

The Role of Surface Morphology and Surface Termination on Diamond Surfaces Exhibiting High Photoelectric Yield

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Abstract

The fabrication of self assembled diamond on a tungsten substrate was found to be successful, using electrostatic adsorption of diamond particles in a suspension at a regulated pH on to a cleaned tungsten surface with positively charged PEI polymer adsorbed on to it, to achieve good surface coverage on the material. The lithium terminated oxygenated surface of the self assembled diamond was found to exhibit a high secondary electron emission yield, in addition to its known thermionic potential. The high yield of secondary electron emission also holds potential for enhancing the thermionic emission potential of such diamond materials.

1.0 Introduction

With the expectation that, within the next two decades, the world demand for fossil fuels will have exceeded annual production and, with the dangers surrounding such heavy reliance on these fossil fuels and nuclear power highlighted, in light of recent events such as the Gulf of Mexico oil spill and the Fukushima nuclear catastrophe, there has never been more emphasis on the need for research into efficient, renewable energy sources. In 2010 renewable sources of energy were estimated to have grown to supply 16% of global energy consumption as a year average, with up to one quarter of global energy estimated to have been provided by renewables by the years end. In spite of global recession, investment in renewable power sources rose in 2010 to \$211 billion, a 32% increase from \$150 billion spent the previous year. The most abundant source of renewable energy we have available to us on earth is solar thermal energy. It is known that more than 7500 times the earth's annual energy consumption falls on the world as solar thermal energy each year and in just one hour the earth receives more energy from the sun than we consume in an entire year^{1,2}. As a result of this, great interest in current research is to develop new ways of harnessing solar radiation that reaches the earth, for the use in efficient energy production methods.

One such method that is subject of intense current research is thermionic emission. Most simply, thermionic emission is the heat induced emission of electrons from the surface of a material. Observations of this phenomenon were observed in the 19th century, but it was first quantified by Owen Richardson, who in 1901 devised the Richardson equation. This equation has been modified several times and is now most commonly presented as the Richardson-Dushman equation.

$$J = A' T^2 \exp\left(-\frac{\phi}{k_B T}\right)$$

(Eq.1)

For which, J is the Current density (Acm^{-2}), A' is the Richardson constant ($\text{Acm}^{-2}\text{K}^{-2}$), T is the Temperature (T), ϕ is the Workfunction (eV) and K_B is the Boltzmann constant³.

To make use of this phenomenon, thermionic emission can be applied in a heat engine known as a thermionic energy converter (TEC). A TEC consists, most basically of a hot emitter and a cooled collector, which are separated by a vacuum gap. It works, as the current produced by the emitter, flows through the vacuum to the collector, across a temperature gradient, which acts as a thermovoltage, generating electrical power. TECs hold great promise for use in energy generation via the conversion of thermal energy into electrical work as they have no moving parts, giving them a great advantage over mechanical generators, as they have the potential to work at high levels of efficiency. The challenges are to produce materials that can be configured in a system, for which high efficiency thermionic converters can be built and then produce these in an economically viable manner.

2.0 Theory

2.1 Band Theory

Band theory is an extension of molecular orbital (MO) theory and is a theory used to help with the explanation and prediction of the electrical behaviour and characteristics displayed by a material. It works, by treating a material as an infinite number of indistinct atoms and similar orbitals on neighbouring atoms, i.e. orbitals which possess the same n and l quantum numbers, as degenerate⁴. These degenerate orbitals are assumed to be able to overlap and form a band of energy levels. Due to the number of orbitals assumed to be in this band the energy gap between these orbitals is taken to be incredibly small and so the band is taken to be continuous. There are three distinct types of electrical conductivity that a material may possess and materials can be divided into metals, semiconductors and insulators because of this. Each different type of material presents a distinct band structure, which can be displayed pictorially by a diagram known as a band diagram. Band diagrams show the energies at which filled and unfilled orbital bands lie in relation to each other, as well as displaying the degree to which electrons have filled a band.

Each material possesses a valence band, it is the bottom band on a band diagram and appears as the only band present in the band diagram for a metallic material. The

valence band is formed from the last filled or partially filled orbital in the molecular orbitals present in a material and is filled by the electrons in these orbitals. The highest energy level at which electrons appear on a band diagram is known as the Fermi level.

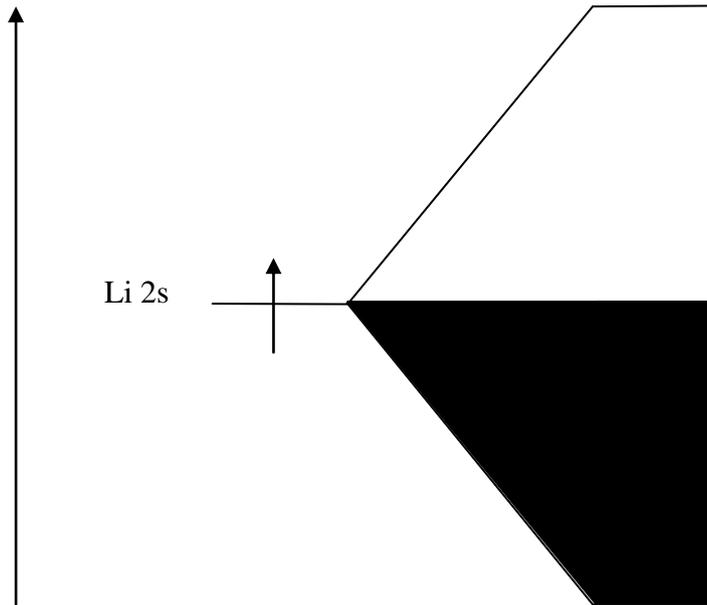


Figure 1- The band diagram for lithium, a typical metal.

Above in figure 1 appears the band diagram of a typical metal, lithium. The valence band here is formed by an infinite number of lithium 2s orbitals, that would in a molecular orbital form a σ bond and a σ^* antibond between two lithium atoms. Each orbital in the material has one electron and as they are half filled orbitals the band created by these 2s orbitals is half filled. The composition of lithium atoms possesses metallic conductivity as a result of this half-filled band as electrons that lie within this band are free to move within the band as it is formed of continuous energy levels. This means electrons are free to move around the material and so lithium is able to conduct electrically, this is the same for any material that displays a partially filled band.

The conduction band appears on band diagrams for both semiconductors and insulators. It lies higher in energy than the valence band, which in both semiconductors and insulators is filled, meaning the Fermi level. The separation in energy from the top of the valence band, termed the valence band maximum (VBM) and the bottom of the conduction band, the conduction band minimum (CBM) is known as the band gap. The band gap is the energy required to be provided to an electron to be promoted from the valence band to the conduction band, which needs to occur in order for a material to conduct electricity.

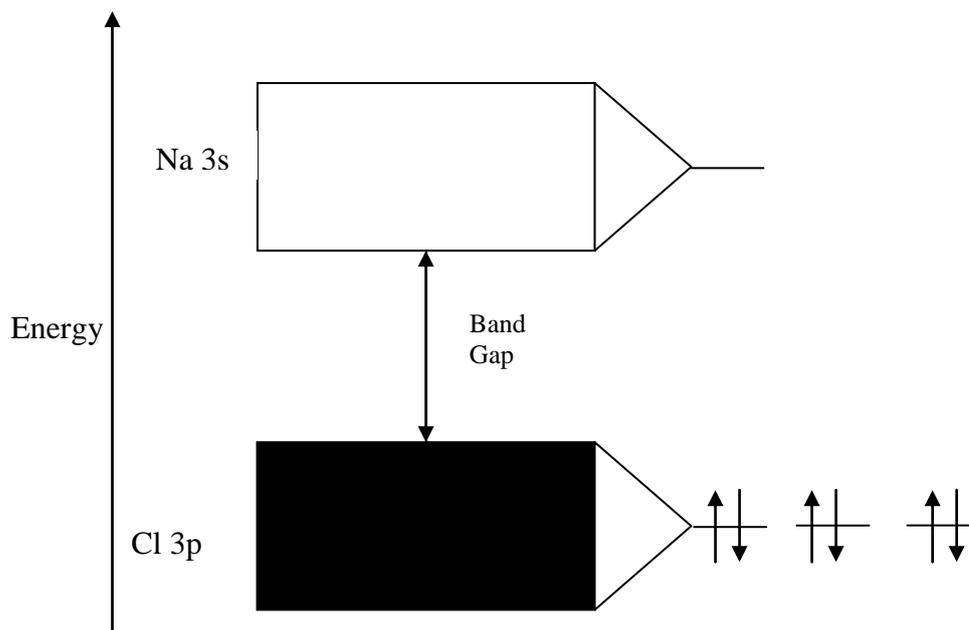


Figure 2- the band diagram of NaCl, a typical electrical insulator.

It is shown in figure 2 that the 3p band of Cl lies below the 3s band of Na which is expected from MO theory, it is also shown that the electron in the 3s orbital of sodium lies in the 3p band of chlorine, as expected for the ionic species NaCl. Here there is a full 3p band, the valence band, which lies below an empty 3s band, the conduction band. For sodium chloride to conduct electrically energy equivalent to the band gap would need to be provided in order to excite electrons into the conduction band. This is true of both semiconducting materials and insulators. However the major factor in whether a material is classed as a semiconductor or an insulator is the size of the band gap separating the conduction and valence bands. If the gap is greater than 3eV then the material is classed an insulator, as it is for NaCl, but if the gap is lower than this

value the material can be classed a semiconductor. Semiconductors, provide a more varied band structure though. Some consists simply of a filled valence band and an empty conduction band separated by less than 3eV, similar to the NaCl structure displayed and described above, these are known as intrinsic semiconductors and gain their semiconducting characteristics from the properties of the bulk of the material. Others, however display semiconductivity as a result of impurities introduced into the material through doping and surface terminations, these are known as extrinsic semiconductors and display a band structure that is slightly more complicated than that of intrinsic semiconductors. Extrinsic semiconductors can be categorized into to separate subsections, known as p-type and n-type semiconductors, both of which gain their semiconducting character through the formation of energy levels within the band gap, either above the valence band or below the conduction band.

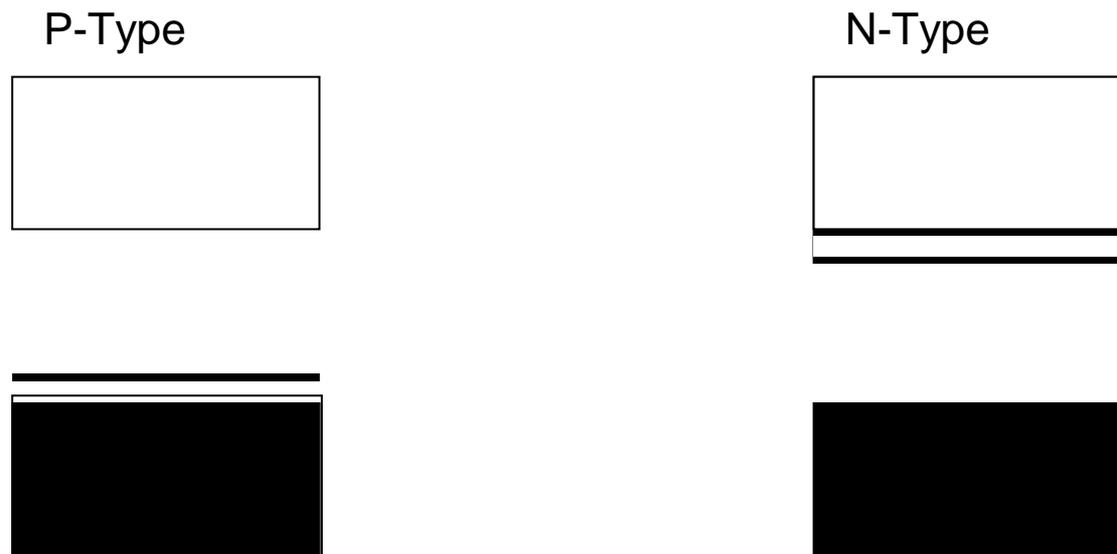


Figure 3- Example band diagrams for p- and n-type semiconductors.

Above figure 3, shows examples for the band diagrams of both p- and n-type semiconductors. It can be seen that, in p-type semiconductors the Fermi level lies just above the VBM with holes appearing at the top of the valence band. This is caused because the impurities that lie in a p-type semiconductor are charge acceptors and so they form acceptor levels that lie above the valence band and pull electron density out from the valence band. The name p-type is derived because there are many more electrons than holes, so to some it may appear as though the holes in the band are the

charge carriers, moving a positive charge. This is not the case as conductivity is still caused by the movement of electrons but this is where the p-type notation is derived from. Figure 3 also shows a model n-type semiconductor band diagram, it displays a Fermi level that lies just below the CBM. It is caused by the introduction of charge donors as impurities into the material. These form donor levels below the conduction band, which require comparatively small excitation energies to allow electrons to move from these levels into the conduction band in relation to the energy required to excite electrons from the VBM to the CBM. N-type semiconductors are promising materials for electron emission applications as they allow electrons to be present in levels just below the CBM. Such materials also often have wide band gaps and so the CBM is close to the level at which electrons are no longer bound to the material and so the barrier to emission is significantly reduced, especially when doping or surface termination can cause a conventionally insulating material into this form of semiconductor.

On a band diagram some important parameters can be defined in addition to the VBM, CBM, Fermi level and band gap. The energy at which electrons are free to be emitted from the material and into the vacuum is known as the vacuum level, once electrons gain sufficient excitation to reach this level they are no longer bound to the material and are free to leave the surface and pass into vacuum. The energy gap between the Fermi level and the vacuum level is known as the workfunction, the surface workfunction is significantly reduced by raising the Fermi level. The energy required to excite the highest energy electrons into emission is reliant on the workfunction and so by consequence the position of the Fermi level. The energy gap between the CBM and the vacuum level is termed the electron affinity. Electron affinity is defined as, the energy that would be required by an excited electron lying at the CBM to overcome the barrier to emission.

2.2 Workfunction

A materials surface workfunction is defined as the energy required to take an electron from the Fermi level to the vacuum level and is an important property to be considered when studying the electron emission properties of a material. The surface workfunction is a property that is specific to each material and different planes of the

same material often have slight variations in their measured workfunctions. Developing materials that have a low or reduced surface workfunction is seen as an important step to providing materials capable of efficient electron emission and many surface treatments have been tested in order to find such materials.

Element	Workfunction	Element	Workfunction	Element	Workfunction
Ag	4.52-4.74	Ce	2.9	Na	2.36
Al	4.06-4.26	Co	5.0	Ni	5.04-5.35
As	3.75	Cr	4.5	Pd	5.22-5.6
Au	5.31-5.47	Cs	1.95	Pt	5.12-5.94
B	4.45	Cu	4.48-5.10	Rh	4.98
Ba	2.52	Fe	4.67-4.81	Se	5.9
Be	4.98	Ga	4.32	Si	4.60-4.91
Bi	4.34	Ir	5.00-5.76	Sn	4.42
C	5.0	K	2.29	Ti	4.33
Ca	2.87	Li	2.93	W	4.22-4.63
Cd	4.08	Mg	3.66	Zn	3.63-4.9

Table 1- A table displaying the workfunction in eV of a selection of elements⁵

The above table shows a series of surface workfunctions for a range of elements and where different crystallographic planes yield different workfunctions the workfunction is presented as a range of values. It can be seen that of the elements for which appear in the table that the alkaline metals, such as caesium, lithium and potassium, display the lowest workfunctions.

2.3 Electron Affinity

The electron affinity is an important property for a material, which goes some way to defining the emission behaviour of a material. Electron affinity is, by definition the energy gap between the CBM and the vacuum level⁶. It is the energy required to take any electrons in the conduction band to the vacuum level and so overcome the barrier to emission. The electron affinity of a semiconductor can also be described by the

energy required to remove an electron from the CBM of the material to a point macroscopically far from its surface and thus materials that possess a low electron affinity are therefore desired for electron emission applications⁷.

2.4 Electron Emission

Studies into the properties of electron emission and research into improving the efficiency of electron emitting materials through the tuning of the surfaces of emitting materials is an area of heightening interest for current research. With materials that display electron emission having uses in current electronic devices and the expectation for electron emitters to have the potential of many more uses for both current and potential applications within the electronics division, research into the advancement of electron emitting materials has seen large investments in recent years.

The area of vacuum electronics and microelectronics for which many electron emitting devices can and have realised potential uses is an incredibly wide field, finding applications for devices that range from uses in flat panel displays to energy conversion engines^{2,7}. There are three major categories of electron emission from a solid and each takes its name from the medium for which the electrons in the material gain the required excitation energy needed for emission. These categories are; thermionic emission, field emission and secondary electron emission⁸. For electron emission to be termed as field emission, the energy provided for electrons to be excited into a state where they are no longer bound to the material, must originate from an electric field applied to the material. Likewise with secondary electron emission, in which the excitation energy is gained by the collision of an incident particle with the surface of the emitting material, with the required energy transferred from the incident particle, which may be among a range of particles, including for example an atom, electron or photon. Thermionic emission is perhaps, the most promising of electron emission modes for use as an efficient source of electrons and it relies on the thermal excitation of electrons in a material to gain sufficient energy to emit from the surface. Due to the abundance of thermal radiation provided by the sun thermionic applications are viewed as an interested method of energy generation for many applications.

2.5 Richardson-Dushman Equation and Thermionic Emission

Owen Richardson undertook work in 1901 on what was then titled, the effect of heat on the interaction between electricity and matter, building on work done by Guthrie (1873), Elster and Geitel (1882-1889) and J. J. Thompson (1899). Richardson's work focussed on the phenomena now known as thermionic emission, which mostly plainly described as the emission of electrons from a surface, stimulated by thermal excitation. Richardson first noticed that when studying electron emission from a platinum surface, the number of electrons emitted was limited per unit area, but this limit was subject to rapid increase as temperature rose⁹. The result of this realisation, was the derivation of an equation that related emission current i , to temperature T .

$$i = AT^{1/2}e^{-w/kT} \quad (\text{Eq.2})$$

In which i was the maximum current, T the absolute temperature (K), w the workfunction of the surface (eV), k the Boltzmann constant and A the Richardson constant ($\text{Acm}^{-2}\text{K}^{-2}$). The value of the parameter, A , was determined as an ideal, to be $123 \text{ Acm}^{-2}\text{K}^{-2}$ and derived as a collection of known constants and presented as;

$$A = emk_B^2/2(\pi^2\hbar^3) \quad (\text{Eq.3})$$

Where e is the electronic charge, m is the mass of an electron, k_B is the Boltzmann constant and \hbar is the Planck constant. Although, A is determined as a constant with the theoretical value of $123 \text{ Acm}^{-2}\text{K}^{-2}$, it is known to vary as the structural surface properties of the emitter also govern the value that A holds¹⁰. For a tungsten emitter with a workfunction of 4.52 eV the experimentally determined value for the A constant was $\sim 60 \text{ Acm}^{-2}\text{K}^{-2}$.

Richardson equation relating the current density produced by thermionic emission was later altered, with input from Dushman, to account for emitted electrons that may not be detected and other such factors that may reduce the observed current, forming what is now the widely accepted Richardson-Dushman equation. For which, J is the Current density (Acm^{-2}), A' is the Richardson constant ($\text{Acm}^{-2}\text{K}^{-2}$), T is the

Temperature (T), ϕ is the Workfunction (eV) and K_B is the Boltzmann constant, this is now presented in the form of Eq.1 (1.0 Introduction).

The phenomenon of thermionic emission is utilized in the energy generation and electronics industries for many current applications. It is envisaged that with advancements of the materials and surfaces used to fabricate these emitters and improvements to the systems that they work within, that these thermionic emitters may be used as the electron source for many more potential applications currently using other less efficient methods for power generation. Within the electronics industry thermionic emitters now have many applications in which they are used to provide a source of electrons, such as for electron guns and high power telecommunications.

Perhaps most interestingly though, is the potential employment of thermionic emission for the generation of electrical work through the direct conversion of thermal energy. This application is employed in a heat engine conventionally known as a thermionic energy converter (TEC). A conventional thermionic energy converter consists simply, of a hot emitter separated by vacuum from a cooled emitter. The temperature gradient over the vacuum gap between the collector and emitter acts as a potential difference or thermovoltage and as a current of electrons are emitted through this thermovoltage, electrical power is generated. A TEC contains no moving parts and so holds a major advantage over traditional mechanical generators due to this, as it possesses the potential for a much greater efficiency. TECs are known to have been fabricated with an efficiency of upwards of 30% but are currently believed to have the potential to reach an efficiency of up to 90%, making them an attractive area for investment into current research.

Research into the high efficiency of thermionic energy conversion intensified in the latter half of the 20th century, as both the US and the Soviet Union recognised the potential of the highly efficient method for energy generation, via this process of conversion from thermal energy, with both nations launching research programs to employ TEC technology as a method for power generation for future space programs, with the building and testing of TEC technologies carried out through much of the 1950s and 1960s. However the first reported successful testing of such a device did

not come until 1971, when research at the Soviet TOPAZ nuclear power system project reported success in ground-testing. The TOPAZ reactor consisted of a flat metal tungsten emitter heated by thermal energy provided by enriched UO_2 fuel rods. The emitter and collector were separated by a vacuum gap, in which caesium vapour was injected in order to negate space charge effects. During 1987 two separate Soviet space missions were successfully launched using the TOPAZ thermionic system as the power source for the space mission. The missions were planned to last for a year and for 6 months after which the TOPAZ energy generator was deemed to have been a success¹¹. However due to the high working temperature of $\sim 1770\text{-}2070\text{K}$ ¹² for which the emitter requires to be heated to, in order to generate sufficient emission for a substantial power to be generated, thermionic energy converters, based on this set up were not deemed suitable for terrestrial or mobile applications.

Traditional TECs also employed a similar system to that of the TOPAZ program, with flat metal electrodes also employed as the material for which the emitters. These metal or metal composite electrodes often require working temperatures of upwards of 1000°C in order to generate an appreciable current of emitted electrons, which again is too high for use in most terrestrial applications, for example an initial demonstration of such a configuration employed a tungsten electrode, impregnated with BaCO_3 and SrCO_3 impurities required a working temperature of 1260°C to gain a substantial emission current¹³. Typical flat metal emitters, commonly used in these traditional TECs, tend to possess surface workfunctions that range from $2\text{-}5.5\text{eV}$, with it accepted that to attain an appreciable current of emitted electrons at low to moderate temperatures sufficient for energy conversion, surface workfunctions need to be lower. Using caesium vapour injected into the interelectrode space was found to reduce the surface workfunction of the emitter by $\sim 1.45\text{eV}$ for a flat tungsten emitter, with a similar result found for a molybdenum emitter, however, even with the lowering of workfunction for metal emitters, appreciable power cannot be generated from conventional TECs at a temperature below 1200K . These high operating temperatures limit the lifetime of the converter¹⁴ and thus these TECs can now only be used for specialist applications until further advancements in the current technology are made.

2.6 The Space Charge Effect

Space charge is an effect that reduces the efficiency of thermionic emission of electrons into vacuum and is known to significantly lower the effectiveness of thermionic emission from flat metal emitters. Space charge builds up as a result of the emission of slow moving low energy electrons from the surface of that material. These slow moving electrons lie in the interelectrode space as a result of either, bouncing back from the collector or failing to fully leave the surface of the emitter and effectively reduces the emission current reaching the collector by blocking electrons as they leave the emitter. A number of techniques have been used to negate this effect, as it is the cause of a large reduction in efficiency for TECs and causes the required temperature for sufficient current to be emitted to be increased, as well as degrading the efficiency of the emitter as usage continues¹⁵. The effect is felt worst by flat metal emitters as a result of the size and shape of the emitter as well as the surface workfunction of the emitter material being too high and thus causing many of the electrons emitted to have a low energy. Methods such as introducing a positive ion species, such as caesium vapour, into the interelectrode space in order to neutralize the charge build up caused by emitted electrons have been used effectively to increase the efficiency of thermionic emission. An added feature of the introduction of this caesium vapour into the interelectrode space was the reduction in the workfunction of the metal emitter and so fewer low energy electrons were emitted into the vacuum as a result of this, meaning the introduction of caesium vapour acts in two ways to create an overall more efficient thermionic emitter. Other methods that have been used in order to mitigate space charge effects include addition of methane into the interelectrode space or reduction of the interelectrode gap, the latter of which was found to be very difficult to fabricate practical devices implementing this specification¹³. Another method that has been used to increase the current of electrons gathered at the collector was to reduce the workfunction of the collector surface. This results in fewer electrons bouncing back from the collector and so works to increase the current collected at the collector relative to number of electrons emitted, as well as reducing the electrons that are free in the electrode space, which results in greater effectiveness of thermionic emission at the emitter and so this method also acts in two separate ways in which to increase the efficiency of a thermionic emitter.

2.7 The NEA Condition

As stated previously (2.3 Electron Affinity) electron affinity is the energy gap between the CBM and the vacuum level, the energy at which electrons are no longer bound to the surface of a material and free to pass into vacuum. For most materials, electron affinity can be defined by the energy required to take an electron from the CBM to the vacuum level, these materials possess a positive electron affinity. However, for some materials, the electron affinity may be negative, a condition termed negative electron affinity (NEA). This condition is found as a result of the CBM lying at higher energy than the vacuum level¹⁶. A material that possesses the NEA condition has certain characteristics, which affect, most significantly the behaviour of the material when concerning electron emission. Due to the positions of the vacuum level and the CBM, any electron density promoted into the conduction band for a material possessing the NEA condition is higher in energy than the vacuum level, meaning that they are not bound to the surface of the material and available for emission¹⁷. The result of this property therefore, is that the barrier to emission is reduced, as energy required for emission, is the energy needed to promote electrons from the Fermi level in to the conduction band, it also results in electrons that are emitted from the material possessing greater energy as their presence in the conduction band means that they have, greater energy than the vacuum level, with the NEA the lowest excess energy they may possess, after emission. Very few materials possess a negative electron affinity and lots of research in the present day surrounds finding materials that display this condition and to improve the condition of current NEA materials. In comparisons of the electron emission performance of materials with NEA and positive electron affinity (PEA) it was found that materials that display a NEA significantly outperformed the materials with PEA, when the conditions were made to be equivalent, by using an NEA material with a barrier to emission equivalent to the workfunction of the PEA material¹⁵. As well as outperforming PEA materials in terms of emission, the use of a material that possesses NEA for emitters, significantly reduces the space charge build up that effects emitter performance. This is a result of the NEA material emitting electrons that have a greater energy and so fewer emitted electrons sit around the surface of the emitter or in the interelectrode space. The use of materials that display an NEA condition thus, hold great potential for the realisation of a thermionic emission device, capable of operating effectively to

provide sufficient emission, for electronic or even energy generation devices at low or moderate temperatures.

2.8 Emission from Semiconductors

In recent years, it has become clear that it is semiconductors and most of all n-type semiconductors that hold the greatest promise as a candidate material for the use in electron emission and most specifically thermionic emission applications. With it known that, in all likelihood a material that possesses an NEA condition or a significantly reduced workfunction is required for substantial emission at moderate temperatures to be achieved, attention has turned to surface treatments and doping of materials in order to achieve such conditions.

It is known that semiconductors that possess wide band gaps have the potential to exhibit NEA conditions⁷. For this reason extrinsic semiconductors, often formed by adding dopants or surface treatments to semiconducting and insulating materials, are of key interest for their electron emission properties. Semiconductors that possess a wide band gap are possible candidates for achieving the NEA condition due to the high energy at which the CBM must lie at for a material that has a large band gap. This increases the possibility that the vacuum level lies below the CBM and so therefore increases the possibility of a material possessing NEA.

Surface treatments to semiconducting materials, such as adsorbing just one monolayer of an alkali metal, Na, K, or Cs, to the surface of semiconductors such as Si and Ge, is known to significantly lower the surface workfunction of the material in question, by between 2 and 3.5eV. This is thought to be caused as a result of the formation of surface dipoles due to the high electropositivity of the alkali metals that are adsorbed. It is also known that adding Cs or Rb to an $(\text{NaK})_3\text{Sb}$ semiconductor, is effective in reducing the workfunction of the material¹⁸. However, the reliance on alkali metal layers adsorbed onto a surface creates a new problem as although they are effective in achieving a lowered workfunction, they are easily contaminated and will not operate after air exposure¹⁶. This complication causes it to be difficult to use such materials and regain a working surface after contamination, which means they are somewhat impractical. As the most highly electropositive element readily available, studies into

the effect of caesium have been undertaken with the greatest regularity and detail¹⁹, its high electropositivity suggests that it should form strong electron donor layers on the surface to which it is adsorbed and create the large dipoles to which the reduction in surface workfunction and achievement of NEA are attributed to. Studies into the effects of the CsO- termination of semiconducting materials such as Si, GeAs, and GeP, have seen an NEA condition activated on surfaces of these materials. For the Silicon example, processing with Cs and O was successful in inducing the NEA condition for the Si(100) face but unsuccessful for the (111) and (110) faces. Whilst surface termination and doping of semiconductors is one way of achieving NEA, some semiconductors are also able to possess NEA. It has been known for boron nitride, BN and also in aluminium-gallium-nitride, AlGaN, when alloys are composed with a high quantity of aluminium, as well as in AlN¹⁶.

2.9 Carbon based Emitters

Carbon based materials have long been of interest for electron emission applications due to a number of properties which they possess. Carbon materials, as a source of electrons tend to have low threshold fields for emission, with applied fields required for field emission for such carbon systems being lesser than for most other materials¹⁷. Carbon materials also tend to possess low electron affinities. Whereas with metals the low electron affinity is caused by the low electronegativity of the metallic elements, carbon is the most electronegative of the group 14 elements and the low electron affinity stems from a wide band gap, which is possessed by many carbon based materials⁶. With diamond, diamond-like carbon and carbon nanotubes proving the most promising of materials for electron emission applications²⁰⁻²².

2.10 Electron Emission from Diamond

Diamond is a useful material for applications concerning electron emission and has been intensively researched in recent years, due to a number of chemical, physical and mechanical characteristics it possesses, mainly as a result of the tetrahedral framework of sp^3 carbon-carbon bonds. Diamond is not only the hardest material known to man, but has a high thermal conductivity, greater than even that of copper, a material that is most commonly used for its thermal conductance. Diamond is

chemically stable and most importantly for electron emission applications is capable of possessing the NEA characteristic. Diamond is naturally an electrical insulator due to the wide band gap present, but can possess certain properties that are promising for electron emission at the surface²³. Tuning of these properties that can be promising for emission can be done by the introduction of chemical dopants into the sp^3 carbon framework, with elements such as nitrogen, boron, phosphorus and sulphur having been successfully introduced in order to reduce the workfunction and induce NEA. Surface terminations have also successfully used to induce an NEA and lowered workfunction, with hydrogen termination and the treatment of an oxygenated surface with alkali metals providing examples of where this has caused an improvement of diamonds emission characteristics.

Diamond has long been noted as showing promise for electron emission applications as a result of its unique properties, with a band gap of $\sim 5.4\text{eV}$ diamond is the only material currently known to possess a NEA when surface terminated by hydrogen. As a result of this, the diamond surface shows huge promise for electron emission as, it is noted that through tuning with other surface terminations and chemical dopants it is likely that an enhancement of the NEA character and low workfunction will be achieved, in order to create a material that will be capable of substantial electron emission at low to moderate temperatures.

Research into the properties of diamond and its possible use as a potential material for electron emission applications has, over recent years intensified. This is due to the development of crystal vapour deposition (CVD), high temperature high pressure (HPHT) and diamond self assembly methods for forming industrially available diamond films, or layers of diamond particles. Such methods have caused the study of diamond surfaces to be a financially viable area of research and so its useful properties are now well documented as a result.

2.11 Hydrogen Termination of Diamond

The electron affinity of a clean diamond surface, with no foreign atoms employed as surface terminations, has an electron affinity of $\sim 0.5\text{eV}$. However, when diamond is terminated at the surface by hydrogen, the hydrogenation layer induces a significant

NEA, causing a drop of almost 2eV in electron affinity. This is the result of the hydrogen surface termination²⁴ forming dipoles at the surface of the diamond. As hydrogen and carbon both have similar electronegativities, there is no great reason for a significant dipole to be formed and an NEA would not be expected to be induced, however the dipole formed in this case is a symmetry dipole, formed through breaking of the symmetry in the carbon framework as a result of the carbon to hydrogen bond at the surface. As charge density moves from the centre of the hydrogen atom to the centre of the C-H bond, symmetry is broken perpendicular to the surface of the material, causing sub-bands to be formed⁶. With the slight difference in electronegativity between carbon and hydrogen causing a small net movement of electrons towards the carbon, a small amount of electron density accumulates in the conduction band. With the NEA a result of the formation of sub-bands and the electron density accumulating in the conduction band electrons become available for emission. Termination by either hydrogen or deuterium has been observed to significantly reduce threshold voltages to emission as well as increasing the emission current by almost a factor of 20¹⁹. The explanation for this improvement in emission characteristic, is not only thought to be as a product of the formation of sub-bands and surface dipoles, but also because the hydrogen treatment that is responsible for this hydrogen termination is expected to remove any areas of oxygen or graphite impurities found within the diamond structure and be responsible for the restoration of the sp³ structure that is necessary for electron emission from diamond to be effective. Oxidised, hydrolysed and aminated surface terminations have all been tested on CVD diamond. The results of each of these surface treatments were found to degrade the performance of electron emission from the surface of the material, with threshold fields raised and emission current reduced by at least 2 orders of magnitude for all terminations.

2.12 Doping of Diamond

Diamond can be doped by a wide range of elements, each of which has varying effects on the workfunction, NEA and electronic behaviour of the surface and material as a whole. The doping of diamond can be used to create both p-type and n-type semiconducting materials, with the introduction of charge donors, to create n-type diamond semiconductors, subject of increasing research.

The p-type doping of diamond is most commonly found with the introduction of boron impurities. Boron is a common impurity in naturally formed diamond and due to the similarity of the atomic radii of boron and carbon can be incorporated into the diamond sp^3 structure with relative ease in comparison with the incorporation of other elements²⁵. The man-made formation of boron doped diamond can be achieved, either by CVD growth or by ion implantation, with both methods successful in producing lightly doped diamond. Boron is a charge acceptor, when incorporated into diamond and so forms acceptor level in the band structure. The acceptor levels formed by boron in diamond lie above the VBM, with the Fermi level raised $\sim 0.35\text{eV}$. The position of the Fermi level in boron doped diamond is as expected for a p-type semiconductor, but also indicates that there will be a large barrier to emission. As a naturally occurring material lightly boron doped type IIb diamond has been researched and studied extensively for its properties, as has CVD grown boron doped diamond. The NEA characteristic and field emission have been observed from these materials when surface terminated by diamond, emission from these surfaces has been attributed to electrons within the valence band. Boron doped diamond has been proposed to have uses in vacuum microelectronics and for cold-cathode applications. However, the barrier to emission for such p-type doped diamond is thought to be larger than for the n-type doped alternatives and due to this and the ease of making boron doped diamond and its occurrence in nature, the incorporation of other elements for the formation of p-type doped diamond have not been studied in depth as a result. It was found that for boron doped diamond that, surface treatments such as excimer laser annealing, hydrogen passivation, argon/oxygen plasma etching and surface coating with gold were all found to reduce the performance of electron emission from the surface. Reasons for the degradation in emission performance have ranged from surface damage to causing the electron current produced from the surface to be unstable.

Nitrogen, phosphorus and sulphur have all been reported to have been used successfully to dope diamond, all forming n-type semiconductors²⁶⁻²⁸. Each of these different elements used for n-type doping of diamond causes donor levels to be formed beneath the conduction band. The donor levels formed for each doping elements are at different positions beneath the conduction band, each of which have different effects on the emission properties of the surface of the diamond. The

formation of n-type semiconductors, through the doping of diamond is particularly promising for electron emission applications due to the material properties of diamond, such as the ability to possess NEA and the position at which, the donor levels form beneath the conduction band. As these donor levels form beneath the CBM the Fermi level is raised by a large energy and the barrier to emission is significantly reduced.

Nitrogen doped diamond is the most thoroughly researched of all of the n-type doped diamond due to its occurrence in nature. Like boron impurities, but to a lesser extent, nitrogen can be found in some naturally occurring diamond and so its properties have been studied intensively. It is known that for nitrogen doped diamond with the appropriate surface termination a strong NEA can be observed, a promising condition for thermionic applications. Electron emission and the NEA character for nitrogen doped diamond can be attributed to the hydrogen termination at the surface, this hydrogen terminated layer shows stability up to $\sim 800^{\circ}\text{C}$, which is a higher temperature than the hydrogen termination on clean undoped surface diamond, is stable to. However, the introduction of metal layers, such as Ti, Hf, or Zr to nitrogen doped diamond, has been found to further increase the stability of thermionic emission from nitrogen doped diamond at temperatures approaching 950°C ²⁹. However, although altering the surface of diamond helps alter some surface characteristics, there are still some problems in relation to doping diamond with nitrogen. Doping with nitrogen results in deep lying donor states, which sit $\sim 1.7\text{eV}$ below the CBM, this energy gap is still too large for thermionic emission to present a substantial current of emitted electrons at mid-to-low temperatures.

It has been found to be more difficult to dope diamond with nitrogen successfully than with boron and methods for efficient nitrogen doping are still under research. To achieve the workfunction lowering displayed by doping with nitrogen atoms, a high concentration of nitrogen must be achieved which has also proved problematic. Doping of diamond with nitrogen can be achieved by ion implantation and CVD methods, much like with boron, however at lower concentrations, but a method involving urea as a gaseous source of nitrogen during CVD growth has been devised, which has achieved high concentrations of diamond³⁰.

Effective workfunctions of 1.3eV and lower have been achieved using nitrogen doped ultra nanocrystalline diamond (UNCD), where the previous lowest workfunction for nitrogen doped diamond had been recorded as 1.5eV, with thermionic emission observed from these UNCD films at temperatures as low as 250°C, these materials exhibit decreasing resistivity with decreasing temperature, suggesting that the doping of these UNCD films with nitrogen plays a role in the decrease in resistivity, however a recorded Richardson constant of $0.8\text{A}^2\text{cm}^{-2}\text{K}^{-2}$ means that efficient thermionic emission at low temperatures with this material is still unlikely to be achieved. Nitrogen doped UNCD films also show promise for thermionics applications as a layer between a metal substrate and a top layer of diamond. This material was found to form an ohmic contact with the top layer, a nitrogen doped diamond film. It also forms a low resistance contact with the metal substrate and so overall allows electrons to flow through the bulk of the material more easily⁸. This is beneficial for applications such as thermionic emission, as it lowers the resistivity throughout the material which limits the flow of electrons through the material towards the surface.

2.13 Different Surface Terminations of Diamond

The electronegativity of the surface terminating species plays an important role, in whether the electron emission character of the diamond is improved or worsened by their chemisorption onto the diamond surface. Terminating the carbon sp^3 framework with highly electronegative species will draw electron density out of the conduction band and towards the terminating species, in-turn reducing the amount of electrons available for emission and so reducing the efficiency of emission from the surface. Alternatively, termination by highly electropositive species causes an increase in the electron density in the conduction band as electrons are donated to the carbon from these species¹⁹. The result of this is an improvement in the NEA condition and emission efficiency of the material. Termination by alkali metals and other metals has been tested and confirmed to improve the electron affinity and emission efficiency of the diamond. The termination of diamond surfaces by Na, K and Cs have all been recorded to improve emission properties of a diamond surface significantly, with very similar results observed for all three metals. The use of the surface dipole model predicts that, the most drastic improvement should be observed for termination by the most electropositive of the metals. However, as such similar results are observed for

all three metals, it has been suggested that in all cases the metal species are effectively chemically bonded to the surface, donating their valence electron into the conduction band of the diamond bonding structure in what can be represented as a pseudo ionic bond. With this the case the only differences in emission behaviour that would be observed would be caused by the size of the atoms of the different metal species, with little difference predicted between, the effects of Na, K, and Cs cations that would be present at the surface for the three examples. The thickness of the metal layer adsorbed on to the surface of the diamond has an affect on the emission observed. The deposition of just a few monolayers of metal onto the surface can lower the emission threshold as well as increasing the emission observed. Emission improves with the increasing thickness of the metal layer, but this improvement levels off as the metal layer reaches 50-100Å¹⁹.

Other surface terminations have also been successful in achieving the NEA condition and improving the emission character of diamond films. Although it is known that oxygenation of the surface of diamond reduces the efficiency of electron emission, such surfaces are able to be treated and further enhance observed emission properties from the diamond surface. Treatment of the oxidised surface with metals has often presented positive results, with regards to the emission characteristics obtained by the surface and often eclipses the performance of the surface formed by the treatment of the hydrogenated diamond surface with the same metal³¹.

The formation of a metal oxygen surface termination, such as the addition of a caesium layer to oxygenated diamond presents favourable properties for electron emission. The chemical and thermal stability of this surface is promising for thermionic applications in particular, as previous diamond materials that have had NEA have relied on surface terminations to induce this characteristic, which have not had such high chemical and thermal stability.

The hydrogen termination which is well known to induce an NEA on diamond is prone to corruption by oxygen, when an electron is emitted from the surface of the diamond with this hydrogen termination in poor vacuum conditions, excitation of physisorbed species at the surface can occur and this in turn can cause the release of atomic oxygen which will corrupt the surface and damage the NEA condition of the

diamond³². The termination of diamond with the alkali metals Na, K and Cs does also induce NEA and improve the emission characteristics, but, like the adsorption of layers of these metals on to other semiconducting materials, this surface is not chemically and thermally stable¹⁶. The comparison of the caesiation of hydrogen terminated surface diamond and oxygenated surface diamond shows that the CsO-terminated surface has a stronger NEA and is thermally stable up to temperatures of 650K, temperatures at which the Cs termination on hydrogenated diamond cannot reach without degradation³². It is also possible to apply different surface terminations to doped diamond films, with an example of nitrogen doped diamond films showing improved emission, as a result of a thin surface termination of titanium, bettering the emission measured from the same nitrogen doped diamond films with hydrogen surface termination¹⁷.

2.14 The LiO- Surface Termination

Although the effects of alkali metals such as Na, K, Rb and Cs on both clean and oxygenated semiconducting surfaces has long been known, the effects of lithium termination on clean and oxygenated surface diamond had not been investigated until 2010. The termination of diamond surfaces by lithium metal was found to produce much the same structures that termination by alkali metals, Na, Rb and K have been observed to with the same surfaces of diamond. However, as a result of the size of lithium atoms in comparison with the other alkali metals the binding energies between the lithium atoms and the diamond surface were found to be higher than those recorded for the other metals measured. However, termination with lithium was found to produce the same lowering in workfunction as the other alkali metals was found to and so the study of the termination of diamond surfaces with lithium is an area of interest for electron emission applications.

Due to its high electropositivity, it was thought that caesiation of oxygenated diamond surfaces, to provide an CsO- surface termination, was the most promising of the alkali metal oxide salt surface terminations available for inducing NEA and a low workfunction on diamond, in order to improve the emission potential of the surface. However, the CsO- terminated surface, although more stable than other surface terminations employing alkali metals and more stable than the hydrogenated diamond

surface is only stable up to 650K, which is not sufficiently high for thermionic emission. As seen with the surface termination of lithium on clean diamond, lithiation of the oxygenated diamond surface has similar properties in enhancing emission to other alkali metals. The LiO surface termination on diamond produces a workfunction 4.52eV lower than that of clean surface diamond, a similar reduction to that of the CsO termination, but due to the high binding energy of lithium 4.7eV per lithium atom, it is possible that this LiO surface termination, is capable of thermal stability to a temperature at which thermionic emission is effective³³. It is also possible that because of the reduction in workfunction due to the surface termination will reduce the temperature required for thermionic emission to become effective.

2.15 Project Aims

The aim of the project is to determine the influence of the morphology of the substrate for which self-assembled diamond is deposited onto, on the overall electron emission from diamond. For applications of thermionic emission that could potentially rely on thermal energy concentrated from solar radiation, it is thought that reducing the thickness of the metal substrate in places will act to improve thermionic emission from the diamond surface. The reasoning for this is that, thermal energy used to excite the electrons for thermionic emission should be transmitted more easily through the metal in areas where it is most thinned and also, because it is thought that solar radiation is a potential source of heat for such applications, by reducing the thickness of the metal substrates in small areas, i.e. by cutting grooves into the back of the metal, light may be frustrated through the grooves.

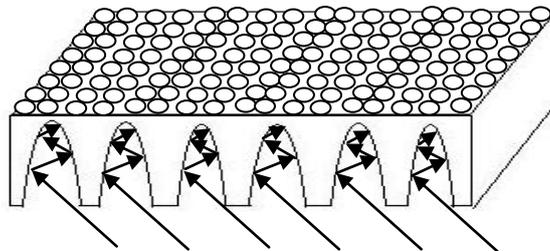


Figure 4- Diagram of how light may frustrate through the machine grooves on the back of a tungsten substrate.

The result of this potentially, is that as light is frustrated through the grooves, the metal substrate in these areas is heated by the concentrated radiation and more thermal energy can be transmitted through from the light into the diamond in order to produce thermionic emission from the surface. It is also thought that by utilizing the secondary emission properties of LiO terminated diamond, in the laser machined grooves at the back of the tungsten substrate, that secondary electron emission caused, by concentrated solar radiation, may also be capable of playing a role in enhancement of thermionic emission from diamond particles on the front face of the tungsten substrate.

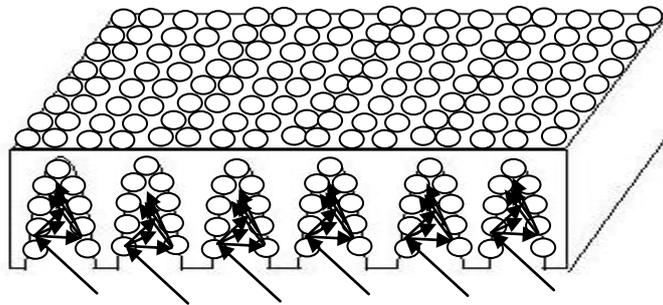


Figure 5- Diagram of how secondary electron emission may be used to increase the potential for thermionic emission.

This would be achieved using light frustrated through the grooves, causing secondary electron emission to commence, with the secondary electrons then in-turn being frustrated through the machined surface, causing the emission of more secondary electrons, in a cascade effect and so transmitting a greater amount of thermal energy through the thin layer of tungsten substrate into the diamond back contact, to thermally excite surface electrons in diamond, whilst also providing electrons to the tungsten substrate to be transmitted into the diamond, in order to achieve a greater amount of thermionic emission from the diamond surface.

3.0 Experimental

3.1 Machining of Tungsten Electrodes

Using the Oxford Laser Micromachining system, squares of 10 x 10mm and 20 x 20mm were cut out from a tungsten sheet of thickness 1.5mm. The tungsten squares were cut out to be used as substrates for which self-assembled diamond may be deposited on to for potential use as an emitter electrode for thermionic applications. Then using a program written on the same laser system, a series of grooves, of dimensions 1mm length by 0.01mm width, were machined into a 7 x 7mm grid, in the centre of the back of the tungsten squares. The grooves were designed to be made as deep as possible, without boring holes through to the other side of the tungsten, so testing was undertaken to find the required laser intensity and the number of passes required for each groove to be machined to this specification.

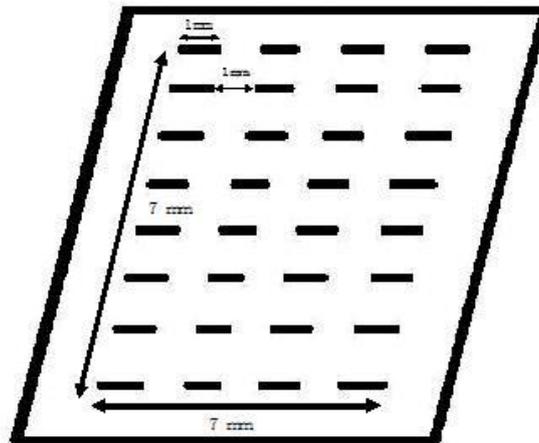


Figure 6- Diagram showing the arrangement of grooves cut into the back of the tungsten electrode.

The program written on the laser machining system cut 32 grooves in the square outlined earlier, with 8 grooves spaced by 1mm parallel to the width and 4 grooves spaced by 1mm parallel to the length. In an attempt to smooth the area on the back of the tungsten electrode around the outside of the grooves, the laser was run around the edges of the grooves at a lower intensity, in order to remove any tungsten deposited as a result of the high laser intensity used for the original machining of the grooves.

3.2 Self Assembly of Diamond

A self assembled monolayer (SAM) of diamond particles were deposited onto the surface of cleaned tungsten electrodes using electrostatic adsorption³⁴. The tungsten electrodes were first cleaned in a 40% solution of KOH, before the adsorption of the positively charged polymer solution PEI (polyethylimine) on to the surface. A diamond suspension, at pH 7.5-8, was prepared using 500nm HPHT diamond and pipetted onto the surface of the tungsten electrode, before being left to dry, with excess diamond washed off using deionised water.

3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a technique that uses the secondary electron emission properties of the material that is being studied in order to show a detailed image of the surface morphology and the species that occupy the surface of the subject of the study. A high energy beam of electrons is concentrated on to a spot on the surface of the material being studied. The energy and intensity of electrons that are then subsequently reflected or emitted from this spot are measured and used to build up an image for the area of the surface being studied, as the electron beam gradually rasters across this area, displaying a brightness for every spot that the beam is focussed on, in order to produce an image for the overall area of focus. When using, SEM, areas on the surface of a material that absorb electrons appear dark as the signal that is recorded in response to the electron beam focussed on this area is lower than a reflective surface. Alternatively, an area on the surface of a material that has a high secondary electron yield will appear bright in the SEM image obtained for that area on the surface as the resultant signal is boosted by the electrons that are emitted from the surface of the material. Changing the energy of the electron beam used in SEM is an effective method in altering the depth at which the microscope probes the surface of the material under study. When using a low energy electron beam, electrons will be reflected off of the surface from a more shallow position on the surface, so the image that will be obtained from such conditions will give more information on the very top of the surface of the studied material. However on using a higher energy electron beam allows the electrons to probe deeper in to the surface of the subject material and

allows a greater understanding to be obtained for a much deeper portion of the surface in question.

3.4 Surface Treatments of Self Assembled Diamond

A series of surface treatments were undertaken on the self assembled diamond deposited on the tungsten electrode in order to reach the lithium oxide terminated diamond surface that was to be studied. First the sample was annealed, in order to fix the diamond monolayer to the tungsten electrodes more securely. This is required for further surface treatments to be successful. Annealing is followed by silver treatment in which a layer of silver is deposited over the diamond monolayer. This was then followed by H^+ plasma treatment, oxygen treatment and then finally treatment with lithium.

3.5 Phosphor Screen Secondary Electron Emission Measurements

After the lithium oxide terminated diamond is obtained, a series of measurements regarding the secondary electron emission from the surface of this material were taken, for a number of samples, using phosphor screen equipment. An electron beam a known energy, created by a hot tungsten filament, was focussed on a point on the sample. The sample was tilted as to deflect the beam focussed on to it towards a collector connected to a photomultiplier tube at which secondary electrons was measured as displayed in figure 7.

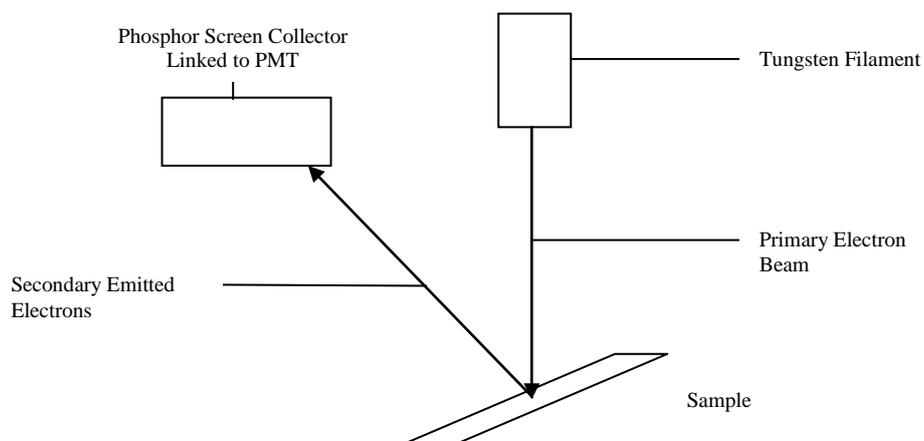


Figure 7- Diagram showing set-up of the phosphor screen equipment.

The results of the secondary electron emission were then compared with the emission recorded for a standard graphite sample and a yield for secondary emission was obtained. The recorded emission from the surface of the diamond sample was measured across a range of electron beam energy and compared with the results from graphite samples over the recorded energy range to calculate a secondary electron emission yield for the sample at varying energy of the primary beam.

4.0 Results and Discussion

The results in this section were obtained as a number of images and graphs using a combination of optical microscopy, SEM and phosphor screen measurements to determine the surface properties of the material.

4.1 Tungsten Electrode Surface

The tungsten electrode surface around the grooved areas was analysed using a combination of optical microscopy and SEM, with images from both methods showing a build up of deposited tungsten around the edges of the machined grooves. On SEM images it can clearly be seen that the build up of deposited tungsten covers over the edges and across some of the groove.

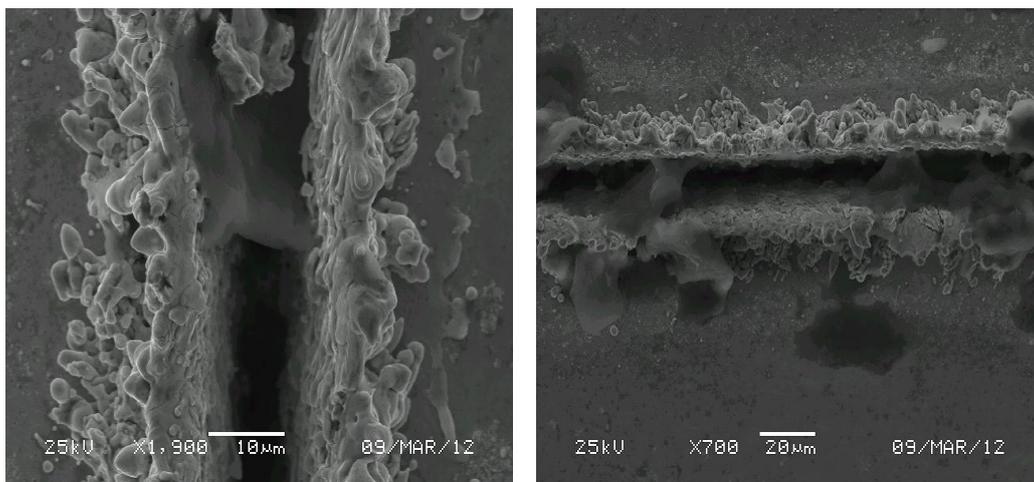


Figure 8- SEM images of laser machined tungsten grooves, taken using the JEOL 5600LV electron laser.

In Figure 8, the images show that the laser machined grooves are cut deep into the metal substrate, but the groove is only cut into the substrate and not through to the other side.

From optical microscopy you can see the build up of the deposited tungsten around the grooves by the appearance of what looks like a shadow around the edges of the grooves.

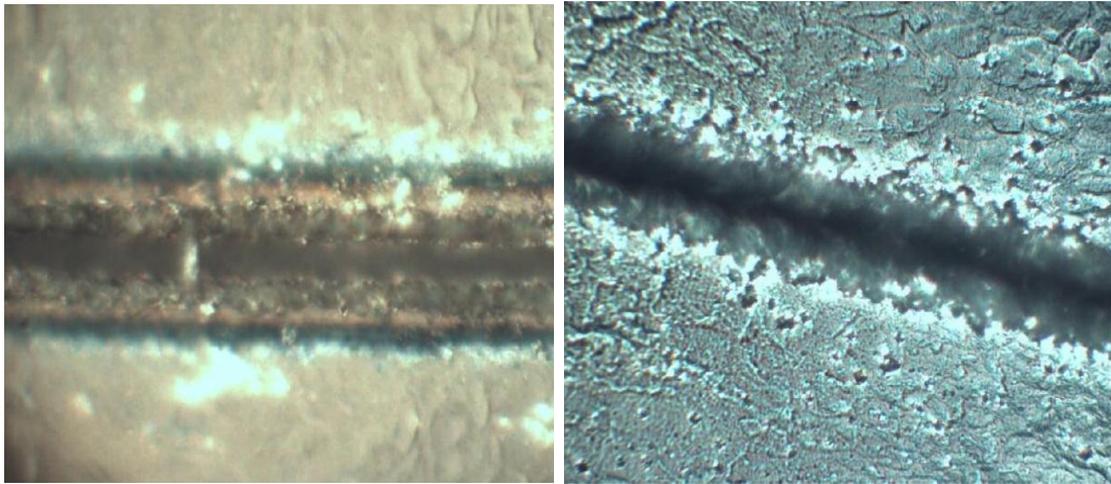


Figure 9- Images of the grooves cut into the back of the tungsten electrode using optical microscopy.

Figure 9 shows two images of grooves cut into tungsten electrodes. The image on the left shows a large shadow around the outside of the groove, caused by the high intensity of the laser cutting the groove. The image on the right shows a groove cut by the laser, but a reduced layer of deposited metal around the outside, as a result of passing the laser over the edges of the groove at a lower intensity.

4.2 SAM Surface Coverage

The surface coverage was studied using optical microscopy to show the areas of the metal substrate in which diamond has been deposited. The images taken using the optical microscope show that good surface coverage has been achieved using the self assembly technique and that self assembly is an effective technique for deposition of diamond particles onto a cleaned metal electrode.

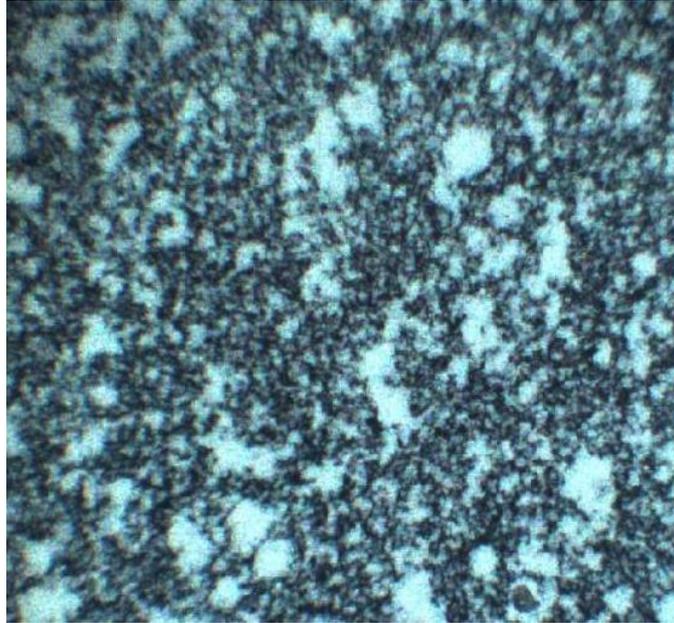


Figure 10- Optical microscopy image of self assembled monolayer of diamond, with good surface coverage, on tungsten substrate.

Images of the grooves were also obtained using the optical microscope, to gauge how successful deposition of the self assembled diamond was on the grooves at the back contact of the diamond, in order to determine whether self assembly is an effective method for creating a diamond surface in small grooves cut within the back face of an electrode.

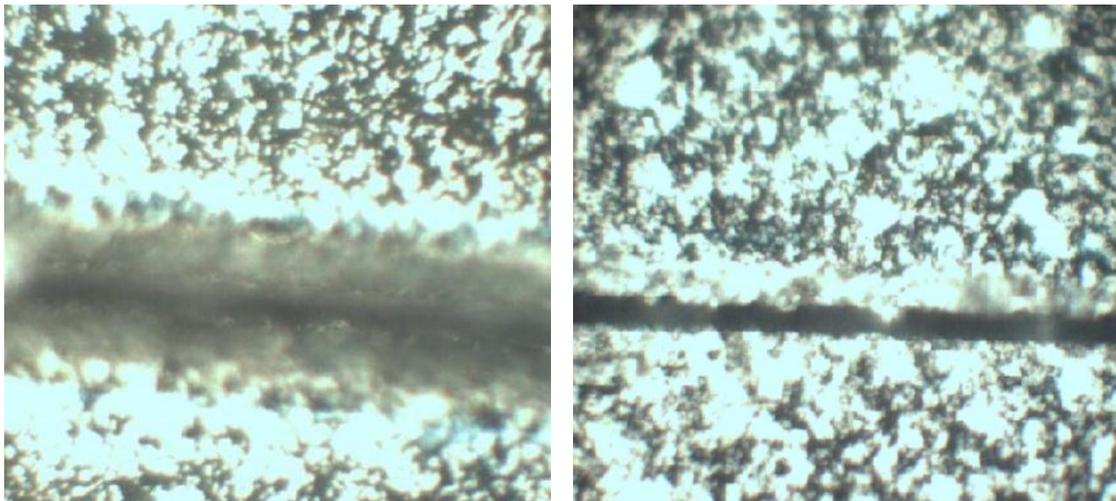


Figure 11- Images of diamond surface coverage on the back of the tungsten electrode and in the grooves cut into the surface.

The images show that diamond is effectively assembled inside the grooves and so self assembly is a method that can be used for depositing diamond into grooves cut into a laser machined irregular surface.

4.3 Secondary Electron Emission from LiO Terminated Diamond

Secondary electron emission from oxygenated diamond terminated by lithium was measured using phosphor screen measurements, which provided a yield for secondary electron emission as a ratio of emission recorded at the collector for this material, compared with the emission recorded for a standard graphite electrode. It is commonly accepted that graphite neither emits or absorbs the electrons from the high energy electron beam and just reflects them to the collector, thus it may be used as the standard for secondary, so a yield for electron emission can be calculated with this parameter known. Electron emission from the surface of the lithiated diamond was also recorded using SEM, with it expected that areas of the diamond surface that have been effectively terminated by LiO, would show up brightest in the SEM images and so therefore the images obtained from SEM would allow the success of the lithiation of the diamond surface to be determined, as well as the morphology and size of the diamond particles. Four tungsten electrodes, with self assembled diamond, surface treated as outlined in the experimental section (3.4 Surface Treatments to Self Assembled Diamond Layer) were tested using both the phosphor screen equipment and the SEM.

Measurements using the phosphor screen equipment were used to measure the degree of secondary emission at which the sample material was capable of emitting, with each sample providing quite similar results in terms of both the peak electron emission yield and the applied electron beam energy at which the peak emission yield is achieved. The measurements were taken with the beam energy increasing 100eV between each measurement and the beam energy ranged from 100-5000eV. However, the tested samples all appeared to show a peak emission yield at comparatively low energies, signalling that at high beam energies, electrons passed through the sample without exciting any electrons for emission. The samples tested also implied that the materials in question showed good characteristics for secondary electron emission applications as they produced a relatively high emission yields.

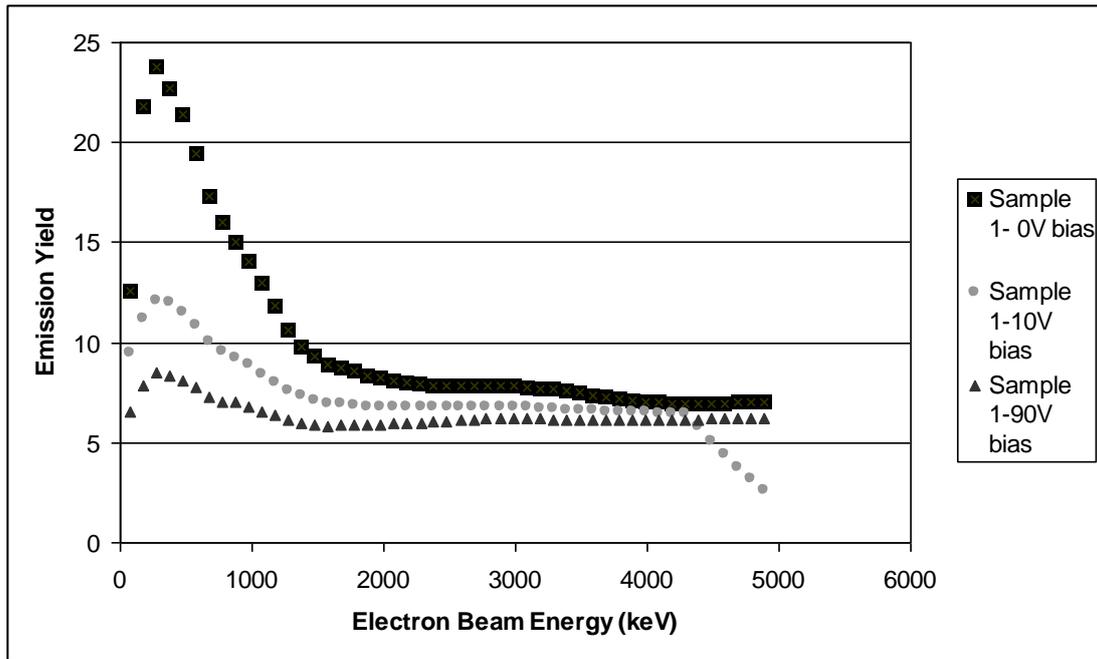


Figure 12- Graph showing the electron emission yield compared with the electron beam energy for 1 sample, with different voltage biases applied.

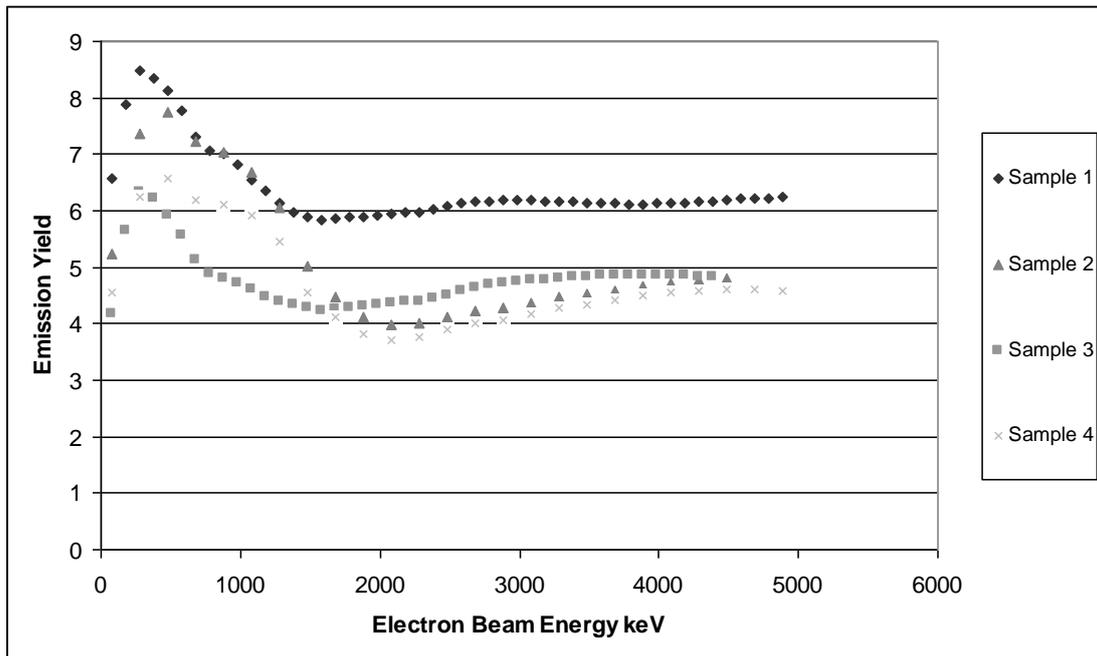


Figure 13- Graph of electron emission yield for 4 samples of LiO terminated diamond on tungsten, when a 10V bias was applied to the sample.

Figures 12 show that when no bias was applied to the sample the electron emission observed from the sample had a very high yield and such materials would have a good potential for electron emission applications. Figure 30 shows 4 samples that all have a

10V bias applied and all the results show an extent of correlation. The peak in electron emission yield comes between 100-1000eV for all samples and the peak emission ranges from 6-9, showing good electron emission character for each sample even when the bias is applied.

Images from the SEM were taken for the 4 samples, with results showing good correlation, areas of diamond with silver coating were visible, as well as areas with just oxygen termination and area of lithium termination on oxygenated diamond all being visible. Areas with lithium at the surface appeared bright on the SEM images as there was a high yield of secondary emitted electrons as known from the phosphor screen testing. The area that had oxygen terminated diamond or remaining silver coating appeared darker on the SEM images as they had lower secondary emission yields. From the SEM images and the scale beside them it can be seen clearly the size of the diamond particles observed and so it can be determined that these particles are indeed diamond.

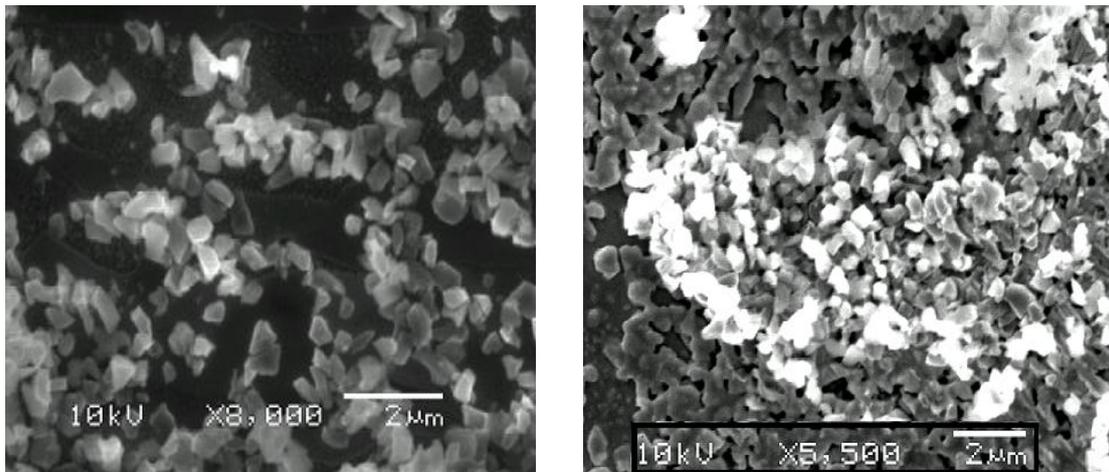


Figure 14- SEM images taken of LiO terminated diamond.

Figure 14 shows images of diamond terminated with LiO, taken under the SEM, the scales clearly show that the particles being imaged are of the order of 500nm and so can be identified as diamond. It can be seen that there are particles that appear much darker than others and some that appear very bright. It is likely that the areas where, the particles are brightest show termination by lithium and the darker areas, have no lithium surface termination and are instead terminated at the surface by oxygen or silver layers.

5.0 Conclusions

Images recorded through optical microscopy show that the method of self assembly has been successful in achieving a good surface coverage of the metal substrate with diamond particles, with SEM images showing clearly that diamond particles of the expected size, 500nm, are present in high concentration on the surface of the area studied of the tungsten substrate. SEM images showed that the laser micromachining system was successful in creating a deep well in the tungsten metal, without creating any holes within the grooves cut, whilst optical microscopy has shown passing a laser at lower intensity around the edges of the grooves, that have been machined by a laser set at high intensity, was also successful in reducing the roughness around the outside of the grooves, caused by deposition of metal around the grooves. Results obtained from the phosphor screen equipment shows that the lithium terminated oxygenated diamond surface exhibits extremely strong secondary electron emission characteristics and that its peak electron emission yield is when a relatively low energy of electron beam is focussed on to the surface, this is promising for secondary emission applications that require concentrated light to stimulate the emission of electrons and so in turn for applications that would use light to begin the process of secondary electron emission in order to increase thermal energy transmitted to diamond through a metal substrate. This is the purpose for cutting grooves into the tungsten, in order to deposit self assembled diamond within them to cause emission through frustrated light in the tunnels that have been machined in the tungsten and thus transmit thermal energy through to the diamond on the surface, for use in improving applications of thermionic emission from the surface. For this to be achieved self assembly of diamond must be improved inside the grooves, by either increasing the width of the grooves so more diamond can be deposited by creating a less restricted area for the deposition of the diamond, or by creating an improved method for self assembly in order to achieve this. Images produced by the SEM show the lithiated surface of diamond with areas of very bright particles, but these areas are not very concentrated throughout the material, indicating that the lithium termination on self assembled diamond could be improved in order to achieve better emission from the surface.

6.0 Future Work

Future work surrounding this subject area should include testing of the thermionic emission properties of this lithium terminated diamond surface, testing should be conducted firstly on a flat no machined tungsten substrate, to which heat is applied to the back of from an infra-red source. The results of this should be compared with thermionic emission from this diamond surface deposited on to the machined tungsten substrate, in order to gauge the effect on emission by, in places reducing the thickness of tungsten to which to which the diamond is deposited on to. Further testing can be conducted on the machining of tungsten substrates and morphologies for the size of grooves to be cut, in order to gain the optimum deposition of self assembled diamond. A suggestion would be to increase the width of the grooves that are cut so to create a wider space for diamond to be deposited into, it could also be suggested that using, thicker tungsten as the electrode material would allow deeper and wider grooves to be made, in an attempt to substantially increase the amount of diamond that could be deposited into the grooves and therefore increase the amount of secondary emission that may be observed within the grooves, in order to increase the thermionic potential of the material. Also further testing could be conducted to use light concentrated from solar sources in order to attain thermionic emission from this diamond surface, a suggestion for testing would be to focus light on to the back of the tungsten substrate, in order to transmit thermal energy through to the diamond in order gain thermionic emission. Testing of this method could focus on frustrating the concentrated light into the grooved areas of the tungsten, and testing whether the deposition of a lithiated diamond surface, that exhibits a high potential for secondary electron emission is a factor in increasing thermionic emission from these surfaces. Other future work concerning this surface termination for diamond could include engineering it in to a practical setup for use in a thermionic emitter. A potential design of this would to use both the surfaces secondary electron emission properties and its thermionic emission ability in order to enhance overall emission from the material. By designing a potential system in which concentrated light from solar radiation could be focussed both on to the diamond surface, to stimulate secondary electron emission and the back surface of the metal electrode, to stimulate thermionic emission, where there is a potential for these emitted electrons to collide with another diamond surface or metal

electrode, emitted electrons could then further enhance emission from another surface to which they collide with. Fabrication of such a design would be a step towards realising a potentially viable method for thermionic energy conversion.

7.0 Acknowledgments

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