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Combined visible light photo-emission and low temperature thermionic emission from nitrogen doped diamond films

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This study reports a photoemission threshold of $\sim 1.5 \text{ eV}$ from nitrogen-doped nanocrystalline diamond, which ranks among the lowest photo-threshold of any non-cesiated material. Diamond films on molybdenum substrates have been illuminated with light from 340 to 550 nm, and the electron emission spectrum has been recorded from ambient to $\sim 320 \,^{\circ}\text{C}$. The results display combined thermionic and photo-electron emission limited by the same low work function and indicate that the two emission processes are spatially separated. These results indicate the potential for a solar energy conversion structure that takes advantage of both photoemission and thermionic emission. © 2011 American Institute of Physics. [doi:10.1063/1.3658638]

Recently, nitrogen doped diamond films have shown low temperature thermionic emission and vacuum thermionic energy conversion at temperatures as low as 500 °C,^{1,2} and these structures have been proposed for improving energy efficiency through reclamation of waste heat.³ In this report we present results on visible light photoemission from n-type doped diamond films with one of the lowest photo threshold of any non-cesiated material. These emitters could enable a solar energy conversion structure that takes advantage of both photoemission and thermionic emission.

Due to the high electric and thermal conductivity, stability of diamond, and the negative electron affinity (NEA) of H-terminated diamond,⁴ it has been considered for electron emitter applications based on thermionic emission,^{1–3,5,6} field emission,⁷ and secondary electron emission.⁸ On the other hand photoelectron emission has typically been limited by the large band gap and consequent large photo-threshold of diamond.^{9–12}

While n-type doping is essential to obtaining a low work function for diamond materials with a 5.45 eV band gap, upward band bending observed on single crystal surfaces has resulted in a work function >3 eV.^{10,13} Yet, in previous studies, it has been shown that hydrogen terminated, n-type doped diamond films exhibit a low effective work function (defined here as the difference between the conduction band minimum (CBM) and the Fermi level, E_F), where a value of 1.3 eV has been achieved with nitrogen doping¹ and 0.9 eVwith phosphorus doping.¹⁴ The impact of band bending is presumably mitigated by the presence of the sp² bonded grain boundaries that can provide sufficient electrons to compensate empty surface states. In addition, the substrate and grain boundaries can provide carriers to sustain the emission current. Such values correspond to photon energies within the visible light regime. Thus the possibility of visible light photo-emission enabled with diamond film emitters is the focus of this report. Moreover, the combination of photoemission and thermionic emission could lead to increased efficiency of thermionic energy conversion devices.

Ambient temperature photoemission spectra¹⁵ from the diamond sample are shown in Fig. 1. The low energy cut-off

at 1.5 eV is evidence of the effective work function, Φ_W . The normalized intensity of the electron peaks changes significantly with the specific photon energy, while the maximum emission energy relative to E_F corresponds approximately to the photon energy. The results indicate that the photoelectrons are excited from states near E_F . The fact that the emission peaks do not match the excitation energy indicates that scattering processes influence the emission. Under the same experimental conditions, neither thermionic (TE) nor photo-emission (PE) is observable from the bare molybdenum substrate, demonstrating that the electron emission involves the diamond film.

The combined effects of thermionic emission and photon illumination were detected by measuring the electron emission spectra while the heated sample is illuminated. We assume that the thermionic emission is not affected by the illuminating photons. Thus, the PE component of each spectrum at a given temperature is obtained by subtracting the thermionic emission from the combined emission, as shown in Fig. 2. The thermionic and photo-emission spectra share the same low energy cut-off, Φ_W . The relationship between photo-



FIG. 1. (Color online) Recorded emission spectra from N-doped diamond showing intensity normalized ambient temperature photo-emission.

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FIG. 2. (Color online) The total emission, thermionic emission, and subtracted photo-emission component from diamond sample #1 at 270 °C and 340 nm illumination.

emission and temperature then becomes of interest. The effect of temperature on both thermionic and photo- emission is shown in Fig. 3. Initially the thermionic emission is negligible but increases above ~220 °C. The PE initially increases slightly as the temperature is increased, but decreases at the temperature where the thermionic emission becomes significant, possibly due to increased absorption by thermally excited free carriers in the diamond film. Such behavior indicates that although thermal ionization and photon excitation are spatially separate processes, there is a more complex interaction between them that needs to be considered.

The photo- and thermionic emission may be understood in terms of the 3-step process suggested by Spicer¹⁶: electrons are excited to states above the vacuum level, transported to the sample surface, and then emitted into vacuum. As shown in the band schematic in Fig. 4(a), electrons in the



(a)

conduction band originate from thermally ionized N-donors and form an equilibrium distribution; thus, the thermionic emission originates from the surface of the diamond film. With illumination, the photons are transmitted through the diamond film and adsorbed in the metal substrate. The process is shown schematically in Fig. 4(b). In this transport process the electrons "thermalize" into a non-equilibrium

scattering

emission w/

5

scattering

4

Energy above E_r (eV)

-Theoretical

Experiment

6

7

χ<0

Ec

Donor

 $\bar{\Phi}_w$

EF



FIG. 3. (Color online) The effect of temperature on thermionic and photoemission. At low T the emission is dominated by the photo-excited carriers; at high T it is dominated by thermionic excitation.

Φw



FIG. 5. (Color online) Experimental and modeled emission spectra of the N-doped diamond film structure showing ambient temperature photoemission with 340 nm illumination.



FIG. 6. (Color online) Schematic of a diamond based energy converter. The emitter (doped diamond film) is heated for thermionic emission, and illuminating photons generate photo-emission.

distribution through scattering. This process is similar to the results reported by Schwede *et al.* on doped GaN.¹⁷ Therefore PE and TE are individually interface or surface limited processes. Based on the observed spectra, the Schottky barrier at the metal-semiconductor interface does not provide an additional barrier that is greater than the surface work function of the diamond film.

Following the theoretical framework of free electron materials,¹⁸ a simplified and optimized model for analyzing the photoemission spectra assumes that the photon flux increases the energy of the electrons with equal probability. This effectively increases the Fermi-Dirac distribution of the metal substrate by the photon energy. The electrons in the diamond conduction band are modeled as the product of the photon enhanced distribution and the parabolic density of states of the diamond conduction band. The electron emission distribution (EED) can be derived for photo-emission¹⁹

$$I_{PE}(E)dE = A \frac{E - E_F - \Phi_W}{1 + \exp[E - E_F - h\nu/k_B T]} \times H(E - E_F - \Phi_W)dE,$$
(1)

where the constant A includes the effective mass and the collecting efficiency and H is the Heaviside step function. The resulting spectrum is the convolution of the EED and a Gaussian spreading function characteristic of the analyzer with a resolution σ

$$G_l = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{E-E'}{\sigma}\right)^2\right].$$
 (2)

The numerically calculated results are shown in Fig. 5, normalized to the actual spectra. A work function of 1.8 eV is used instead of the low energy cuts off, due to smearing from the convolution. Disagreement of modeled and experimental spectra is believed to be evidence of a strong "thermalizing" effect.¹⁹ To include this effect, we assume all electrons are scattered by optical phonons (1332.5 cm⁻¹ or 165 meV) with equal probability, hence the EED is then shifted to lower energy. For each scattered electron, its kinetic energy is reduced by the phonon energy, and the number of scattering events is assumed to follow a Poisson distribution with an expectation *p*

$$\Delta I_{\text{mod},\text{PE}}(E; E' \to E) dE = B(E') \cdot \frac{\exp(-p)}{\left\lfloor E' - E/E_{phonon} \right\rfloor!} \cdot p^{\left\lfloor E' - E/E_{phonon} \right\rfloor} \cdot I_{PE}(E') dE'.$$
(3)

Equation (3) shows the contribution to the modified EED at energy E from an equal or higher energy E', and an integral of all these contributions represents the final EED. In the calculation, electron relaxation below the CBM is forbidden (modified through a probability-normalization coefficient B). At ambient temperature this model provides a best correspondence with experimental data when p is equal to 8. Further improvement of the model would require consideration of the interaction between the photo- and thermionic emission and include the photon absorption as a function of sample temperature.

To conclude, a mechanism is clearly established for electron emission from nitrogen-doped, hydrogen-terminated NCD emitters: the combined photo-emission and thermionic emission. As photo and thermal excitation are combined in this emissive process without the need of field enhancement, the NCD emitters are potentially candidates for applications in thermal and solar energy conversion. A schematic of such an energy converter is shown in Fig. 6. The quantum efficiency of the diamond photo-emission still needs to be examined and will certainly be dependent on the properties of the substrate material. The efficiency of these integrated energy conversion devices may be further enhanced by including phosphorus-doping¹⁴ and molecular transport mechanisms.²⁰

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