

Photoemission tuning of nanodiamond particles treated in variable percentages of H₂-N₂ plasmas

L. Velardi¹, A. Valentini² and G. Cicala¹

¹ P.LAS.M.I. Lab@CNR NANOTEC, Via Amendola 122/D, 70126 Bari, Italy, luciano.velardi@le.infn.it

² Dipartimento di Fisica, Università di Bari, Via Orabona 4, 70126 Bari, Italy

Abstract

This work deals with photo-cathodes (PCs) based on as-received and treated nanodiamond (ND) particles, 250 nm in size. The aim of this study is the hydro-, hydro-/nitro- and nitro-generation of NDs performed in microwave plasmas adding different N₂ percentages (0, 50 and 100 %) to pure H₂ gas. Untreated and treated NDs are dispersed in solvents such as 1,2-dichloroethane and deionized water, and then deposited, as continuous layers, on p-Si and kapton substrates by the pulsed spray technique. The produced layers are characterized by Raman, photoluminescence spectroscopies and photoemission measurements. The quantum efficiency (QE), a merit figure for photocathodes, is assessed in the UV spectral range from 146 to 210 nm. The results show an enhancement of the photoemission for PCs based on hydro-, hydro-/nitro- and nitro-generated NDs that exhibit at 146 nm QE values of about 23, 21 and 13 %, respectively. The advantage of nitrogenated PCs is the good stability to air exposure against their lowest QE values.

Introduction

In the field of UV photocathodes (PCs), the required material properties are a low/negative electron affinity (NEA) and a low work function, to facilitate the electron escape from their surfaces. Caesium Iodide (CsI) is the reference material for UV PCs thanks to its wide band gap of 6.2 eV and low electron affinity of 0.1 eV [1]. Nevertheless, CsI possesses the disadvantage to be hygroscopic and consequently chemically unstable upon exposure to air [2]. The diamond represents a good alternative to CsI for its band gap of 5.5 eV and low electron affinity [3] that becomes negative (down to –

1.27 eV) when its surface is hydrogenated [3-5]. If the diamond is also doped with nitrogen or boron atoms, its work function decreases and the photoemission further enhances [4, 5]. Since the 1990s, several papers are concerned with diamond based photocathodes [5-9]. The highest quantum efficiency (QE) reported in literature (12-14 % at 140 nm) was achieved by PCs based on microwave plasma enhanced chemical vapor deposited (MWPECVD) polycrystalline diamond films [6, 8]. Nevertheless, these films show a strong aging effect that reduce the QE down to 5% after about 1000 hours.

In the last years, nitrogen has been used not only for doping the diamond, but also for the

modification and termination of its surfaces. On this last topic, few studies [10-12] are reported in the literature. Two works concern with theoretical [10] and experimental studies [10, 11] of N- and N/H- terminated diamond surfaces. These termination are attractive for stabilizing the emission of N-V⁻ centers close to the surface. These authors predict also that nitrogenated surfaces exhibit a positive electron affinity (PEA) of 0.32 and 3.46 eV for *N/H- and full N-terminated diamond surfaces*, respectively.

Hamers and Bandy [12] found that amino- (NH₂-) terminated surfaces, via RF plasma and successively protonated to form surface NH₃⁺ group, act as emitters better than H-terminated ones at atmospheric pressure of gases such as Ar, air and SF₆. The authors observe also a photoemission in inert Ar gas higher than that in electronegative O₂ and SF₆ gases, able to trap the emitted free electrons. Additionally, the enhanced emission based on NH₃⁺, containing a full positive charge, confirms the key role recognized and already played by partial positive charge (δ^+) in C ^{δ^-} - H ^{δ^+} heteropolar bonds at the hydrogenated surfaces.

This work deals with nanodiamond (ND) particles utilized as electron emitters [13-17]. In the year 2015, the authors of this work have patented [16] very high efficient UV PCs based on layers of hydrogenated NDs (250 nm size), deposited by the pulsed spray technique [17-19], an easy, inexpensive methodology working at low temperature.

The present study represents a step forward of this patent and investigates the hydro-/nitro- and nitro-generated surfaces of NDs performed in H₂-N₂ and N₂ microwave plasmas.

Materials and methods

ND layers for photocathode fabrication. A diamond powder with an average grain size of 250 nm, marketed by *Diamonds & Tools srl*, was used in the experiments and examined. Four types of photocathodes were

manufactured using layers deposited by means of the pulsed spray technique [17-19]: a device with as-received powder (*as-rec ND*), and three devices obtained by powders treated in H₂ (100%, *H-DISP*), H₂-N₂ (50-50%, *NH-DISP*) and N₂ (100%, *N-DISP*) microwave plasmas for 1 h. Each treated powder was dispersed in two kinds of solvent: 1,2-dichloroethane (DCE) and deionized (DI) water. After that, the dispersions were sonicated for 30 min by a Bandelin Sonoplus HD2070 system and then sprayed on substrates of 12 x 12 mm²: p-doped Si (500 μ m of thickness) and metalized kapton (50 μ m of thickness with an Al layer of 20 μ m).

Details of the pulsed spray apparatus and experimental conditions employed are already described in refs [17-19]. The holder temperature was set at 120 and 150 °C during the spray process, to evaporate easily the DCE and H₂O, respectively. All the samples were obtained with 400 spray pulses, giving a homogeneous layer formed by ND particles.

ND treatments in MW plasmas. The modification of the NDs was performed in microwave plasmas of hydrogen adding different percentages of nitrogen (0, 50 and 100 %) to hydro-, hydro-/nitro- and nitro-generate the nanoparticles, respectively. The powders were placed in tungsten boats, 12 mm long, resistant to the high deposition temperatures. The plasmas were generated in a home-made cylindrical stainless steel *ASTeX*-type reactor, typically used for the growth of diamond films by MWPECVD technique [20].

During the plasma treatments, the working pressure, the microwave power, the total flow rate and the further heating temperature were held constant at 25 mbar, 800 W, 20 sccm and 650 °C, respectively. The deposition temperature increases up to about 1100 °C for the further heating due to the MW power, as measured by IR pyrometer (Williamson Pro 9240).

Raman and photoluminescence (PL) spectroscopy. Raman and PL spectra were measured at room temperature by means of a

Raman confocal micro-spectrometry apparatus (Labram from Jobin-Yvon Horiba) in the backscattering configuration using an Ar-ion laser beam at 488 nm. The Raman signals were obtained by a 100x objective, focusing the beam on a spot of about 1 μm diameter and sent to spectrometer with a 1800 grooves/mm grating. For each sample, the Raman spectra were performed on three regions.

The PL emissions were collected by a 10x objective focusing the beam on a spot of about 10 μm diameter on the sample surface and sent to spectrometer with a 600 grooves/mm grating.

The laser power on the sample was set at 0.6 and 6.5 mW for the acquisition of Raman and PL spectra, respectively; the collection time was 1 s. Both Raman and PL signals were detected by means of a cooled CCD.

QE measurements of photocathodes. Photoemission measurements were carried out in the Vacuum Ultra Violet (VUV) spectral range from 146 to 210 nm. The measurements were acquired in reflective mode, under vacuum (10^{-5} mbar) and at room temperature (20°C). The samples were irradiated with a 30 W deuterium lamp (Mc Pherson TM) coupled to a monochromator for the wavelength selection. The samples were mounted in a multi-wire proportional chamber, not operating in electron multiplication mode. Then, the photocurrent was collected on a grid of wires placed in front of the sample and biased at +90 V, corresponding to the value where the current plateau was reached. The photocurrent was measured by means of an electrometer with a sensitivity of 10^{-16} A. The absolute QE values were assessed using an NIST calibrated standard Si photodiode (AXUV-100G) for the normalization.

Results and discussion

Figure 1 shows the Raman spectra of the untreated (*as-rec ND*) and treated ND particles (*H-DISP*, *NH-DISP* and *N-DISP*)

deposited on p-Si starting from DCE dispersions.

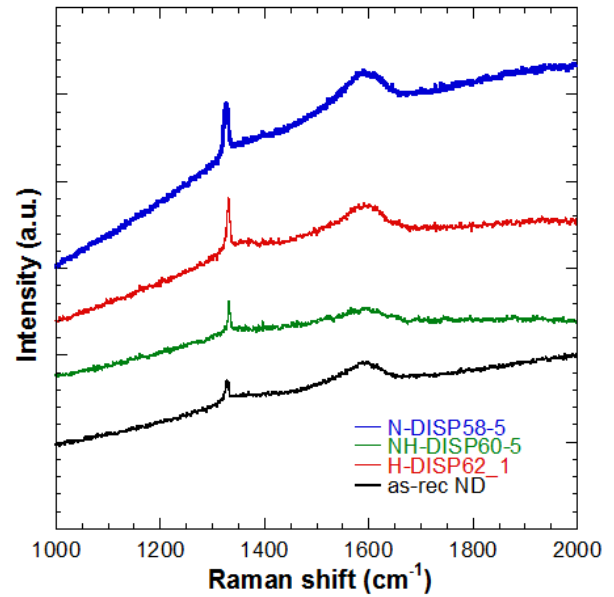


Figure 1: Raman spectra of NDs untreated (*as-rec ND*) and treated in H_2 (*H-DISP*), $\text{H}_2\text{-N}_2$ (*NH-DISP*) and N_2 (*N-DISP*) plasmas, deposited on p-Si substrate.

The spectra show the sharp diamond (sp^3 bonded carbon) peak at 1332 cm^{-1} and the graphite band (sp^2 bonded carbon, G-band) centered at 1586 cm^{-1} . In particular, the high content of sp^2 carbon hybridization for the as-received and treated ND layers points out the defective nature of the *Diamond and Tools srl* powder. The sp^2 percentage (P_{sp^2}) is calculated by the following expression:

$$P_{\text{sp}^2} = 100 \times A_{\text{sp}^2} / (A_{\text{sp}^3} + A_{\text{sp}^2})$$

where A_{sp^3} and A_{sp^2} are the areas of diamond peak and G-band, respectively. Table 1 reports the values of P_{sp^2} and sp^2/sp^3 intensity ratio ($I_{\text{sp}^2}/I_{\text{sp}^3}$) assessed by Raman analysis.

Table 1: sp^2 percentage (P_{sp^2}) and sp^2/sp^3 intensity ratio ($I_{\text{sp}^2}/I_{\text{sp}^3}$).

Sample	as-rec ND	H-DISP	NH-DISP	N-DISP
$P_{\text{sp}^2}(\%)$	90 ± 3	85 ± 1	87 ± 3	89 ± 2
$I_{\text{sp}^2}/I_{\text{sp}^3}$	0.88	0.50	0.56	0.75

Figure 2 shows the PL spectra of the untreated and treated ND particles deposited on p-Si

starting from H₂O dispersions. All the spectra are very similar each one.

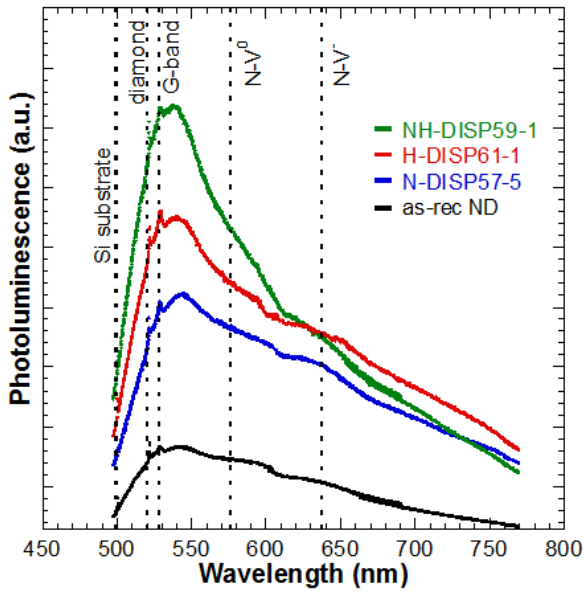


Figure 2: Photoluminescence spectra of NDs untreated (as-rec ND) and treated in H₂ (H-DISP), H₂-N₂ (NH-DISP) and N₂ (N-DISP) plasmas, deposited on p-Si substrate.

The dashed lines reported in Fig. 2 indicate the positions of the silicon substrate (Si peak at 500.5 nm, corresponding to a Raman shift of 520 cm⁻¹), of the Raman lines due to the nanodiamond layer (diamond peak at 522 nm and G-band at 528 nm, corresponding to a Raman shift of 1332 cm⁻¹ and 1586 cm⁻¹, respectively). No emission from nitrogen-

vacancy optical centers (N-V⁰ at 575 nm and N-V⁻ at 637 nm) [21] was observed in the PL spectra of the untreated and treated powders.

Table 2: QE values at 146 nm.

Sample	as-rec ND	H-DISP		NH-DISP		N-DISP	
Solvent	DCE	DCE	H ₂ O	DCE	H ₂ O	DCE	H ₂ O
QE _{pSi} (%)	7.0	22.6	24.4	20.6	22.3	14.5	13.2
QE _{kapton} (%)	-	23.2	20.2	20.8	22.5	12.9	12.7

Figs. 3a-c show the QE trends of the PCs as a function of wavelength. Devices produced starting from NDs dispersed in DI water and DCE exhibit very close QE values, probably due to the similar stability of aqueous and DCE dispersions. This result is important because suggests the use of an *eco friendly* solvent such as DI water instead of the toxic DCE. In fact, layers of hydrogenated NDs deposited by unstable dispersions of ethanol, not reported here, show low QE values (~12% at 146 nm).

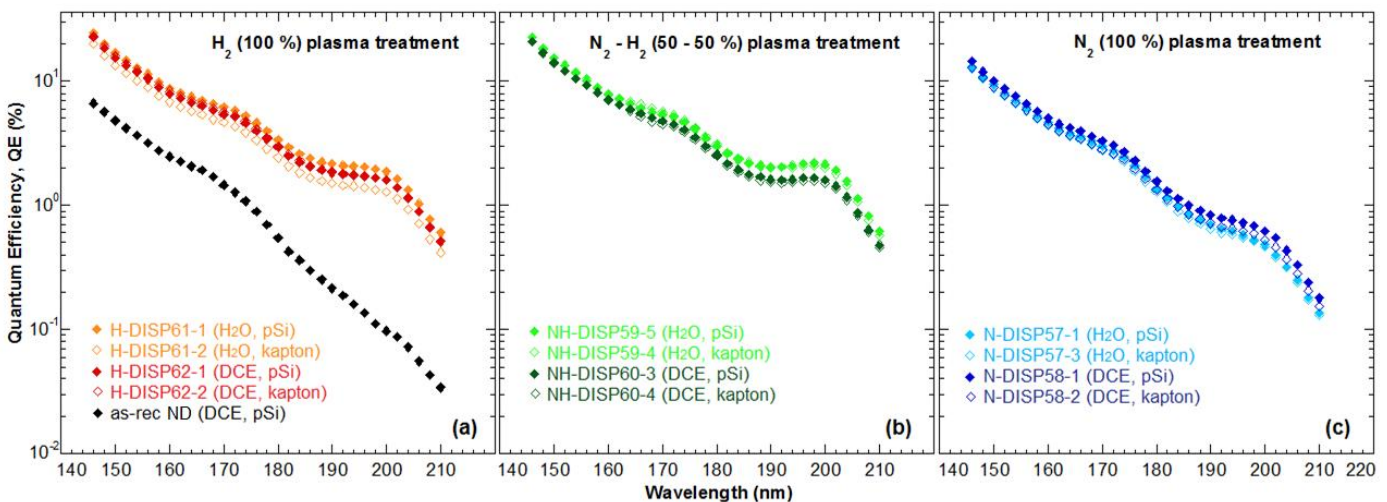


Figure 3: Quantum efficiency (QE) of layers by (a) untreated (as-rec ND) and treated NDs in H₂ (H-DISP), (b) H₂-N₂ (NH-DISP) and (c) N₂ (N-DISP) plasmas.

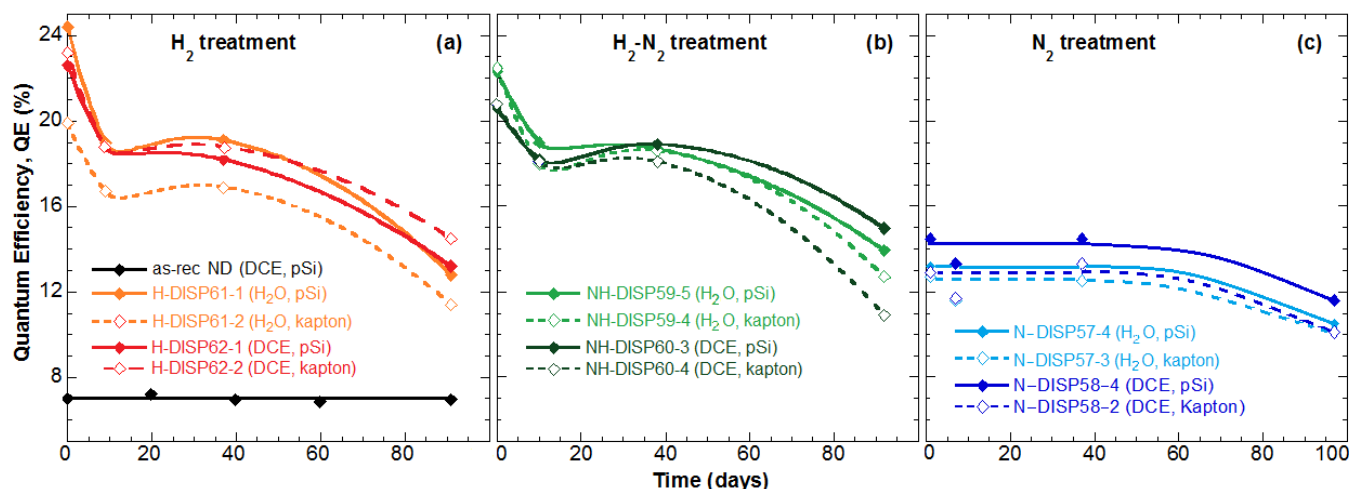


Figure 4: QE values measured at 146 nm of (a) untreated (as-rec ND) and treated nanodiamonds in H₂ (H-DISP), (b) H₂-N₂ (NH-DISP) and (c) N₂ (N-DISP) plasmas versus time.

In the same Figs. 3a-c, the p-doped Si or metalized kapton substrates on which are manufactured the PCs do not seem to affect the QE. This point is also interesting because the fabrication of these PCs is possible on cheap substrates including polymers (e.g. kapton). In Table 2 the QE values at 146 nm of the examined PCs are summarized. Photocathodes based on hydrogenated NDs show the highest QE values (20.2-24.4 % at 146 nm), whereas hydro-/nitro- and nitro-generated ones exhibit QE slightly (20.5-22.5%) and heavily (12.7-14.5%) decreased, as reported in Table 2. These QE values are explained by considering the electron affinity that increases from -1.27 [3, 5] up to 0.32 [10] and 3.46 eV [10] for H-, H/N- and N-terminated diamond surfaces, respectively, hindering the photoemission of electrons. Figures 4a-c show the evolution of QE values as a function of the time. The aging effects of hydro- and hydro-/nitro-generated PCs are more marked than that of nitrogenated one. After about 100 days all the PCs based on NDs and treated differently achieve a QE value around 11 % that however is higher than 7 %, typical QE value of PC based on as-received NDs.

Conclusions

A comparative study of photocathodes based on sprayed layers of ND particles employed as-received and/or treated in microwave plasmas, adding different nitrogen percentages (0, 50 and 100%) to H₂ gas is presented in this paper. The surface treatments in H₂-N₂ and N₂ plasmas, the ND dispersion in water (*eco friendly solvent*) instead of toxic DCE and metalized kapton substrates alternative to the expensive p-Si are the main novelties of this work. The photoemission measurements have shown no influence of solvent and substrate within the error range. The photocathodes based on hydro-, hydro-/nitro- and nitro-generated NDs exhibit QE values of about 23, 21 and 13 % at 146 nm, respectively, against the 7% of as-received one. These results are certainly superior to that reported for a MWPECVD photocathode (12-14% at 140 nm), and they represent the maximum QE achieved by a diamond-based device in the state of international art.

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