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# Electron emission measurements from CVD diamond surfaces

S.P. Bozeman<sup>a</sup>, P.K. Baumann<sup>a</sup>, B.L. Ward<sup>a</sup>, M.J. Powers<sup>a</sup>, J.J. Cuomo<sup>a</sup>, R.J. Nemanich<sup>a</sup>, D.L. Dreifus<sup>b</sup>

\* Department of Materials Science and Engineering and Department of Physics, North Carolina State University, Raleigh, NC 27695-7919, USA

<sup>b</sup> Kobe Steel USA Inc, Electronic Materials Center, PO Box 13608, Research Triangle Park, NC 27709, USA

#### Abstract

Electron emission measurements on diamond films synthesized by chemical vapor deposition are reported. UV photoemission spectroscopy indicates that the samples exhibit a negative electron affinity after exposure to hydrogen plasma. Secondary electron emission yields vary from 2.2 to 9.2. Field emission current-voltage measurements indicate threshold voltages ranging from 28 to  $84 \text{ V} \mu m^{-1}$ . The film with the highest secondary yield also exhibits the lowest emission threshold.

Keywords: Field emission; CVD diamond; Secondary electron yield; UV photoelectron spectroscopy

### 1. Introduction

The electron emission properties of diamond make it an attractive material for cold cathode applications such as high-power high-frequency electronic devices, flat panel displays and electron multipliers [1,2]. In general, electron emission studies have used UV photoemission spectroscopy (UPS), secondary electron emission (SEE) or field emission (FE), but comparison of these three types of electron emission characterization techniques has been limited. In this study we employ all three types of characterization techniques (UPS, SEE and FE) to examine chemical vapor deposited (CVD) diamond films on silicon. Photoemission and secondary emission are similar techniques in that they generate both electrons and holes in nearly equal numbers, and electron emission clearly originates from the conduction band. In an ideal field emission measurement only electrons participate and electron emission also occurs from the conduction band. However, for p-type semiconductors it is possible that emission occurs from the valence band and that holes transport through the semiconductor. Thus it is of interest to investigate correlations between the other measurements and field emission.

# 2. Experimental

The samples examined were diamond films grown on silicon via microwave plasma chemical vapor deposition.

The study included four films ranging from insulating to highly conductive and varying in surface morphology. The films were characterized using standard scanning electron microscopy, Raman spectroscopy and secondary ion mass spectroscopy (SIMS) techniques. The properties of the films, including thickness, atomic boron concentration, surface morphology and Raman full width at half maximum (FWHM) are listed in Table 1.

The first type of electron emission measurement employed was UPS. In UPS, UV light incident on the sample excites electrons from the valence band into the conduction band [3]. Electrons with sufficient energy to overcome the electron affinity of the material are emitted into the vacuum. For a semiconductor with negative electron affinity (NEA), a distinctive peak may be observed at the lowest kinetic energy in the spectra [4]. This low-energy feature corresponds to the large number of secondary and scattered electrons that have thermalized to the conduction band minimum and escaped into vacuum. UPS can also be used quantitatively to determine the electron affinity of a material by measuring the width of the spectrum from the valenceband turn-on to the low-energy cut-off. If the electron affinity is positive, this width is given by W = $hv - E_g - \chi$ , where hv is the excitation energy,  $\chi$  is the electron affinity and  $E_g$  is the bandgap. If the electron affinity is negative,  $W = hv - E_g$  and the magnitude of the electron affinity cannot be determined from the spectrum.

Sample	Thickness (µm)	10 <sup>18</sup> Boron content <sup>a</sup> (cm <sup>-3</sup> )	Surface morphology	Raman FWHM (cm <sup>-1</sup> )
A	3.2	1.1	(110) texture	9.4
В	4.2	1.2	(110) texture	6.5
С	5.8	_	(110) texture	6.6
D	4.3	3.7	Mix of large and small grains	5.7

Table 1 The CVD films used in the study

<sup>a</sup> Boron content was measured using SIMS. The boron content of sample C was below the SIMS detection limits.

UPS measurements were performed in a UHV chamber (base pressure below  $2 \times 10^{-10}$  Torr) connected in vacuo to a hydrogen plasma system. Excitation in this system was provided by 21.2 eV (He I) light from a He resonance discharge lamp and a hemispherical analyzer was used to measure the energy spectrum of the photoemitted electrons. The sample was biased at -3 V with respect to the analyzer to allow the electrons to overcome the work function of the analyzer and to facilitate the measurement of low-energy electrons. The UPS system is described in more detail elsewhere [5]. UPS measurements of the diamond films were made under three conditions: (1) as-loaded, (2) after exposure to hydrogen plasma to clean and hydrogen-terminate the surface and (3) after annealing in UHV at 1000 °C for 10 min. In step (2), the samples were exposed to a remote hydrogen plasma at a sample temperature of 500 °C and a H<sub>2</sub> pressure of 50 mTorr.

Secondary electron emission involves the ejection of low-energy electrons from a surface which is exposed to a primary energetic beam of electrons [6]. The secondary electron yield of a material is defined as the ratio of the total number of secondary electrons ejected per incident primary electron. The secondary electron yield generally depends on both the penetration depth of the primary beam and the escape depth of the secondary electrons.

Secondary electron emission measurements were obtained with the samples in a separate high vacuum chamber (pressure below  $10^{-5}$  Torr). A primary beam current of 250 nA was applied over a spot of diameter 1 mm, giving a current density of approximately  $32 \,\mu\text{A cm}^{-2}$ , and the primary beam energy was varied from 0.5 to 1.25 keV. The primary beam current  $I_p$  was measured by directing the beam into a Faraday cup, and both the secondary electron current  $I_c$  and the current drawn by the sample mount  $I_m$  were measured by deflecting the beam into a separate enclosure containing the sample [7]. The collector which draws the secondary electron current was biased at +30 V with respect to the sample mount to ensure collection of all secondary electrons emitted. The secondary electron yield was calculated as the ratio  $I_c/I_p$  and the equality  $I_{\rm p} = I_{\rm c} + I_{\rm m}$  was verified for consistency. The secondary electron yield was determined at five incident energies for each of the samples.

Field emission measurements were obtained within a third high vacuum chamber (pressure below  $10^{-5}$  Torr). During the experiment, samples were placed beneath a 2 mm diameter movable platinum anode with a flat tip. The anode was controlled by a stepper motor such that one step yielded a translation of 0.44 µm. The currentvoltage (I-V) measurements were taken at several distances ranging from 2 to 20 µm and for bias voltages in the range from zero to 1100 V. The relative travel of the probe was determined by the number of steps and the step size was established by the translation stage. I-Vcurves were measured at intervals as the probe approached the sample, and the absolute distance was calculated when the probe tip touched the sample. Using this procedure, the measurements were made before the probe tip touched the sample. In all three techniques employed in this study, the sample area probed was 2-3 mm in diameter. While the field emission properties of the samples may not be uniform, this nonuniformity is expected to be on a microscopic scale so that the probe area averages over the variation in emission sites.

#### 3. Results and discussion

UPS spectra of the CVD diamond films were measured as-loaded, after a hydrogen plasma clean and after annealing. The UPS spectra for samples A and B did not vary substantially among the three treatments except for a small increase in the width of the spectrum after the hydrogen plasma clean as would be expected from hydrogen surface termination. The spectra for samples C and D varied significantly in intensity and exhibited shifts of about 1 eV indicative of charging. All postannealing spectra have widths which are consistent with NEA. The spectra for sample A are shown in Fig. 1; the results for all four samples are summarized in Table 2. Some of the spectral widths are greater than  $hv - E_g$ , suggesting emission within the bandgap. Two possible explanations for these spectral widths are the exciton effects discussed by Bandis and Pate [8] and variations in the surface Fermi level of these polycrystalline films.

Sample	UPS <sup>a</sup>			Peak SEE	Field emission	Effective barrier
	As-loaded	Plasma-cleaned	Annealed	yleid	threshold (v µm )	neight (ev)
A	W = 15.0  eV	W = 15.6  eV	W = 15.9  eV	9.2	$28 \pm 2$	$0.16\pm0.04$
	PEA, $\chi = +0.7$	PEA, $\chi = 0.1$	NEA, χ<0			
В	W = 14.6  eV	W = 15.9  eV	W = 16.3  eV	8.6	$84 \pm 26$	$0.33 \pm 0.12$
	<b>PEA</b> , $\gamma = +1.1$	NEA, $\gamma < 0$	NEA, $\gamma < 0$			
С	W = 13.1  eV	W = 14.1  eV	W = 15.7  eV	2.2	43 + 17	0.15 + 0.01
	PEA, $\gamma = +2.6$	PEA, $\gamma = +1.6$	NEA, $\gamma < 0$		_	—
D	Weak signal	W = 15.2  eV	W = 15.8  eV	5.3	44 + 2	$0.19 \pm 0.03$
	e e e e e e e e e e e e e e e e e e e	PEA, $\chi = +0.5$	NEA, $\chi < 0$			

 Table 2

 Summary of electron emission results

W is the width of the UPS spectrum,  $\chi$  is the electron affinity and  $E_g = 5.45$  eV is the band gap of diamond. The values given for the emission threshold and barrier height are the averages and standard deviations of the measurements at different distances.

<sup>a</sup> PEA, positive electron affinity; NEA, negative electron affinity.



Fig. 1. UPS spectra for sample A as-loaded, after a hydrogen plasma clean and after annealing. The hydrogen plasma exposure induces NEA which causes the spectrum to become broader.

The measured secondary emission yields of the samples ranged from 2.0 to 9.2. The yields are shown in Fig. 2 as a function of energy, and peak yields are given in Table 2. For each sample, the yield decreased from the peak value within minutes. Possible explanations for the decrease are removal of the hydrogen termination or electron beam effects such as surface graphitization or electron-beam-induced deposition. The secondary yield



Fig. 2. Secondary electron yield as a function of incident beam energy for samples A, B, C and D.

was independent of beam energy over the energy range covered. This result is in contrast to the reports of SEE energy dependence for Cs-coated GaAs NEA emitters for which the yield increases with beam energy [9]. The lack of energy dependence of the secondary yield could be caused by a short electron diffusion length. It is known that electron transport properties are affected by grain boundaries in polycrystalline films [10]. The presence of grain boundaries may also result in a short electron diffusion length.

Field emission I-V curves were measured for each of the four samples, and the curves for sample A are shown in Fig. 3 for six distances. Emission thresholds were estimated by the electric field at which the current exceeded 0.1  $\mu$ A. This method yielded threshold fields ranging from 28 to 84 V  $\mu$ m<sup>-1</sup> which are summarized in Table 2. These threshold values are consistent with values reported for diamond by other authors [11]. The threshold fields at different distances agreed well for samples A and D, while the other samples exhibited more scatter. Possible sources of the scatter are varia-



Fig. 3. Field emission I-V curves for sample A at distances of (a) 2.6  $\mu$ m, (b) 5.3  $\mu$ m, (c) 8.8  $\mu$ m, (d) 11.4  $\mu$ m, (e) 15.8  $\mu$ m and (f) 19.8  $\mu$ m. The threshold electric fields from these curves are averaged to give the threshold value in Table 2.

tions in distance caused by vibration and changes in the density of emitting sites. Other reports have indicated that the emitting sites are a small fraction of the total film surface, making the true current density difficult to estimate [12].

These field emission results can be analyzed in terms of Fowler-Nordheim theory describing emission via barrier tunneling [13]. The Fowler-Nordheim equation has the form

$$I = k \left(\frac{\beta V}{d}\right)^2 \exp\left(\frac{-6530d\phi^{3/2}}{\beta V}\right)$$
(1)

where k is a constant related to the emission area  $\alpha$ , V (V) is the voltage applied,  $\phi$  (eV) is the barrier height,  $\beta$ is the geometric field enhancement factor and d ( $\mu$ m) is the distance from the anode to the cathode. Fig. 4 is a plot of  $I/V^2$  vs. 1/V for sample A. The straight lines are fits to Eq. (1) and are used to determine values for the effective barrier heights  $\phi/\beta^{2/3}$  which are given in Table 2.

For these films, emission typically occurs from a large number of sites with different values of  $\phi$  and  $\beta$  so that the I-V curve is most appropriately described by an integral over the distribution of emission sites [11]. Even assuming a single type of emission site, one can obtain from the Fowler-Nordheim plot sets of solutions with low  $\beta$ , low  $\phi$  and small emission area, or alternatively with high  $\beta$ , high  $\phi$  and large emission area. From the data in Fig. 4(d), for example, one can either assume  $\beta = 1$  (no field enhancement) and obtain  $\phi = 0.15$  eV and  $\alpha = 1.14 \times 10^{-12} \text{ cm}^2$ , or one can assume  $\phi = 5 \text{ eV}$ (carbon work function) and obtain  $\beta = 190$  and  $\alpha =$  $4.6 \times 10^{-6} \text{ cm}^2$ . The latter value for  $\beta$  is well within the range which has been reported for polished surfaces [14]. The actual field emission properties of the semiconductor are influenced by factors such as field penetration, band bending, surface states and the electron effective mass [15,16]. However, the focus of this paper is the comparison of field emission with other types of emission measurements, and a detailed analysis of all the factors influencing field emission should be the subject of future studies.



Fig. 4. Fowler-Nordheim plot of the field emission I-V data presented in Fig. 3.

Samples A and B have both the highest SEE yields and the most robust UPS signals, while sample C had the lowest yield and the weakest UPS signal. Sample C was also the only one of the samples that was insulating (see Table 1). The low conductivity of sample C may also explain the low secondary yield as charging of the diamond surface would reduce the emission of the low energy secondary electrons. However, sample D also has a yield which is lower than A and B but its dopant level is the highest of all. Thus the dopant level is not the only factor determining the electron emission characteristics of the diamond. The surface of sample D contains large diamond crystals scattered on top of smaller grains. This unusual morphology may be related to the low secondary yield. The film with the lowest field emission threshold also exhibits the highest secondary yield, but this correlation is not valid in the other three samples.

## 4. Conclusions

Results of electron emission measurements for CVD diamond films are reported. UV photoemission spectroscopy indicates that the samples exhibit NEA after exposure to hydrogen plasma. Secondary electron emission yields vary from 2.2 to 9.2. Field emission I-V measurements indicate threshold voltages ranging from 28 to 84 V  $\mu$ m<sup>-1</sup>. Preliminary results indicate a complex combination of excitation, transport and emission processes. Additional samples of various types need to be evaluated and compared in order to understand these mechanisms.

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