

Polycrystalline diamond films grown by MWPECVD technique and application in photocathodes

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Abstract

Diamond is an extremely interesting material for photoemission applications, due to the negative electron affinity which can be obtained after suitable surface treatments. In the present work, two sets of polycrystalline diamond films, characterized by different thickness and deposition conditions, are analyzed. In particular, the relationship among the grain size, the amount of non-diamond carbon (sp^2) located at the grain boundaries and the film sensitivity as a photocathode has been found and carefully investigated. The photoemission yield in the UV range has been evaluated for all the samples, before and after hydrogenation process, and after air exposure. The critical parameter for the photocathode performances has been found not to be the film thickness, but the properties of polycrystalline diamond films, tunable with the plasma modulation and the methane percentage in the gas mixture.

INTRODUCTION

Natural diamond and synthetic polycrystalline diamond (PCD) films are of great interest to the scientific community due to their wide indirect band gap (5.5 eV), heat dissipation properties, chemical stability, radiation hardness and very low electron affinity (EA=0.5 and 0.35 eV for bare (100) and (111) diamond surfaces, respectively [1]). The surface EA is the barrier that prevents the electrons in the conduction band from escaping into vacuum. Negative electron affinity (NEA) is obtained when the surface of natural diamond and PCD films is coated with a caesium (Cs) [2] or caesium iodide (CsI) [3] layer and/or terminated with hydrogen [1-4], making them attractive as field emitters in displays and cold cathodes in vacuum microelectronics. The NEA allows an efficient escape of generated photo-

electrons without an energy barrier at the surface because the vacuum level has moved down to the conduction band minimum [4]. The NEA is one of the most important parameters causing an easy photoemission [5-7] and a low threshold field emission [8,9] of electrons excited in the conduction band and therefore affecting positively the diamond photocathode performance.

High efficiency diamond photocathodes have been demonstrated to be more stable than conventional materials such as CsI [10]. Natural diamond, poly- and nano-crystalline diamond films have been still investigated and tested [11-12]. Many research groups found that photoemission [7,13] and field emission properties [1,8] can depend on the defects within the grain boundaries and on the co-deposition of diamond (sp^3 component) and non-diamond (sp^2 component) phases. For poly-, micro- and nano-crystalline diamond the non-diamond phases are mainly located at the grain boundaries that are considered more conductive than the grains, being principally sp^2 bonded. According to Robertson et al. [1] the grain boundaries supply electrons to the grains from which surface they later escape into vacuum.

Later Laikhtman et al. [6] reported that the surface treatment of PCD films in hydrogen microwave plasma is responsible for the quantum efficiency (QE) enhancement. However, they observed that the structure, the crystallite sizes and the defects induced by grain boundaries do not affect the photoemission of the hot filament (HF) and micro-wave (MW) polycrystalline diamond films. In fact, they found that only the chemical composition of the surface affects the electronic structure and therefore the efficiency of a given film.

In the present work, the photocathode QE measurements on two sets of PCD films deposited by Micro-Wave Plasma Enhanced CVD (MWPECVD) technique are reported and the correlation existing be-

tween QE and the deposition conditions of PCD films is evidenced.

The photoemission behaviour of PCD films is correlated to the morphological and chemical-structural properties, as determined by means of Scanning Electron Microscopy (SEM) and Raman spectroscopy, respectively, in order to identify the reasons of the best emission performances.

Furthermore, the surface of all PCD films has simultaneously been hydrogen terminated in MW hydrogen plasma.

EXPERIMENTAL

Two sets of PCD films were produced in a homemade cylindrical stainless steel Astex-type reactor by MWPECVD technique using CH₄ as a carbon source diluted in H₂. The PCD films were deposited on polished p-doped (boron) silicon (100) substrates 2x2 cm² in size, pretreated ultrasonically for 1h in an ethanol suspension of diamond powder (40-60 μm).

During the deposition process, the total flow rate, the pressure and the peak power were fixed at 200 sccm, 50 mbar and 1250 W, respectively. More details are summarized in Table 1. The deposition temperature was controlled by an additional radiative heating system located in the susceptor and was measured on the sample surface by a dual-wavelength infrared pyrometer (2.1 and 2.4 μm). In order to interrupt the deposition process when the desired value was reached, the thickness was monitored at the centre of the sample in real-time using pyrometric interferometry technique [14].

The set I includes two PCD films with a thickness between 3.8 and 5 μm. The samples 1 and 2 were deposited by using continuous wave (CW) and pulsed wave (PW) discharges, respectively. The CH₄ percentage in the gas mixture was kept constant at 1% throughout the deposition process of the CW sample 1, while it was set at 1% for the bottom layer (2.76 μm thick) and 0.5% for the upper layer (0.94 μm thick) of the PW sample 2.

The set II comprises two 30 μm thick PCD films. The samples 3 and 4 were deposited using the same deposition parameters except for the CH₄ percentage in the gas mixture: for sample 3 it was held constant at 1%, while for sample 4 it was changed during the deposition and was fixed at 1% for the bottom layer (17 μm thick) and 0.5% and 0.4% for the upper layers (9.7 and 3.4 μm thick, respectively).

The deposition conditions for the four PCD samples are summarized in Table 1.

Sample	CH ₄ (%)	DC (%)	Power (W)	Temp. (°C)	Thickness (μm)
Set I					
1	1	100 (CW)	1250	750	4.85
2 ^a	1 0.5	75 (PW) 50 (PW)	937.5 ^b 625 ^b	830	2.76 0.94
Set II					
3	1	100 (CW)	1250	867	30.02
4	1 0.5 0.4	100 (CW)	1250	832	17.04 9.74 3.35
Hydrogenation^c					
	0	100 (CW)	1250	780	---

^a Pulse frequency 100 Hz.

^b Time-average microwave power (see eq. 1 of ref. 14).

^c H₂ flow rate 200 sccm and pressure 57 mbar.

Table 1: Discharge conditions of the four diamond films grown on pretreated Si substrates at total flow rate, pressure and peak microwave power of 200 sccm, 50 mbar and 1250 W, respectively, and variable CH₄ percentage and duty cycle (DC). Discharge conditions of the hydrogenation process are also shown.

The film surface hydrogenation was obtained by a microwave hydrogen plasma for 1 h at 780°C surface temperature, setting the microwave power at 1250W, the hydrogen flow at 200 sccm and the pressure at 57 mbar.

The film surface morphology was observed by using an EVO scanning electron microscope (SEM model Zeiss 50XVP) in secondary electrons mode, with an operating voltage of 15 kV.

The chemical-structural features of PCD films were examined at room temperature by means of a Raman confocal micro-spectrometry apparatus (Labram from Jobin-Yvon Horiba) in the backscattering configuration and using an Ar-ion laser beam (488 nm, laser output power 4.5 mW). The spot size on the samples was approximately 1 μm in diameter using a 100x objective.

QE measurements of the diamond-based photocathodes were performed in reflection mode and normal incidence in the UV spectral range (150–210 nm) by means of a 30 W deuterium lamp (Mc Pherson TM) under vacuum (about 1x10⁻⁶ mbar). The photocathode was mounted in a multi wire proportional chamber, not operating in electron multiplication mode. The diamond photocathode was fixed in front of a trans-

missive golden tungsten mesh set at 4 mm and positively biased at 90 Volts. For the photoelectron detection the sample was connected to ground through a custom-made electrometer with a sensitivity of 10^{-16} A. The absolute QE was evaluated by means of a NIST calibrated standard photodiode (Hamamatsu R1460 PM). Details of the photoemission characterization set-up are found in ref. [10]. The QE measurements were done on untreated, hydrogenated and aged (in air for one month) PCD films.

RESULTS

Scanning Electron Microscopy (SEM)

The SEM images of the four samples are reported in Fig.1. All the samples are polycrystalline and made of randomly oriented grains with a pyramidal structure and variable sizes. A rough estimation of grain sizes has been done by analyzing ten SEM images for each sample, neglecting the secondary nucleation, where present.

The samples 1 and 2 of set I have grain sizes smaller than those (samples 3 and 4) of set II, as expected due to their low thickness (see Table 1). Moreover, the comparison of the two samples within each set evidences differences of the crystallite sizes likely due to the growth conditions. The effect of CH_4 percentage on the morphology of the samples 3 and 4 of set II is clear although the CH_4 change was carried out only on the upper 13 μm layer. Secondary nucleation is observed in sample 3 and is absent in sample 4 grown at lower CH_4 percentage on the topmost layer (see Table1).

On the contrary, the dilution effect on the thin film set (CW samples 1 and PW sample 2) is less evident and the secondary nucleation is absent or hard to see due to the small grain sizes. The pulsed conditions seem to delete the effect of CH_4 dilution because the grain sizes of the PW sample 2 are smaller than those of CW sample 1, grown at higher CH_4 percentage.

SEM analyses of the samples after hydrogenation and aging do not show any appreciable variation in the surface morphology of the films.

Raman spectroscopy

The Raman spectra of the samples of set I and set II are shown in Fig. 2a and 2b respectively, and the polycrystalline diamond features are well evident. All the spectra show a typical diamond sharp peak around 1332 cm^{-1} [15], and a low broad signal at ap-

proximately 1500 cm^{-1} (graphite G band) due to sp^2 bonds localized principally at the grain boundaries. In the thin samples (see Fig. 2a) a peak at 520 cm^{-1} due to the Si substrate is also evident, absent in the thick samples (Fig. 2b).

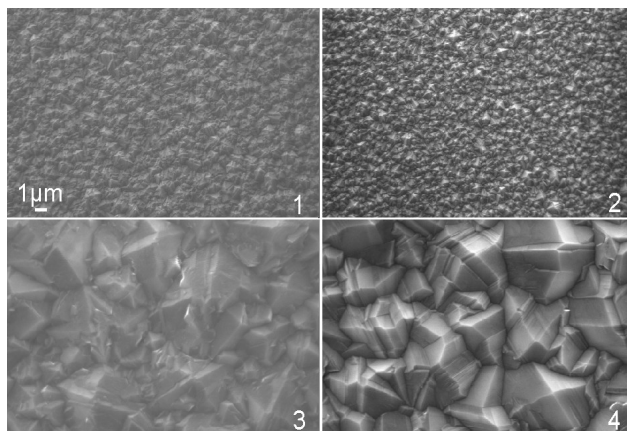


Fig. 1: Secondary electron micrographs of the four analysed PCD films.

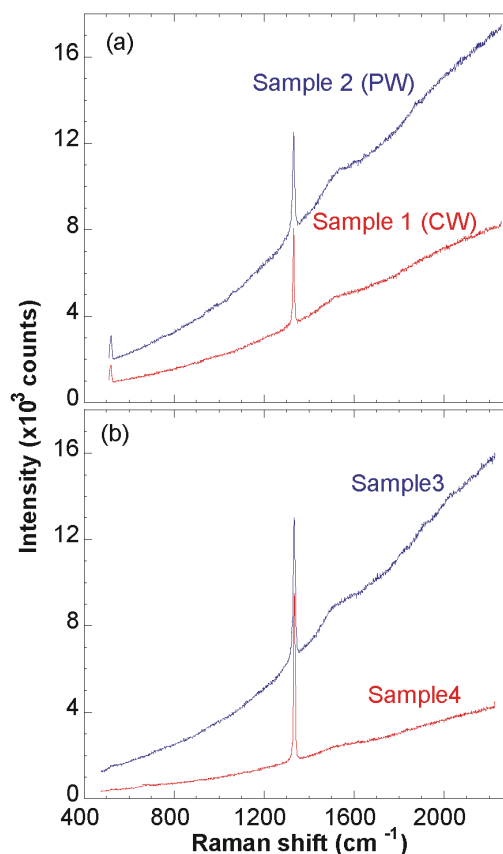


Fig. 2: Micro-Raman spectra recorded on the four investigated PCD films, coupled according to the growth set. a) Set I: samples 1 and 2; b) set II: samples 3 and 4. Raman spectra of samples 2 and 3 show a higher fluorescence background due to more defective films.

A quality factor, R , is determined by the equation where I_{sp^3} is the intensity of the diamond peak at

$$R = 100 \cdot \frac{I_{sp^3}}{I_{sp^3} + I_{fl} + \sum_k I_k}$$

1332 cm^{-1} , $\sum_k I_k$ is the intensity of the non-diamond phases and I_{fl} is the intensity of the fluorescence background at the position of the diamond peak, as reported in ref. [15].

For the PW sample 2, with the $0.94 \mu\text{m}$ upper layer deposited at low CH_4 percentage (0.5%), the Raman spectrum is dominated by a higher fluorescence background indicating that this sample is more defective than the CW sample 1. The PW sample shows also a higher graphitic component. The low quality (i.e. low R value) of the PW sample with respect to the CW one is due to the smaller size of crystalline grains which leads consequently to a higher amount of grain boundaries.

The samples of set II show the same features as those of set I, but the sample 4, deposited lowering the CH_4 percentage (from 1% to 0.5-0.4 %) on the $13 \mu\text{m}$ top layer of the film, has a Raman spectrum indicating a better quality and an R factor higher than sample 3. The hydrogenation and the aging of the samples have not changed the quality and composition of the films as observed in Raman spectra.

Photoemission

The QE results of the photocathodes based on PCD films of the two sets, in the UV spectral range 150–210 nm, are reported in Fig. 3a and 3b. All the samples untreated, hydrogenated and aged, show an increase in QE with decreasing wavelength in the explored range, as reported in literature [3,6]. The untreated sample 2 and sample 3 present QE values of 4.1% and 3.6% at 150 nm, respectively, higher than those of the untreated sample 1 and sample 4, having QE values of 2.3% and 2.6%, respectively. In the same figures the QE curves of the hydrogenated samples (pointed lines) and air-exposed hydrogenated samples (dashed lines) are reported. A careful inspection of Fig.3a and 3b leads to the following further remarks:

- the QE response of hydrogenated samples is improved in both sets;
- the QE values of the hydrogenated samples of each set increase and reach the same value;
- the improvement extent of QE of thicker ($30 \mu\text{m}$) samples is higher than thinner ($4.5 \mu\text{m}$) ones;
- the QE of the aged samples decreases to values ap-

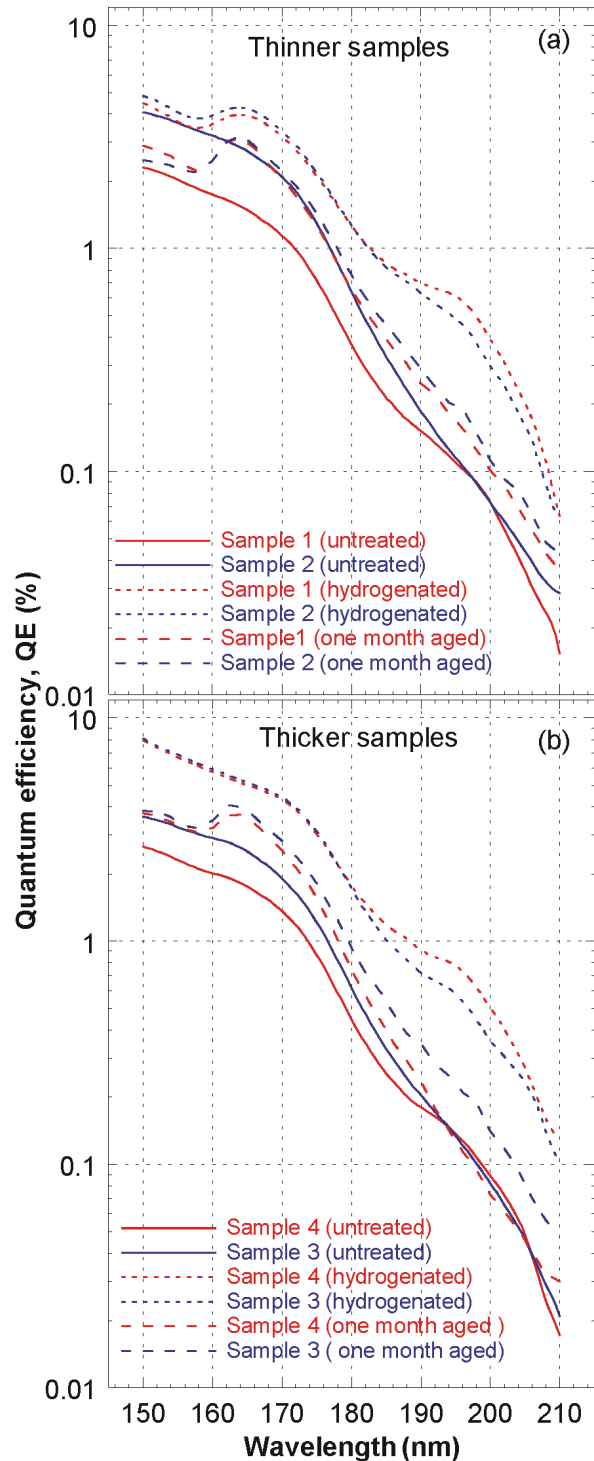


Fig. 3: QE values as a function of the wavelength measured in the near-ultraviolet spectral region (150-210 nm) for the photocathodes based on PCD films of set I (a) and set II (b). Continuous, pointed and dashed lines refer to untreated, hydrogenated and one-month air-exposed samples, respectively.

proaching those of the untreated ones. Figures 4a and 4b show the QE values at 150 nm of

untreated samples as a function of the quality factor R and grain size. The samples having a quality factor $R < 55\%$ (sample 2 and 3) exhibit the highest QE values, whereas the films with grains of different size seem not to affect the photoemission properties. In figure 5a and 5b the calculated relative quantum efficiency ($RQE = QE_{\text{hydrogenated}} / QE_{\text{untreated}}$) at 150 nm are reported as a function of the quality factor R and the grain size, respectively. The figures show that the thicker films have the higher relative QE gain.

DISCUSSION

On the basis of the above results, our discussion is focused to answer to the following questions:

what are the factors that cause higher QE values (see Fig. 4a) in untreated samples 2 and 3 with respect to samples 1 and 4?

why are the QE curves of the samples 1 and 2 of set I and samples 3 and 4 of set II coincident after hydrogenation?

why is the hydrogenation more effective in the thicker samples?

To answer the first question we must consider the role of PCD quality on the QE. The non-diamond phase is mainly localized at the grain boundaries (see Fig. 1) and, as reported in Fig. 2a-b and Fig. 4a, samples 2 and 3 have higher sp^2 component and smaller R compared to samples 1 and 4, respectively. A positive effect on the photoemission properties seems related to the presence of sp^2 carbon phases at the grain boundaries of diamond films, so a suitable combination of sp^2 and sp^3 components would enhance the photoemission. In fact, the photoelectrons should originate from the graphite–diamond contact and can easily leave the material (as required by a high QE) via the diamond vacuum level. We can conclude that the smaller R (see Fig.4a), the higher the sp^2 component (see Fig.2a-b), the better the photoemission properties (see Fig.3a-b and Fig.4a). Consequently sample 2 and sample 3 (set I and set II, respectively) are better electron emitters than sample 1 and sample 4. The different thickness of the films seems not to affect the photocathode performance.

To answer the second and the third questions we must consider the influence of hydrogenation on the non-diamond and diamond phases. The QE improvement after hydrogenation of all the samples (Fig. 5a,b) is due to the activation of the photocathode surface into a negative electron affinity and for each set the QE values of hydrogenated samples are roughly identical. It is evident inside each set that the QE increase is greater for the best quality films (higher R),

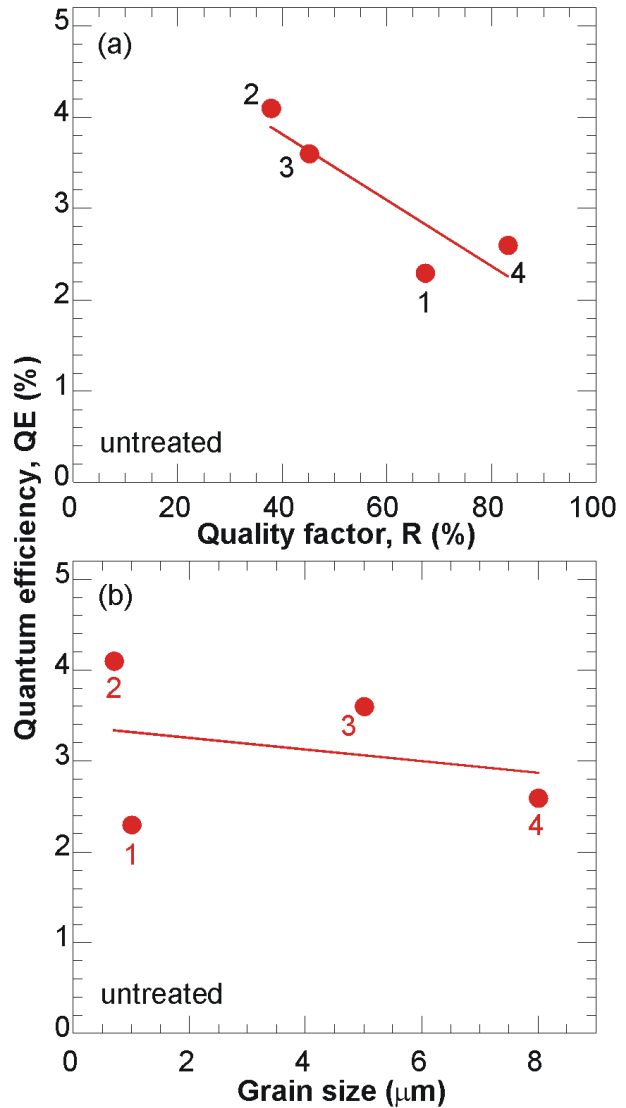


Fig. 4: QE values measured at 150 nm versus quality factor R (a) and grain size (b) for the untreated samples.

sample 1 and sample 4 (Fig. 5a). In fact the QE enhancement after hydrogenation of these samples is about twice and three times as much as their initial value, respectively. This result can be explained considering that the hydrogenation of graphite makes no difference to the photoyield from this non-diamond material, whilst it has a strong effect on photoemission from diamond [4, 8]. Moreover, samples 3 and 4 (set II) have a greater relative QE gain after hydrogenation (Fig. 5a,b). This can be explained by the high thickness (30 μm) and by the consequent greater grain dimensions (see Fig. 1 and Fig.5b) [1] that should give higher diamond percentage as regards the thinner films. It is worthy to underline that sample 3 (set II) has a quality factor R lower than sample 1 (set I), and this is due to the presence of secondary nucleation on sample 3 well evident in Fig.1, that

causes the increase of the graphitic component, but at the same time sample 3 incorporates grain sizes larger than those of sample 1. These two contrastant factors (non-diamond content in the deeper layers and grain size on the surface) lead to hydrogenated materials whose photoemitting response is almost the same.

After the QE measurements the hydrogenated films are exposed to air for one month and subsequently re-measured. The aged samples exhibit an evident QE decay (Fig. 3a-b) due to the low stability of hydrogenated PCD surface that is independent of the film quality within each set and on the grain sizes of the examined samples. The worsening in the QE could be due to the oxidation of hydrogenated surface. The same high sensitivity can be easily and reversibly

recovered many times by subsequent hydrogen-plasma activation treatments.

CONCLUSIONS

In the present work, two sets of pairs of PCD films have been investigated. The difference between the two sets is the thickness range, while inside each set the samples are characterized by different deposition conditions. The samples show similar morphologies (microcrystalline structure and random orientation) but different crystal size and relative content of non-diamond (sp^2) component, related to the presence of the grain boundaries.

The photoemission QE results can be explained based on the characteristics of the films. The comparison between the QE values of the untreated samples points to a fundamental effect of the sp^2 component in the film: an higher sp^2 content seems to improve the photocathode performance, independently on the grain size.

After hydrogen plasma treatment the expected increase in QE, reported already in literature, is found for all the analyzed films. In this case the best relative improvement is observed in films with larger grains and lower relative sp^2 content. This can be easily interpreted in that the hydrogenation affects only the diamond component of the film, therefore the larger size and the lower sp^2 component must clearly correspond to the higher QE improvement. The decay of photoemission properties of the air-exposed hydrogenated samples is around 50% and is found to be independent of the grain size and the quality factor R.

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REFERENCES

- [1] J. Robertson, M.J. Rutter, *Diamond Relat. Mater.* 7 (1998) 620.
- [2] L. Diederich, O.M. Kuttel, P. Aebi, E. Maillard-Schaller, R. Fasel, L. Schlapbach, *Diamond Relat. Mater.* 7 (1998) 660.

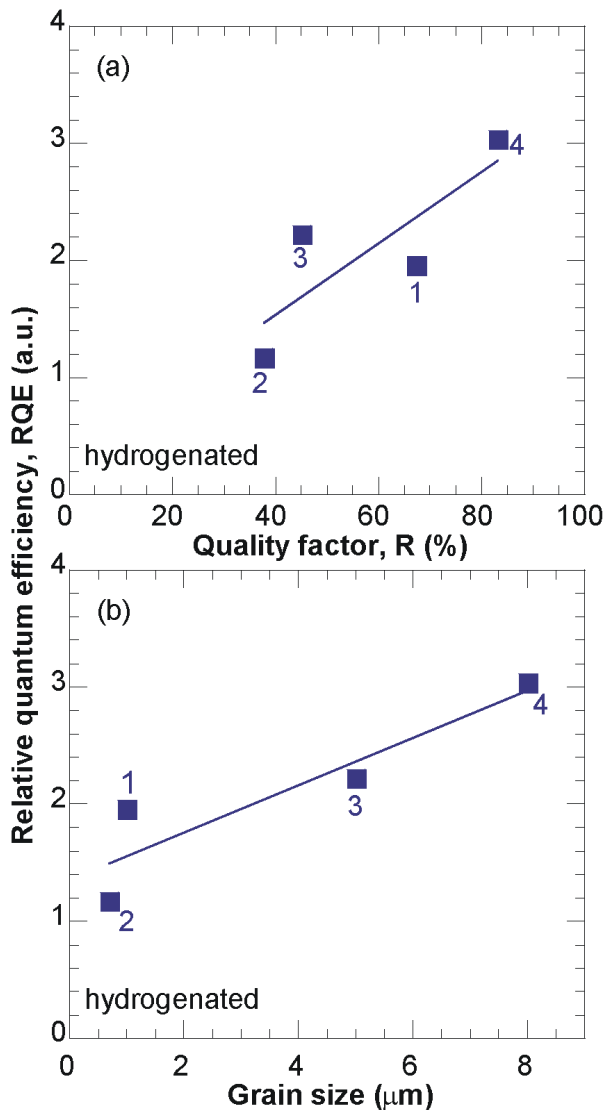


Fig. 5: RQE values calculated at 150 nm as a function of quality factor R (a) and grain size (b) for the hydrogenated samples.

- [3] A.S. Tremsin, O.H.W. Siegmund, *Diamond Relat. Mater.* 14 (2005) 48.
- [4] J. Ristein, F. Maier, J.B. Cui, L. Ley, *Phys. Status Solidi A* 181 (2000) 65.
- [5] A. Breskin, R. Chechik, E. Shefer, D. Bacon, Y. Avigal, R. Kalish, Y. Lifshitz, *Appl. Phys. Lett.* 70 (1997) 3446.
- [6] A. Laikhtman, Y. Avigal, R. Kalish, A. Breskin, R. Chechik, E. Shefer, Y. Lifshitz, A. Hoffman, *Diamond Relat. Mater.* 8 (1999) 725.
- [7] J.S. Foord, C.H. Lau, M. Hiramatsu, A. Bennett, R.B. Jackman, *Diamond Relat. Mater.* 11 (2002) 437.
- [8] J.B. Cui, M. Stammler, J. Ristein, L. Ley, *J. Appl. Phys.* 88 (2000) 3667.
- [9] N. Koenigsfeld, R. Kalish, A. Cimmino, D. Hoxley, S. Praver, I. Yamada, *Appl. Phys. Lett.* 79 (2001) 1288.
- [10] A. Valentini, E. Nappi, M.A. Nitti, *Nucl. Instr. and Meth. A* 482 (2002) 238.
- [11] D. Takeuchi, C. E. Nebel, S. Yamasaki, *J. Appl. Phys.* 99 (2006) 086102.
- [12] M.A. Nitti, M. Colasuonno, E. Nappi, A. Valentini, E. Fanizza, F. Benedic, G. Cicala, E. Milani, G. Prestopino, *Nucl. Instrum. Methods Phys. Res. A* 595 (2008) 131.
- [13] J.B. Cui, J. Ristein, L. Ley, *Phys. Rev. B* 60, (1999) 16135.
- [14] G. Cicala, R. Brescia, M.A. Nitti, A. Romeo, D. Altamura, C. Giannini, M. Capitelli, P. Spinelli, S. Schutzmann, *Surf. Coat. Technol.* 204 (2010) 1884.
- [15] H. Chatei, J. Bougdira, M. Rémy, P. Alnot, C. Bruch, J.K. Krüger, *Diamond Relat. Mater.* 6 (1997) 107.