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The effect of diamond surface termination species upon field emission properties

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Abstract

Undoped CVD diamond films on Si substrates have been chemically treated in order to change the surface termination species. Treatments used include hydrogenation, deuteration, oxidation, hydrolysis, amination, chlorination, fluorination, and metallisation, using Na, K and Cs layers. The effect of these treatments upon field emission characteristics has been measured. In general, it is found that emission currents increase and threshold voltages decrease as the electronegativity of the surface species decreases. The best field emission properties were observed for the films with metal layers, with threshold voltages of ~15 V/μm. © 1998 Elsevier Science S.A.

Keywords: Diamond films; Field emission; Surface dipole; Surface treatments

1. Introduction

Diamond has been suggested as a possible material for application in electron emission devices because of its negative electron affinity (NEA), coupled with its chemical inertness. NEA is a term used to describe the situation whereby the conduction band minimum lies above that of the vacuum level at the surface [1]. It is believed that diamond possesses this property either due to the presence of a dipole on the surface [2] or band bending [3]. The surface dipole arises as a result of the termination of the dangling sp^3 bond by a species other than carbon. Experiments by Waclawski et al. [4] and Pate et al. [5] show that on most natural diamonds and CVD diamond films the surface terminating species is hydrogen. Photoemission studies on the (111) surface of single crystal diamond by Himpsel [6] showed that the hydrogen termination was directly responsible for NEA, and the influence of the surface dipole upon the electron affinity of diamond and other carbon systems has formed the basis of a model by Robertson [7]. In this model, the hydrogen termination has two effects. First, the difference in electronegativity between H and C causes a net movement of charge through the C–H bonds towards the C. Consequently, some electron density is forced into the conduction band, and since this lies above the vacuum level any electron density accumulating there is readily available for emission into the vacuum. The surface dipole is not the sole effect in operation though. The C–H terminations also lead to a breaking of the symmetry of the diamond structure, resulting in the formation of sub-bands, as shown in Fig. 1. Other theoretical studies [8,9] show that the presence of sub-bands provides an explanation for the experimentally observed field emission characteristics of CVD diamond. If this model is accurate, it is expected that modifying the nature of the surface termination species should greatly affect the field emission characteristics. Termination of the diamond surface by highly

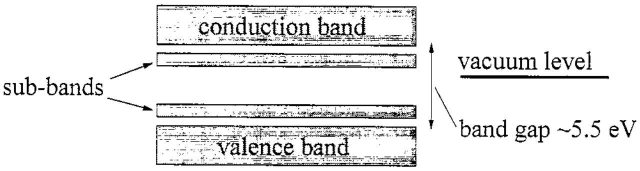

Fig. 1. A schematic diagram of the band structure close to the diamond surface, with sub-bands forming just below the conduction band and just above the valence band.

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electronegative atoms, such as oxygen or halogens, should draw electron density away from the conduction band, decreasing emission efficiency and current, and increasing the threshold voltage necessary to initiate emission. Conversely, highly electropositive atoms, such as alkali metals (Cs, Na) should be expected to donate their electrons into the conduction band and sub-bands, improving emission characteristics.

However, only a small number of studies have been performed to test this hypothesis, and the number of surface terminating species tried to date have been limited. Oxidation of CVD diamond films has been achieved by suitable acid or oxygen plasma treatments [10], and the resulting surface terminations consist of various carbon–oxygen single, double and bridging (ether) bonds, or OH attachments. Photoemission and other studies [10–12], show that oxidation in this way removes the NEA associated with as-grown hydrogenated diamond surfaces, but the NEA can be re-established by hydrogenation using a hydrogen plasma.

Halogenation of diamond surfaces is more problematic, since molecular chlorine and fluorine cannot be directly added to the diamond surface. One solution is to utilise radical reactions [13–15], which may be initiated by either thermal excitation or by ultraviolet photoexcitation. These treatments both cause homolytic fission of the halogen–halogen bonds, resulting in the formation of reactive atomic species which are capable of attacking the diamond surface and substituting for the hydrogen. The fluorinated surfaces have been analysed to reveal a mixture of CF and CF_3 terminating species and are air stable, unlike chlorinated samples which hydrolyse (OH addition) within a period of hours. The reactivity of such chlorinated samples can, however, be utilised to provide a route to more exotic surface terminating species. Exposure of chlorinated diamond surfaces to water vapour or ammonia at temperatures above 400 °C leads to respectively, carbonyl or NH_2 terminations. The electron emission characteristics of such films have yet to be reported, and this forms one aspect of the work presented here.

Addition of electropositive species to diamond surfaces usually involves evaporation of an alkali metal in vacuum to form a thin (<100 Å) layer on the surface. The diamond surface is often maintained at elevated temperatures (>200 °C) to ensure the metal chemically reacts with the diamond, or alternatively the evaporation may be done cold and the film post-annealed in an inert atmosphere. Being the most electropositive metal that is readily available, caesium has been the most studied of the alkali metals. Caesiated diamond surfaces have been shown to be air stable, and have excellent field emission properties [11]. However, the electron emission yield is critically dependent upon the surface treatment of the diamond prior to caesiation, and several recent studies have been devoted to investigating the effect of caesiating oxidised or hydrogenated diamond surfaces [16–18].

However, what is lacking in the literature is a systematic study of the effects upon field emission characteristics of a number of different surface terminating species, ranging from very electronegative to very electropositive character. The aim of this present study is, therefore, to use a series of identical CVD diamond films and modify their surface terminations in a systematic way. Measurement of their subsequent electron emission properties may provide an insight into the validity of the surface dipole model mentioned above.

2. Experimental

Undoped diamond films were grown on Si(100) substrates using standard hot filament CVD methods. The substrates were abraded prior to deposition with 1–3 μm diamond grit, and the CVD conditions used 1% methane in hydrogen at 20 Torr for 6 h. This produced polycrystalline diamond films with thickness 3 μm and a hydrogenated surface. The films were then treated in a variety of methods to modify the surface chemistry.

2.1. Hydrogenation

Additional hydrogenation of the as-grown films was performed in a 1 kW microwave plasma CVD reactor operating at 20 Torr and ~800 °C using H_2 gas for 30 min.

2.2. Deuteration

This was also performed in the MW CVD reactor using D_2 gas and the same conditions as above. The D_2 plasma was surprisingly difficult to strike compared with the H_2 plasma, and was very unstable.

2.3. Oxidation

A CVD film was placed into a test tube containing a 50:50 mixture of concentrated nitric and sulphuric acids and heated to 85 °C for 15 min. It was then thoroughly rinsed in water.

2.4. Hydrolysis

A CVD film was placed into a test tube containing four pellets of solid potassium hydroxide and 4 cm^3 of water and heated to 90 °C for 15 min. It was then thoroughly rinsed in water.

2.5. Halogenation

This was performed by two methods.

2.5.1. Thermal reaction

A diamond film was placed into a quartz reaction vessel which was then evacuated to a pressure of less than 10^{-4} Torr before being filled with 200 Torr of either Cl_2 gas, or 0.16% F_2/6.3% Ar in Ne (excimer laser gas). The reaction vessel was placed into a tube furnace and heated to 600 °C for 90 min. The samples were then cooled to room temperature and placed into a vacuum desiccator. Electron emission characteristics were measured on these films within 30 min of the halogenation process in order to minimise possible oxidation of the unstable surface. This was found necessary for the chlorinated samples, but the fluorinated ones remained air stable for weeks.

2.5.2. UV photolysis

The diamond film was placed into a quartz vessel, which was evacuated and filled with the appropriate gas, as above. The vessel was then irradiated with UV radiation from a high power mercury discharge lamp for 90 min, before being tested for electron emission in the same way as above.

2.6. Amination

A chlorinated diamond film produced using UV photolysis was placed back into the quartz reaction vessel, which was filled with 200 Torr of ammonia. UV photolysis was performed as above.

2.7. Metallisation

Three types of metal were used, Na, K and Cs, and all were supplied using a standard alkali metal dispenser (SAES Getters, UK). The metal coatings were produced by passing an electrical current of 7 A through the dispensers in high vacuum for typically 30 min. This caused the metal to evaporate from the dispenser and uniformly coat the diamond film positioned 1 cm below it. The diamond films were then placed into an oven and heated in argon for 20 min at 320 °C for Na or 125 °C for K or Cs. The thickness of the evaporated layer was calibrated using Auger depth profiling.

XPS analysis was performed upon the treated films to ascertain the effectiveness of the various treatments. Analysis of deuterated and hydrogenated samples was performed using SIMS and the results are shown in Table 1. Field emission analysis was performed using a specially designed high vacuum apparatus, in which the film is positioned on a grounded electrode, and the electrons that are emitted from the film surface are attracted to a nearby positively biased anode. The emission arises from an area on the surface of the film approximately the size of the anode. This is estimated to be ~0.5 mm in diameter by measuring the size of the damaged area on the film using an SEM. The anode-to-film distance is varied using a micrometer, and by ramping the anode voltage and measuring the current, I–V curves can be obtained. A current limit of 0.3 mA was set to prevent excessive damage to the film surface during emission. It was found that in order to obtain reproducible I–V curves it was necessary to ramp the voltage up and down several times to 'condition' the surface. The I–V characteristics continually improved throughout these conditioning runs, and when they had stabilised to reproducible values, measurements were recorded.

3. Results and discussion

From Table 1, it can be seen that the attempts at modifying the surface termination met with varying degrees of success. XPS is very sensitive to even slight oxygen contamination on the surface, and so nearly all of the samples analysed show the presence of some O. This is especially true for samples treated in the oven method. Even though the bake was performed in a nominally oxygen-free inert atmosphere, even trace amounts of oxygen at these temperatures are able to react with and oxidise the diamond surface. Thus, for the halogenation experiments, the UV photolysis method is preferable. Oxidation using the acid treatment has resulted in 28% of the surface being covered with O, however there is also evidence of the presence of N and S, probably as residues from the nitric and sulphuric acids.

An example of a field emission I–V curve is shown in Fig. 2 and the same data are plotted as a Fowler–Nordheim plot in Fig. 3. Curve fitting allows the threshold voltage to be obtained (defined as the voltage for which a current greater than 10 nA is first observed). The average of threshold voltage values obtained at anode–film separations of 20, 40 and 60 μm are plotted for the various treatments in Fig. 4, together with an estimate of the uncertainty in the measurement based upon this run-to-run reproducibility. The emission currents measured at a fixed voltage of 1.5 kV and anode-to-film separation of 20 μm are shown in Fig. 5. From these a number of general conclusions can be made. First, hydrogenation and deuteration both equally improve the emission characteristics from the as-grown film. The threshold voltage is reduced by ~10 V/μm and the emission current is increased by almost a factor of 20. This can be attributed to removal of any graphite or oxygen impurities present on the surface after growth, as confirmed by the XPS and SIMS data. Also, the hydrogen treatment is expected to clean up any areas of

Table 1
Surface treatment and compositional analysis

Film treatment	Surface composition (ignoring carbon)	($\phi/\beta^{2/3}$) /eV	Comments
As-grown	O 1%, H 3%	0.15	
Hydrogenated	H 4%	0.12	
Deuterated	D 4%	0.11	
Oxidised	O 28%, N 2%, S 9%	0.16	The N and S are probably remnants from the nitric and sulphuric acids used in the oxidation.
Hydrolysed	O 5%	0.23	
Chlorinated (oven)	Cl 2%, O 13%, Si 7%	0.18	The Si is from the substrate which was slightly etched by the Cl_2 gas and redeposited onto the surface.
Chlorinated (UV)	Cl 9%, O 1%	0.18	
Fluorinated (oven)	F 1%, O 16%, Si 5%	0.20	The Si is from the substrate which was slightly etched by the F_2 gas and redeposited onto the surface.
Fluorinated (UV)	F 1%, O 4%	0.20	The low percentage of F probably results from the low percentage of F_2 in the source gas.
Aminated	N 2%, O 3%	0.23	
Metallised			(40 min evaporation, oven bake 20 min). The surface work function values for the unbaked metallised samples were identical to the ones shown here for the baked ones.
Na	Na 1–2%, O 9%	0.13	
K	K 1–2%, O 12%	0.14	
Cs	Cs 1–2%, O 10%	0.14	

SIMS was used for hydrogenated and deuterated surfaces and XPS was used for the other treatments. The metallisations were also analysed using Auger depth profiling. Note that XPS is not sensitive to H and so the percentages given are only for the heavier elements present in the first few atomic layers of the surface. The percentages shown are made up to 100% with C. The values for the surface work function, ϕ are estimates from Fowler–Nordheim plots and are presented as $\phi/\beta^{2/3}$, where β is assumed to be 1 for a planar surface. From reproducibility experiments, the variability in each calculated value is ±0.02 eV, however, the absolute magnitude of the values rely upon the assumptions about β and the size of the emission area mentioned in the text.

the surface which may have undergone reconstruction, and re-establish the sp^3 configuration necessary for efficient electron emission.

The oxidised, hydrolysed and aminated surfaces all degraded the electron emission performance considerably. Threshold voltages increased by ~20 V/µm with a corresponding decrease in emission currents of two orders of magnitude. This agrees with what is expected from the surface dipole model for highly electronegative species. For the same reasons, the halogenated surfaces also have much worse emission characteristics than the as-grown films. The degradation is roughly dependent upon the electronegativity of the species, F is worse than Cl. Furthermore, the reluctance of these oxidised

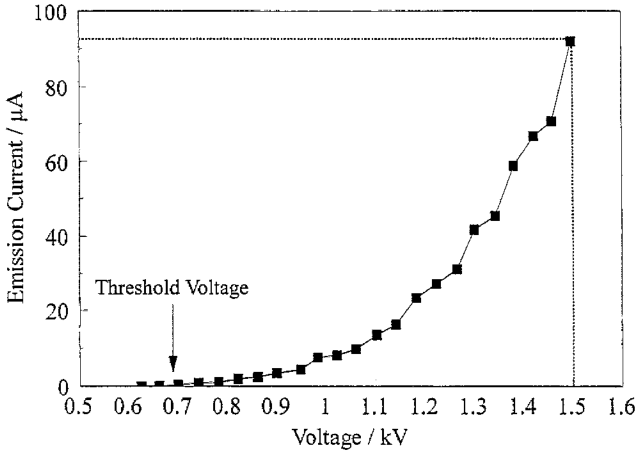

Fig. 2. Representative *I–V* plot of emission current vs anode potential for a CVD diamond film. This particular curve was for a hydrogenated surface. The dotted lines show the value of the current at an anode voltage of 1.5 kV used in Fig. 5.

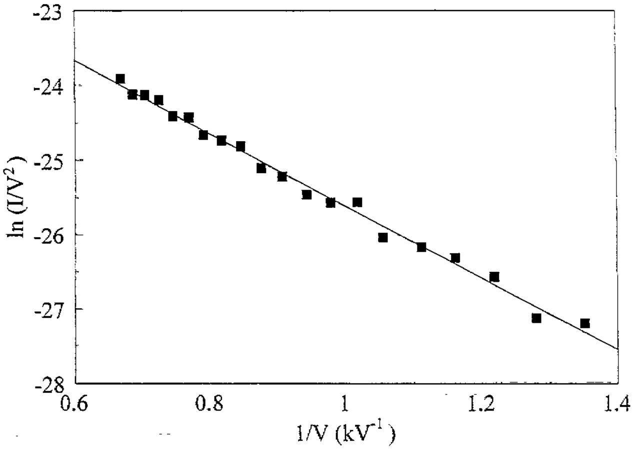

Fig. 3. A Fowler–Nordheim plot of the data in Fig. 2, showing a linear relationship indicative of good field emission characteristics. The gradient of this line can be used to calculate the surface work function, if assumptions are made about the area of the emission site and the geometrical enhancement factor (which is related to the flatness of the surface).

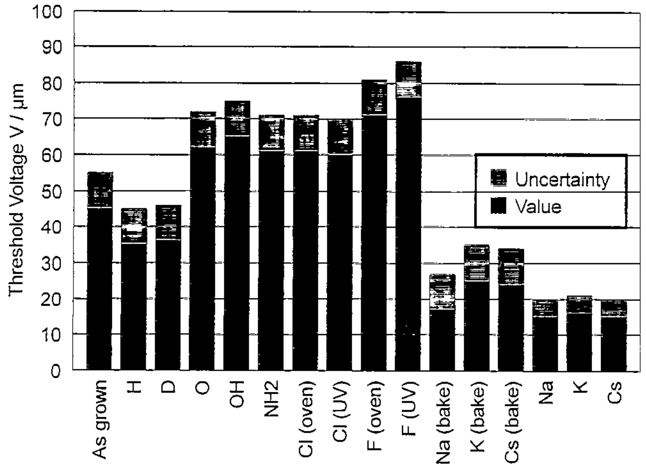

Fig. 4. Threshold voltage measured for each of the surface treatments described in section 2. The uncertainties in the measurements are shown by the shaded bars, so, for example, for the first bar, the value should be read as 50 ± 5 V/μm. The different surface treatments are described by the major terminating species: H, hydrogenated; D, deuterated; O, oxidised; OH, hydrolysed; NH2, aminated; Cl, chlorinated via the oven or UV processes; F, fluorinated via the oven or UV processes; Na, K, Cs, metallised with a 100 Å layer, with and without a 40 min oven bake.

and halogenated films to emit electrons is highlighted by the fact that for some of them emission could not be obtained at anode-to-film separations of >40 μm, without applying such large voltages (>5 kV) that sparking and discharging occurred in the vacuum vessel.

The metallised surfaces all showed improved electron emission characteristics, giving threshold voltages around half that of the as-grown films. The oven baked metal surfaces were all inferior to the unbaked ones; this could be due to slight oxidation, which occurred due to trace oxygen impurities in the inert atmosphere within the oven. Evidence for this is seen in the XPS results shown in Table 1. Curiously, for the unbaked metal surfaces there appears to be very little difference between the electron emission characteristics of the three alkali metals. Within experimental error, the threshold voltages and the emission currents are almost the same. This is somewhat unexpected, as the surface dipole model might predict that the surface terminated with the more electropositive metal would have the better field emission properties. This could, however, be explained if the metal is effectively chemically bonded to the diamond surface by a pseudo-ionic bond. In this case, the valence electron from the metal will have been donated into the conduction band of the diamond and be available for emission. The presence of the remaining metal 'cation' will alter the surface band structure, but the differences between the three metals will be small. One factor which does appear to influence the emission characteristics is the thickness of metal deposited. Even a few monolayers of metal on the surface can lower the threshold voltage by a factor of almost two. The emission properties improve with increasing metal thickness, but level-off at ~50–100 Å, as shown in Fig. 6. The reason for this is uncertain, but one suggestion is that the value of 50 Å is the smallest needed to ensure a contiguous coating from a possibly non-uniform deposition source.

Analysis of the Fowler–Nordheim plots for the various surface treatments allows the surface work function to be estimated (see Table 1). These values are calculated assuming that the geometrical field enhancement factor $\beta = 1$ (i.e., a planar surface [19]) and that the emission area is identical in each case. A value for the emission area was estimated at $\sim 2 \times 10^{-7}$ m^2 from SEM analysis of the damaged area observed on the film surface following emission [20]. The values in Table 1 should be treated with caution, however, since estimates of the surface work function using the Fowler–Nordheim method are notoriously unreliable, owing to difficulties in obtaining trustworthy values for both β and the emission area [21]. If we assume that β and the emission

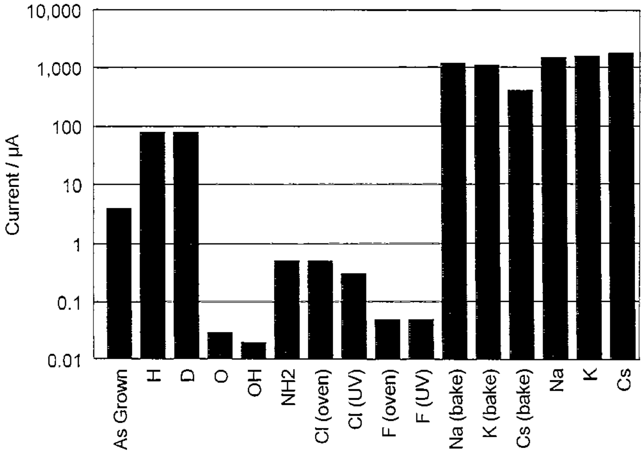

Fig. 5. Emission current measured at an applied voltage of 1.5 kV and an anode-to-film separation of 20 μm for each of the various surface treatments. The values for the metallised films were estimated from an extrapolation of the I–V curve at lower voltages.

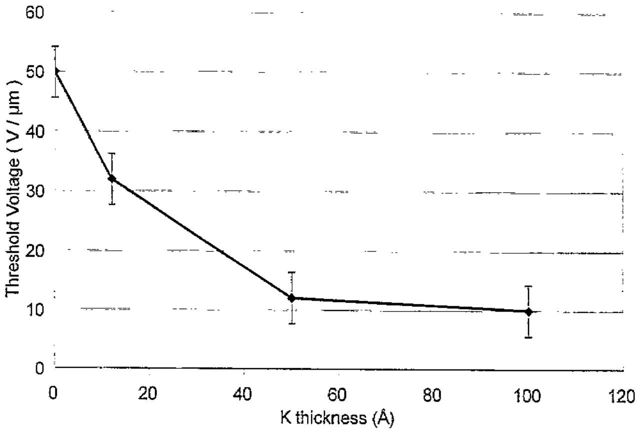

Fig. 6. Threshold voltage measured for different thicknesses of K deposited onto a CVD diamond film.

area do not change significantly with the surface treatments used, then Table 1 shows a general trend of increasing work function with increasing electronegativity of surface species, as expected. However, the differences in absolute magnitude between the various samples seem small compared with the large differences observed in their *I–V* behaviour. This is a consequence of the logarithmic nature of a Fowler–Nordheim plot.

4. Summary

In this paper we have shown that the terminating species upon a CVD diamond surface has a marked influence upon the electron emission characteristics of the film. In general, the more electronpositive the species, the better the emission properties, both in terms of low threshold voltage and high emission currents. Thus, oxidised and halogenated films give poor characteristics compared with as-grown films, but hydrogenated films or films treated with alkali metals give improved results. This agrees well with a model for electron emission based upon surface dipoles.

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