface energy structure which can either have 1 or 3 dangling bonds. [7]

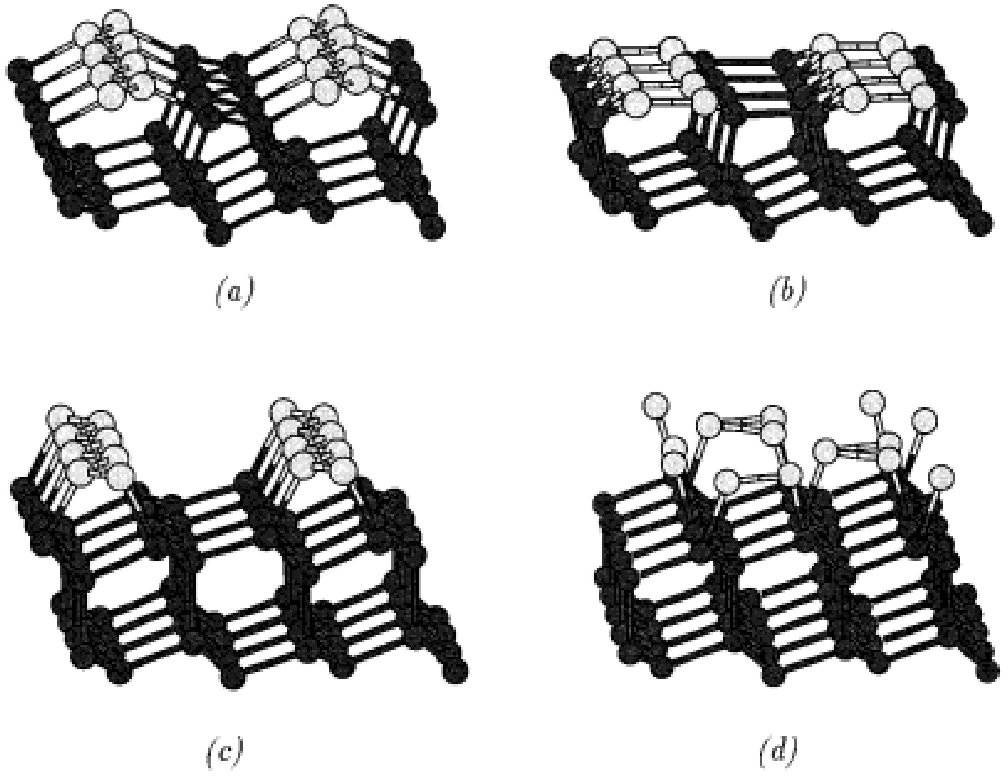

Figure 1: Demonstrating the energy minimum structures of (111) diamond surface.
(a) Pandey p-bonded chain model (b) Chadi p-bonded molecule model at the C(111) single-dangling-bond surface; (c) the Seiwatz single-chain model; and (d) the hollow (H) site trimer model at the C(111) triple-dangling-bond surface. White circles represent surface carbon atoms whereas black circles indicate those in the bulk. [27]

1.4 - Theoretical Background

1.4.1 - Work Function

The work function of a material is the amount of energy required to excite an electron from the Fermi energy (E_F) into the vacuum level. If a material has a negative electron affinity, the conduction band lies above the vacuum level such that electrons can be emitted from the material with relative ease.

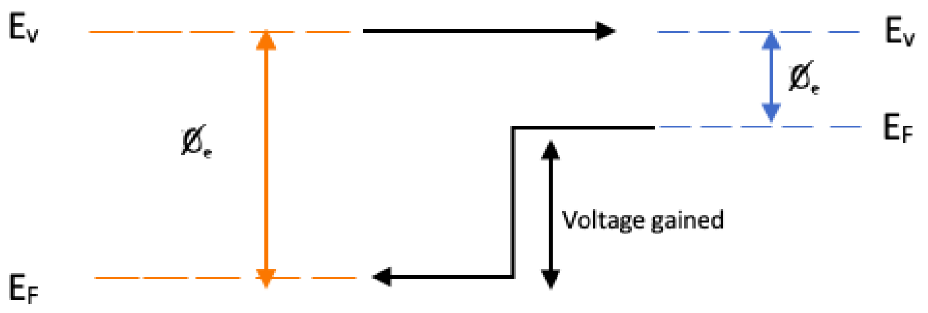

Figure 2: The energy bands as a resultant work function of a thermionic energy converter. Modified from [8].
E$_V$ is the vacuum energy
E$_F$ is the Fermi energy
ϕ_e Is the Work function

The surface of diamond contains dangling bonds, or surface radical sites. Unless these bonds are terminated with a monovalent species, such as H, they may crosslink forming a graphitic surface. H termination stabilises the surface in the sp$_3$ structure. In most materials other than diamond, the conduction band minimum lies below the vacuum level -a situation known as positive electron affinity. Electrons which have been promoted into the conduction band are prevented from escaping into a vacuum by this energy barrier. However, for diamond, the monolayer of hydrogen on the diamond surface creates a surface dipole with the H layer slightly more positively charged than the diamond bulk. This raises the energy of the conduction band above that of the vacuum level, forming a negative electron affinity (NEA) between the surface and the bulk of the diamond. This means that electrons excited into the conduction band of diamond have no energy barrier to escape into vacuum. NEA has been extensively studied on the C(100), C(110) and C(111) surfaces [9] A calculated NEA for hydrogen terminated diamond is to be ~-2.2eV for a C(100)-(2x1) diamond surface [10]. The downside of using hydrogen terminated diamond is that it thermally degrades at relatively low temperatures (~700 °C in a vacuum and ~200°C in air) making electron emission devices problematic (see later). Although H-terminated diamond may have an NEA, the electrons still need to be promoted from the (full) valence band into the (empty) conduction band before electron emission can take place. Thus, even with a NEA surface, the workfunction is not zero, but may still be a few eV. Nevertheless, this is significantly smaller than would be the case in other materials, and the workfunction may be lowered further by using n-doped diamond.

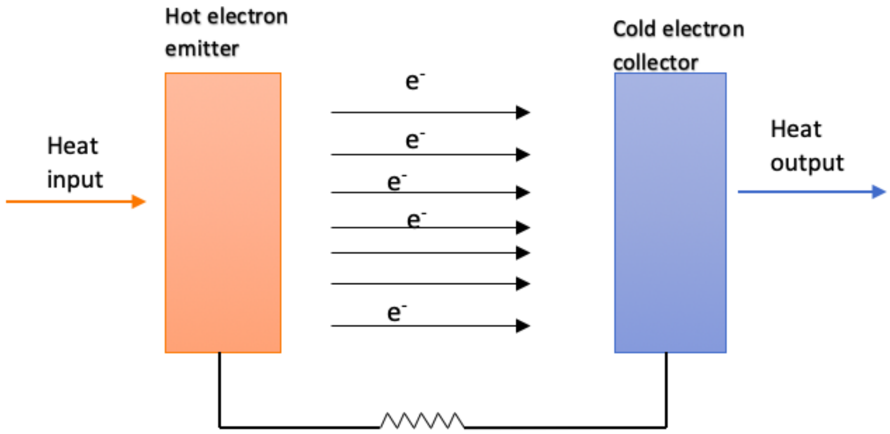

Figure 3: A thermionic energy converter. Modified from [8].

Low work function materials with NEA surfaces are essential for fabrication of a thermionic energy converter (TEC). [11] A TEC relies on thermionic emission of electrons - an important process also used in fluorescent lamps and mass spectrometers. Having a low work function material is key as it means less energy is needed to heat the thermo-emitting cathode in order to create a current, as shown in Figure 3. The lower the work function of the electron emitter the more efficient a TEC becomes.

1.4.2 - Electron affinity

The electron affinity is the band gap between the conduction band minimum and the vacuum energy level. Hydrogen terminated diamond has a NEA because the introduction of hydrogen to the surface of the diamond moves the conduction band above the vacuum level, as shown in Figure 4.

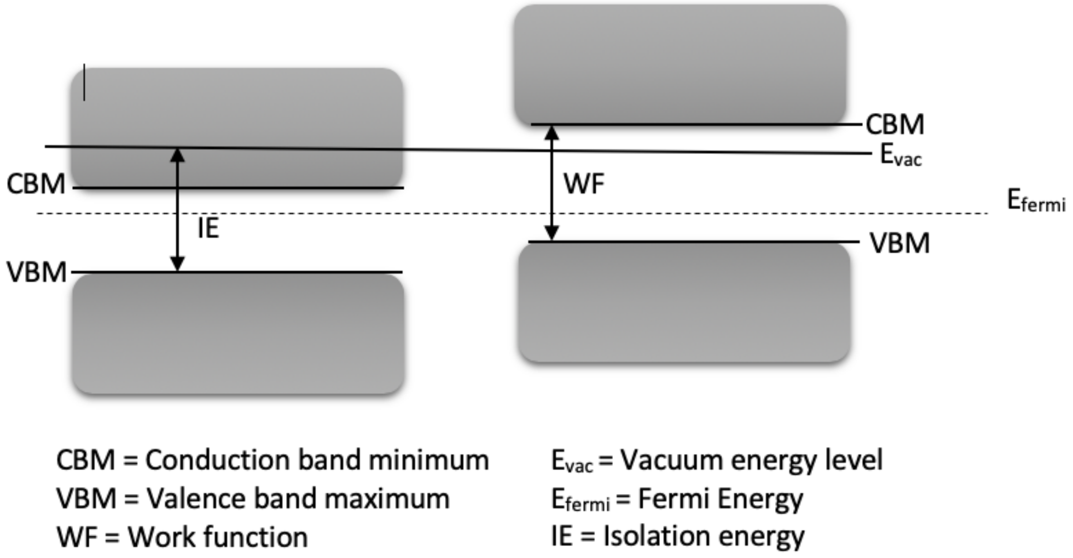

Figure 4: Diagram showing how the conduction band moves as the diamond is hydrogen terminated.

1.4.3 - Hydrogen termination

Hydrogen is less electronegative than carbon, which creates a partial dipole between the surface carbon and the hydrogen termination which can act as a p-type semiconductor layer. During the diamond CVD process there is an abundance of atomic hydrogen, and the highly reactive hydrogen bonds to the dangling bonds of the surface carbons allowing them to stay sp_3 hybridised and not cross link on the surface. [12]

The problem with a hydrogen-terminated system is that the H atoms desorb from the surface at a relatively low temperature. Experiments measuring the thermionic emission from polycrystalline CVD diamond with increasing temperature (between 600-800°C) showed the desorption of hydrogen followed a first-order rate while following Arrhenius behaviour with an activation energy of 1.23 eV. [13]

1.4.4 - Oxygen Termination

Diamond can be oxygen terminated by using a hot plasma as described in more detail in A.Vazir's work on Cell adhesion [14]. Oxygen can bond to diamond in 2 ways. The 'ketone' arrangement and the 'bridged' or 'ether' arrangement (see Fig.4). In the ketone arrangement, the oxygen doubly bonds to a single surface carbon atom, whereas in the ether arrangement the oxygen bridges the surface of two carbon atoms forming a single bond to each. [4]

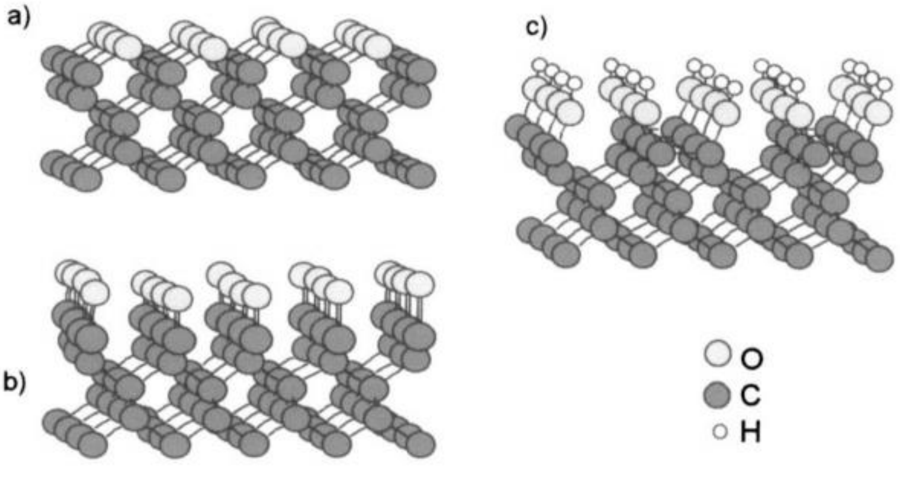

Figure 5: The different ways in which oxygen can terminate diamond.
(a) bridged ether structure
(b) The ketone arrangement
(c) hydroxyl termination [31]

1.5 - Metal oxide termination

Alkali metals, with their high electropositivity, can also form surface dipoles when bonded to semiconductor surfaces. An example of these includes the introduction of potassium on a silicon semiconductor. [15]

Previous work has shown that smaller highly charged ions are the most effective at creating a lower work function or creating a more negative NEA on a diamond surface. There has therefore been study into using metals such as Mg-O or Ti-O_x. Mg-O was recorded to show an NEA of -2.01±0.05eV which was the largest recorded NEA to date. [16]

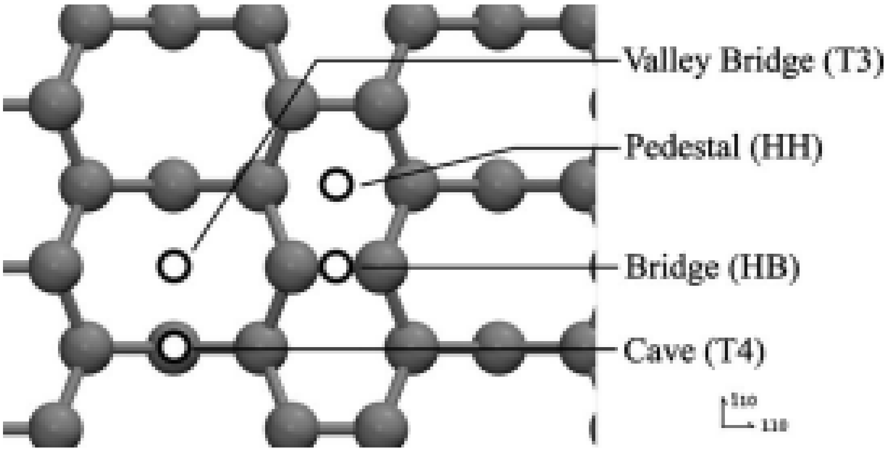

Figure 6: The positions at which an alkali metal would bond based on previous work on silicon. [17]

1.5.1 - Li-O Termination

Figure 6 shows the sites where alkali metals are most likely to be adsorbed based on previous work on alkali metals on the surface of Si(100) [17]. It is shown that with a 1.25 monolayer (ML) coverage of Li on C(100)-(1x1):O not only does the Li fill these Hexagonal Hole sites (HH) but also on top of the 3rd layer carbon (T3). This causes the carbon to undergo (2x1) reconstruction, as shown in figure 7.

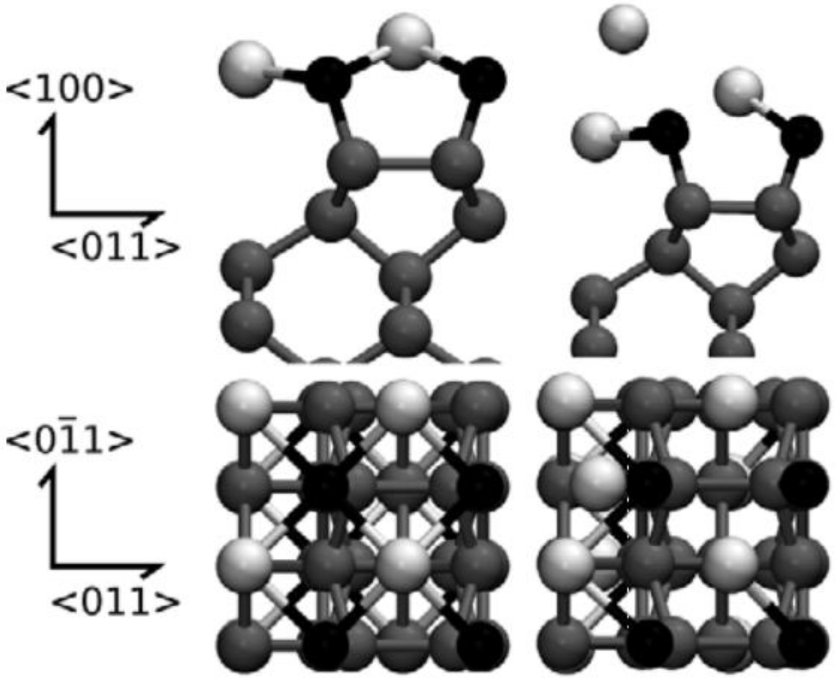

Figure 7: The top and side view of the T3 adsorbed Li (Left) 1 ML Li coverage and (right) 1.25 ML coverage [26]

Using AIMPRO code and Local Density Approximation (LDA) , a monolayer of LiO on C(100)and C(111) diamond was predicted to create an NEA of -3.89 eV and -2.70 eV, respectively. However, under UPS and XPS analysis it was found to have an NEA of -2.10eV for C(100) diamond [18] in comparison to hydrogen which was calculated to have an NEA of -1.3 eV [19] This was a significant increase.

1.5.2 - Mg-O Termination

Magnesium is not only similar in size to lithium, it also demonstrates a similar electronic structure of delocalised electrons. However, it should be able to donate twice as many electrons, due to the fact that magnesium forms a 2+ charge and lithium forms a 1+ charge. The sizable dipole that this creates across the surface lowers the NEA. When Mg or Li are adsorbed onto a surface they must be annealed (heated to a high temperature and cooled slowly) to form a chemical bond. Magnesium doesn't have to be heated to as high a temperature to be adsorbed in comparison to lithium.

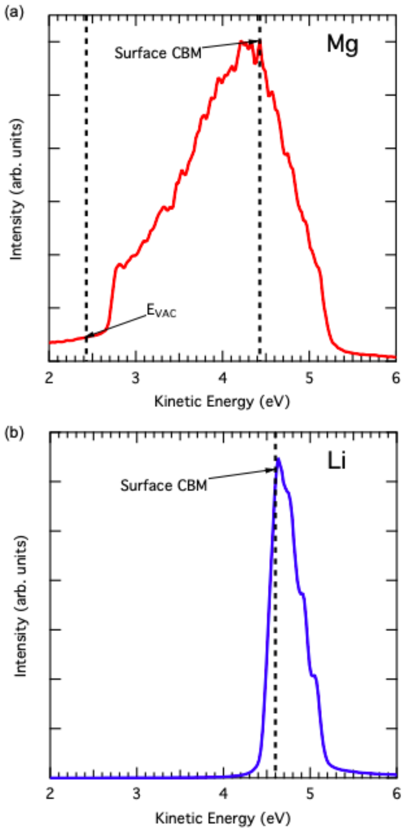

Figure 8: a) The kinetic energy spectrum of a 0.5 ML coverage of Mg on oxygenated diamond [16] compared with b) a 1 ML coverage of Li on oxygenated diamond. [25]

It can be seen in Figure 8 that, although the conduction band moves to a higher kinetic energy, there is a broad emission below the conduction band of magnesium. This is evidence for a low NEA of magnesium on oxygenated diamond allowing thermionic emission above the vacuum band, compared to Li-O termination which doesn't emit until the conduction band minimum is reached.

1.5.3 - Ti-O Termination

There has been little published experimental work of titanium adsorbed on oxygenated diamond, however there has been extensive theoretical research into the field using Density Functional Tight Binding (DFTB) methodology. It was found that, due to the 4+ charge on the titanium ion, a quarter-monolayer of Ti (as shown in figure 9) was the most effective, creating a calculated NEA of -3.10 eV. [20] This was one of most negative calculated NEA values to date.

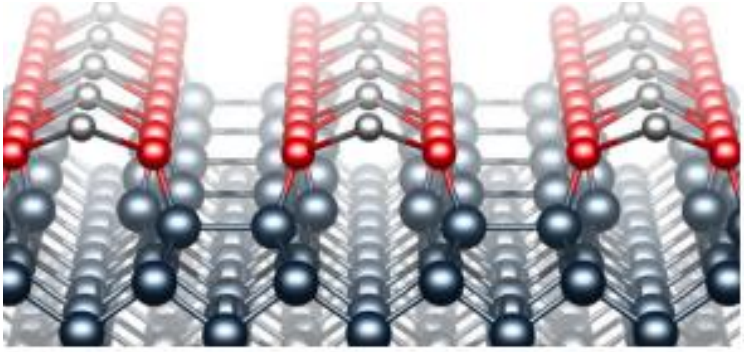

Figure 9: The bonding of a quarter monolayer of Ti on oxygenated diamond. [20]

1.5.4 - Cs-O Termination

Caesium on oxygenated diamond has been studied extensively due to the low work function displayed by caesium oxide. Coating oxygenated diamond with a half monolayer of Cs moves the conduction band 0.85 eV above the vacuum level [21].. The binding energy of Cs on an oxygenated surface is small meaning that the caesium is desorbed from the diamond surface at only ~400-500°C. [22] This is a lower temperature than hydrogen-terminated diamond, and almost useless for TEC applications.

1.5.5 - Al-O Termination

Extensive research has been done into the NEA of aluminium on oxygenated diamond surfaces. Table 2 shows that aluminium only creates a NEA when in a quarter monolayer. Even so, the NEA is rather small. [23]

Coverage	**Electron Affinity** (eV)	**Binding energy** (eV)
Quarter monolayer	-0.37	-6.36
Half Monolayer	+1.06	-5.99
Full Monolayer	+0.54	-4.58

Table 1: The binding energy per atom and the electron affinity displayed with different surface coverages of Al on oxidised diamond. [23]

1.6 - Project aims

There has been increased research in recent years on using a metal terminated diamond as the electron emitter in a thermionic energy converter. So far, the most promising metal seems to be some preliminary work done by the university of Bristol with Titanium. [24]

In this project I will be terminating oxygenated diamond with scandium. Following the previous success of titanium, it is predicted that scandium will give similar results. This reasoning follows scandium having a relatively highly charged ion (3+) but also has a smaller atomic radius than that of titanium. These two factors are ideal for creating a large NEA together with a temperature-stable surface.

2 - Experimental

2.1 - Project aim

There were 2 main project aims. The first was to cover the Single Crystal Diamond (SCD) which was purchased from ElementSix with a monolayer of scandium. The second was to use a Photoemission electron microscopy to determine the work function and whether the sample had a negative electron affinity.

All samples that were used were 5mmx5mm in size.

2.2 - Acid Cleaning

The samples were acid cleaned in a combination of sulphuric and nitric acid, and heated under reflux for 90 minutes while being checked every 20 minutes. The sample was then washed with deionised water.

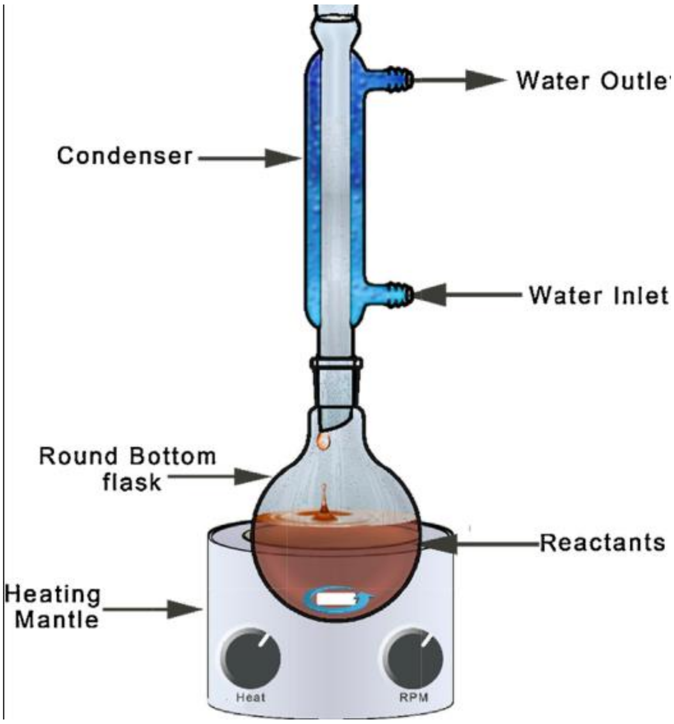

Figure 10: The reflux set-up where the reactants are the diamond sample and the sulfuric acid mix [28]

2.3 - Hot Filament

The samples placed in the hot filament boron reactor. Shown in figure 11. The reactor doped the surface of the diamond in boron. This is in order to make the surface of the material conductive so analysis could be done. Boron is a p-type donor and will donate electrons into the diamond sample.

A Boron doped diamond was obtained using a hot filament with a flow of diborane (B_2H_6), Methane (CH_4) and hydrogen gas (H_2). The methane flow was set to 1% of that of hydrogen and the diborane at 1375 ppm.

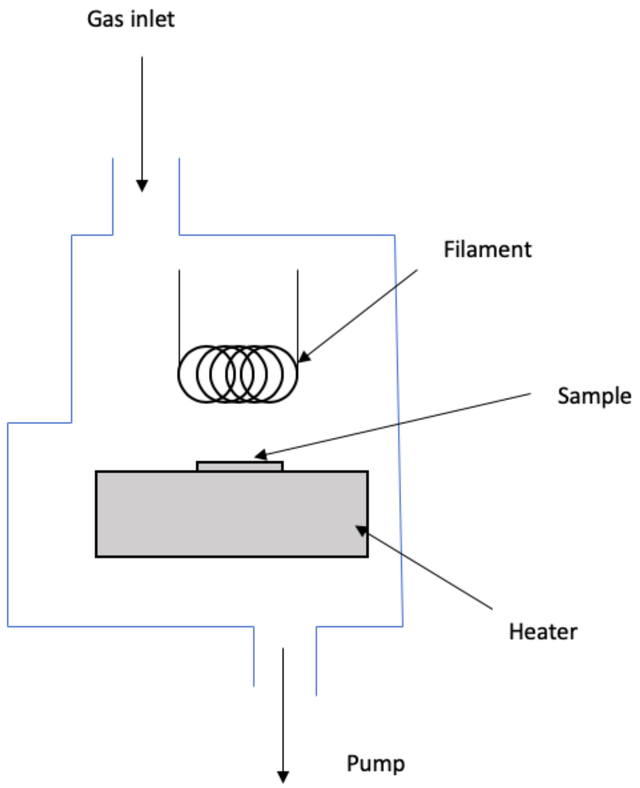

Figure 11: Setup of the hot filament reactor where a pump processes the gas over the sample and the heater is made up of a molybdenum substrate plinth, a heated plate and a stainless-steel substrate holder at the bottom.

2.3.1 - Standard operating procedure

The pre-oxygenated diamond samples were placed on the molybdenum plinth and 3 tantalum filaments were placed above the sample at the beginning of the CVD growth. The sample holder and lid were placed into the reaction chamber separated by a rubber “O” ring and secured with bolts to ensure an airtight seal. Once the chamber was stabilised at a pressure of 20.0 Torr, current of 25A was passed through the filaments. This was then left for 1 hour, resulting in a thin boron layer.

2.4 - NanoESCA

The NanoESCA consists of two combined parts, analysis and a high energy electron beam and is shown schematically in Figure 12. . The sample was put under X-ray photoelectric spectroscopy in order to make sure the sample was oxygenated whilst ensuring it was not contaminated with molybdenum from the hot filament. The high energy electron beam was used for volatizing the scandium. Initial experiments were done to ensure that a full monolayer of scandium was deposited on to the surface of the diamond. XPS was then repeated to confirm the monolayer and scandium had been deposited and UPS analysis in order to determine the work function.

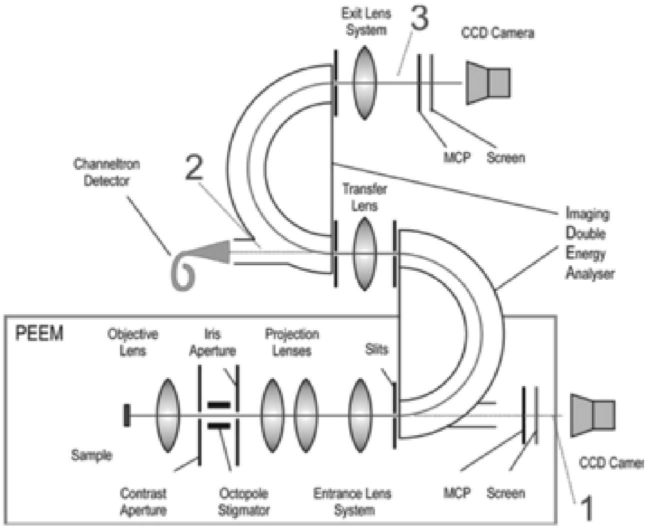

Figure 12: The setup of the analysis section of the NanoESCA which is capable of 3 types of analysis.

1. NanoESCA II energy filtered photoemission electron microscope (PEEM)
2. X-ray photoelectron spectroscopy (XPS)
3. Spot profile analysis low energy electron diffraction (SPA-LEED) [29]

2.4.1 - X-ray Photoelectron Spectroscopy

The samples were rotated to an angle of 90° relative to the analyser, an aluminium x-ray source was to produce photons with an energy of 1486 eV.
The XPS was done in 2 sections; the survey and core level scan. The initial survey is done to see which elements are present in the sample and to reduce the amount of background noise in the core level scan. The core level scan looks at the elements that are of interest. In this case, the Carbon 1s, Oxygen 1s and Scandium 2p. The core level scans are repeated in order to further reduce background noise. Table 3 describes the conditions used to analyse the sample.

Voltage bias /kV	14
Filament Current /A	2
Emission Current /mA	16.3

Table 3: List of XPS conditions from the aluminium X-ray source used in this experiment

2.4.2 - Ultraviolet Photoelectron Spectroscopy

Ultraviolet Photoelectron Spectroscopy (UPS) was only used to determine the work function of the sample. This works by dividing the sample into pixels where each pixel represents a spectrum and the work function is determined by the energy of the valence electrons emitted by the sample. It was done under a pressure of approximately $1x10_{-7}$ Torr.

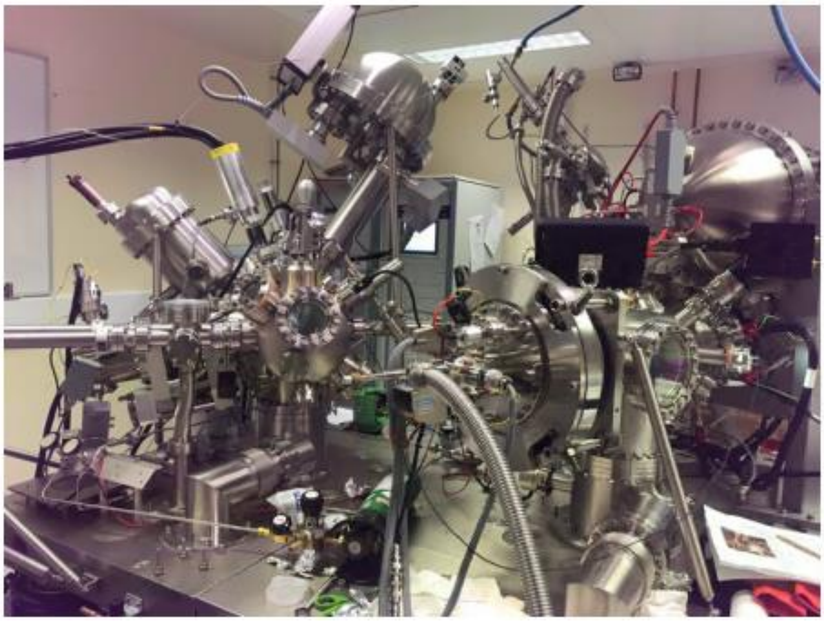

Figure 13: The Machine used for the XPS and UPS [30]

2.5 - Sonication Cleaning

Sonication cleaning was employed to wash the sample in deionised water, acetone and isopropyl alcohol. By agitating the sample this method removes any dirt or dust on the sample before it was put under the scanning electron microscope. All the samples were dried using an air gun with ambient N_2 gas.

2.6 - Scanning Electron Microscopy

Scanning electron microscopy was done on the sample before and after the scandium deposition.
The sample was placed on a podium under vacuum at a working distance of 10mm with a 15kV. Three images were taken of the sample at different magnifications 30x 900x and 4000x. Each of the images have been taken at different positions of the sample in order to restrict the damage the electron beam does to the sample.

3 - Results and Discussion

3.1 - Hot Filament

The sample was placed in the hot filament as shown in figure 14. As previously stated, the flow of H_2 gas was significantly higher than that of the CH_4 or B_2H_6. This was done since the surface of diamond has a lot of dangling bonds and atomic hydrogen can quickly bond to these dangling bonds and keep the diamond sp_3 hybridized and restrict the growth of amorphous diamond or graphene. The filament was made of thallium due to its ability to temperatures needed for this experiment and its low cost compared to alternatives such as molybdenum or rhenium

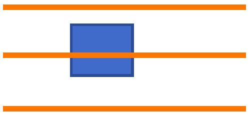

Figure 13: the placement of the oxygen terminated diamond in the hot filament Where the blue square is the Single Crystal diamond and the orange lines are the filaments

The filament is heated to a temperature of 2200 °C. This is hot enough to dissociate the hydrogen gas and form atomic hydrogen which can bind to either dangling bonds on the diamond, or the oxygen.

Thallium has the ability to form thallium carbide in the hot filament following reaction with the methane gas. Thallium carbide is a lot more brittle than thallium and is prone to snap under the current of 25A. This means that it needs to be checked every 15-20 mins, however the diamond was only under hot filament for an hour, as only a thin boron layer was required, so the chances of it snapping in that short timeframe is minimal.

3.2 - Scanning Electron Microscopy

Figures 14,15 and 16 show the images taken by the microscope. They show a fairly uniform growth with a few discrepancies.
These are shown in more detail in figure 16 where the irregularity of the growth can be seen by the cracks on the surface. These are most likely nanocrystalline growths of diamond.

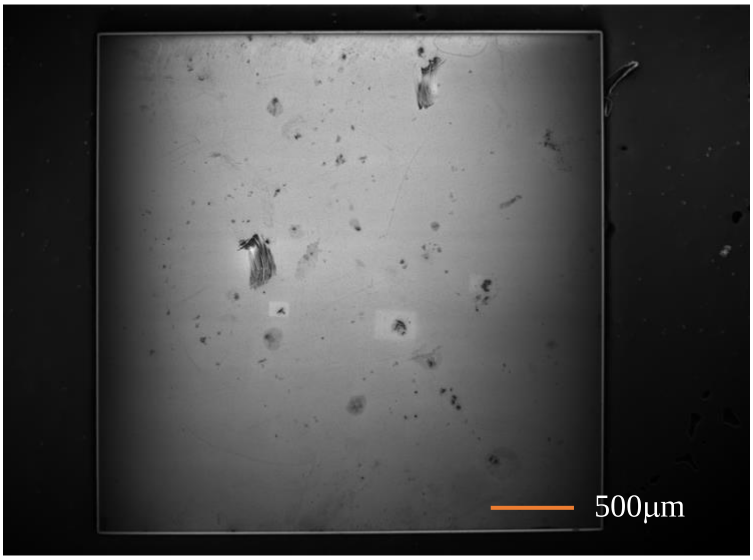

Figure 14: shows the SEM image at 27x magnification

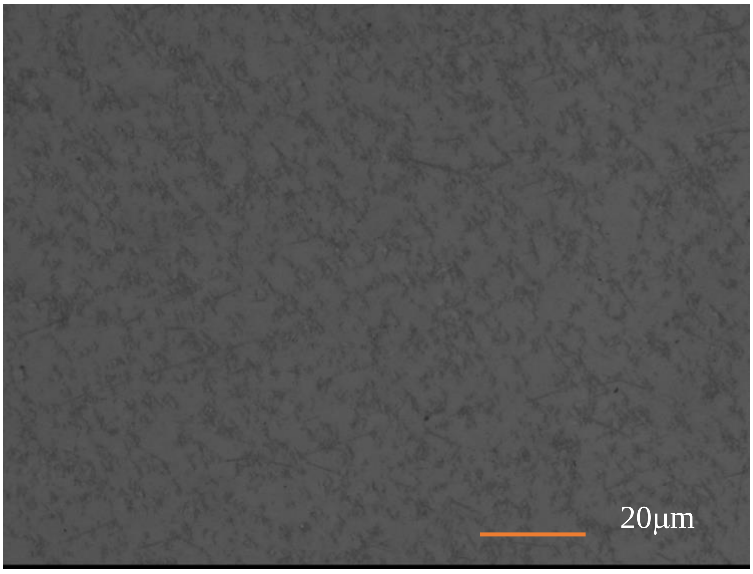

Figure 15: SEM image at 900x magnification

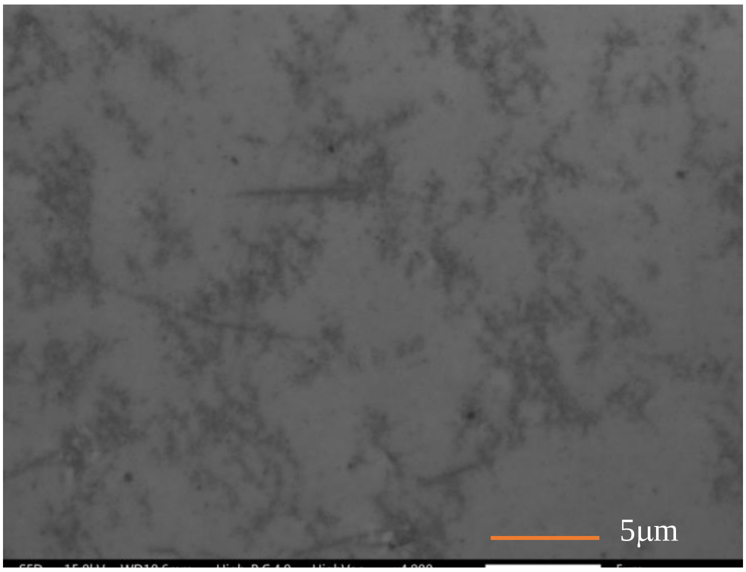

Figure 16: SEM Image of the boron doped diamond surface at 4,000x magnification

3.3 - NanoESCA

3.3.1 - X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was performed on the sample before the deposition. It was seen that there were two strong peaks, one at 532 eV and another at 284 eV. These relate to the oxygen and carbon peaks respectively.

3.3.2 - Scandium deposition

A high energy electron beam with a power of 8 W was used to vaporise the scandium and deposit it on the diamond.

Prior experiments were done in order to ascertain how long the diamond would take to form a full monolayer. The results are shown in figure 17. The point where the two lines cross is the point is the time needed for one complete monolayer of scandium. That point was found to be 9 minutes 25 seconds.

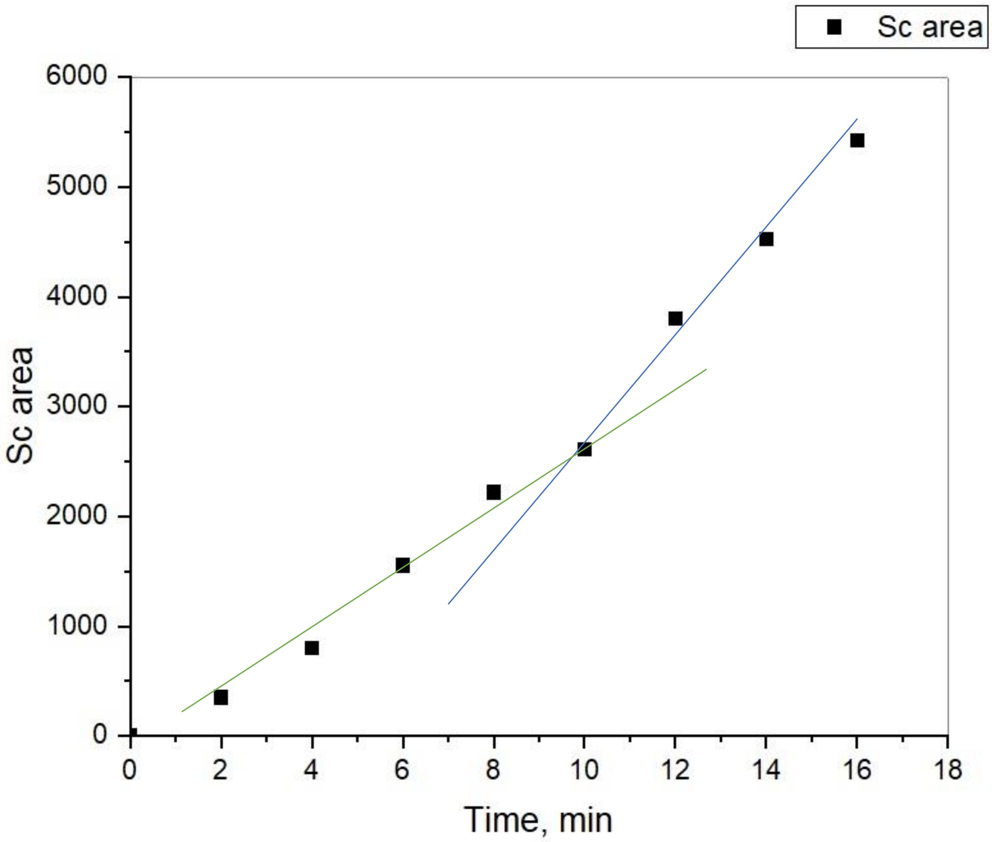

Figure 17: The green line shows the deposition of the first monolayer and the blue line shows that of the second monolayer

3.3.3 - X-ray Photoelectron Spectroscopy

The second time XPS was done on the sample was to check the scandium was deposited and also to check the area of the curve to see how much coverage was on the sample. Figure 18 shows the survey and figure 19 shows the scandium 2p peak.

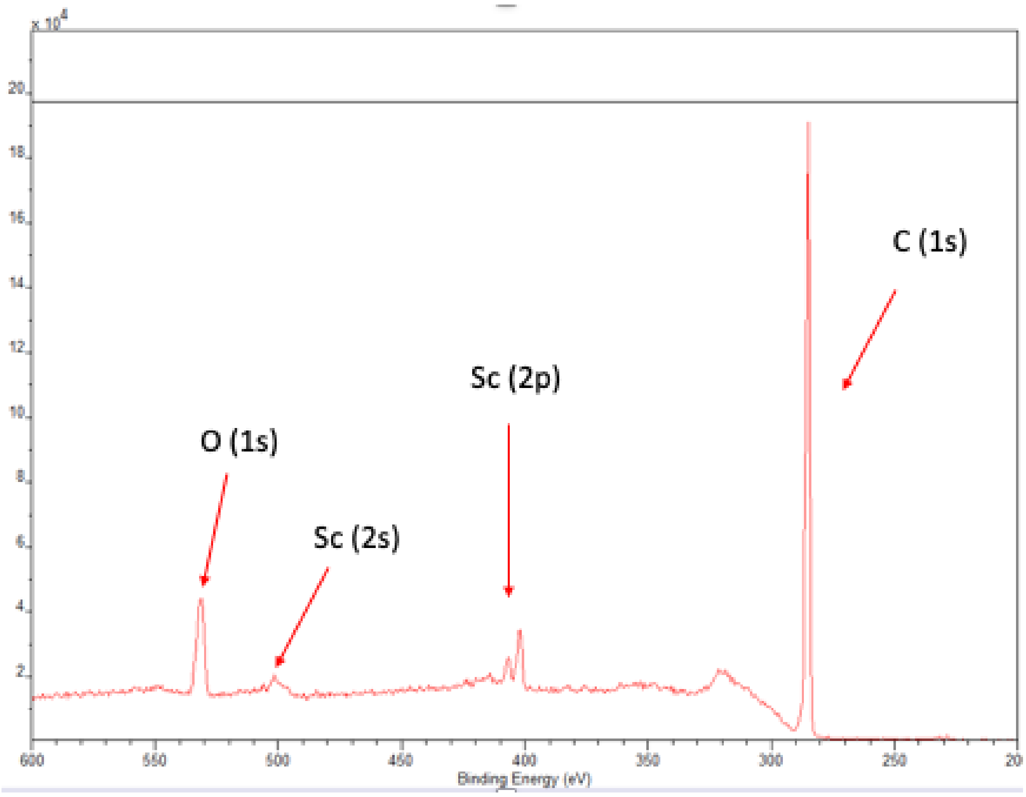

Figure 18: The survey results of the initial XPS.

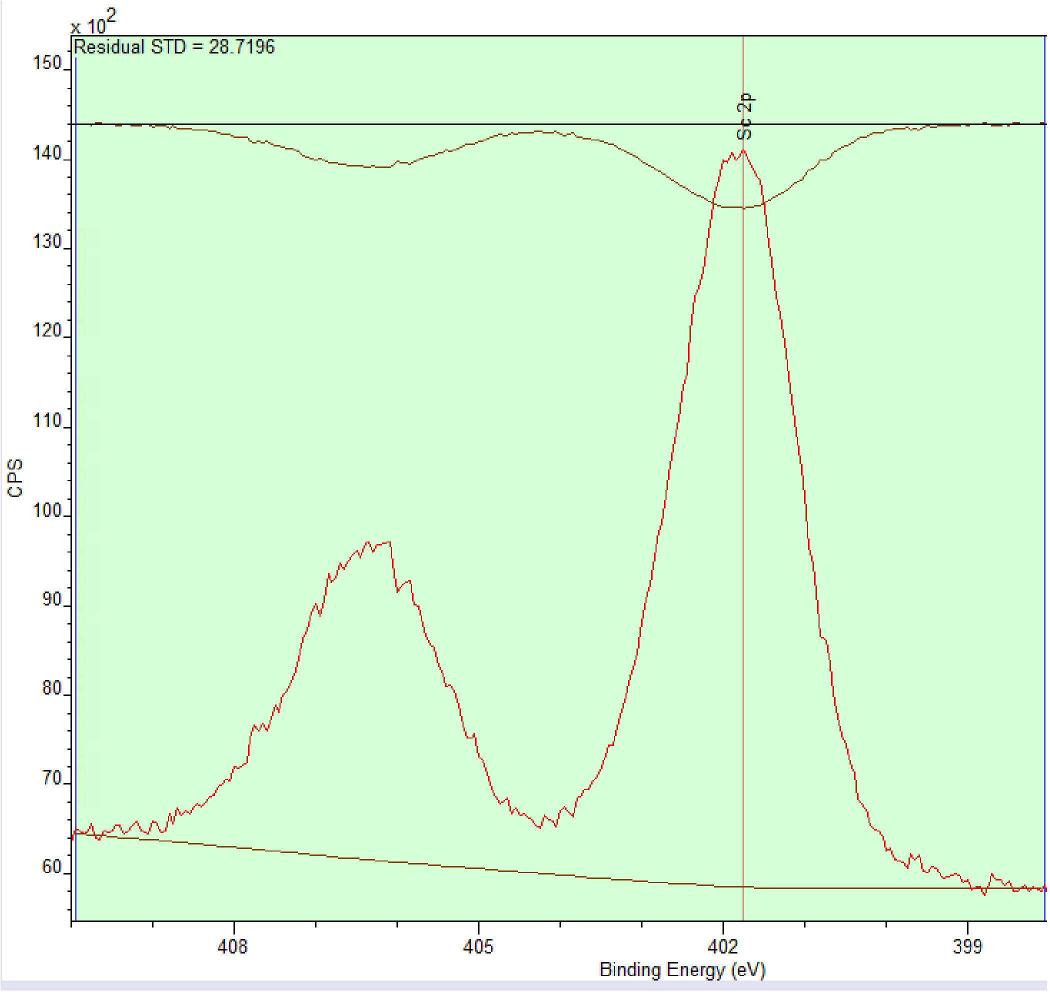

Figure 19: shows the scandium peak with an area of 1862.5 Arbitrary units

The area of the Scandium peak was 1862.5 meaning although a full monolayer was aimed for the experiment ended with only 72% coverage.

3.3.4 - Ultraviolet Photoelectron Spectroscopy

The UPS data give a graph with a large steep peak where the valence electrons cease their emission from the sample. This energy is the work function of the sample.
The energy was approximately 4.6 eV.

A work function map was created for this as shown in Figure 20 each pixel is a spectrum where the Colour relates to the work function
The UPS has a sensitivity of 20 meV meaning that all the spectrums obtained are sure to be highly accurate.

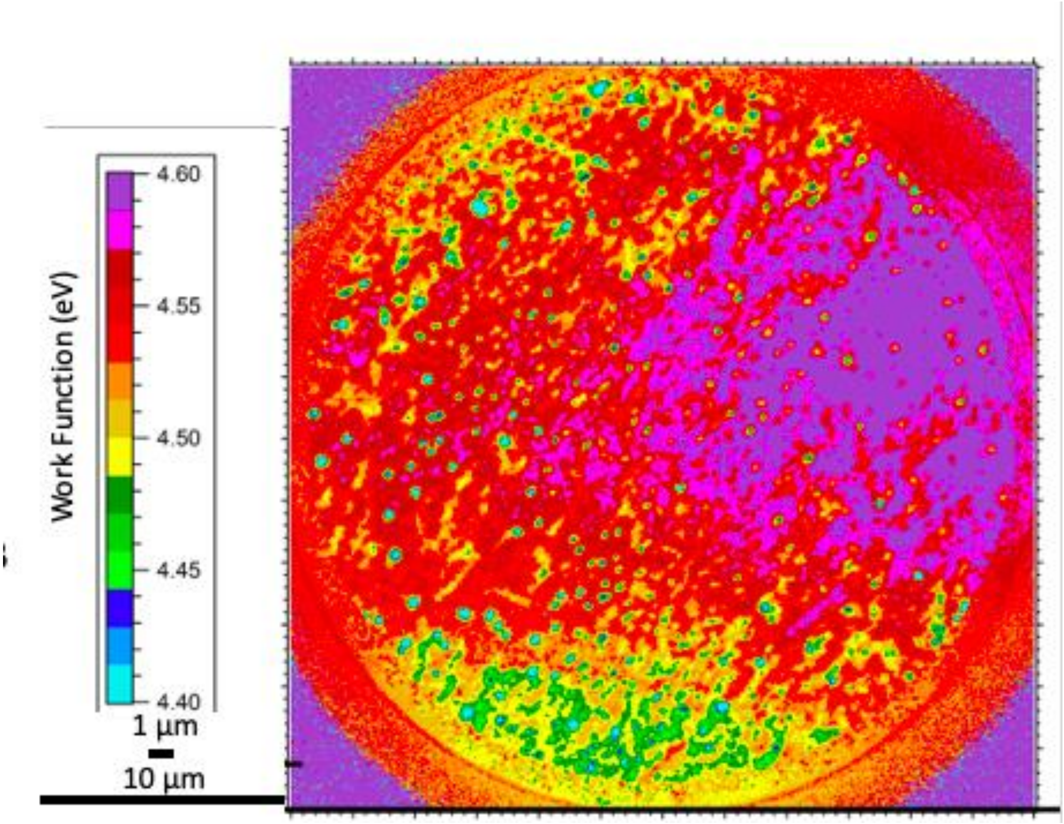

Figure 20: Energy filtered work function map of scandium deposited onto diamond surface with a 72% coverage.

3.4 - Scanning Electron Microscope

The sample was placed under the scanning electron microscope again. it can be seen that as the scandium evaporated onto the single crystal diamond it formed a smooth surface shown in figures 21 and 22.

Figure 21 shows a circle, this corresponds to where the washer was placed on the sample in order to hold it in place whilst in the NanoESCA.

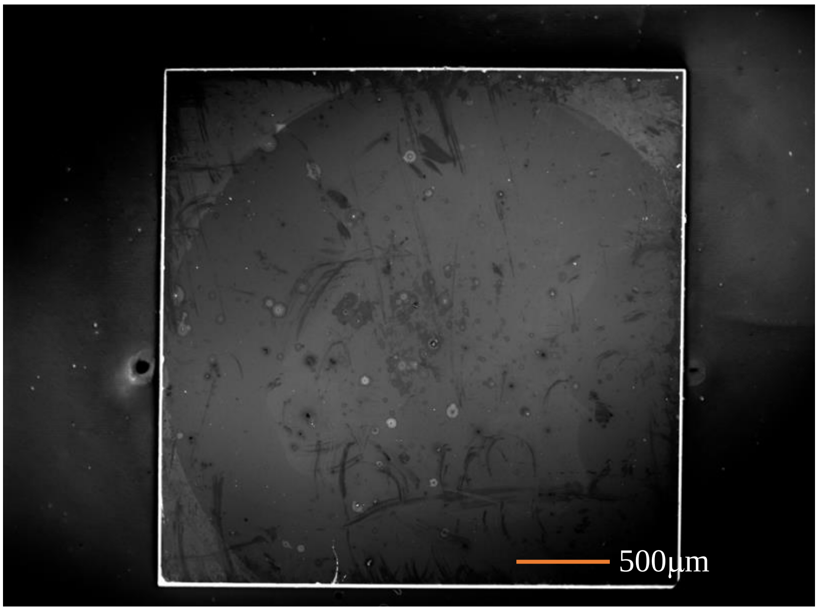

Figure 21: Scandium onto diamond surface under scanning electron microscope at 77x Magnification.

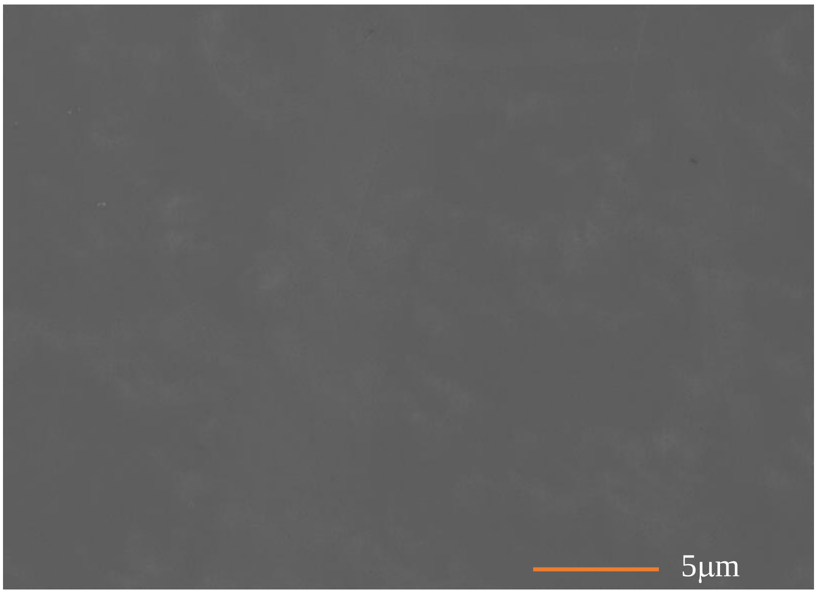

Figure 22: Scandium onto diamond surface under scanning electron microscope at 4000x Magnification

4 - Conclusion

A level of coverage of 72% doesn't constitute a negative electron affinity on C(100) diamond. However, the UPS of the sample was skewed as the thin boron layer of the diamond was not thick enough, meaning that under UPS the sample began to charge. This then changed the properties of the sample meaning a truly accurate work function was not obtained.

5 - Future work

Due to a University wide closure, there were unforeseen time constraints the project couldn’t be repeated with a full monolayer coverage, and the UPS data was left in the NanoESCA with no way of access. This means the error, which would have been found from taking the range from the steep drop of the UPS graph could not be obtained.

The experiment could have been repeated with a Full monolayer and a thicker Boron layer.

Results from a thesis that at the time of writing has yet to be published showed that titanium oxide had the lowest work function at a quarter monolayer due to its 4+ charge. Since scandium naturally forms a 3+ charge it may be found that a 1/3 monolayer would have been the closest to a NEA.

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