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Field emission conduction mechanisms in chemical-vapour-deposited diamond and diamond-like carbon films

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Abstract

The observed current–voltage relations from the field emission of electrons from a number of different types of diamond and diamond-like films have been fitted to a variety of mathematical models for charge transport through poor conductors. We find that the Fowler–Nordheim model provides no better a description for the overall conduction mechanism than three alternative mechanisms involving transport through the bulk, and this holds for emission from natural diamond, various doped and undoped CVD diamond films, and diamond-like carbon (a-C:H). © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The emission of electrons from the surface of diamond and diamond-like carbon (DLC) films is currently of much interest due to potential applications in cold cathode devices. The negative electron affinity (NEA) of the hydrogenated diamond surface plays an important role [1], and different surface terminating species can greatly affect the emission characteristics [2]. However, since most of the results from low field emission experiments are from chemically vapour-deposited (CVD) diamond with poorly characterized surfaces, it is clear that NEA is not solely responsible for the emission process. A recent paper by Geis et al. [3] states that the emission observed from CVD diamond films may actually arise from the triple junction at the substrate–diamond–vacuum interface. The electrons from the substrate tunnel into surface states of the diamond whereupon they are accelerated along the edge of the diamond film (or through a conducting channel at the grain boundaries) to a sufficiently high energy to be emitted from the surface — a process termed 'surface electron emission'. If this model is true, then the overall mechanism describing this process will almost certainly have a more complicated mathematical form than has hitherto been assumed.

In most recent literature on field-induced emission from diamond or DLC films, the current–voltage relation is simply fitted to a Fowler–Nordheim model, and a good fit has been taken as evidence that the process occurring is cold field emission. However, there are problems with the Fowler–Nordheim model when applied to diamond films. It was originally developed [4,5] as a model to explain emission from metals, and its application to materials with different band structures, such as semiconductors, is questionable. Further extending its application to wide band gap semiconductors or insulators, such as diamond, is therefore even more dubious. Other problems are that parameters extracted from the 'Fowler–Nordheim plot' of $\ln(I/V^2)$ against $1/V$ (where I and V are the emission current and applied voltage, respectively) often have physically unrealistic values [6]. A question mark, therefore, hangs over the validity of using the Fowler–Nordheim model for diamond-based films, and also, therefore, over whether the dominant emission mechanism is really cold field emission at all.

In previous reports [7,8], we have shown that field emission from diamond and diamond-like carbon films can be described accurately by four independent models for charge transport: the Fowler–Nordheim model for emission through a potential barrier at a surface, the Schottky emission model for ejection over a surface barrier, the space-charge-limited current (SCLC) model for transport through the bulk, and the Poole Frenkel

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hopping model modified by SCLC (PF+SCLC). Two other models that were investigated, the standard Poole Frenkel (PF) mechanism and Hill's Law conduction, were found to be poor fits to the data.

In those reports, we used data measured from our own undoped CVD diamond and diamond-like carbon (DLC) films. We now apply the same analysis to the emission data from a variety of other films reported in the literature from many different authors. We aim to show that our conclusions about the inappropriate use of the Fowler–Nordheim equation and the values for parameters derived from its use are generally applicable to emission from most types of carbon film, irrespective of doping, manufacture method, or graphitic content.

2. Experimental

We have used current–voltage (I–V) data obtained from field emission experiments from a variety of different sources reported in the literature over the past few years (see Table 1) . These include natural diamond and diamond grit particles attached to a Si or metal substrate, CVD diamond films, and doped and undoped DLC or a-C:H films. In choosing these data sets, we have selected samples for which raw I–V data are published, and which are representative of many different types of carbon surface and bulk material.

Following the procedure given in Refs. [7,8], the expected current–voltage relations for various models for conduction mechanisms at the surface of and in the bulk of insulators are given in Table 2. By plotting the appropriate mathematical form of these relations as abscissa and ordinate, a straight line plot can be obtained. The correlation coefficient of the least-squares line of best fit then gives a direct measure of how well each model represents the experimental data.

Fig. 1 shows the results of plotting these I–V data for the first five CVD diamond films described in Table 1. Data for the PF model and Hill's law model are not shown since these always gave r^2 values <0.7 and so were never good fits to the data. For the other four models, despite the gradients and intercepts of the fitted lines being different in each case (due to differences in the local work function, film surface, or substrate material), it is clear that an extremely good correlation can be achieved for all four models and all five data sets. The same is true for similar plots using the I–V data sets from DLC or natural diamond (not shown). The correlation coefficients for all the various film types tested are given in Fig. 2. Note that the exact values of r^2 obtained from these plots depend somewhat on the number of data points included in the calculation — since some points at low field and effectively zero emission current have to be ignored. This introduces a certain amount of subjective judgement to the plots, which will contribute to random errors in the r^2 values. This is particularly important when the number of data

Table 1
Details and references for the various diamond and diamond-like carbon films and their I–V data[a]

Film number	Description	Reference
CVD 1	Undoped diamond-coated Mo tips, annealed at 430°C, 0.5 h	[9]
CVD 2	As above but annealed at 430°C, 2.5 h	[9]
CVD 3	As above but annealed at 500°C, 15 h	[9]
CVD 4	Initial test of CH_4/air-treated B-doped CVD diamond made by MW PECVD on a Si substrate	[10]
CVD 5	Nitrogen-doped MW PECVD fine-grained diamond films on Si	[11]
CVD 6	B-doped homoepitaxial layer on type Ib HPHT diamond, array of tips, 100-μm testing gap	[12]
DLC 1	a-C on a Cr plate	[13]
DLC 2	a-C:H on Si	[14]
DLC 3	a-C:H:N with 15% N content, 300 nm thick on Si	[6]
DLC 4	a-C:H:N with 14% N content, 300 nm thick on Si	[6]
DLC 5	a-C:H:N with 11% N content, 300 nm thick on Si	[6]
DLC 6	a-C:H:N with 7% N content, 300 nm thick on Si	[6]
DLC 7	a-C:H:N with 0% N content, 300 nm thick on Si	[6]
DLC 8	a-C:H:N	[14]
DLC 9	a-C:H:N with 11% N content	[15]
DLC 10	ta-C:N with 7.5% N content	[16]
DLC 11	ta-C:N with 0.56% N content	[16]
DLC 12	ta-C:N gown with 170-eV ion beam energy	[16]
Natural type Ib 1	400-μm testing gap	[12]
Natural type IIb 1	(100) diamond, 3.3-μm testing gap	[17]
Natural type IIb 2	(100) diamond, 4.3-μm testing gap	[17]
Surface emitter 1	Natural Ib diamond, acting as a surface emitter in darkness	[3]
Surface emitter 2	Natural Ib diamond surface emitter in light	[3]

[a] MW PECVD: microwave-plasma-enhanced CVD; HPHT: high-pressure, high-temperature synthetic diamond; a-C: amorphous carbon; ta-C: tetrahedral amorphous carbon.

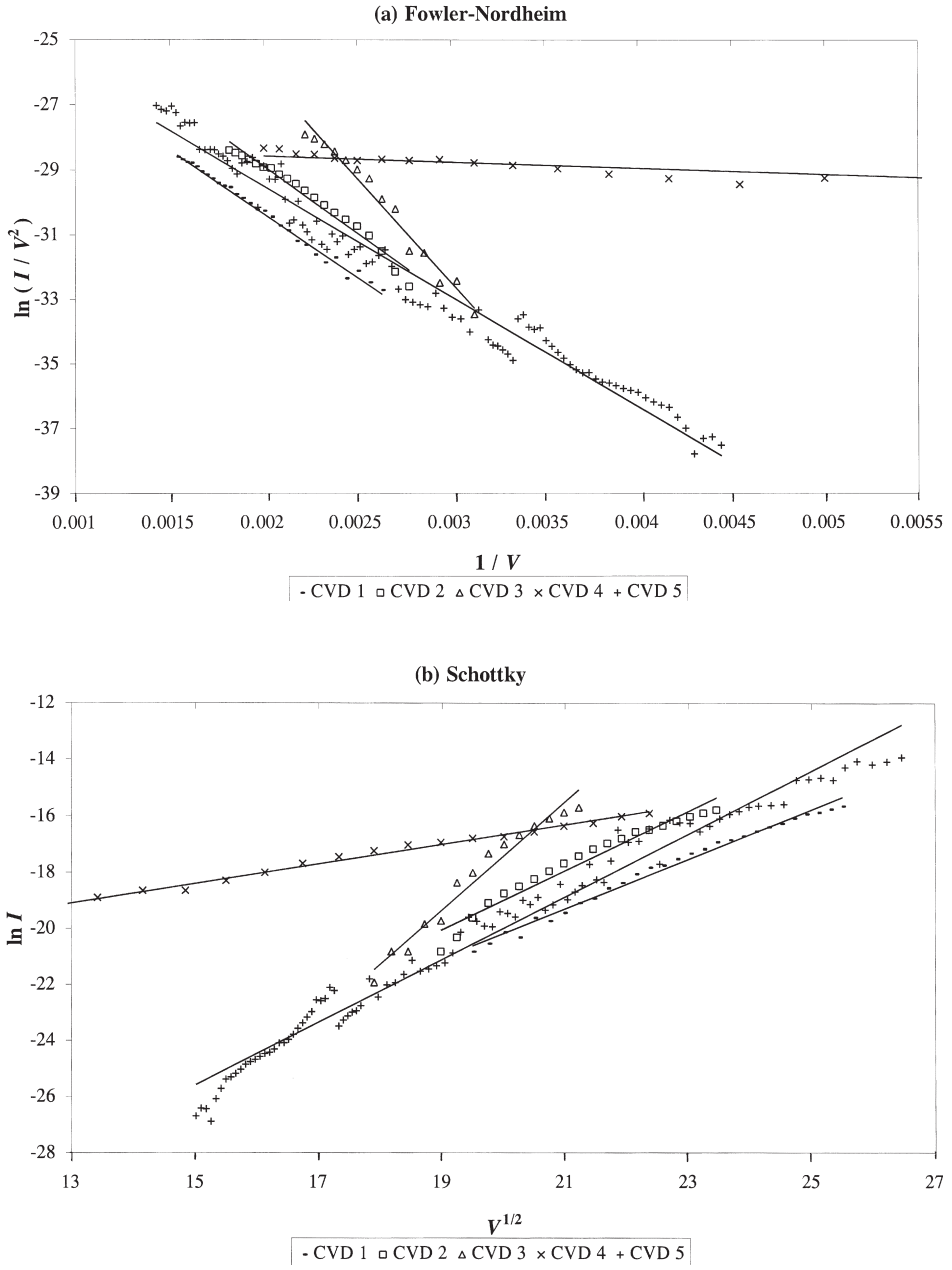
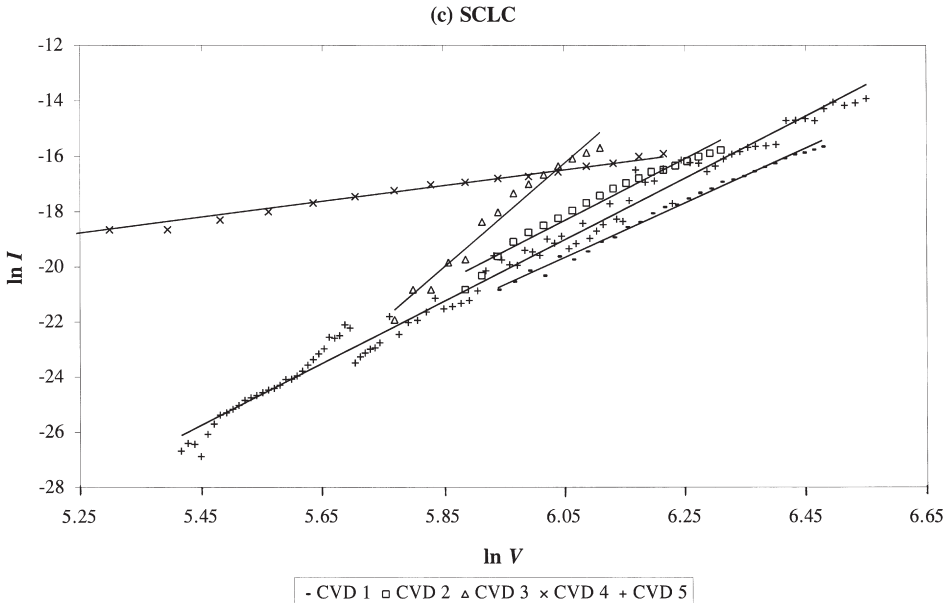


Fig. 1. Current–voltage data for five CVD diamond films plotted in such a way as to test the appropriateness of (a) the Fowler–Nordheim model, (b) the Schottky model, (c) the SCLC model and (d) the SCLC+PF model. The current (I) is measured in amps, and the voltage (V) in volts. The least-squares lines of best fit for each of these data sets are also plotted, showing that all four models provide good fits to the data.

points in a set is small — some I–V curves (e.g. DLC6, DLC7 and the Type IIb data) had <20 data points in the region with non-zero current, making accurate statistical analysis of the straight line plots problematic. Nevertheless, from Fig. 2, we can see that apart from a few such statistical variations or measurement errors, the field emission data from almost every type of carbon surface fit all four models closely, with r^2 values in virtually every case >0.8 and most >0.9. In fact, for the 23 samples studied, the SCLC model provided the best fit 14 times, the Schottky model four times and the Fowler–Nordheim only five times. Clearly, the justification for choosing the Fowler–Nordheim model in preference to any of the other models is questionable in almost all of these cases. Only in the data from the surface emitting material do we find different behaviour. Here, the Fowler–Nordheim model is a poor fit to the data, with the SCLC model being the closest fit. Interestingly, we obtained r^2 values for the Hill's law model of >0.98 for both of the surface emitter samples, comparable to that for the SCLC. This suggests that there is some difference in emission characteristics between the emission observed from normal CVD or DLC samples and that specially fabricated to enhance surface emission.



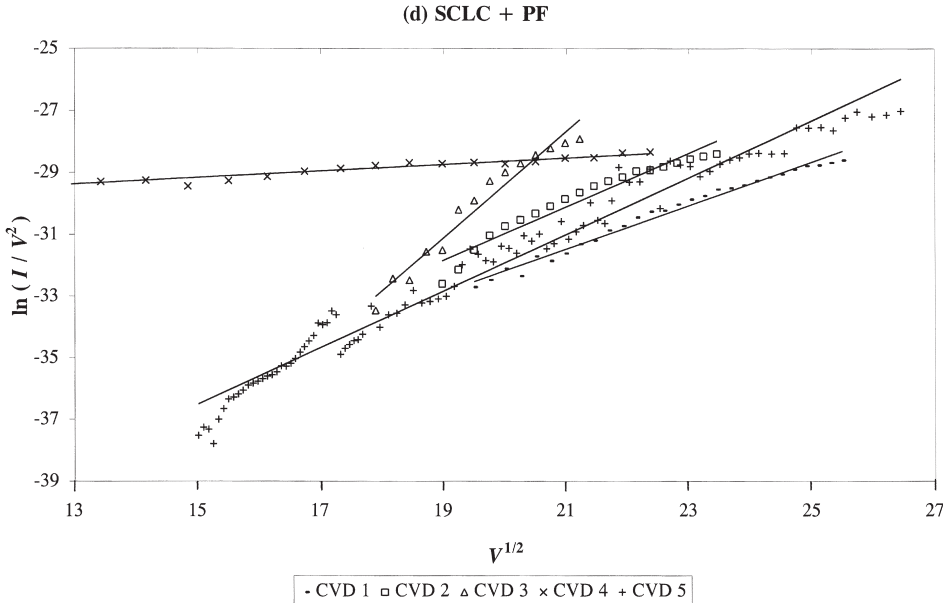


Fig. 1. (*continued*).

Table 2
Most usual mechanisms of conduction in insulators, their expected current–voltage relations [18], and mathematical relations required for a straight-line plot [7][a]

Conduction model	Current–voltage relation	Ordinate	Abscissa
(1) Fowler–Nordheim	$I \sim V^2 \exp(-a/V)$	$\ln(I/V^2)$	$1/V$
(2) Schottky	$I \sim \exp(aV^{1/2}/kT)$	$\ln I$	$\sqrt{V}$
(3) SCLC	$I \sim V$ (low fields)	I	V
	$I \sim V^n$ ($n>1$, high fields)	$\ln I$	$\ln V$
(4) SCLC + PF	$I \sim V^2 \exp(aV^{1/2}/kT)$	$\ln(I/V^2)$	$\sqrt{V}$
(5) PF	$I \sim V \sinh(aV^{1/2}/kT)$	$\sinh^{-1}(I/V)$	$\sqrt{V}$
(6) Hill's Law	$I \sim \sinh(aV/kT)$	$\sinh^{-1} I$	V

[a] SCLC: Space-charge-limited current; PF: Poole Frenkel models.

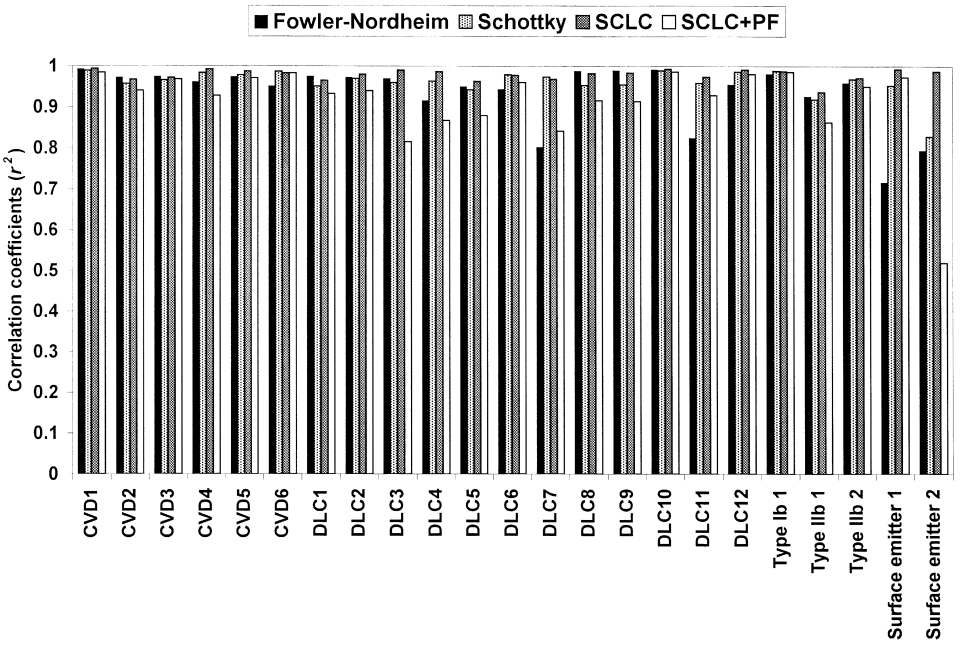


Fig. 2. Correlation coefficients (r^2) for the lines of best fit for the four conduction models and the 23 types of carbon cathode described in Table 1. The r^2 values for all four conduction models are very similar and >0.9, except for the surface emission devices, for which the SCLC model is superior.

Some recent reports [7,8] have suggested that surface damage may be a necessary requirement of low field emission. This may be another reason for the variation in r^2 values from film to film. It is interesting to note that the r^2 values for the Fowler–Nordheim and Schottky models show a good deal of film-to-film variation, whereas those for the SCLC model appear to show much less variation. This would be consistent with the above hypothesis since the first two models would be more sensitive to the exact surface condition of the film being tested than the SCLC model, which is based upon conduction through the bulk.

3. Conclusions

A general conclusion from this work is that a straight line obtained in a Fowler–Nordheim plot of *I–V* data obtained from *any* type of carbon surface does not necessarily prove that the electron emission process is cold field emission. This appears to be true for natural diamond, CVD diamond, DLC or a:C:H films, and for both doped and undoped samples. Indeed, with four different mechanisms based on entirely different models for the carrier transport mechanism, all giving good fits to the emission data, it is not obvious why one model should be used in preference to any other. Clearly, in future, if the Fowler–Nordheim model is to be used in preference to any other model, authors will need to justify their decision carefully. This will be especially important if reliable (and physically realistic) values for the emission area, surface work function and field enhancement factor are extracted from the gradient and intercept of such a plot.

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