Available online at www.sciencedirect.com
ScienceDirect
Diamond & Related Materials 15 (2006) 2006–2009
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Field penetration and its contribution to field enhanced thermionic electron emission from nanocrystalline diamond films

F.A.M. Koeck *, R.J. Nemanich

Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA

Available online 18 September 2006

Abstract

Field emission from sulfur doped nanocrystalline diamond films is characterized by intense emission sites with nm scale diameters. Field emission measurements were obtained at room temperature and analyzed in terms of the Fowler–Nordheim expression where electron emission is due to tunneling through a diminished barrier. The electron emission versus temperature was also recorded at a series of applied fields from 0.5 to 0.8 V/μm. These results were analyzed in terms of a modified Richardson–Dushman relation which describes field dependent thermionic emission. It was found that both sets of data could be fit with a work function of 2.0 eV and a field enhancement factor of ~1750. The large field enhancement could not be correlated with specific structures on the relatively flat surfaces. The field and thermionic-field emission from the sulfur doped nanocrystalline diamond films is evaluated by a model which includes barrier lowering as a result of field penetration effects.

Keywords: Field emission; Thermionic emission; CVD; Nanocrystalline diamond

1. Introduction

Electron emission from the surface with an applied electric field has been employed over decades as a way to form high brightness electron sources. As surface properties of the emitter are crucial to electron field emission, extensive studies have described this solid–vacuum interface under the influence of an electric field. A formulation of the field emission process proposed by Fowler and Nordheim (FN) was based on tunneling phenomena from cold metals [1]. The emission current density, J, as a function of the applied field, F, was then quantified by

$$J(F) = A'F^2 e^{\frac{-B'\varphi^{3/2}}{F}}, \quad (1)$$

where φ is the work function and A' and B' are slowly varying functions defined elsewhere [3]. For planar emitter geometries the local field at the emitter is distributed uniformly across its surface without spatial variation. Introducing a surface protrusion results in a re-distribution of the applied field at these geometric features which are then coupled to a strong variation in the local field distribution. This non-uniform field can then be described by a field enhancement factor, β, which modifies the applied field, F, to $\beta(x,y)\cdot F$. The field enhancement factor has then become a spatially dependent function. To determine the work function of the emitter from a $J(F)$ dataset requires a fitting procedure using Eq. (1) where a simultaneous computation of φ and β is possible but with limitations.

In a separate mechanism, electrons can be released from a solid by application of thermal energy, a process termed thermionic emission formulated by Richardson and Dushman with the expression

$$J(T) = A_R T^2 e^{-\frac{\varphi}{k_B T}}, \quad (2)$$

where T is the emitter temperature, A_R is the Richardson constant with a theoretical value of 120 A/cm^2 K^2 and k_B is the Boltzmann constant [2,3]. Exposing a thermionic emitter to an external electric field modifies the exponent in Eq. (2) by a term proportional to the applied field, which results in

$$J(T,F) = A_R T^2 e^{-\frac{\varphi - 3.79\cdot F^{1/2}}{k_B T}}, \quad (3)$$

where F [V/Å] is the applied electric field. This expression is referred to as the Schottky equation and it accounts for the field dependent barrier lowering.

We have prepared sulfur doped nanocrystalline diamond films by plasma assisted chemical vapor deposition to study the

* Corresponding author.
E-mail address: fakoeck@ncsu.edu (F.A.M. Koeck).

0925-9635/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2006.08.002

emission mechanism. Field emission from nanostructured carbon films, in general, has been described by field enhancement effects where high field enhancement factors on the order of several 1000s have been reported [4,5]. While the emission observed as intense emission sites is indicative of field enhancement effects, it is difficult to detect morphological features which would account for the unusually large deduced field enhancement factors. In this study we present temperature dependent emission data from sulfur doped nanocrystalline diamond films and discuss the results with respect to field penetration effects.

2. Experimental

An AsTex® HPMS deposition system equipped with a 1.5 kW, 2.45 GHz microwave power source and induction heater was utilized for diamond film growth. Sulfur doped nanocrystalline diamond films were synthesized employing microwave plasma assisted chemical vapor deposition. The films were deposited on 1 in. diameter Mo substrates. Pretreatment included a 30 minute ultrasonic abrasion step in a diamond/titanium/methanol suspension with 0.1 μm diamond and 30 μm titanium powder [6]. The substrate was then rinsed with methanol, dried with nitrogen gas and loaded into the CVD reactor.

The sulfur source was a 50 ppm hydrogensulfide in hydrogen (H_2S/H_2) mixture. The emitter films were synthesized with 5 to 40 sccm of the (H_2S/H_2) mixture and 20 sccm methane at 20 Torr chamber pressure, 900 W of microwave power, and ~900 °C substrate temperature. Laser reflectance interferometry was employed for in situ monitoring of the film growth. Sample preparation was concluded by simultaneously terminating gas flows, shutting off the microwave plasma and substrate heating. The final film thickness was determined by in situ laser interferometry to be ~0.3 μm.

Field and field thermionic emission was characterized in a UHV environment with a base pressure $<5\times10^{-10}$ Torr. For thermionic emission, a radiatively heated sample stage is utilized while a cooled, moveable collector is positioned near the emitting sample. The electric field was determined by applying a measured voltage across the known emitter–collector separation of typically 500–1000 μm. A moveable sample stage with a 25 μm vertical resolution allowed accurate collector positioning. Current/voltage sweeps were recorded at various fields and temperatures using an SRS PS350 source measuring unit.

3. Results and discussion

A non-uniform distribution of the field enhancement factor, β, typical for nanostructured carbon materials, i.e. nanocrystalline, ultrananocrystalline and carbon nanotube (CNT) films, results in a non-uniform electron emission behavior. This singularity can be directly observed in a projection of the emissivity where individual emission sites appear as bright sources. The size of a single emission site has been estimated to be ~10 nm while no direct correlation between surface topography and emissivity could be observed [7]. This indicates that the field enhancing characteristics are not solely governed by structural properties where the high aspect ratio features such as tips exhibit high field enhancement factors.

Sulfur doped nanocrystalline diamond films exhibit a similar emission behavior at room temperature, additionally a strong temperature dependence in the emission is observed. With an increase in emitter temperature, the electron emission intensity of an individual site increases significantly over its room temperature value. This emission behavior suggests a thermionic component to the field emission, where electrons can overcome a diminished emission barrier in addition to the field induced tunneling current. These processes are shown schematically in Fig. 1. With an increase in the applied electric field the emission barrier is reduced by an amount proportional to the field strength and local field enhancement. The work function φ of the region of emission is then substituted by the effective work function $\varphi-\Delta\varphi$.

At room temperature emission from sulfur doped nanocrystalline diamond films is described by a tunneling process with a typical current/applied field dependence shown in Fig. 2a.

Plotting the I/V data with respect to the Fowler–Nordheim functionality allows the extraction of the ratio of work function φ and field enhancement factor β with the result $\beta=631\cdot\varphi^{3/2}$. It is often suggested that an evaluation of this functionality is valid for a work function of 5 eV, typical for graphitic species. However, this would result in a field enhancement factor β of 7054 which is in contrast to morphological observations by scanning electron and atomic force microscopy. These surface characterization techniques of nanocrystalline diamond films have indicated a roughness of 10–65 nm [8,9]. Alternatively, with moderate geometric field enhancement factors of about 100, a work function significantly less than 1 eV would be necessary to describe the observed emission. Thus, field enhancement alone cannot provide the mechanism for a significant emission barrier lowering.

To complement the room temperature field emission measurements, thermionic emission characterization was employed providing an additional means of determining the emission barrier. Here, the emission current was recorded as a function of emitter temperature while an applied electric field was held constant during the temperature sweep. Similar $I(T)_{F=\text{const}}$

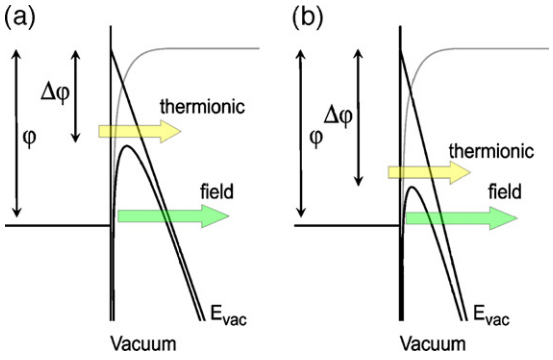

Fig. 1. Band schematic of field induced barrier lowering due to high field enhancement effects (a). With an increase in the applied field the emission barrier is reduced lowering the effective work function and increasing the thermionic emission component (b).

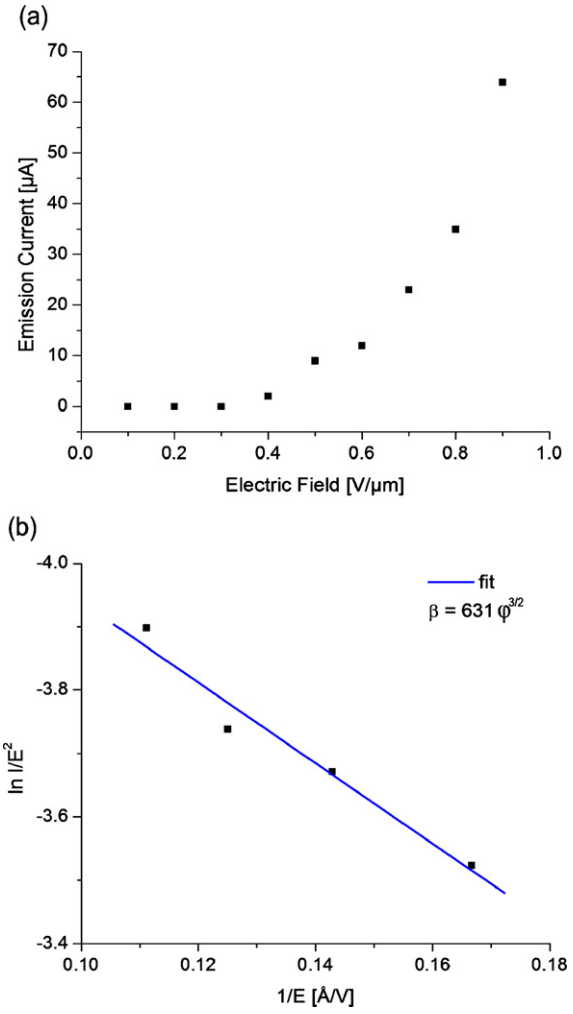

Fig. 2. Field emission characteristic from a sulfur doped nanocrystalline diamond film. Current/applied field plot with small threshold fields (a) and Fowler–Nordheim plot (b).

curves were then acquired for various applied fields which were fitted by the Richardson equation as shown in Fig. 3. At an applied electric field of 0.5 V/μm an effective work function of 2.3 eV was computed. Increasing the applied electric field from 0.5 V/μm to 0.8 V/μm results in a significant reduction of the effective work function by 0.3 eV to 2.0 eV. This is accompanied by a shift of the $I(T)_{F=\text{const}}$ curve to higher values over the same temperature range.

The Fowler–Nordheim relation for room temperature field emission and the Richardson equation for thermionic emission are based on different emission mechanisms with the emission barrier, the effective work function φ, as a common parameter. An accurate computation of φ after the Fowler–Nordheim relation requires an estimate of the field enhancement factor β which determines the value of the work function. The continuous, strictly monotonic function $\varphi(\beta)$ increases at a faster rate with small to moderate β which translates to greater uncertainties in the work function in this field enhancement regime. Topographical investigations of nanocrystalline diamond films indicate that moderate field enhancement factors occur at the surface which necessitates an additional characterization step for a more comprehensive description of the emissive material. Employing thermionic emission, a process independent of field enhancement effects due to negligible extraction fields, presents a viable method to determine the emission barrier. However, sulfur doped nanocrystalline diamond films are field thermionic emitters, i.e. temperature dependent emission commences at a small threshold field described by the field modified Richardson relation (3). A typical field thermionic dataset, $I(T)_{F=\text{const}}$, corresponds to emission at a constant applied field or more accurately $I(T,\varphi)_{F\cdot\beta=\text{const}}$, where the applied field F, emitter temperature T and the emission current I are measured. The Fowler–Nordheim and field modified Richardson relation can then be solved consistently with a unique solution for the effective work function φ and field enhancement factor β. Thus, for the sulfur doped nanocrystalline diamond film a field enhancement factor of 1748 is computed with a work function of 2 eV.

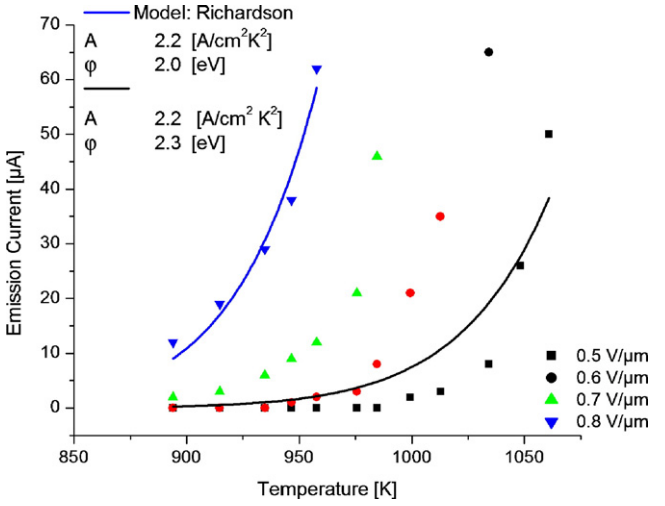

Fig. 3. Field thermionic emission data from a sulfur doped nanocrystalline diamond film at various fields. An increase of the applied field results in a significant lowering of the effective work function.

This significantly reduced field enhancement factor is still considerably larger than that suggested by evaluating the effect of topographic features. To account for this discrepancy we are proposing that an additional mechanism is necessary to provide

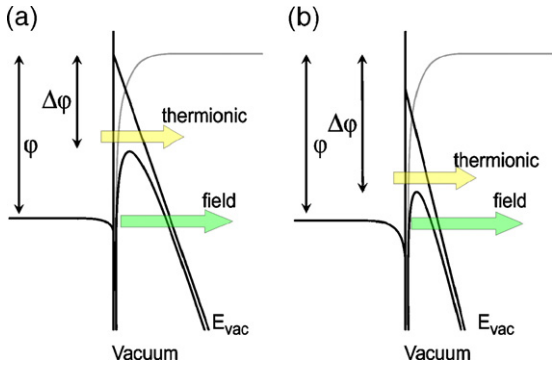

Fig. 4. Field penetration effects can result in barrier lowering where field enhancement structures can provide increased localized fields (a). With an increased applied field the effective work function is significantly reduced (b).

means of lowering the emission barrier. Fig. 4 presents a schematic of the effect of field penetration in a field enhancement based emitter geometry. With an increase in the applied field, the field can penetrate into the film which results in a reduction in the potential of the electronic levels at the surface (i.e. band bending). The net result is a reduction in the work function. For a metal with a carrier density of $\approx 5\times10^{22}$ cm^{-3}, the Thomas–Fermi screening length is <0.1 nm, and the potential reduction for an applied field of 1 V/μm would be negligible. However, for a material with a lower electron density the effect can be much more significant.

The graphitic nature of the grain boundary matrix in nanocrystalline diamond films and their respective field emission properties suggests emission phenomena comparable to carbon nanotube films. While the exact carbon bonding configuration in the grain boundaries is still under investigation various studies indicate the presence of thin graphitic sheets between the sp^3 bonded grains [10,11]. A reported boundary width of <0.5 nm is supportive of a comparison with a theoretical approach based on carbon nanotubes [12]. One crucial aspect in the emission mechanism from carbon nanotubes is their structural configuration including termination of the tube. Extensive experimental and theoretical approaches to the field emission from single- and multi-wall carbon nanotubes have focused on the emission mechanism [13–15]. Computational results for a (5,5) carbon nanotube indicated that the closed structure was not a disadvantage with respect to field emission as a result of diminished field penetration effects [16]. This was attributed to a more efficient screening of the electric field by the closed nanotube tip configuration. In a separate study a closed (5,5) nanotube exposed to an electric field of 0.33 V/Å was considered. The small height of the nanotube resulted in a small geometric field enhancement with $\beta\approx3$ inducing a local field at the tip of the nanotube of ~1 V/Å. The simulation of this configuration presented an effective work function of ~3 eV [17].

This strong reduction in the work function (4.78 eV at zero field) by 1.76 eV was attributed mainly to field penetration effects. In an analogy with nanocrystalline diamond films where we estimate the geometric field enhancement factor to be ~100, the effective field enhancement factor of 1748 indicates a contribution from field penetration. The non-geometric field enhancement of 1648 arises from neglecting the geometric contribution to β. We also neglect the geometric field enhancement effects to the capped (5,5) nanotube with an applied field of 0.33 V/Å. Assuming a similar emission phenomenon for a nanocrystalline diamond film and a nanotube film, this high effective field enhancement will then appear in the Fowler–Nordheim emission characteristics. Consequently, the applied field for the nanotube would then be $F_{\text{applied}}=(F_{\text{local}}/\beta)=$ 0.33 V/Å/1648 ≈ 2 V/μm.

This result indicates that an applied field of 2 V/μm with small geometric field enhancement can give rise to a significant effective field enhancement factor which is attributed to field penetration effects and which in turn can significantly lower the effective work function. Thus, our results from nanocrystalline diamond films with an applied field of 1 V/μm are at least consistent with a model where field penetration is the major contributor to emission barrier lowering.

4. Conclusion

Sulfur doped nanocrystalline diamond films were synthesized by plasma assisted chemical vapor deposition and field and field thermionic emission was characterized in a UHV environment. Field emission as described by Fowler–Nordheim suggests a high field enhancement factor in contrast to experimental observations. Field thermionic emission indicates a low effective work function of 2 eV which is consistent with Fowler–Nordheim emission results where a high field enhancement factor is assumed. This high effective field enhancement factor indicates field penetration effects which can significantly lower the effective work function. Simulations for single wall carbon nanotubes with small geometric field enhancement can result in a Fowler–Nordheim characteristic with high field enhancement β where the grain boundary work function is reduced to ~3 eV under the exposure of an electric field of 2 V/μm which is in agreement with our results.

Acknowledgement

This research is supported by the Office of Naval Research through the TEC MURI project.

References

[1] R.H. Fowler, L. Nordheim, Proceedings of the Royal Society of London. Series A 119 (1928) 173.
[2] O.W. Richardson, Physical Review 23 (1925) 153.
[3] S. Dushman, Physical Review 21 (1923) 623.
[4] O. Gröning, L.-O. Nilsson, P. Gröning, L. Schlapbach, Solid-State Electronics 45 (2001) 929.
[5] J.-M. Bonard, M. Croci, I. Arfaoui, O. Noury, D.I. Sarangi, A. Châtelain, Diamond and Related Materials 11 (2002) 763.
[6] R. Shima, Y. Chakk, A. Hoffman, Carbon 38 (2000) 1839.
[7] F.A.M. Köck, J.M. Garguilo, R.J. Nemanich, Diamond and Related Materials 13 (2004) 1022.
[8] H. Yoshikawa, C. Morel, Y. Koga, Diamond and Related Materials 10 (2001) 1588.
[9] K. Subramanian, W.P. Kang, J.L. Davidson, et al., Journal of Vacuum Science and Technology B 23 (2005) 786.
[10] D.M. Gruen, Annual Review of Materials Science 29 (1999) 211.
[11] H. Ogi, N. Nakamura, H. Tanei, H. Masahiko, Applied Physics Letters 86 (2005) 231904.
[12] P. Keblinski, D. Wolf, S.R. Phillpot, H. Gleiter, Journal of Materials Research 13 (1998) 2077.
[13] J.-M. Bonard, J.-P. Salvetat, T. Stöckli, L. Forró, A. Châtelain, Applied Physics A 69 (1999) 245.
[14] A. Mayer, N.M. Miskovsky, P.H. Cutler, Physical Review B 65 (2002) 155420.
[15] C. Adessi, M. Devel, Physical Review B 62 (2000) R13314.
[16] A. Mayer, N.M. Miskovsky, P.H. Cutler, Applied Physics Letters 79 (2001) 3338.
[17] C.-W. Chen, M.-H. Lee, S.J. Clark, Applied Surface Science 228 (2004) 143.