Thermionic electron emission from low work-function phosphorus doped diamond films

Franz A.M. Koeck [a,*], Robert J. Nemanich [a], Andrada Lazea [b,c], Ken Haenen [b,c]

[a] Department of Physics, Arizona State University, Tempe, AZ 85287 USA
[b] Institute for Materials Research (IMO), Hasselt University, Wetenschapspark 1, B-3590 Diepenbeek, Belgium
[c] Division IMOMEC, IMEC vzw, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

ARTICLE INFO

ABSTRACT

Thermionic electron emitters are a key component in applications ranging from travelling wave tubes for communications, space propulsion and direct energy conversion. As the conventional approach based on metallic emitters requires high operating temperatures the negative electron affinity (NEA) characteristic of diamond surfaces in conjunction with suitable donors would allow an electronic structure corresponding to a low effective work function. We have thus prepared phosphorus-doped polycrystalline diamond films on metallic substrates by plasma assisted chemical vapor deposition where an NEA surface characteristics was induced by exposure of the film surface to a hydrogen plasma. Thermionic electron emission measurements in an UHV environment were conducted with respect to the Richardson–Dushman relation observing an emission current at temperatures <375 °C. Measurements were terminated at 765 °C without significant reduction in the electron emission current indicating a stable hydrogen passivation of the diamond surface. A fit of the emission data to the Richardson equation allowed for the extraction of emission parameters where the value of the materials work function was evaluated to 0.9 eV. This value could well be the lowest measured work function of any known material.

Published by Elsevier B.V.

1. Introduction

Electron emission from carbon based materials has long been under investigation due to prospects of providing efficient electron sources. These emitters, diamond, nanocrystalline and carbon nanotube films, were mainly characterized with respect to electron field emission at room temperature. The emission mechanism for the nanostructured materials was based on field enhancement and penetration effects. Diamond thin films with small rms roughness exhibit negligible field enhancement effects and emission originated from states due to dopants as well as negative electron affinity (NEA) effects. Doping of diamond films is of ongoing interest as it is the crucial step for developing diamond electronics. While natural diamonds can occur in various formations boron and nitrogen doped varieties were studied due to their electronic properties. Boron, an acceptor forms states ~0.35 eV above the valence band maximum (VBM) making it a suitable p-type semiconductor. N-type conductivity in diamond can be achieved by nitrogen doping, however, states 1.7 eV below the conduction band minimum (CBM) form deep donors making electronic applications not feasible. Identifying shallow donors has been of ongoing interest with recent interest in phosphorus which theoretical calculations have shown

should form states 0.2 eV below the CBM [1]. Phosphorus doping of CVD diamond has been reported for films grown on (111) type Ib substrates with a carrier activation energy of 0.43 eV [2].

Shallow donor states in conjunction with NEA properties of diamond would significantly lower the barrier for thermionic electron emission for operation at low to moderate temperatures.

2. Experimental

Sample preparation included ultrasonic abrasion of metallic substrates in a nanodiamond - dimethyl sulfoxide (DMSO) suspension for 60 min. This was followed by a rinse in methanol and drying with nitrogen gas. Growth of the emitter structure was performed by plasma assisted chemical vapor deposition utilizing PH_3 as phosphorus source and low methane concentration. In order to increase the phosphorus doping concentration which prefers the (111) oriented growth direction, the sample temperature was adjusted accordingly to about 1130–1200 °C [3]. A more detailed report on the growth procedure can be found elsewhere [4,5].

Prior to emission measurements the samples were exposed to a hydrogen plasma with microwave power at 600 W, sample temperature <600 °C and chamber pressure at 20 Torr. This results in NEA properties of the diamond [6].

Thermionic emission characterization was performed in a specially designed UHV test and measurement system with a base pressure

$<5 \times 10^{-10}$ Torr. The apparatus included an anode moveable in all 3 spatial directions and a radiatively heated sample stage capable of temperatures up to 1200 °C. Temperature readings were recorded employing a 2-color pyrometer. Electron emission current and applied bias were controlled by a Stanford Research I/V source and measure unit.

3. Results and discussion

A thermionic electron source is based on the phenomenon of thermionic electron emission where electrons gain sufficient kinetic energy to escape the surface and are thus released into vacuum. Establishing an emission current from a metallic solid is depended on materials parameters, the work function φ and an emission parameter A_R. Richardson and Dushman, in a theoretical approach, formulated a relation between the emission current $J(T)$ and material parameters in their corresponding law expressed by

$$J(T) = A_R T^2 e^{-\frac{\varphi}{k_B T}}, \tag{1}$$

where φ is a the material work function and A the Richardson's constant, with the emitter at temperature, T, and k_B Boltzmann's constant [7,8]. Dushman first deduced a universal value for A considering pure metallic emitters [9]. However, an experimental evaluation of various materials presents significant deviations from the universal value of 120 A/cm^2 K^2 [10,11].

Despite its wide band-gap characteristics diamond has long been studied for applications focusing on electron sources. With a set of promising material properties, i.e. the possibility for its surfaces to gain a negative electron affinity (NEA) and doping, it should be feasible to engineer an emitter where a low emission barrier as key parameter could be achieved. Exposing diamond surfaces to a hydrogen plasma results in a negative electron affinity characteristics resulting in the vacuum level referenced below the CBM [12]. For a (111) diamond surface a widely accepted value for NEA has been reported to $\chi < -1.2$ eV [13]. Similarly, for the (100) diamond surface χ has been evaluated to ~ -1.3 eV [14]. In a different study performed on (111) n-type, phosphorus doped CVD diamond films an NEA was observed with $\chi < -1.1$ eV [15]. While nitrogen has been widely used as dopant, its deep states 1.7 eV below the CBM would still present a significant emission barrier. We have previously reported an effective work function of 1.5–1.9 eV for nitrogen-doped diamond films grown on molybdenum substrates [16]. The shallow states introduced by phosphorus would further reduce the effective work function.

Growth of phosphorus doped diamond films showed positive results by using (111) oriented substrates prepared by high pressure, high temperature (HPHT) synthesis [17]. While (100) oriented substrates are easier to obtain, deposition was observed to promote hillock-like morphology including crystallites deviating from epitaxial structure. Utilizing plasma assisted CVD under PH$_3$ addition growth on (111) substrates was observed to follow a step-flow process resulting in smooth (111) facets with increased growth rate [18]. Furthermore, an oxidation of the surface prior to deposition has shown to improve film properties with respect to defect density.

Regarding diamond electronics, (111) structures are not desirable due to limitations in substrate size and preparation as well as device-based properties [19]. In a device oriented approach Kato *et al.* were successful in preparing P-doped films grown on (001) HPHT synthetic Ib type substrates [20]. Film morphology grown on substrates with misorientation angle of $\theta_{off} \approx 2.0°$ exhibited step-bunching along crystal orientations. Phosphorus concentration as determined by SIMS was similar for (001) and (111) prepared samples with a value of $\sim 10^{18}$/cm^3 and an activation energy of ~ 0.58 eV.

Field electron emission from phosphorus doped diamond films has been evaluated from (111) oriented samples with an observed emission barrier of 1–1.5 eV where the doping concentration was
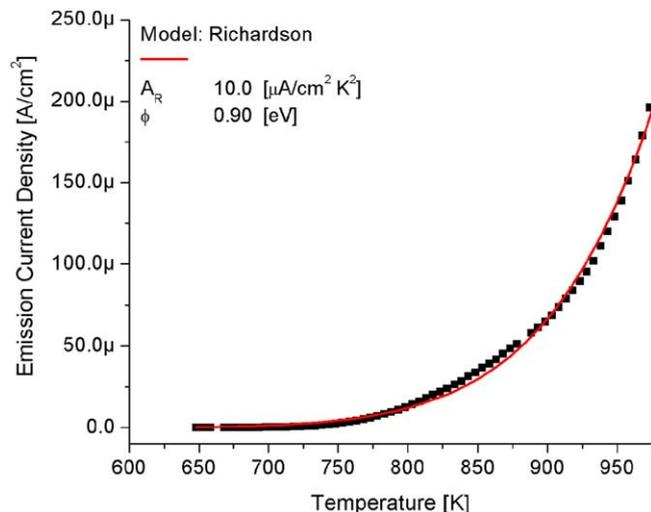
Fig. 1. Thermionic electron emission data (squares) and fit to the Richardson relation (line) from phosphorus-doped polycrystalline diamond.

$\sim 5 \times 10^{19}$/cm^3 [21]. For efficient thermionic emitters metallic substrate materials have shown preferred emission properties. This was partly due to the reduction of the overall emitter resistivity which resulted in a significant increase of the emission current density. In conjunction with an optimized growth process a phosphorus based emitter structure should present a significant improvement with respect to effective work function. P-doped polycrystalline diamond films grown on a metallic substrate were characterized with respect to the Richardson–Dushman relation. The emission current was recorded as a function of emitter temperature and the data-set fit to Eq. (1) as shown in Fig. 1.

Electron emission from this structure commences at temperatures <375 °C and increases following the law of Richardson–Dushman. Evaluation of the data-fit presents an effective work function of 0.9 eV significantly lower than results from previously reported nitrogen-doped diamond emitters. Concurrently with the small work function a reduced Richardson's constant is observed. From previous SIMS measurements of polycrystalline diamond films an active donor concentration of $\sim 5 \times 10^{18}$/cm^3 has been determined. However, the corresponding low mobility of ~ 15 cm^2/V^1 s^1 and a typical high resistivity due to hopping-conduction may result in the observed small value of the emission constant [22].

At elevated temperatures of 765 °C the emission current was observed to exhibit stability within the measurement intervals of ~ 1 h indicating stability of the NEA surface. In a study of hydrogen desorption from a (111) oriented diamond surface the original value of the NEA was observed to evolve towards a positive value after ~ 1 h when annealed at 700 °C [23].

4. Conclusion

We have prepared phosphorus-doped polycrystalline diamond films on metallic substrates by plasma assisted chemical vapor deposition using PH$_3$ as phosphorus source. Prior to characterization the sample surface was exposed to a hydrogen plasma to induce NEA surface characteristics. Thermionic electron emission measurements with respect to the Richardson–Dushman relation presented an effective work function of 0.9 eV. A reduced Richardson's constant was suggestive of low mobility and increased film resistance. Thermionic emission sustained a stable current up to 765 °C.

Acknowledgment

References

[1] S.A. Kajihara, A. Antonelli, J. Bernholc, R. Car, Phys. Rev. Let. 15 (1991) 2010.
[2] S. Koizumi, M. Kamo, Y. Sato, H. Ozaki, T. Inuzuka, Appl. Phys. Lett. 71 (1997) 1065.
[3] A. Lazea, V. Mortet, J. D'Haen, P. Geither, J. Ristein, M. D'Olieslaeger, K. Haenen, Chem. Phys. Lett. 454 (4–6) (2008) 310–313.
[4] M. Nesládek, K. Meykens, K. Haenen, L.M. Stals, Phys. Rev. B 59 (1999) 14852.
[5] M. Nesládek, K. Haenen, J. D, Haen, S. Koizumi, H. Kanda, Phys. Status Solidi A 199 (1) (2003) 77.
[6] D. Takeuchi, S.G. Ri, H. Kato, C.E. Nebel, S. Yamasaki, Phys. Status Solidi A, Appl. Res. 202 (11) (2005) 2098 [0031-8965].
[7] O.W. Richardson, Phys. Rev. 23 (1924) 153.
[8] S. Dushman, Rev. Mod. Phys. 2 (1930) 381.
[9] S. Dushman, Phys. Rev. 21 (1923) 623.
[10] P.W. Bridgman, Phys. Rev. 27 (1926) 173.
[11] E.B. Hensley, J. Appl. Phys. 32 (1961) 301.
[12] J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc, R.J. Nemanich, Phys. Rev. 50 (8) (1994) 5803 [0163-1829].
[13] J.B. Cui, J. Ristein, L. Ley, Phys. Rev. Lett. 81 (2) (1998) 429 [0031-9007].
[14] F. Maier, J. Ristein, L. Ley, Phys. Rev. B, Condensed Matter Mater. Phys. 64 (16) (2001) 165411 [1098-0121].
[15] D. Takeuchi, H. Kato, G.S. Ri, T. Yamada, P.R. Vinod, D. Hwang, C.E. Nebel, H. Okushi, S. Yamasaki, Appl. Phys. Lett. 86 (2005) 152103.
[16] F.A.M. Koeck, R.obert J. Nemanich, Diamond Relat. Mater. 15 (2–3) (February–March 2006) 217.
[17] S. Koizumi, K. Watanabe, M. Hasegawa, H. Kanda, Science 292 (2001) 1899.
[18] M. Nesladek, K. Haenen, J. D, Haen, S. Koizumi, H. Kanda, Phys. Status Solidi A 199 (2003) 77.
[19] H. Okushi, H. Watanabe, S.-G. Ri, S. Yamanaka, D. Takeuchi, J. Cryst. Growth 237–239 (2002) 1269.
[20] H. Kato, S. Yamasaki, H. Okushi, Appl. Phys. Lett. 86 (2005) 222111.
[21] T. Yamada, C.E. Nebel, B. Rezek, D. Takeuchi, N. Fujimori, Appl. Phys. Lett. 87 (2005) 234107.
[22] N. Casanova, A. Tajani, E. Gheeraert, E. Bustarret, J.A. Garrido, C.E. Nebel, M. Stutzmann, Diamond Relat. Mater. 11 (3–6) (March–June 2002) 328.
[23] J. Ristein, Diamond Relat. Mater. 9 (3–6) (April–May 2000) 1129.