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Field Emission and Display Applications

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FIELD EMISSION FROM CARBON SYSTEMS

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ABSTRACT

Electron field emission from diamond, diamond-like carbon, carbon nanotubes and nano-structured carbon is compared. It is found that in all practical cases that emission occurs from regions of positive electron affinity with a barrier of ~5 eV and with considerable field enhancement. The field enhancement in nanotubes arises from their geometry. In diamond, the field enhancement occurs by depletion of grain boundary states. In diamond-like carbon we propose that it occurs by the presence of sp2-rich channels formed by the soft conditioning process.

INTRODUCTION

Various forms of carbon such as carbon nanotubes, diamond and diamond-like carbon (DLC) can show electron field emission at low applied fields of order 2-20 V/μm. This opens up a number of opportunities for electronic devices. Each device requires a different set of material parameters and so this favours the use of a different type of carbon.

The electronic device of primary interest in vacuum microelectronics is the microwave power amplifier [1,2]. The high frequency limit of semiconductor devices is set by their dimensions and the relatively small limiting velocity of electrons in semiconductors, eg 10^5 m.s^{-1} for Si. Vacuum microelectronic devices can in principle operate up to THz, as the limiting electron velocity in space is 3.10^8 m.s^{-1}. These devices require a large, stable emission current density, but place no limits on the substrate or emission site density. It is likely that carbon nanotubes are best here, as they can carry the largest current.

Field emission displays (FEDs) are flat panel displays in which the image is formed from a large array of pixels each addressed by field emission sources [3,4]. The use of thin film emitters rather than Spindt tips allows the use of wider gate holes. This makes lithography easier and lower cost for large display areas. A significant constraint is that glass substrates are used for low cost, so deposition and processing temperatures must be kept under about 500°C or lower. The cathodes are ~2 μm in diameter, so it is necessary that there is one emission site per source, equivalent to an emission site density (ESD) of 10^6 cm^{-2}. FEDs require emission current densities of about 1 mA.cm^{-2}.

Carbon field emitters could be used in vacuum power switches [5,6]. Solid state power switches have considerable difficulty in simultaneously withstanding the large breakdown voltages and having small forward voltage drops, as this places opposite constraints on the doping density of the semiconductor. A vacuum emission device can separate these two requirements – the vacuum withstands the off voltage, while the forward voltage drop can be low for a good field emitter.

Carbon nanotubes can make field emission electron guns with extremely high brightness and narrow energy distributions for use in scanning transmission electron microscopes [7]. The sharp energy distribution helps to minimise the chromatic aberration.

Finally, the decreasing size of Si devices is reaching the limits of UV lithography. Various high resolution methods such as electron beam writing are impractical, because it is necessary to write the images in two dimensions to transfer the image information in a reasonable time. This problem can be resolved by using parallel electron beam writing, for example from a controllable array of field emission cathodes. The electron beams should be sharply focused for high resolution, which is easier for flat cathodes rather than tips. This favours carbon cathodes over Spindt tips [8].

The requirements for each application are summarised in Table 1; more dots signify a greater need.

	Current density	Low Field	Site density	Current stability	Energy width
Microwave amp	**			**	
FE Display		*	**	**	*
Power switch	**	**			
FE gun	***			**	**
Lithography		*	**	*	*

The emission properties of the various types of carbon are summarised in Table 2. Again, the more dots the better.

	Current density	Low Field	Site density	Current stability	Deposition Temperature
Diamond				*	
Nano-diamond	*	**	**	**	
Diamond-like carbon		*			**
Nano-structured Carbon	*	**	**	**	**
Nanotubes	***	**	**	*	(*)

DIAMOND

We now consider the emission properties of each of the various forms of carbon in more detail. The original motivation for the study of field emission from diamond was its negative electron affinity [9-11]. Diamond is a semiconductor with a band gap of 5.5 eV. When its surface is terminated by hydrogen it has a negative electron affinity (NEA), so that its conduction band edge lies above the vacuum level. This means that any electrons in its conduction band could pass into the vacuum with no energy barrier. However, field emission requires electrons to travel round a complete circuit. This is a problem, as there is still a large potential barrier at the back contact [15](Fig. 1), and diamond has a very high resistivity. To date, the best electron emission from diamond phases is from microcrystalline and nano-crystalline diamond [16-20]. In this case, the emission is found to vary inversely with the grain size.

Emission should be possible from n-type diamond as this places electrons near the conduction band. However, the most soluble donor is nitrogen, but this gives a deep donor level at 1.7 eV below the conduction band, so the film remains highly resistive [21]. Phosphorus has a more shallow donor level ~0.5 eV below the conduction band [22]. This system could finally test the ideas of NEA field emission. However, to date, even phosphorus doped films still have a high resistivity, which will limit emission. In addition, phosphorus doping has only been carried out on homo-epitaxial films on single crystal diamond, so that making electrical contact to the back of the doped film is difficult and has required back-side etching of the diamond substrate [23].

The origin of the field emission can be determined by measuring the electron energy distribution (EED) of the emitted electrons in conjunction with for example a photoemission measurement (Fig. 2). The mean energy can show if the electrons originate from the conduction band, valence band, gap states or the Fermi level, while the EED width is proportional to the size of the local field. Bandis and Pate [24] found that emission from boron doped single crystalline diamond originates from the valence band. They later found that emission from some N-doped diamond originated from states in the lower gap [25], but it turned out that the material has a large tungsten impurity. Recently, Groning et al [20] have shown that emission from nano-crystalline diamond originates from the Fermi level, which in that case lies about 1 eV above the valence band edge. Thus, to date, no field emission has truly utilised the NEA property of diamond.

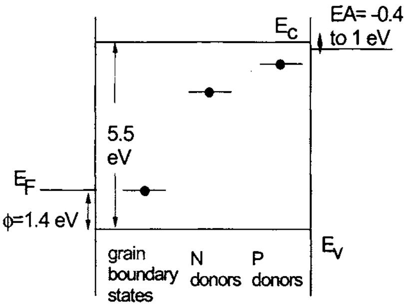

Fig. 1. Schematic band diagram for diamond [12,14], showing large barrier for electrons at the back contact, and the energy levels of grain boundary states and N and P donors.

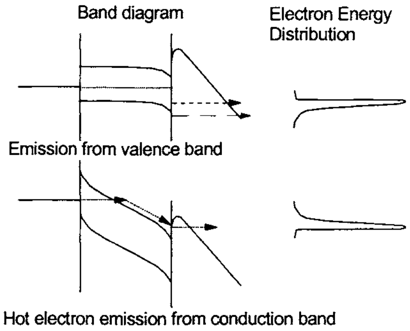

Fig. 2. Schematic electron energy distributions for (a) emission from the valence band or Fermi level, and (b) hot electron emission from the conduction band.

The spatial location of emission can be deduced by using a scanning tunnelling microscope arrangement. Karabutov et al [26] has correlated the more emitting regions with the topological features of micro-crystalline diamond. They found that emission tends to come from the troughs rather than the peaks of the surface. This is consistent with emission from the grain boundaries, rather than the grains. Similar results were found by Rakhimov et al [27]. The grain boundaries of diamond are more conducting, sp^2 bonded and have states lying about 1.4 eV above the valence band edge. Thus, the results suggest that electrons cross the film along the grain boundaries and are emitted from them. This is consistent with early reports of preferential emission from the positive affinity, sp^2 regions of CVD diamond films [28,29]. It is also consistent with the observed EED.

On the other hand, some groups such as Groning et al [20] find that emission comes mainly from the grain peaks, not dips. While diamond is usually very resistive, CVD diamond taken from a hydrogen plasma can have a large, hydrogen-induced p-type conductivity [30]. The origin of this conductivity is not yet understood, but it could allow conduction from the grain boundary to the peaks and emission from the grain peaks.

Emission from grain boundaries is consistent with a field enhancement model [19]. The grain boundary is sp^2 bonded, and it gives rise to π states on either side of the Fermi level, which lies about 1.4 eV above the valence band edge. If the grain boundary is very narrow, these states are simply localized π states in the diamond band gap. The π states are neutral when half filled. When filled, they are negatively charged and when empty they are positively charged. The emission barrier is 4-5 eV, the energy from Fermi level to the vacuum level - the work function.

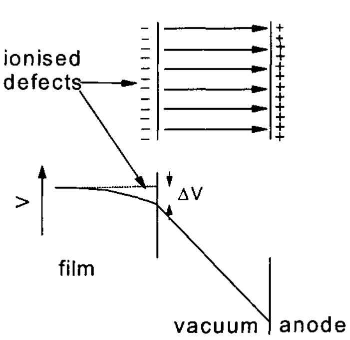

Fig. 3. A uniform applied field creates a depletion layer in the diamond. The field penetration depth is small for fields of 10-20 V/μm.

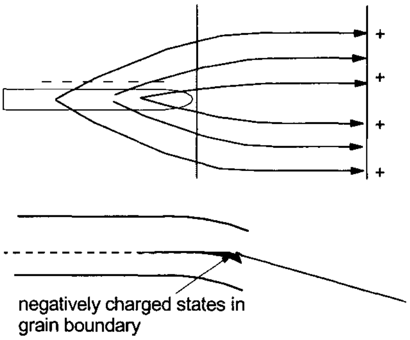

Fig. 4. Field lines focusing to the negatively charged gap states of a grain boundary in micro-crystalline diamond.

Consider applying an external field by a flat anode. For a single crystal diamond containing no defects, the field will be lower in the diamond by the dielectric constant. If the diamond possessed a uniform distribution of these π defect states, the field would induce negative charges on the states, and form a negatively charged depletion layer at the diamond surface (Fig. 2). This results in field penetration, but the depth is quite small (~1 nm) for the fields of interest (10 V/μm) as the defect density is quite large. Hence this field penetration does not result in a significant band bending or lowering of the surface potential barrier (<0.1 V). If instead, the defects are concentrated in grain boundaries, the field lines focus into these regions (Fig. 3). This produces strong local fields, which extends along the grain boundary. The grain boundary acts like an *internal tip*. This mechanism can provide an adequate narrowing of the 5 V barrier, and this allows the easy emission by tunneling.

DIAMOND-LIKE CARBON

Diamond-like carbon (DLC) is amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) containing a substantial amount of sp^3 bonding [31]. It consists of very smooth films, usually grown at room temperature, which is a great advantage for displays. Two main types of DLC have been studied, the a-C:H grown by plasma enhanced chemical vapour deposition (PECVD), and the highly sp^3 bonded tetrahedral amorphous carbon (ta-C) grown by filtered cathodic vacuum arc (FCVA) or by pulsed laser deposition (PLD).

DLC is a reasonable emitter, when doped with nitrogen [32-38]. However, the emission site density from DLC tends to be low, which limits its use in field emission displays [39]. Many types such as undoped a-C:H are not very useful for emission because their resistivity is too high (10^{14} Ω.cm). The hydrogen can also lead to rather unstable emission, so many groups have focused on hydrogen-free a-C. Emission from ta-C has been found to depend strongly on its sp3 content, the incorporation of nitrogen, and on any plasma surface treatment [33-35]. The emission when tested in the parallel plate configuation can occur at threshold fields as low as 5 V/μm.

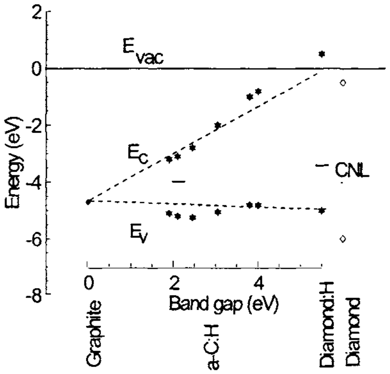

Fig 5. Schematic band diagram for a-C:H [14], from photoemission data [42]. The valence band edge remains at roughly 5 eV below the vacuum level, for all band gaps.

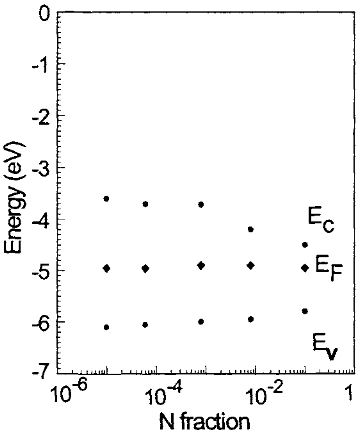

Fig. 6. Fermi level, valence and conduction band edge energies from Kelvin probe and photemission measurements [41,42]

Emission, particularly from the more resistive types of DLC, requires a forming or conditioning process in which the voltage is applied in cycles of increasing size [34]. For highly resistive a-C:H which has a large threshold field, it is clear that the conditioning process creates surface damage, which is then the cause of the emission. In ta-C's with lower threshold field, there is a form non-destructive conditioning. STM experiments suggest that this acts to increase the local conductivity at the emitting spots by a local conversion of sp^3 to sp^2 bonding [38]. The need for conditioning indicates that the film conductivity is still too high for the most efficient emission.

The emission mechanism in DLCs has been difficult to understand. The macroscopic emission current densities roughly obey the Fowler-Nordheim equation.

$$J = af\,\frac{(\beta F)^2}{\phi}.\exp(-\frac{b\phi^{3/2}}{\beta F}) \qquad (1)$$

where ϕ (eV) is the barrier height, F is the applied field, β is a dimensionless geometric field enhancement factor, f is the fraction of area over which emission occurs and a and b are constants. The slope of the Fowler-Nordheim plot of 0.01 to 0.4 eV derived [12] from the Fowler-Nordheim plots by taking $\beta=1$ is clearly not the real barrier, as such small barriers would allow temperature-dependent thermionic emission or Schottky emission which is not observed.

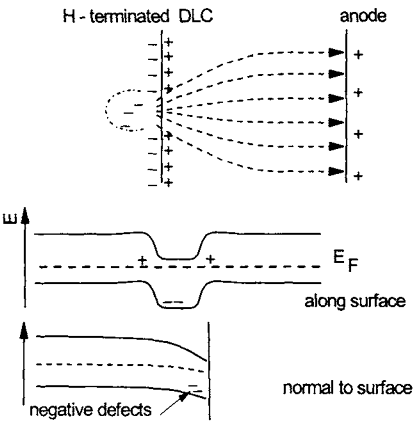

Fig. 7. (a) Schematic of the field lines focusing to a surface region unterminated by H on a ta-C surface. (b) Associated band diagram along and normal to surface [14].

It is necessary to construct a band diagram for ta-C to understand the emission mechanism [12-15]. A-C:H films have a band gap which varies with their sp^3 content. The energy of their valence band below the vacuum level has been measured by photoyield experiments [40]. The resulting band diagram (Fig. 5) shows that a-C:H always has positive electron affinity. Recently, photoemission [41] and Kelvin probe [42] have been used to find the valence band energy and work function of ta-C. Ta-C is a semiconductor whose band gap varies with its sp^3 content [31,43]. A typical band gap is ~2.5 eV for 80% sp^3 content [43]. The work function is found to be 4.9 eV and the electron affinity is 3.4 – 3.6 eV [41,42]. The variation of band energies with nitrogen addition is shown in Fig. 6 [42]. These results emphasise that ta-C always has a sizeable positive electron affinity, and that its work function is relatively independent of sp^3 content and nitrogen addition at 4.8 to 4.9 eV. This value is quite similar to that of graphite 4.9 eV [20].

The EED of a-C with a large nitrogen incorporation has been measured, and emission is found to occur from ~5 eV below the vacuum level [44]. The EED width is consistent with the presence of a high local internal field. This indicates the existence of a strong field enhancement mechanism.

It has been suggested that emission from DLC is due to hot electrons created by strong band bending at the back contact [32], as shown schematically in Fig. 2(b). However, photoemission measurements of the valence band energy of ta-C films of increasing thickness show no evidence of any band-bending at the back contact [41]. The EED also shows no evidence of hot electrons as a high energy tail. Thus, this mechanism does not seem to be relevant to DLC.

The band diagram and the absence of hot electron effects mean that there is a large, ~5 eV emission barrier at the front surface, and that there are large local fields. The main problem in any emission model is that DLC films are very smooth and generally homogeneous, so the origin of a large field enhancement is not clear [14]. The first proposal [14] was based on the observation that the EA and work function of diamond could be shifted by 1.5 eV by varying the surface coverage of hydrogen. A local surface region without hydrogen termination would have a more positive EA than the surrounding H-terminated surface. Ta-C has a large density of amphoteric defects. The common Fermi level leads to charge transfer to create negatively charged defects behind the un-terminated