

Electron emission from nitrogen-doped polycrystalline diamond/Si heterostructures

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The field electron emission from polycrystalline diamond/silicon and nitrogen-doped polycrystalline diamond/silicon structures obtained by HF CVD deposition method has been investigated. Electron emission currents from the samples were measured in a chamber at the pressure equal to $2 \cdot 10^{-6}$ Pa in sphere-to-plane diode configuration with the 5 μm distance between electrodes. As expected, the results confirm the relation between the structure of diamond films and their emission properties. The type of silicon substrate also influences the value of emission currents and the diamond/n-Si heterostructures exhibit better electron emission than diamond/p-Si ones. The nitrogen doping significantly enhances the electron emission from the heterostructures and their emission parameters. The values of the threshold field between 2 V/ μm and 3 V/ μm were registered, the values of emission current close to 1 mA/cm² at 5 V/ μm for the nitrogen-doped films were obtained. The shape of current-voltage characteristics for nitrogen-doped polycrystalline films may be interpreted in terms of stochastic distribution of diameters of conducting channels which form the emission centers.

Keywords: *HF CVD, diamond films, nitrogen-doping, Raman spectroscopy, electron emission*

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1. Introduction

Diamond is one of the most interesting materials for field emitters due to its very attractive physical and chemical properties such as high hardness, very high thermal conductivity, good adhesion, chemical stability and its electron affinity which can be tuned in the range between -1.3 eV and $+1.7$ eV by various surface terminations [1, 2]. The tuning of electron affinity becomes the more important that the negative electron affinity (NEA) not necessarily supports the electron emission (EE) because the NEA leads to formation of an internal depletion layer by ionized donors. Such a depletion layer may prevent electrons from approaching the surface which in turn leads to an increase in electric field necessary for field emission.

The electron emission from diamond and doped diamond surfaces is defined by two basic phenomena. The first one is related to the band structure of diamond emitter which strongly influences the emission phenomenon. It seems that n-type doping

of diamond enhances the values of emission currents [3]. Nitrogen is the most commonly considered n-type dopant for diamond and diamond-like carbon (DLC) [4–6]. The major difference in the electron emission between pure DLC and nitrogen-doped DLC films is that the emission in the doped film can occur without the electrical breakdown [7]. In the case of nitrogen-doped diamond films we have to do with strong upward band bending at the very surface, leading to the value of work function (obtained by photoelectron spectroscopy or thermionic emission) in the range between 1.5 eV ÷ 3.0 eV [8–10]. The second problem is related to the influence of diamond nanostructure on the electron emission and the emission parameters. In particular, the role of conducting channels formed of graphite inclusions and their influence on the emission parameters and current-voltage characteristics is of crucial importance [11]. It seems that in order to obtain efficient diamond electron emitters one should combine optimal (not necessary extremely low) electron affinity with a nanostructure suitable for efficient electron emission.

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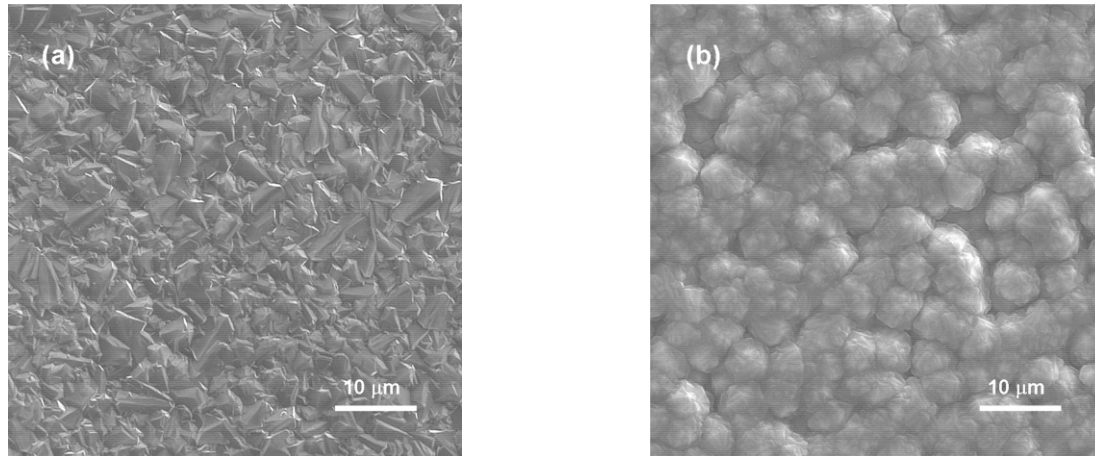


Fig. 1. SEM pictures of the polycrystalline diamond films. (a) undoped small-grained film grown from the mixture of methanol vapor and hydrogen; (b) nitrogen-doped film grown from the mixture of methanol vapor and hydrogen with the ammonium hydroxide added to the working gas.

The cold cathode emission from CVD diamond films has been demonstrated experimentally, but the mechanism of EE from CVD polycrystalline diamond films still remains under discussion, although a number of models of EE from diamond films have been proposed (see for instance [11]). This is probably due to a great variety of CVD polycrystalline diamond films characterized by various surface morphology, conductivity and different concentration of dopants. It has been shown the EE from CVD diamond films may depend on a surface treatment [12, 13], thermal history [14], microstructure [15], crystalline orientation [16], and presence of non-diamond carbon phases [17, 18]. The preparation of silicon substrate can also influence the electron emission from polycrystalline diamond films [19].

In this paper the basic structural properties and emission currents from undoped and nitrogen-doped HF CVD (Hot Filament CVD) polycrystalline diamond films deposited on both p-type and n-type silicon are presented. The analysis of the influence of film microstructure on the shape of current-voltage characteristics and comparison with some other experimental results is also shown.

2. Experimental

The polycrystalline undoped diamond films (DF) and nitrogen-doped diamond films (N-DF) were

deposited on n-type and p-type silicon substrates using HF CVD technique [20, 21]. The mixture of methanol vapour and hydrogen ($\text{CH}_3\text{OH}/\text{H}_2 = 0.5\% \div 2.0\%$) was used as a working gas. In order to synthesize the nitrogen-doped films the ammonium hydroxide was added to the working gas. The main parameters of the deposition process were as follows: total pressure in the reaction chamber 50 hPa, the substrate temperature 1000 K, the working gas flow rate 100 sccm. In order to enhance the diamond nucleation density, the substrates were scratched with diamond paste before the deposition process.

The surface morphology of the samples was examined using Tesla BS 301 Scanning Electron Microscope working at the voltage 25 kV. T64000 Jobin-Yvon Raman spectrometer was used to study the quality of the films; 514.5 nm argon laser was used for excitation.

Electron emission from the samples was measured in a chamber at the pressure equal to $2 \cdot 10^{-6}$ Pa in a sphere-to-plane diode configuration with the 5 μm distance between electrodes.

3. Results and discussion

As it is mentioned above, the surface morphology is very important for EE from diamond films, both due to varying amount of graphite-like phase forming well conducting channels and because the

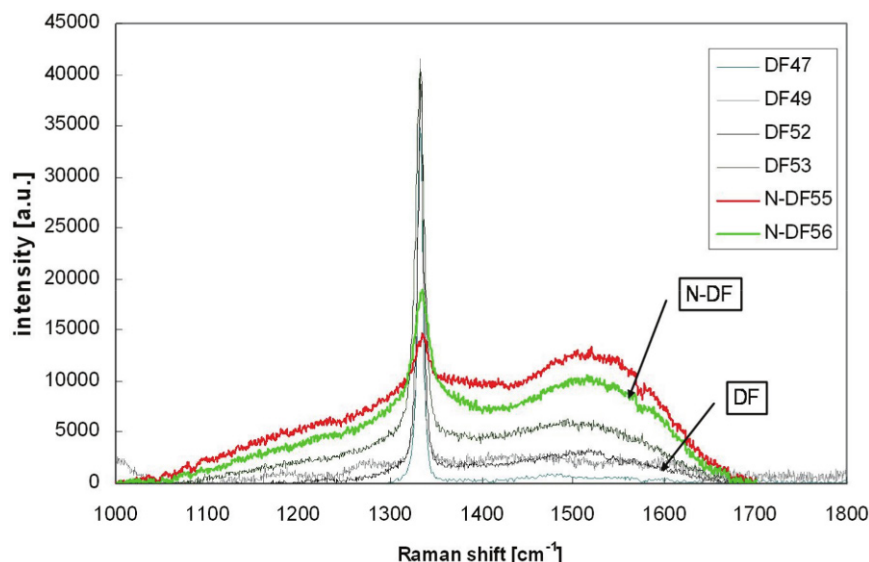


Fig. 2. Raman spectra for undoped diamond films (DF) and nitrogen-doped diamond films (N-DF).

morphology influences the distribution of the electric field at the very surface. The surface morphology of the investigated diamond films was found to depend on the concentration of methanol in the working gas. For the working gas containing 0.5 % of methanol, large-grained films were obtained. For the higher concentration of methanol the size of crystallites becomes smaller, but there is no clear relation between the size of crystallites and the concentration of methanol in the working gas. The nitrogen doping changes the film morphology significantly (see Fig. 1a, b).

The nitrogen-doped films are composed of very small microcrystallites and show cauliflower character, the crystal features are not clearly pronounced. The doped films contain comparatively high concentration of grain boundaries and, as a consequence, comparatively high concentration of defects.

The changes in morphology of the films are reflected in their Raman spectra (see Fig. 2).

It is known that a monocrystalline diamond is characterized by the sharp line at 1332.5 cm^{-1} with full width at half maximum (FWHM) equal to $2 \text{ cm}^{-1} \div 2.5 \text{ cm}^{-1}$ [22]. The Raman diamond lines of the investigated HF CVD diamond films are much broader than that of single crystal diamond (see Fig. 2 and Table 1).

The broadening of diamond line is characteristic of diamond structures containing high concentration of defects. Apart from the main diamond line, an additional line at about 1550 cm^{-1} is observed for the investigated films. This line is called G-line and is typical of carbonaceous structures containing high concentration of graphite-like amorphous carbon phase. Relatively high intensity of the G-line registered for the nitrogen-doped films (see Fig. 2) indicates that these films contain higher concentration of disordered graphite-like phase, probably localized at the grain boundaries first of all.

The relation between the emission currents from large-grained and small-grained films obtained by HF CVD method was discussed earlier [23]. It has been shown that the currents from the small-grained films are substantially higher than those from the large-grained films.

The comparison of emission currents from the undoped and nitrogen-doped films deposited on n-type and p-type silicon substrates are shown in Fig. 3a.

It results from the figure that the type of silicon substrate influences the value of emission currents significantly. The currents for DF46/p-Si, DF47/p-Si, DF48/p-Si and DF49/p-Si samples (curves 1 in Fig. 3a) are considerably smaller than those for sam-

Table 1. Full width at half maximum (FWHM) of Raman diamond line and basic parameters of electron emission calculated from Fowler-Nordheim Equation (1) for the investigated heterostructures.

Sample/ substrate	thickness [μm]	FWHM [cm^{-1}]	ϕ_{ef} [eV]	E_{t-on} [V/ μm]	E_T ($I = 1\text{nA}$) [V/ μm]	Current density at turn-on field j_{t-on} [A/ cm^2]	Current density at 40 V/ μm or maximal measured values j_E [A/ cm^2]
DF46/p-Si	2.80	10.0	0.032	12.0	–	$7 \cdot 10^{-11}$	$4 \cdot 10^{-9}$
DF47/p-Si	2.10	8.5	0.070	22.0	–	$4 \cdot 10^{-10}$	$9 \cdot 10^{-9}$
DF48/p-Si	1.85	11.0	0.057	24.0	36.0	$4 \cdot 10^{-10}$	$6 \cdot 10^{-8}$
DF49/p-Si	1.20	5.5	0.062	20.0	42.0	$7 \cdot 10^{-11}$	$4 \cdot 10^{-8}$
DF52/n-Si	3.00	7.5	0.052	10.0	15.0	$4 \cdot 10^{-10}$	$9 \cdot 10^{-6}$
DF53/n-Si	2.90	11.0	0.056	8.0	11.0	$4 \cdot 10^{-11}$	$6 \cdot 10^{-5}$
N-DF55/n-Si	1.20	18.0	0.041	3.4	2.7	$1 \cdot 10^{-10}$	$7 \cdot 10^{-4}$ (7V/ μm)
N-DF56/n-Si	1.60	20.5	0.039	2.2	2.8	$3 \cdot 10^{-9}$	$5 \cdot 10^{-4}$ (5V/ μm)

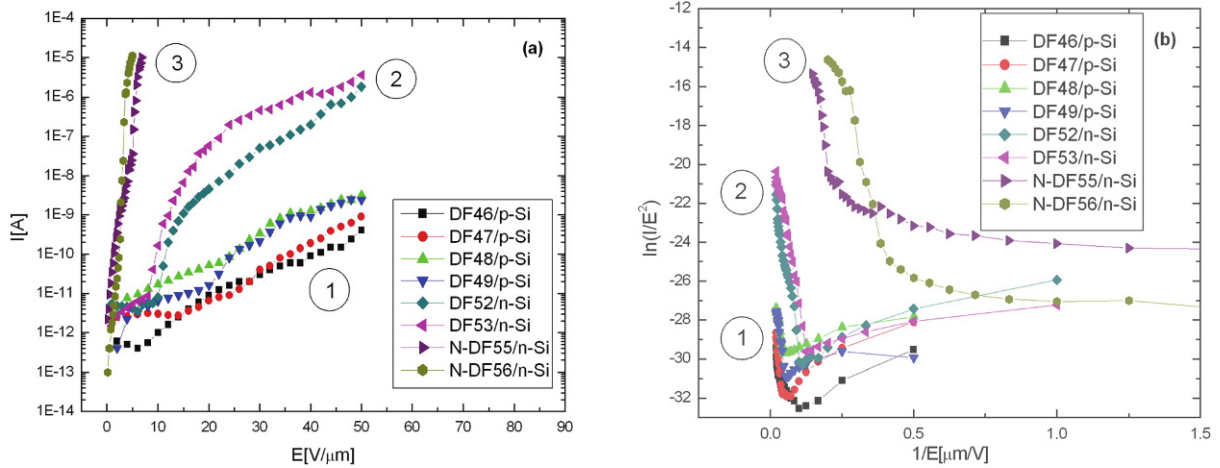


Fig. 3. (a) Current-field characteristics of the investigated diamond/Si heterostructures. Curves 1: small-grained diamond films deposited on p-Si substrates; curves 2: small-grained diamond films deposited on n-Si substrates; curves 3: small-grained nitrogen-doped films deposited on n-type substrates. (b) The same results in Fowler-Nordheim coordinates.

ples DF52/n-Si and DF53/n-Si (curves 2 in Fig. 3a). It is worth noting that the values of emission currents corresponding to 40 V/ μm for the undoped diamond films deposited on n-type silicon are approximately 3 orders of magnitude higher than for the films deposited on p-type silicon (see Table 1).

The highest emission currents have been registered for the nitrogen-doped N-DF55/n-Si and N-DF56/n-Si heterostructures (Fig. 3a, curves 3). From comparison of the curves 1 and 2 (Fig. 3a) it appears that n-Si substrate supports the electron emission from the investigated silicon/diamond heterostructures. This is probably due to better conduction of diamond/n-Si junction in comparison with

diamond/p-Si one. Similar results were reported earlier [24] and this is probably the reason for which electron emitters composed of CVD diamonds deposited on n-type silicon have received more attention [25, 26]. The same relation between the conductivity of DLC/n-Si and DLC/p-Si junctions was found earlier and interpreted in terms of band model of DLC/Si junctions [27].

Fig. 3b shows the data in Fowler-Nordheim coordinates:

$$\ln\left(\frac{I}{E^2}\right) = -b \frac{\phi_{ef}^{\frac{2}{3}}}{\beta_0} \frac{1}{E} + \ln a, \quad (1)$$

where I is the EE current, E is the electric field, ϕ_{ef} is the effective work function, β is the geometric field enhancement factor, a and b are the constants independent of electric field ($b = 6.83 \cdot 10^9 \text{ eV}^{-3/2} \text{ m}^{-1}$). In order to compare the emission properties of the investigated heterostructures, the basic emission parameters such as the effective work function ϕ_{ef} and the turn-on field E_{t-on} resulting from application of Fowler-Nordheim equation were calculated and are presented in Table 1. The turn-on field E_{t-on} is defined as the field at which the field emission described by Fowler-Nordheim relation starts. The Table 1 also shows the threshold field E_T which corresponds to the emission current 1 nA as well as the current densities j_{t-on} corresponding to the turn-on field E_{t-on} and the current densities j_E corresponding to the field 40 V/ μm . Because the current densities at the field 40 V/ μm in nitrogen-doped films are not available, the maximal measured current densities j_E are given additionally. Table 2 summarizes the data for polycrystalline diamond films obtained by a number of other Authors.

For comparison the results obtained for single-crystal diamond with various surface terminations are also presented.

It is not quite easy to compare our results with those obtained by other Authors, because the definitions of threshold field E_T are very often imprecisely specified and, in consequence of this, different definitions of E_T are taken into account. However, having in mind the limitations resulting from possible differences in definitions of emission parameters, the following conclusions may be put forward:

- The electron emission depends on microstructure of polycrystalline films [18, 19, 31, 32]. In particular the increasing amount of graphitic sp^2 phase supports the emission currents [18, 31]. This is consistent with our results published earlier [34] which suggest that the emission is related to grain boundaries and increases with increasing structural disorder and amount of graphite-like phase.
- Doping leads to improvement of electron emission from diamond films [28, 29, 32]. The lowest turn-on fields and the highest emission currents are obtained for nitrogen

doping, though boron and phosphorus doping also improve the emission properties [28, 32]. However, the results obtained by Lacher *et al.* [29] show that boron-doped diamond films may, in certain circumstances, exhibit better emission properties than nitrogen-doped films. The Authors suggest that this may result from existence of large amount of non-diamond carbon in the films examined by Lacher *et al.* Hence, the improvement of the field emission is rather due to structural changes related to introduction of doping atoms and does not result from changes of electronic band structure. Both the values of turn-on field and the values of emission current densities for our nitrogen-doped film (see Table 1) are in good agreement with results obtained by other Authors [29, 32]. The values of current densities at which the field emission starts are in the range between $4 \cdot 10^{-10}$ and $4 \cdot 10^{-11} \text{ A/cm}^2$ for the undoped films and between $3 \cdot 10^{-9}$ and 10^{-10} A/cm^2 for nitrogen-doped diamond films.

- The values of effective work function shown in Table 1 are in the range between 0.032 eV and 0.070 eV. These values are much lower than that for single crystal diamond and polycrystalline diamond films determined by photoelectron spectroscopy [8]. Such low values of the effective work function, resulting from application of F-N equation, are typical of polycrystalline diamond structures and were found for many diamond polycrystalline materials [7, 35]. These low values of effective work function confirm the suggestion that the electron transport and electron emission in polycrystalline diamond films are related to grain boundaries regions containing comparatively well conducting graphite-like carbon, because for such systems the electric field becomes strongly inhomogeneous and leads to strong field enhancement at the surface.

Fig. 3b shows very smooth transition between Fowler-Nordheim emission currents and the low-field emission currents in the nitrogen-doped films, which is not typical of most field-emission sys-

Table 2. Summary results of a number of other Authors.

Characteristic of sample and deposition method (as described by the Authors)	Basic emission parameters	Refs.
Undoped, phosphorus-doped and boron-doped diamond films covering silicon microtips, (Microwave Plasma-Enhanced CVD)	$E_T = 33.6$ V/ μm for the undoped diamond-clad tips; $E_T = 30.0$ V/ μm for the boron-doped diamond-clad tips; $E_T = 22.3$ V/ μm for the phosphorus-doped diamond-clad tips; Threshold field E_T defined as the field needed to generate current 20 μA .	[28]
Undoped, nitrogen-doped and boron-doped polycrystalline diamond films, (Microwave Plasma-Assisted CVD)	The emission depends on deposition conditions. The dopants improve the electron emission. The field E_T necessary to get the current 1 nA decreases from 22 to 5 V/ μm for the increasing boron concentration. The field E_T decreases from 120 to about 25 V/ μm for the increasing nitrogen concentration. Currents of the order of several mA/ cm^2 at 5 V/ μm .	[29]
p-type single crystal diamond	Threshold field E_T defined as the field needed to generate current 100 nA. E_T depends on the value of electron affinity and decreases with decreasing electron affinity. The affinity can be tuned by termination of diamond surface. For C(100) with oxygen adsorbed $E_T = 79$ V/ μm For C(110) with oxygen adsorbed $E_T = 81$ V/ μm For C(110) with hydrogen adsorbed $E_T = 25$ V/ μm .	[30]
Polycrystalline diamond films grown on n-doped silicon substrates, (d.c. Arc Discharge Plasma CVD from) CH_4/H_2 gas mixture	The field emission registered at $3 \div 10$ V/ μm for films composed of well-crystallized diamond with a considerable amount of nanocrystalline graphitic phase; no detectable nanocrystalline graphite leads to relatively poor emission at fields of $30 \div 200$ V/ μm . The emission centers are associated with grain boundaries.	[31]
nitrogen-doped, phosphorus-doped and boron-doped polycrystalline diamond, (Hot Filament CVD)	Emission currents and turn-on field strongly depend on the kind of dopant. The best emissive properties are found for nitrogen-doped films. Threshold field for the nitrogen-doped films less than 0.5 V/ μm .	[32]
Polycrystalline diamond films deposited on silicon wafer pre-seeded with diamond powder and on scratched silicon (Microwave-Plasma CVD)	The seeded samples show an obvious decrease in threshold and increase in emission current than that on scratched Si at the same voltage. Current density 1 mA/ cm^2 at 30 V/ μm for diamond film deposited on pre-seeded substrate and 0.6 mA/ cm^2 at 30 V/ μm for diamond film deposited on scratched substrate.	[19]
Polycrystalline boron-doped diamond deposited on n-type silicon wafers (Hot Filament CVD)	The threshold field (defined as the field for a current density of 500 nA/ cm^2) decreases to 4 V/ μm with increasing doping level.	[33]
Polycrystalline diamond films deposited on p-type silicon wafer (Microwave-Plasma Enhanced CVD)	Films containing more sp^2 phase concentration exhibit better field electron emission property including lower turn-on electric field and larger emission current. The turn-on field (the electric field at which the emission current reaches 0.01 μA) was 6 V/ μm .	[18]

tems. As presented above, it is widely accepted that field emission in polycrystalline diamond films is via the system of conducting channels formed at the grain boundaries. If we accept that there exists

some stochastic distribution of size of the channels, there has to exist some stochastic distribution of the field enhancement factor which inevitably leads to stochastic distribution of the effective work function

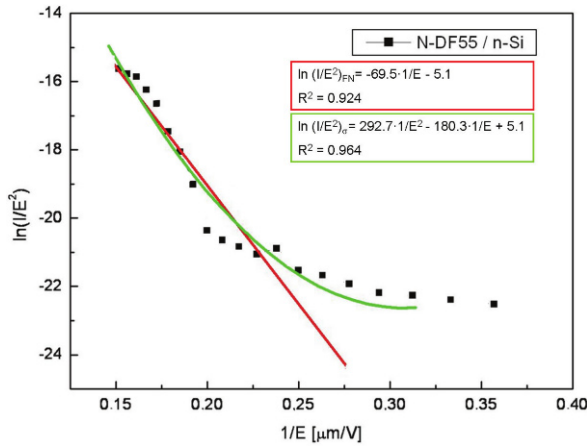


Fig. 4. Results of fitting of the emission currents for sample N-DF55/n-Si with Fowler-Nordheim Equation (1) (straight red line) and with the Equation (3) suggested by Obraztsov *et al.* [36] (green line).

and turn-on field. Assuming the normal distribution of radius of the conducting channels:

$$n(r) = \frac{N}{\sqrt{2\pi}\sigma^2} \exp \left[-\frac{(r-r_0)^2}{2\sigma^2} \right], \quad (2)$$

where r_0 is the average size of the radius and σ is the standard deviation, we get the following current-field characteristics [36]:

$$\ln \left(\frac{I}{E^2} \right) = A\sigma - \underbrace{\frac{0.95b\varphi_{ef}^{3/2}}{\beta_0}}_{B_\sigma} \cdot \frac{1}{E} + \underbrace{\frac{z^2}{2} \left(\frac{0.95b\varphi_{ef}^{3/2}}{\beta_0} \right)}_{C_\sigma} \cdot \frac{1}{E} \quad (3)$$

where A_σ , B_σ and C_σ are the constants independent of the field, β_0 is the average geometric field enhancement factor, $z = \sigma/r_0$. The Equation (3) contains an additional component proportional to $1/E^2$ in comparison with the classical F-N formula (1).

Fig. 4 shows the fittings of our experimental data (sample N-DF55/n-Si) made both using the classical F-N formula (1) and the modified formula given by Equation (3). The standard deviation $\sigma_0 = 0.13r_0$ was assumed for the comparison. The results pre-

sented in Fig. 4 clearly show that the modified formula (3) much better describes the experimental data.

4. Conclusions

The following basic conclusions resulting from the presented data may be put forward:

1. Depending on preparation conditions it is possible to obtain polycrystalline diamond films exhibiting different emission properties. The greater amount of disordered graphite-like phase supports the electron emission from polycrystalline diamond films.
2. The best emission properties, the turn-on field between 2 V/μm and 3 V/μm and the current density at 5 V/μm close to 1 mA/cm² are obtained for the nitrogen-doped films. It suggests that HF CVD deposition technique is appropriate to obtain diamond films of good electron emission properties.
3. The shape of current-field emission characteristics obtained for nitrogen-doped films deviates from typical Fowler-Nordheim characteristics. This deviation may be explained assuming stochastic distribution of size of conducting channels formed at grain boundaries.

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