Diamond & Related Materials 50 (2014) 151–156

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

In situ reactivation of low-temperature thermionic electron emission from nitrogen doped diamond films by hydrogen exposure

Vincenc Nemanič [a,*], Marko Žumer [a], Janez Kovač [a], Franz A.M. Koeck [b], Robert J. Nemanich [b]

[a] Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[b] Department of Physics, Arizona State University, Tempe, AZ 85287–1504, USA

ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 16 September 2014
Accepted 4 October 2014
Available online 12 October 2014

Keywords:
Thermionic electron emission
Nitrogen doped diamond films
Hydrogen exposure
Thermionic electron energy distribution

ABSTRACT

Nitrogen doped, hydrogen terminated diamond films have shown a work function of less than 1.5 eV and thermionic electron emission (TE) has been detected at temperatures less than 500 °C. However, ambient exposure or extended operation leads to a deterioration of the emission properties. In this study thermionic electron emission has been evaluated for as-received surfaces and for surfaces after 18 months of ambient exposure. The initial TE current density of the freshly deposited diamond film was ~5×10^{-5} A/cm^2 at 500 °C. In contrast, the initial TE current density of a film aged for 18 months was ~1.8×10^{-9} A/cm^2 at 500 °C. The decreased emission current density is presumed to be a consequence of oxidation, surface adsorption of contaminants and hydrogen depletion from the surface layer. *In situ* reactivation of the aged film surface was achieved by introducing hydrogen at a pressure of 1.3×10^{-4} mbar and using a hot filament of a nearby ionization gauge to generate atomic and/or excited molecular hydrogen. After 2 h of exposure with the sample at 500 °C, the surface exhibited a stable emission current density of ~2.3×10^{-6} A/cm^2 (an increase by a factor of ~1300). To elucidate the reactivation process thermionic electron energy distribution (TEED) and XPS core level spectra were measured during *in situ* hydrogen exposure at 5×10^{-8} mbar. During the isothermal exposure it was determined that atomic or excited hydrogen resulted in a much greater increase of the TE in comparison to exposure to molecular hydrogen. During exposure at 400 °C the surface oxygen was substantially reduced, the TEED cut-off energy, which indicates the effective work function, decreased by ~200 meV, and the TE intensity increased by a factor of ~100. The increase in thermionic emission with hydrogen was ascribed to the reactivation of the surface through the formation of a uniform surface dipole layer and a reduction of the surface work function.

1. Introduction

Thermionic energy converters (TECs), consisting of a hot cathode and cooler anode in a diode setup, are heat engines that can be employed for direct conversion of heat into electrical energy [1–3]. The TEC devices are based on thermionic electron emission from the cathode or emitter surface. The electrons transit the vacuum gap and are collected at the cooler surface. The potential that develops between the emitter and collector surfaces can provide power to a circuit. Because of the low mass of the electrons, TEC systems can achieve relatively high conversion efficiencies. Previously, TEC devices were developed based on refractory metal surfaces, which were operated at hot side temperatures greater than 1000 °C. Recent research has suggested that low temperature operation (<600 °C) could be achieved with low work function emitter and collector surfaces based on doped diamond films.

Nitrogen doped diamond films as hot cathodes have shown low-temperature vacuum thermionic energy conversion at temperatures as low as 500 °C [4,5], and these structures have been proposed for improving energy efficiency through reclamation of waste heat among other applications [6,7]. The efficacy of these low work function, nitrogen doped diamond films is based on three properties: 1) the negative electron affinity of the hydrogen terminated surface, 2) the mitigation of upward band bending apparently due to the presence of sp^2 bonded grain boundaries, and 3) the achievement of n-type character due to the incorporation of nitrogen in the films. The negative electron affinity of hydrogen terminated diamond films has been established for many years and is attributed to the formation of a surface dipole due to the partially ionic C–H bond [8,9]. Upward band bending has been observed for single crystal nitrogen doped diamond surfaces indicating the presence of acceptor like surface states [10]. It has been suggested that the sp^2 bonded grain boundaries provide sufficient charge to compensate for the surface states. Doping of diamond films with nitrogen has been proposed to occur through two mechanisms: single substitutional N in the diamond domains, and/or nitrogen incorporation in the grain boundaries [11,12]. It is still an open question as to which is most significant for nanocrystalline diamond films.

In vacuum operation it has been observed that the initial performance of diamond cathodes degrades with time and temperature. In

---

* Corresponding author.
E-mail address: vincenc.nemanic@ijs.si (V. Nemanič).

http://dx.doi.org/10.1016/j.diamond.2014.10.003
0925-9635/© 2014 Elsevier B.V. All rights reserved.

both cases, the loss of hydrogen from the subsurface and surface region was assumed to be the main reason for emission loss. Attempts to recover cathodes by hydrogen plasma processes have been successful, while the detailed mechanism responsible for the recovery of these cathode surfaces has not been confirmed [13]. Hydrogen regeneration and surface termination is a well studied process with a typical goal of restoring the negative electron affinity of the surface. In many studies single crystal surfaces have been employed. This study also explores the role of hydrogen regeneration of the emitter surface, but in this case the focus is on the thermionic emission and work function of nitrogen doped diamond films. In this paper we present results on the reactivation process of these cathodes by *in situ* exposure to excited hydrogen, and the process is explored in two different UHV systems.

2. Experimental details

The nanocrystalline diamond cathodes were synthesized utilizing microwave plasma chemical vapor deposition (MPCVD). Substrates were 25 mm diameter polished molybdenum discs, which were employed for their stability and lower electrical resistance compared to Si. The nitrogen-doped diamond layer was grown using 400 sccm hydrogen, 2 sccm methane, 100 sccm nitrogen, 80 mbar chamber pressure, 1300 W microwave power and 827 °C substrate temperature for ~32 min. Sample preparation was concluded by a 1-min hydrogen passivation step where the methane and nitrogen flows were terminated. The final film thickness was determined by *in situ* laser interferometry to ~0.3 μm.

The thermionic emission of the films was characterized using two systems: one that quantified the emission current in a diode configuration and the other that provided spectroscopic measurements. The diode thermionic emission setup was equipped with a heater block incorporated into a ceramic disc (HeatWave Labs, Inc.) and a molybdenum mesh as the collector with a 0.5 mm spacing gap. The heater and collector were mounted in a vacuum chamber with a base pressure around 10^{-7} mbar. A turbomolecular pump was used for this system. No heat shield was placed around the heater block to prevent radiative heat loss. The temperature of the heater was controlled by a K-type thermocouple embedded 1 mm below the top surface and modulated by a PID power supply. The actual temperature at the surface of the samples and the effect of thermal radiation and thermal contact via ceramic insulators on the collector temperature were measured beforehand by two thin K-type thermocouples directly contacted to the sample surface and the collector, respectively. The temperature of the collector reached ~300 °C at the highest sample temperatures of 500 °C.

In this study *in situ* reactivation of the surface is achieved by introducing molecular hydrogen through a leak valve into the vacuum chamber. Atomic and excited hydrogen are generated by the hot filament cathode of the ionization gauge which was mounted relatively close to the leak valve. The hot cathode filament is made of ThO_2:Ir, and it is kept at $T \sim 1400$ °C by the Bayard–Alpert ionization gauge power supply.

The spectroscopic system was also used to elucidate the reactivation process. The measurements were performed in an XPS analytical system (PHI-XPS TFA) which is based on the model PHI 5701. The thermionic electron energy distribution (TEED) spectra were measured during hydrogen exposure. The samples were mounted on a steel sample holder which was resistively heated to 400 °C with temperature increased at a rate of 3 °C/min. The temperature was controlled by a K-type thermocouple mounted inside the sample holder. The TEED scans were recorded using the 290 mm diameter hemispherical energy analyzer operated with a pass energy of 2.75 eV. The energy resolution was estimated to be less than 100 meV. During TE measurements the samples were biased with a negative potential of 3.95 V, and the base pressure in the XPS system was $\sim 8 \times 10^{-10}$ mbar. During the measurements and hydrogen exposure, this system was pumped by an ion pump. The chamber was configured in such a way that the sample surface was not in a direct line to the pump. The distance between the pump and the electrostatic analyzer was ~0.5 m. Flowing hydrogen during the spectroscopic measurements was performed through a leak valve mounted above the ion pump. There was still a small possibility that ions produced in the ion pump may enter into the electrostatic analyzer and contribute to the measured energy distribution. Also this vacuum system was equipped with an ion gauge with a thoriated iridium filament, which was used to crack or excite the hydrogen. The emitted thermionic electrons were collected by the electron analyzer, and the signal was measured in arbitrary units which could not be directly converted to current density. The relative TE intensity for each scan was obtained by digitally integrating the TEED scans.

For surface activation hydrogen was introduced at a pressure of $\sim 5 \times 10^{-8}$ mbar. The electron analyzer was calibrated against the Ag Fermi energy in a separate experiment. The analyzed spot was ~0.4 mm in diameter. For the aged sample with a low initial TE current, the surface was heated to 400 °C and pre-exposed to hydrogen at 5×10^{-8} mbar for 15 min with the ion gauge switched on. This process partially activated the surface to initiate measureable TE. This pre-activation was necessary to produce a TE signal for spectrometer alignment. After the TE signal was established, hydrogen introduction was either stopped or continued while the measurements of the TEED scans were recorded. During the long sequence of measurements of TEED spectra in the XPS system (few days) the stability of the work function of the analyzer was not directly checked with a reference material since the diamond sample was the whole time at the fixed position in front of the analyzer. Throughout the measurements the analyzer was continuously held at the measurement electrical potentials to avoid the warm-up transient effects. Consequently, we do not anticipate that the analyzer work function would change by greater than 0.2 eV during the 4–5 days typically used in the described measurements.

3. Results

3.1. Thermionic electron emission

In this study four similarly prepared samples, termed A, B, C and D, were investigated. The samples differ in their history and in the method that was applied for TE evaluation. The TE was measured from an as-received nitrogen doped, hydrogen terminated diamond film (sample A) within a few days after preparation. The measurements were made between 300 and 500 °C using the diode setup with an applied electric field of 0.2 MV/m and a base pressure of $\sim 3 \times 10^{-7}$ mbar. The applied field is well below the threshold for field emission from these films. The measured TE signal was quite intense (Fig. 1) showing an average TE current density of $\sim 5 \times 10^{-5}$ A/cm^2 at 500 °C.

The same procedure has been performed on a similar sample (sample B), which was stored in ambient conditions for 18 months after deposition. The TE current density of the aged film was $\sim 1.4 \times 10^{-9}$ A/cm^2,

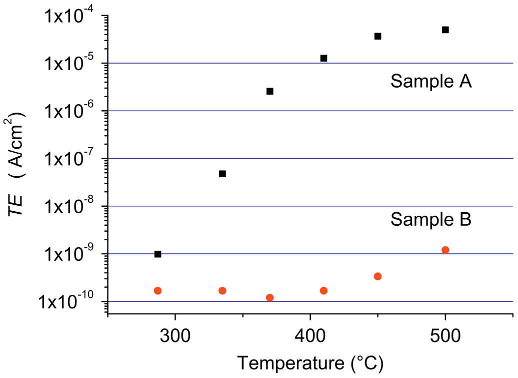

Fig. 1. TE signal measured from sample A a few days after deposition of the diamond film, and from sample B after 18 months of storage in ambient conditions.

which was obtained at 500 °C and 0.2 MV/m, Fig. 1. The emission was stable but substantially lower than the value measured from the as-deposited film. This low TE current density is presumed to be a consequence of oxidation, surface adsorption of contaminants and hydrogen depletion from the surface layer; all processes that occur during the extended ambient atmosphere exposure. We expect that this phenomenon is not related to a particular sample but is a general feature of ambient surface exposure. Therefore, we characterized different samples treated with similar procedures.

3.2. Reactivation of the thermionic emission with activated hydrogen exposure

Given the role of hydrogen in establishing an NEA, the aged surfaces were exposed to an activated hydrogen atmosphere in an attempt to reactivate the TE. The *in situ* reactivation of the surface was achieved by introducing atomic and/or excited molecular hydrogen, generated by the hot filament cathode of a Bayard–Alpert ionization gauge. Fig. 2a shows the time evolution of the TE during exposure to hydrogen at a pressure of 1.3×10^{-4} mbar with the sample at 500 °C and field of 0.2 MV/m. During the 2-hour exposure, the TE current density increased to 2.3×10^{-6} A/cm^2, which represented an increase by a factor of ~1300 (Fig. 2a). The sample was cooled to ~200 °C while the hydrogen flow continued, and the Bayard–Alpert ionization gauge was on.

After cooling to room temperature, the TE characteristics of sample B were measured again in vacuum to establish if the surface was changed during the activated hydrogen exposure, Fig. 2b. The TE current density at 500 °C and 0.2 MV/m was ~6×10^{-7} A/cm^2, which is substantially greater than before the reactivation. We note that these results were obtained without ambient exposure after the reactivation.

To further explore the effect of ambient exposure, the TE characteristics of the same sample were measured after an additional ambient exposure for 9 days, Fig. 2b lower curve. The TE current density was reduced to a value that approached the emission after 18 months of ambient exposure. The loss of TE emission evidently shows that the reactivated surface has greater sensitivity to oxidation, contaminant adsorption or surface hydrogen depletion than the as-grown surface.

A similar trend in the thermionic emission could be deduced from the time dependence of the integrated TEED spectra which were obtained in the XPS system. Fig. 2c shows the time dependence of the thermionic emission during hydrogen exposure obtained from the TEED spectra on sample A. The sample was heated to 400 °C in a hydrogen atmosphere at 5×10^{-8} mbar. A large increase of TE by a factor of ~15,000 was observed during hydrogen exposure for 20 h at 400 °C. Overall the trend is similar to that observed for sample B.

3.3. Chemical characterization of the diamond surface

The surface of a freshly prepared diamond film was compared to one after hydrogen activation with XPS through measuring the O 1s and C 1s core level spectra, Fig. 3. The XPS spectra before and after hydrogen activation of sample D were similar. The results indicated atomic percentages of 99.0 at.% of C, 0.8 at.% of O and traces of N in the 3–5 nm surface layer sampled by XPS. After the activation procedure the oxygen concentration was decreased to 0.4 at.% which shows that annealing at 400 °C and exposure to hydrogen induce desorption of oxygen species from the surface. We presume that this is one of the reasons for the change of the electronic properties of the surface and for the increase of the TE signal.

The carbon C 1s spectrum shown in Fig. 4a has its maximum at 285.8 eV (FWHM = 1.05 eV). It is quite symmetric as is expected for diamond while there is a small asymmetry on the higher binding energy side which can be fit with an additional peak. This peak could be assigned to C–O based groups or shake-up processes due to filled electronic states at the Fermi energy resembling a graphite-like feature. The O 1s spectrum, Fig. 4b, displays a maximum at 532.5 eV which can be assigned to C–O, H_2O or OH bonds. After the hydrogen activation the carbon C 1s spectrum remains essentially identical whereas the O 1s peak decreased significantly indicating desorption of the oxygen based species. Due to the low O 1s signal from sample A after annealing, it was not possible to deconvolve the XPS spectra and obtain more detail about the oxygen bonding configurations.

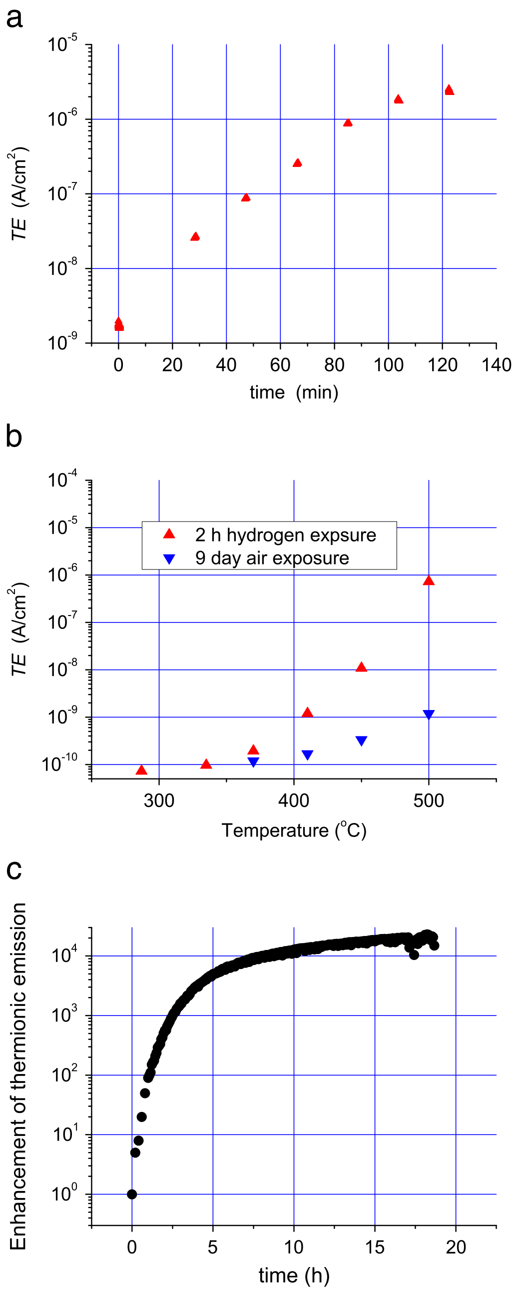

Fig. 2. a. The time dependence of the TE signal from sample B during exposure to hydrogen at 1.3×10^{-4} mbar while heated to 500 °C. An increase by a factor of ~1300 was achieved. b. The TE characteristics of sample B in vacuum, after being reactivated in hydrogen (upper curve) and after a new exposure to ambient atmosphere for 9 days (lower curve). c. Time dependence of the TEED intensity variation during thermionic emission from sample A heated at 400 °C in hydrogen at 5×10^{-8} mbar. An increase of a factor of ~15,000 was achieved within 20 h.

3.4. Dynamics of hydrogen surface interactions

Additional experiments were carried out in the diode setup on an aged sample (sample C) to understand the dynamics during the hydrogen exposure and the role of the filament. For the results shown in

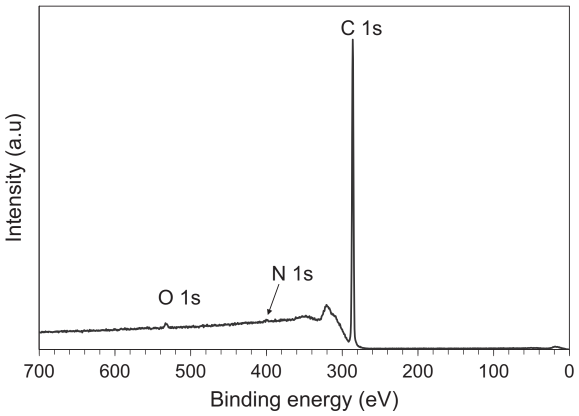

Fig. 3. Typical XPS survey spectrum obtained from an as-received freshly prepared diamond film (sample A) before activation in hydrogen.

Fig. 5, hydrogen gas was introduced at a pressure of ~1.3×10^{-5} mbar with the sample at 500 °C, and the ion gauge filament was controlled as indicated. In the initial step with the hydrogen and filament on, the TE current density was stable at ~1.15×10^{-6} A/cm^2. When the hydrogen flow was terminated, the TE current was reduced by more than a factor of 1.6 within 15 min. After the hydrogen supply was restored to the same base pressure, the TE current density increased to a stable condition with a value near that of the first step. Switching off the ion gauge filament while keeping the hydrogen base pressure constant, resulted in a similar decay of the TE current density. This shows that molecular hydrogen does not have a significant influence on the TE current density at this base pressure. Apparently, molecular hydrogen must be atomized or excited by the hot cathode of the Bayard–Alpert ionization gauge before it affects the characteristics of the nitrogen doped, hydrogen terminated diamond film.

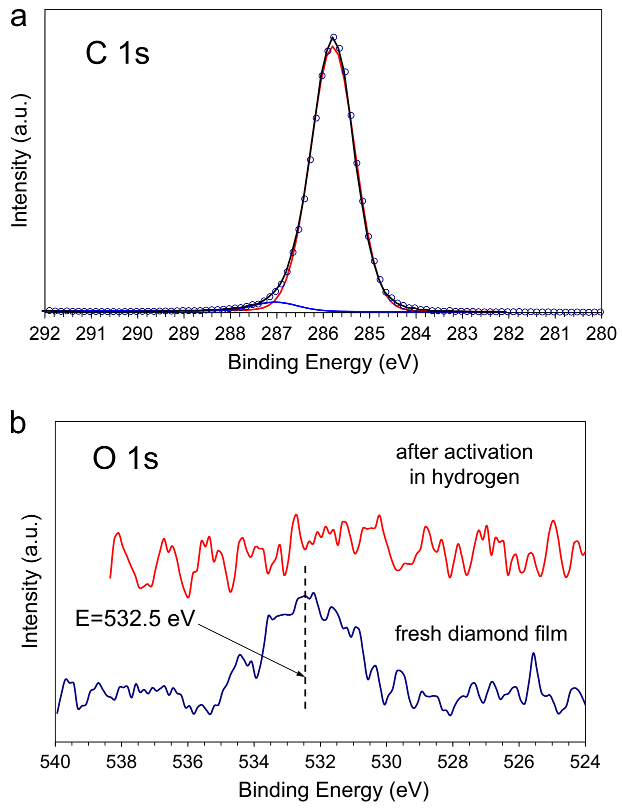

Fig. 4. a. XPS spectrum of C 1s from the freshly prepared diamond film (sample A) before annealing in hydrogen. b. XPS spectra of O 1s from the freshly prepared diamond film (sample A) before annealing and after activation in hydrogen.

In order to understand the reactivation process in more detail, a parallel experiment was performed on an aged sample (sample D), and the thermionic emission energy distribution (TEED) spectra and X-ray photoelectron spectra (XPS) were recorded during the reactivation process. The sample was loaded into the XPS system with a base pressure of 4×10^{-10} mbar. The sample was heated to 400 °C, and due to the low TE current, it was necessary to pre-expose the surface to hydrogen at 5×10^{-8} mbar for 15 min with the ion gauge switched on. This pre-activation was needed to produce a small TE signal that was necessary for alignment of the spectrometer. After this was accomplished the hydrogen flow was stopped.

Fig. 6 shows the time dependence (over 15 h) of the TE current from the diamond surface at a temperature of 400 °C. During the initial 75 min a very low TE was detected, which was attributed to the emission after the pre-activation period. The ion gauge was on during this time period, and the low emission established that electrons from the ion gauge did not contribute to the emission. After 75 min the ion gauge was turned off and hydrogen was introduced at a pressure of 4.6×10^{-8} mbar. From 75 to 300 min, the TE intensity gradually increased. It is possible that in this period the sample heater in the form of hot W wire mounted behind the sample holder caused a small amount of atomic or excited H which activated the TE. At the 300 min point, the ion gauge was switched on in the presence of hydrogen. This resulted in a much stronger increase of the TE for the next 10 h. This time sequence demonstrates that the atomic and/or excited molecular hydrogen is largely responsible for the increased thermionic electron emission from the diamond surface. The total increase of TE over 15 h for sample D was about a factor of 100 with respect to the TE in the first 75 min time period before hydrogen exposure. After 15 h of exposure at 400 °C, the sample was cooled to 230 °C and again reannealed to 400 °C. From the temperature variation of the TE and using the Richardson equation, the effective work function of sample D was deduced to be (1.1 ± 0.1) eV.

3.5. Spectral characteristics of the TE

Characteristic TEED spectra obtained during the 15 h sequence on sample D are shown in Fig. 7. The TEED spectra were continuously recorded during the activation sequence, and the results indicated that the cut-off energy decreased during the exposure. The TEED spectra are asymmetric to the higher kinetic energy side. The full width at half maximum (FWHM) of the TEED spectra were ~0.20 meV. Such a spectral shape reflects the TE process described by the equation $I(E) = \mathrm{A} \times (E - E_\mathrm{f} - \mathrm{WF}) / (1 + \exp(-E - E_f) / \mathrm{kT}))$, where E_f is the Fermi energy, WF is the work function, E is referenced to E_f and A is an arbitrary constant. The cut-off energy in these spectra should correspond to the effective work function (measured from the Fermi energy which is within the diamond band gap) of the annealed diamond surface. After the initial hydrogen introduction the cut-off energy decreased by ~0.05 eV with respect to the weak TE before hydrogen exposure. After switching the ion gauge on (300 min), the cut-off energy was further reduced by ~0.05 eV. With the hydrogen and ion gauge on, the cut-off energy was gradually and continuously reduced and after 350 min of exposure it stabilized at a value ~0.20 eV lower than before exposure. In total, a decrease of 0.20 eV was observed in the cut-off energy (work function) during the exposure to hydrogen.

The XPS scans of the C 1s peak showed a similar shift in energy to higher binding energy. This change may be interpreted as indicating that the surface Fermi level is at a higher energy relative to the valence band maximum. Taken together with the TEED scans the results suggest that the reduction in work function was due to a change in band bending.

This was accompanied by an increase of the total TE intensity on sample D by a factor of 100 with respect to the initial value in the 15 h

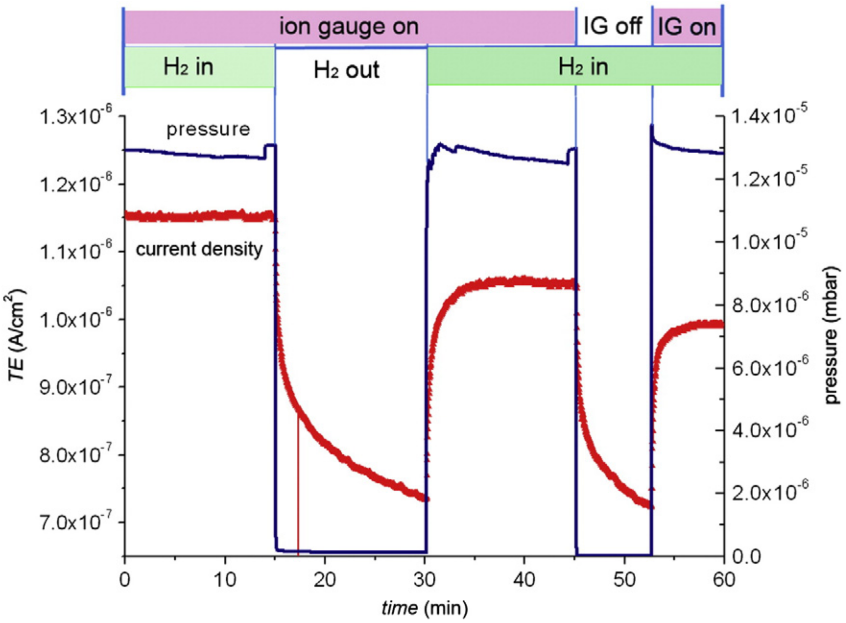

Fig. 5. TE from sample C exposed to hydrogen at ~1.3 × 10^{-5} mbar with the ionization gauge switched on and off as indicated. The sample was held at 500 °C.

period. The expected theoretical relative increase in TE (expression above for $I(E)$) for a change in WF energy of 0.20 eV at 400 °C would be 31. This value is less than the experimentally observed TE enhancement at these conditions. This shows that enhancement of TE at constant temperature is only partly related to lowering of the WF due to hydrogen interaction with the diamond surface. Therefore we deduce that the TE enhancement occurred due to desorption of contaminants and adsorption of atomic hydrogen and the formation of a surface dipole layer.

We note another interesting observation in the TEED spectra. After hydrogen introduction, a weak broad peak appeared at ~1.0 eV beneath the apparent cut-off energy and at energy above 1.6 eV. This feature is possibly related to hydrogen ions probably generated by the ion pump or other sources.

4. Discussion

As shown above we observed that the TE can be enhanced by exposure of the diamond film at elevated temperature to atomic or/and excited molecular hydrogen. A decrease of the hydrogen pressure or absence of the ion gauge hot cathode results in a rapid drop of the TE. The question is then how does the hydrogen influence the TE? There have been several studies of the hydrogen interaction with surfaces of monocrystalline diamond related to basic phenomena during growth of diamond films with the CVD procedure or to the very special diamond property, i.e. NEA. Pepper [14] was among the first who demonstrated that the diamond (110) surface is transformed during vacuum annealing and that new band gap states appear at 900 °C. After the exposure of the transformed surface to excited hydrogen atoms these band gap states were removed. The so-called “regeneration” was observed when the ion gauge filament was switched on. However, it is not clear whether the atomic hydrogen or/and excited molecular hydrogen is responsible for this transition. Later, the group of Ley [15,16] intensively studied electron affinity of bare and hydrogenated single crystal diamond (100) and (111) surfaces. They demonstrated that the electron affinity is dependent on the hydrogen coverage of the surface and explained it by the formation of the C–H surface dipole layer due to a charge transfer between H ad-atoms and the topmost layer of C atoms. They measured a positive electron affinity of +0.38 eV for the hydrogen free reconstructed (2 × 1) diamond surface and a negative electron affinity of −1.27 eV for the fully hydrogen terminated (1 × 1) diamond surface. In a similar way they found out that oxidation of the diamond (100) − (1 × 1) surface resulted in an increased electron affinity of 1.7 eV. Electron affinities of diamond surfaces were theoretically studied also by Robertson and Rutter [17,18].

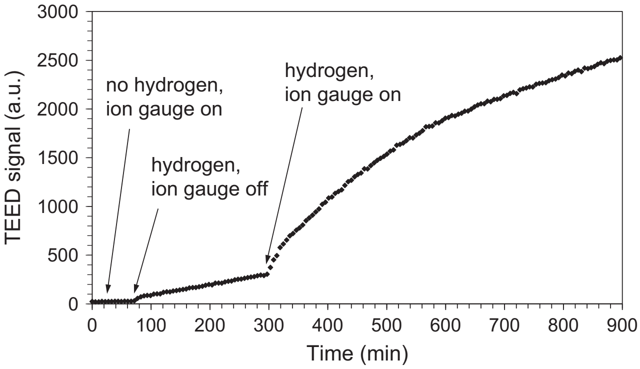

Fig. 6. TEED intensity variation during thermionic emission from sample D annealed at 400 °C and exposed in different sequences to hydrogen.

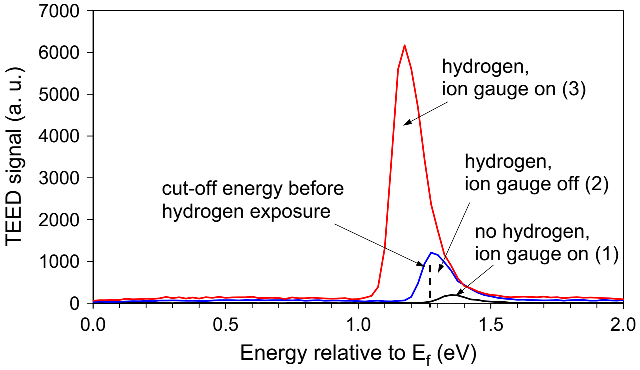

Fig. 7. Typical TEED spectra obtained from sample D in the course of the activation process as shown in Fig. 4. Spectra are indicated in each of the three periods 1) at the beginning (60 min), 2) after hydrogen introduction (170 min) and 3) after switching on the ion gauge (350 min).

In this frame we explain our results on the N-doped polycrystalline diamond film where a similar phenomenon occurs as on the single crystal diamond surfaces. During annealing and simultaneous exposure of our samples to the molecular hydrogen flow with the ionization gauge on, including the hot filament cathode, the surface regeneration was observed. We suppose that the hydrogenation occurs via conversion of the topmost C–C dimer double bonds to single bonds, resulting in one H-atom attached to each carbon surface atom and the formation of a layer of C–H dipoles. This was observed as an increase of the total TE intensity (Figs. 2a, c and 6) and by a change of the electron affinity and work function of the diamond film surface (Fig. 7). A decrease of the hydrogen concentration or an absence of excited molecular or/and atomic hydrogen atoms leads to a decrease of the TE as can be seen in Fig. 5. The TE reduction could be an effect of desorption of hydrogen from the film surface. The low TE observed on our cathodes after exposure for a longer period at ambient conditions is presumed to be an effect of surface contamination and passivation. Partial adsorption of oxygen-based species like water or other contaminants is also expected to occur which would result in a lower TE current.

On the other hand it was suggested [19] for diamond single crystals that the surface layer may suffer from transition from sp^3 hybridization to sp^2 hybridization (during thermal adsorption–desorption cycles). Consequently, it is expected that surface graphitization decreases the TE. This effect may be irreversible and is potentially responsible for the permanent decrease of the TE level obtained after each regeneration process.

5. Conclusions

We performed a systematic study of the influence of hydrogen exposure on *in situ* reactivation of thermionic electron emission from nitrogen doped diamond films after being exposed for different times to an ambient air atmosphere. We showed that it is possible to reactivate thermionic electron emission by annealing cathodes at temperatures of 400–500 °C for 30–100 min in hydrogen in a pressure range of 10^{-4} to 10^{-8} mbar. This process can be performed *in situ* during operation of TE cathodes which can replace *ex situ* pretreatment of cathodes in hydrogen plasma. Our results show that recovery of thermionic electron emission is more efficient when atomic or/and excited hydrogen generated by the hot filament cathode of the ionization gauge is present over the hot cathode surface leading to effective adsorption of atomic hydrogen on the diamond surface as has been suggested in the literature. Based on these data we suggest that the TE enhancement is related to the formation of a C^{-}–H^{+} surface dipole layer through an increase of the surface density of the C^{-}–H^{+} dipoles during hydrogen exposure, which is more efficient in the presence of excited/atomic hydrogen. Our TEED results as a function of hydrogen exposure show that TE activation is related to a decrease of the cut-off energy and effective work function for TE. We assume that other effects may also be involved during activation in hydrogen atmosphere including desorption of oxygen based chemical species. Specifically, XPS analysis of the chemical composition of film surface during TE reactivation showed that a portion of the adsorbed oxygen is desorbed during the cathode activation which may further contribute to the magnitude of the NEA and larger TE current.

Prime novelty statement

In situ reactivation of the aged film surface was achieved by introducing hydrogen at a pressure of 1.3×10^{-4} mbar and using a hot filament of a nearby ionization gauge to generate atomic and/or excited molecular hydrogen. After 2 h of exposure with the sample at 500 °C, the surface exhibited a stable emission current density of ~2.3×10^{-6} A/cm^2 (an increase by a factor of ~1300).

Acknowledgments

This work was supported by the Slovenian Research Agency (P2-0056, J2-4287). FAM Koeck and RJ Nemanich appreciate helpful discussions with Dr. Tianyin Sun, and they acknowledge the support of the US Office of Naval Research through grant number N00014-10-1-0540.

References

[1] G.N. Hatsopoulous, E.P. Gyftopoulos (Eds.), Thermionic Energy Conversion, vol. 1, MIT Press, Cambridge, MA, 1973.
[2] J.R. Smith, R.J. Nemanich, G.L. Bilbro, Considerations for a high-performance thermionic energy conversion device based on a negative electron affinity emitter, Phys. Rev. B 76 (2007) 245327.
[3] J.W. Schwede, I. Bargatin, D.C. Riley, B.E. Hardin, S.J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R.T. Howe, Z.-X. Shen, N.A. Melosh, Photon-enhanced thermionic emission for solar concentrator systems, Nat. Mater. 9 (2010) 762–767.
[4] F.A.M. Koeck, R.J. Nemanich, Low temperature onset for thermionic emitters based on nitrogen incorporated UNCD films, Diamond Relat. Mater. 18 (2009) 232.
[5] M. Kataoka, C. Zhu, F.A.M. Koeck, R.J. Nemanich, Thermionic electron emission from nitrogen-doped homoepitaxial diamond, Diamond Relat. Mater. 19 (2010) 110.
[6] M. Suzuki, T. Ono, N. Sakuma, T. Sakai, Low-temperature thermionic emission from nitrogen-doped nanocrystalline diamond films on n-type Si grown by MPCVD, Diamond Relat. Mater. 18 (2009) 1274.
[7] K. Uppireddi, T.L. Westover, T.S. Fisher, B.R. Weiner, G. Morel, Thermionic emission energy distribution from nanocrystalline diamond films for direct thermal-electrical energy conversion applications, J. Appl. Phys. 106 (2009) 043716.
[8] F.J. Himpsel, D.E. Eastman, P. Heimann, J.F. van der Veen, Surface states on reconstructed diamond (111), Phys. Rev. B 24 (1981) 7270.
[9] J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc, d R.J. Nemanich, Negative-electron-affinity effects on the diamond (100) surface, Phys. Rev. B 50 (1994) 5803–5806.
[10] L. Diederich, O.M. Kuttel, P. Ruffieux, Th. Pillo, P. Aebi, L. Schlapbach, Photoelectron emission from nitrogen- and boron-doped diamond (100) surfaces, Surf. Sci. 417 (1998) 41–52.
[11] J. Birrell, J.A. Carlisle, O. Auciello, D.M. Gruen, J.M. Gibson, Morphology and electronic structure in nitrogen-doped ultrananocrystalline diamond, Appl. Phys. Lett. 81 (2002) 2235.
[12] P. Zapol, M. Sternberg, L.A. Curtiss, T. Frauenheim, D.M. Gruen, Tight-binding molecular-dynamics simulation of impurities in ultrananocrystalline diamond grain boundaries, Phys. Rev. B 65 (2002) 045403.
[13] W.F. Paxton, M. Howell, W.P. Kang, J.L. Davidson, Influence of hydrogen on the thermionic electron emission from nitrogen-incorporated polycrystalline diamond films, J. Vac. Sci. Technol. B 30 (2) (2012) 021202.
[14] S.V. Pepper, Transformation of the diamond (110) surface, J. Vac. Sci. Technol. 20 (2) (1982) 213.
[15] J.B. Cui, J. Ristein, L. Ley, Electron Affinity of the Bare and Hydrogen Covered single Crystal Diamond (111) Surface, Phys. Rev. Lett. 81 (1998) 429.
[16] F. Maier, J. Ristein, L. Ley, Electron Affinity of Plasma – Hydrogenated and chemically oxidized Diamond (100) Surfaces, Phys. Rev. B 64 (2001) 165411.
[17] J. Robertson, M.J. Rutter, Band diagram of diamond and diamond-like carbon surfaces, Diamond Relat. Mater. 7 (1998) 620.
[18] M.J. Rutter, J. Robertson, Ab initio calculation of electron affinities of diamond surfaces, Phys. Rev. B 57 (1998) 9241.
[19] K. Hoffman, B. Bobrov, H. Fisgeer, M. Shechter, Folman, Effects of deuterium adsorption-desorption on the state of diamond: surface degradation and stabilization of sp3 bonded carbon, Diamond Relat. Mater. 5 (1996) 977–983.