DAGMARA JARZYŃSKA[1], ELŻBIETA STARYGA[1], ZBIGNIEW ZNAMIROWSKI[2], KAZIMIERZ FABISIAK[3], TEODOR GOTSZALK[2], MIROSŁAW WOSZCZYNA[2], WŁODZIMIERZ STRZELECKI[4], MACIEJ DŁUŻNIEWSKI[1]

[1] Institute of Physics, Technical University of Lodz
  Wólczańska 219, 90-924 Łódź, Poland
[2] Wrocław University of Technology, Faculty of Microsystems Electronics
  and Photonic, Janiszewskiego 11/17, 50-372 Wrocław, Poland
[3] Chair of Physics, Kazimierz Wielki University
  Weyssenhoffa Sq.11, 85-072 Bydgoszcz, Poland
[4] TUV Rheinland of North America
  12 Commerce Road, Newtown, Connecticut, 06470, USA

FIELD EMISSION AND MICROSTRUCTURAL CHARACTERIZATION OF DIAMOND FILMS DEPOSITED BY HF CVD METHOD

Electron emission from diamond films (DF) deposited using HF CVD technique on silicon substrates has been studied. The field emission characteristics were analyzed using the Fowler-Nordheim model. The diamond films were also characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Raman Spectroscopy (RS) and Electron Spin Resonance (ESR) techniques.
The correlation between electron field emission of investigated films, Raman spectra and concentration of paramagnetic centres has been discussed. The electron emission properties of diamond films improved after doping with nitrogen. The field emission was obtained at turn-on electric field equal to about 10 V/μm and about 3 V/μm, for undoped diamond films and N-doped diamond films, respectively. It seems that the change of turn-on field values and other emissive properties of thin diamond layers may be caused by different content of non-diamond phase (e.g. graphite phase) induced by doping.

Keywords: diamond film, doping, electron emission.

1. INTRODUCTION

In the last years one can notice increased interest in the field of carbon materials in general and especially in diamond films (DF), which are attractive due to their good electron emission properties. Diamond film has many excellent properties such as, chemical inertness, high hardness, high thermal conductivity [1], large intrinsic breakdown field (10^9 V/m) [2]. It was shown that properly prepared diamond surface exhibits a negative electron affinity (NEA) [3]. The chemical inertness and high mechanical strength due to strong inter atomic $\sigma - \sigma$ covalent bonds and NEA property make DF as material appropriate for field emission (FE) cathode materials operating in vacuum under strong electric field of the order of $10^7 \div 10^8$ V/m [4].

In order to get high and stable electron emission current the diamond films should be continuous and synthesized on large area. Despite the existence of many deposition methods of carbon films, the problem of emission stability is still hard to solve.

The undoped chemical vapour deposited (CVD) diamond films have relatively high electron emission turn-on field due to their insulating property. Incorporation of dopants into the diamond films in order to improve their conductivity is necessary for the purpose of enhancing their electron field emission behaviour. However, the understanding of how dopants modify the materials characteristics and electronic properties of the diamond is still in its primitive stage.

The problem of the field emission from DF and other carbon layers is a subject of many papers containing interesting results but only few of them consider the mechanism of electron emission. In a few papers [5-7] authors indicate that the electron emission depends on concentration of carbon atoms bonded by sp^2 bonds and in the case of n-doping, on the kind of donor. It was proposed in few models that the field emission from diamond nanocrystals [8] take place at grain boundaries [9-14]. Arora and Vankar [15] show strong dependence of the emission threshold voltage on both nucleation density and surface coverage by diamond crystallites.

This work presents the results of field emission measurements from CVD diamond films. In order to improve emissive ability the films were doped with nitrogen. The influence of diamond film morphology, grain boundary and nitrogen doping on the emissive properties are shown. The role of the graphite-like phase and paramagnetic centres in diamond films on its electron emission efficiency is also considered.

2. EXPERIMENTAL DETAILS

Diamond films were synthesized by the Hot Filament Chemical Vapour Deposition technique (HF CVD) from a mixture of methanol and hydrogen. The concentration of CH_3OH in the source gas was 1.0%, 1.2% or 1.5% (for undoped DF) and 1.5% (for nitrogen doped DF), the flow rate was 150 cm^3/min. The NH_4OH gas at flow rate 1.0 cm^3/min or 1.5 cm^3/min was used for doping of diamond layers. The gas pressure was 5500 Pa. The filament and substrate temperature were kept at 2200°C and 750°C, respectively. The tungsten filament was placed 8 mm above the substrate. The details of deposition parameters of the investigated DF's were described elsewhere [16].

Diamond films were deposited on n-type or p-type silicon substrates which were cut from single crystal silicon wafer. In order to enhance diamond nucleation density the standard procedure was performed i.e. the substrate surface was polished mechanically and than cleaned in acetone, methanol and distilled water. The thicknesses of DF's are shown in Table 1.

The structure of diamond films and their crystalline quality were evaluated using Raman spectroscopy. The Raman spectra were recorded at room temperature in back scattering geometry using Jobin-Yvon T6400 Raman microspectrometer. The instrument is equipped with a microscope whose focal spot diameter is ~ 1.5 μm. The 514.5 nm line from argon laser was used for excitation. The spectral resolution was set below 1 cm^{-1}.

ESR measurements were carried out at room temperature in the air by using X-band spectrometer with 100 kHz field modulation and modulation amplitude of 0.05 mT. The absolute number of spins in the samples was obtained by comparison, under the same experimental conditions, with an α, α`-diphenyl-β-picrylhydrazyl (DPPH) reference.

The emissive characteristics of diamond films were measured under 10^{-5} Pa pressure in oil-free vacuum chamber using diode configuration. As an anode the copper cylinder with base of sphere placed 50 μm distance from the sample surface was used. The voltage in the range of 50 V ÷ 2500 V was applied between the electrodes during the emission measurements and was changed up and down several times in order to stabilize I-V curve. The electron field emission properties were analyzed using Fowler-Nordheim theory [17].

The surface morphology of diamond films was studied using Tesla type BS 301 SEM microscope, before and after current emission measurements.

Table 1

The parameters of process HF CVD and parameters calculated from Raman spectrum and FN plot of I-E characteristics of the investigated samples

Sample		DF47/ p-Si	DF49/ p-Si	DF52/ n-Si	DF53/ n-Si	N-DF55/ n-Si	N-DF56/ n-Si
Gas mixture in HF CVD method		(1.0%) CH_3OH $+H_2$	(1.2%) CH_3O $H+H_2$	(1.0%) CH_3OH $+H_2$	(1.5%) CH_3OH $+H_2$	(1.5%) CH_3OH+H_2 $+NH_4OH$ (1.5cm^3/min)	(1.5%) CH_3OH+H_2 $+NH_4OH$ (1.0cm^3/min)
Thickness of the film [μm]		2.1	1.2	3.0	2.9	1.2	1.6
Max. of peak [cm^{-1}]	diamond	1333.3	1332.8	1333.4	1332.6	1335.2	1334.7
	G	1510.7	1579.6	1524.3	1557.1	1532.2	1526.9
FWHM [cm^{-1}]	diamond	8.95	5.46	7.55	11.55	18.22	19.82
	G	75	203	203	133	149	154
Quality [%]		99.71	99.12	98.34	96.45	94.99	92.78
Residual stress [GPa]		-1.45	-0.84	-1.07	-0.60	-3.46	-2.92
E_{t-on} [V/μm]		22.0	20.0	10.4	8.3	3.4	2.2
φ_{ef} [eV]		0.070	0.062	0.056	0.052	0.041	0.039
A_{diam}/A_G		6.5	13.6	11.6	7.2	1.1	1.8

3. RESULTS AND DISCUSSION

SEM micrographs (Fig. 1) show that the diamond films consist of some submicron grains about 3 μm in size. These crystallites form continuous polycrystalline diamond films, which cover silicon substrate.
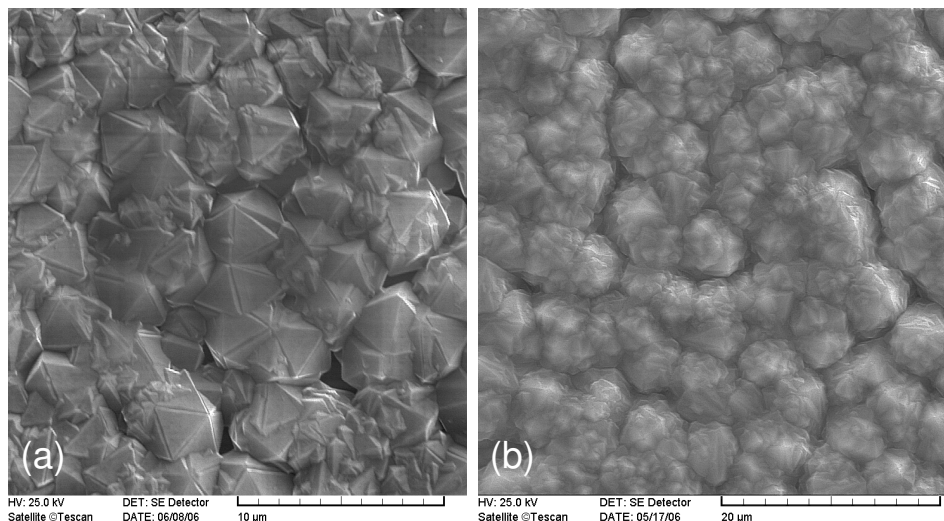
Fig. 1. SEM micrographs of (a) undoped and (b) N-doped diamond films

The coverage ratio of the silicon substrate depends on the conditions of HF CVD process and the time of film deposition. As we can see in Fig. 1b, nitrogen doping of the diamond film causes modification of its structure. Namely, the undoped diamond layer consists of regular crystallites (Fig. 1a), while N-doped diamond films contain crystallites with a cauliflower-like morphology. The clear crystal feature of undoped diamond film indicates that this layer has better quality in comparison to that having non-regular structure. Raman and EPR spectra (see Fig. 2 and Fig. 3) give the information about structure modification which is observed in investigated diamond films.

Raman spectroscopy is commonly used to identify the presence of the diamond phase of carbon in polycrystalline CVD diamond films grown on non-diamond substrates [18]. Raman spectra of DF show, except of well defined diamond Raman peak at 1332 cm^{-1}, the slightly broaden band peaked between 1480 cm^{-1} and 1580 cm^{-1} which is attributed to the non-diamond (amorphous carbon) form of carbon [19]. The broadening of the diamond Raman peak is caused by decrease of the grain size to the nanometer scale, and also by increasing concentration of π bonded carbon (broad Raman band at about 1560 cm^{-1}) at the grain boundaries [20].
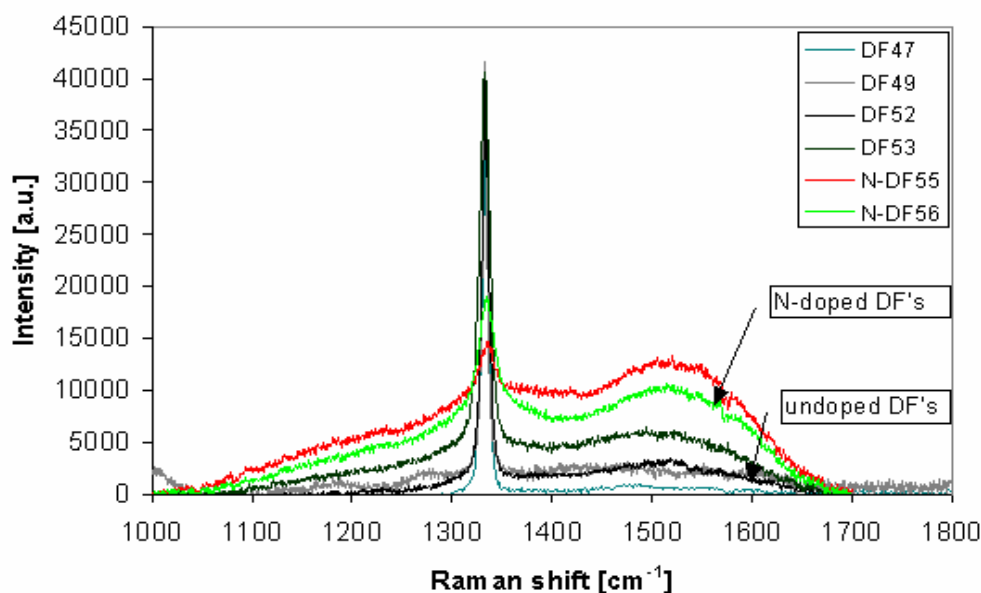
Fig. 2. Raman spectra of investigated undoped and N-doped diamond films

A single peak at 1332 cm^{-1} on a flat background is an indication that given material possesses diamond structure and that no other allotropes of carbon are present. Fig. 2 presents the Raman spectra of investigated diamond film. The Raman spectra for undoped diamond films possess only one sharp peak at 1332 cm^{-1} (Fig. 2, spectra for the samples DF47-DF53), which corresponds to the diamond layer composed mainly from sp^3 C-C bonding carbon atoms. The Raman spectra of nitrogen doped diamond films represented in the Fig. 2 by the curves for sample N-DF55 and N-DF56 show the small peak at 1332 cm^{-1} and the relatively large G band at about 1500 cm^{-1}. It may indicate that diamond film is poor quality and its structure, modified by introduced nitrogen dopant, may contain relatively high amount of graphite-like phase [21]. Probably the doping process causes creation of defects and graphitization [22] of diamond film so the crystallites of N-doped film change their structure and the doped diamond surface become smoothest.

The various parameters of Raman spectra and other parameters like diamond quality (calculated from property formulae - see e.g. [23]) and residual stress (calculated from formula - see e.g. [24]) and the ratio of diamond peak intensity to intensity of G peak are presented in Table I. Reports in literature

ascribe dependence of field emission on size of diamond grain and contents of non-diamond phase [25]. Residual stress in films deposited on solid substrates may lead to delamination of the films and may influence the emission current in this way. That is why the results at residual stress may be important for understanding the results of emission measurements [15]. As we can see in the Table I the residual stress in N-doped diamond films is higher than the stress in undoped films.

ESR spectra recorded for natural and synthetic diamonds are characterized by g-values in the range of $2.0023 \div 2.0027$ and peak-to-peak line width in the range of $0.1 \div 0.3$ mT [26] and concentration of paramagnetic centers about 10^{17} spins/cm^3. It was also found that the spin concentration depends on grain size and is directly proportional to the reciprocal of the particle size [27]. In the case of CVD diamond films it was observed that spin concentration was proportional to the intensity of the Raman band at $1530 \div 1580$ cm^{-1} [19], and paramagnetic defects were mainly distributed at grain boundaries [28].

ESR signal for undoped diamond film (Fig. 3a) forms a symmetrical resonance line which can be decomposed into two components: Lorentzian, are responsible for point defects in diamond lattice, and Gaussian one responsible for C-related defects, as for example dangling bonds, H1 defects associated with amorphous carbon phase [29].
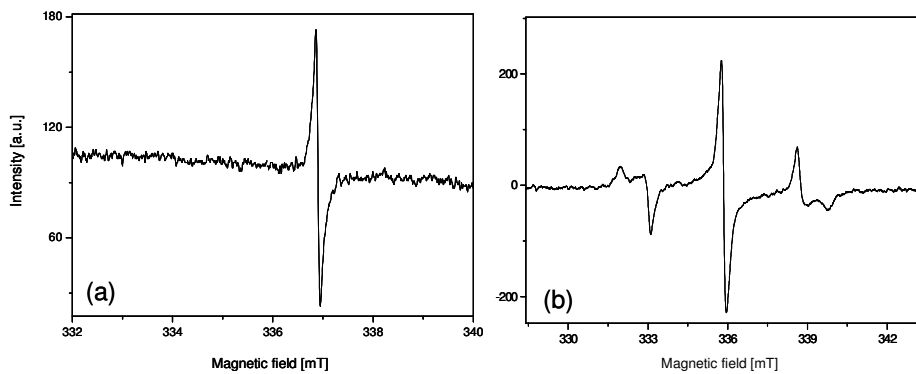

Fig. 3. ESR spectra of investigated (a) undoped and (b) N-doped diamond films

The natural diamond, which contain nitrogen atoms at the substitutional site, exhibit a hyperfine structure, because nitrogen has a nuclear spin 1 [30]. For N-doped HF CVD diamond film, the central line of ESR spectrum is

accompanied by satellite lines (Fig. 3b) that can be attributed to the N_S^0 (P1-substitutional nitrogen) center, as in natural diamond type Ib, and to the paramagnetic centre associated with C-related centres [31]. The position of the hyperfine lines (at ±3.1 and ±4.0 mT) in Fig. 3b indicates that the nitrogen atoms in diamond lattice are present in the substitutional form creating N_S^0 paramagnetic centers [32]. These substitutional nitrogen atoms act as donors [33].

The concentration of paramagnetic centers increases from 10^{17} spins/cm^3 (for undoped diamond films) to about 10^{18} spins/cm^3 (for N-doped diamond films). A large concentration of defects in N-doped diamond films show that nitrogen promotes amorphous carbon phase deposition and cause degradation of diamond quality [34].

Diamond films were investigated by Atomic Force Microscope using conductive probe tip [35]. In this technique it was possible to obtain not only the topography of the surface (Fig. 4a), but also biasing voltage which had to be applied between tip and the sample to maintain constant tunneling current (Fig. 4b). In this case, we were able to acquire information about electrical surface properties correlated to the surface topography. The lowest value of the biasing voltage on grain boundaries indicates that the electron emission from these regions is more effective in comparison with the emission from the surface at diamond crystallites.

It results from the above data that in only to obtain high electron emission from diamond films one should produce small-grain films containing great amount of graphite-like carbon. As results from Fig. 1 and Fig. 3, doping with nitrogen also leads to desirable modification of diamond films. Our results presented above are in agreement with the results obtained by Geis [14] and Okano [36] who pointed out that the occurrence of such defects in the diamond films enhances their emissive properties.

The electron emission current *I* from cathode can be written down according to Fowler-Nordheim (F-N) model, as:

$$I = \frac{a\,A\,\beta^2 E^2}{\varphi} \exp\left(\frac{-b\varphi^{3/2}}{\beta E} \right) \tag{1}$$

where: *A* – the emitting area, *φ* – the work function of emitting surface, *a* and *b* – the constants ($a = 1.54 \cdot 10^{-6}$ eV $\cdot$A $\cdot$V^{-2}, $b = 6.83 \cdot 10^9$ eV$^{-3/2}$ $\cdot$V$\cdot$ m^{-1}), *β* – the geometrical field enhancement factor, *E* – the applied electric field.
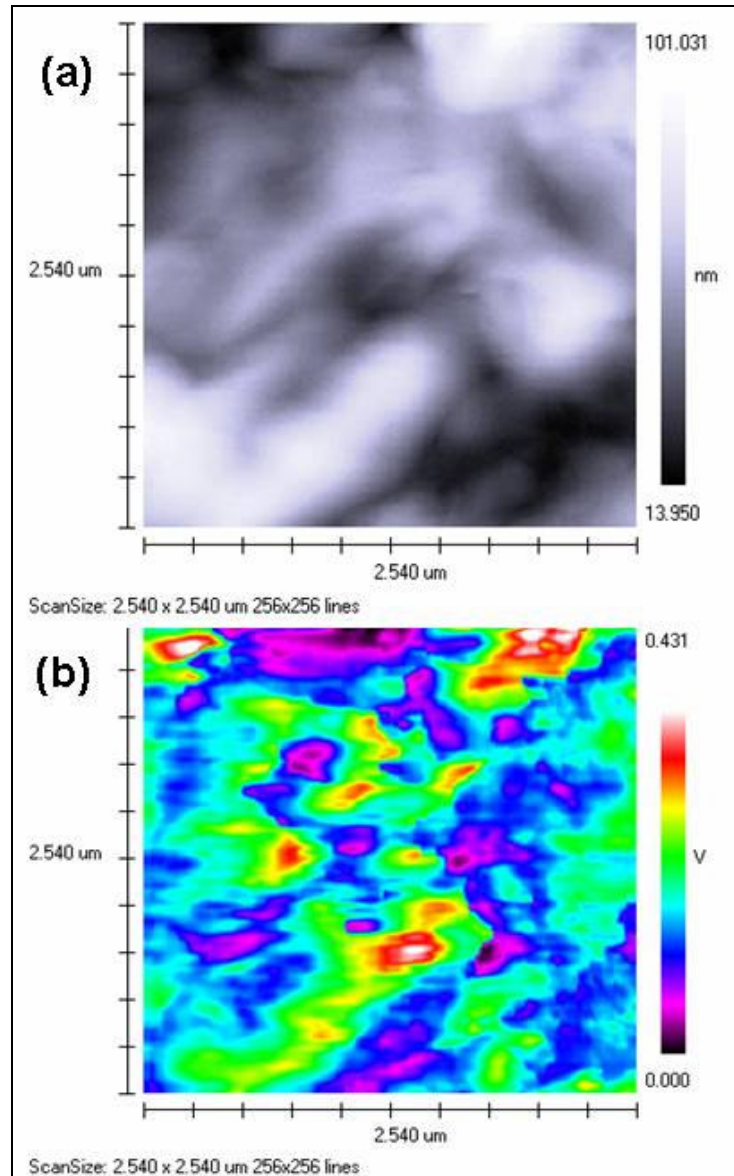
Fig. 4. Illustration of the correlation between (a) the surface topography and (b) electrical surface properties of diamond films

The dependence of the emission current (I) on the applied electrical field (E) for undoped and N-doped DF's is shown in Fig. 5. As can be seen the I-E characteristics of undoped DF's differ significantly from the results for N-doped films. Although the range of magnitude of the emission current for both kind of diamond films is almost the same, the values of the electrical field for which the high current is reached are definitely different. These results indicate that N-doped diamond films should have better field emission properties due to the high current reached at low value of the electric field.

The results of the electron emission were analyzed using Fowler-Nordheim model. If the electron emission is controlled by the tunneling mechanism, Fowler-Nordheim plot $\ln (I/E^2)$ versus $1/E$ presents almost a straight line with negative slope. The recorded I-E data obtained for DF specimens (Fig. 5a) were used to generate F-N plots shown in Fig. 5b. Field emission properties were characterized by the parameters such as turn-on electric field and effective work function. The turn-on field was defined by the intersection of two straight lines extrapolated from the low-voltage (thermionic and leakage currents) segment, and the high-voltage (cold emission current) segment of the F-N plots [37]. This indicates the beginning of the cold electron emission current (see Fig. 5). The effective work function φ_{ef} ($\varphi_{ef} = \varphi/\beta^{2/3}$) can be deduced from the F-N plots in cold emission region.

The calculated values of the turn-on electric field and effective work function were shown in Table I. Let us note that the emission turn-on field for the undoped diamond films is comparatively high for the system DF/p-Si and about two times lower for DF/n-Si system. The turn-on field value decreases to about 3 V/μm after nitrogen doping of diamond film. The value of the effective work function is relatively high for undoped DF's, while for N-doped films the effective work function is equal to about 0.04 eV. The important parameter for characterization of the properties of material for cold emission is the value of emission current at given electric field. The emission current close to about 1 nA is reached at the electric field equal to about 15 V/μm (DF/n-Si), 4 V/μm for N-doped films, and excesses 50 V/μm for DF/p-Si system.

The mechanism of electron emission from DF's is still not clear, but obtained results suggest that the cold emission from diamond, especially from N-doped diamond films may be enhanced by conductivity improvement. The increase of conductivity probably results both from the increase in concentration of charge carriers due to nitrogen-related donor states and from higher amount of disordered graphite-like states in the N-doped films. The later is confirmed both by Raman and ESR spectra discussed above [38].
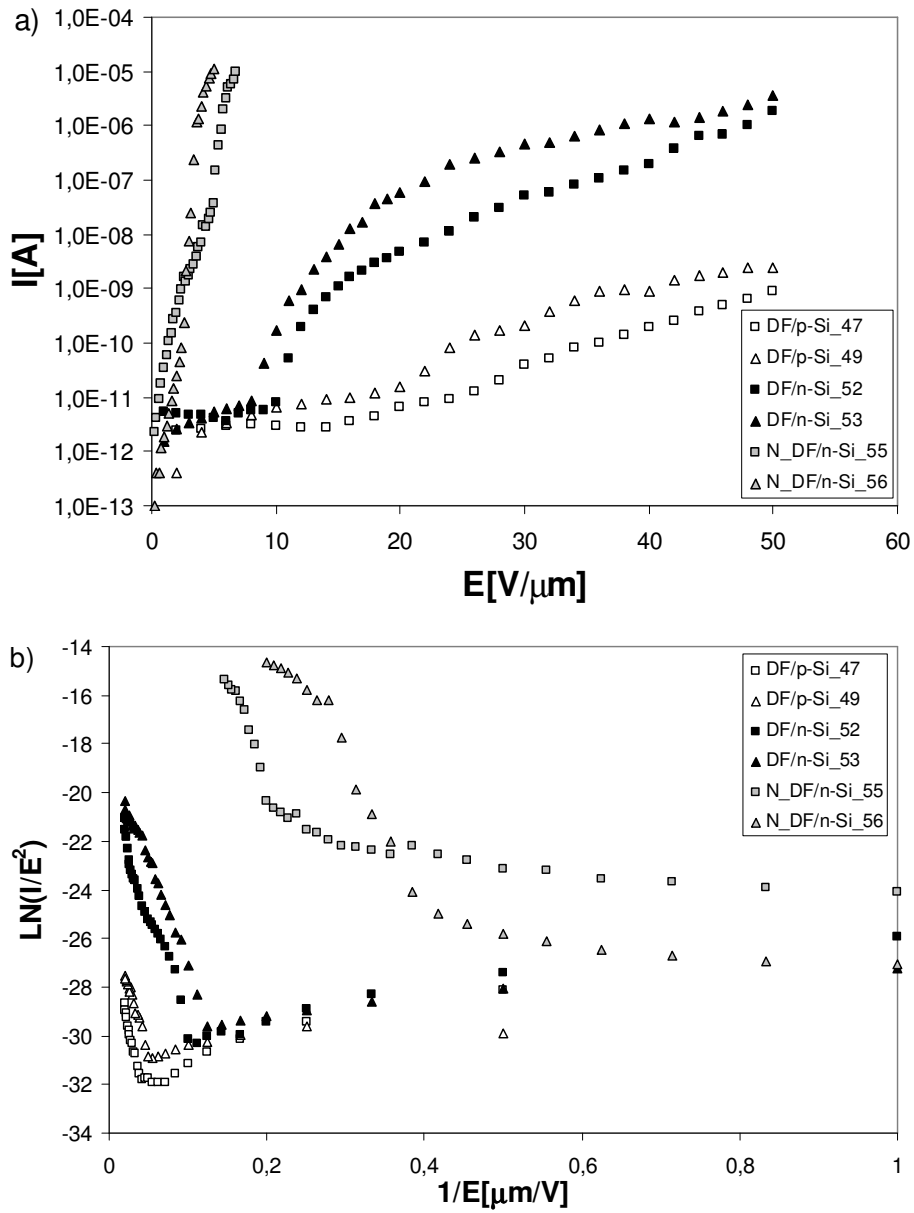
Fig. 5. Emission current vs. electrical field: (a) as I-E characteristics and
(b) Fowler-Nordheim plot

The electrons in the defective diamond films are effectively transported from the back of the diamond film to surface through the defect-induced energy bands by hopping conduction [39]. Therefore, the improved electron emission is observed from defective diamond films. The results in this study showed the nitrogen doping introduced the paramagnetic defects in the diamond film and increased the electron emission current.

4. CONCLUSIONS

This work reports the results of a series experiments on microcrystalline diamond films deposited by HF CVD method. The electron emission measurement confirms that diamond films with some graphite-like phase admixture show better field emission properties than the diamond films of good quality. The graphite-like regions play very important role, because as illustrating microphotography in Fig. 4 electron emission from this regions is more effective then emission from diamond crystallites. The current-voltage characteristics show a good fit to Fowler-Nordheim model. The emission turn-on fields are equal to about 20 V/μm, 10 V/μm and 3 V/μm for undoped DF/p-Si, undoped DF/n-Si and nitrogen doped diamond films in system N-DF/n-Si, respectively. It indicates that N-doping causes changes of diamond films properties which improve their emissive ability. The analysis of Raman and ESR spectra and F-N characteristics revealed that the diamond films with high-density defects more effectively emit the electrons at applied low electric fields.

Acknowledgments

REFERENCES

[1] **Graebner J.E., Jin S., Kammlott G.W., Herb J.A., Gardinier C.F.:** Nature **359** (1992) 401.
[2] **Bogdanov A.V., Vikulin I.M., Bogdanova T.V.:** Sov. Phys. Semicond. **16** (1982) 720.
[3] **Bachmann P.K., Nemanich R.J.:** Diamond. Relat. Mater. **7** (1998) 612.
[4] **Obraztsov A.N., Zakhidov Al.A.:** Diamond Relat. Mater. **13** (2004) 1044.
[5] **Robertson J.:** Thin Solid Films **296** (1997) 61.

[6] **Carey J.D., Forrest R.D., Khan R.U.A., Silva S.R.P.:** Appl. Phys. Lett. **77** (2000) 2006.

[7] **Kang W.P., Wisitsora-at A., Davison J.L., Kerns D.V., Li Q., Xu J.F., Kim C.K.:** J. Vac. Sci. Technol. B **16** (1998) 684.

[8] **Roberson J.:** J. Vac. Sci. Technol. B **17** (1999) 659.

[9] **Forbes R.G.:** Solid State Electronics **45** (2001) 779.

[10] **Xu N.S., Tzeng Y., Latam R.V.:** J. Phys, D: Apel. Phys. **26** (1993) 1776.

[11] **Xu N.S., Latam R.V., Tzeng Y.:** Electron Lett. **29** (1993) 1596.

[12] **Zhu W., Kochanski P.G., Jin S., Seibles L.,** J.Vac. Sci. Technol. B **14** (1996) 2011.

[13] **Gröning O., Küttel O.M., Gröning P., Schlapbach L.:** J. Vac. Sci. Technol. B. **17** (1999) 1064.

[14] **Geis M.W., Twichell J.C., Macaulay J., Okano K.:** Appl. Phys. Lett. **67** (1995) 1328.

[15] **Arora S., Vankar V.D.:** Thin Solid Films, **515** (2006) 1963.

[16] **Fabisiak K., Banaszak A., Kaczamarski M.:** Functional Material **10** (2003) 117.

[17] **Fowler R.H., Nordheim L.:** Proc. Roy. Soc. Lon. Ser. *A*. **119** (1928) 173.

[18] **Knight D.S., White W.B.:** J. Mater. Res. **4** (1989) 385.

[19] **Fabisiak K., Patyk J.K., Rozpłoch F.:** Acta Physica Polonica A **87** (1995) 145-149.

[20] **Gruen D.M.,** Annu. Rev. Mater. Sci. **29** (1999) 211.

[21] **Li J.J., Zheng W.T., Gu C.Z., Jin Z.S., Gu G.R., Mei X.X., Mu Z.X., Dong C.:** Appl. Phys. *A* **81** (2004) 357.

[22] **Kalish R., Lifshitz Y., Nugent K., Prawer S.:** Appl. Phys. Lett. **74** (1999) 2936.

[23] **Sails S.R., Gardiner D.J., Bowden M., Savage J., Rodway D.:** Diamond Relat. Mater. **5** (1996) 589.

[24] **Ralchenko V.G., Smolin A.A., Pereverzev V.G., Obraztsova E.D., Korotoushenko K.G., Konov V.I., Lakhotkin Yu.V., Loubnin E.N.:** Diamond Relat. Mater. **4** (1995) 754.

[25] **Toyama T., Koide Y., Murakami M.:** Diamond Relat. Mater. **11** (2002) 1897.

[26] **Loubser J.H., Van Wyk J.A.:** Rep. Progr. Phys. **41** (1978) 1203.

[27] **Smith M.J.A., Angel B.R., Emmons R.G.:** Nature **210** (1966) 692.

[28] **Fabisiak K., Rozpłoch F.:** Appl. Magn. Reson. **12** (1997) 53.

[29] **Fanciulli M., Moustakas T.D.:** Phys. Rev. B. **48** (1993) 1498.

[30] **Loubser J.H.N., Wyk J.A.V.:** Rep. Prog. Phys. **41** (1978) 1201.

[31] **Samlenski R., Haug C., Brenn R., Wild C., Rocher R., Koidl P.:** Diamond Relat. Mater. 67 (1996) 947.

[32] **Smith W.V., Sorokin P.P., Gelles I., Lasher G.J.:** Phys. Rev. **41** (1959) 1546.

[33] **Iakoubovskii K., Adriaenssens G.J.:** Diamond Relat. Mater. **9** (2000) 1349.

[34] **Banaszak A., Fabisiak K., Kaczorowski M., Kozanecki M.:** Cryst. Res. Technol. **41** (2006) 535.

[35] **Jarzynska D., Znamirowski Z., Starga E., Gotszalk T., Woszczyna M., Fabisiak K.:** Proc. International Conference Vacuum and Plasma Surf. Engineering, 26-27th October 2006, Liberec-Hejnice, Czech Republic, Abstract p. 25.

[36] **Okano K., Koizumi S., Ravi S., Silva P., Gehan A., Amaratunga J.:** Nature **381** (1996) 140.
[37] **Luo J.Y., Liu K.S., Lee J.S., Lin I.N., Cheng H.F.:** Diamond Relat. Mater. **7**. (1998) 704.
[38] **Orzeszko S., Bała W., Fabisiak K., Rozpłoch F.:** Phys. Stat. Sol.(a). **81** (1984) 579.
[39] **Staryga E., Bąk G.W.:** Diamond Relat. Mater. **14** (2005) 23.

EMISJA POLOWA I CHARAKTERYSTYKA MIKROSTRUKTURY WARSTW DIAMENTOWYCH NANOSZONYCH PRZY UŻYCIU METODY HF CVD

Streszczenie

Przeprowadzono badania emisji polowej z warstw diamentowych osadzonych przy użyciu metody HF CVD na podłożach krzemowych typu n i p. Charakterystyki emisyjne analizowano na podstawie modelu Fowlera-Nordheima. Wytworzone warstwy scharakteryzowano przy użyciu następujących metod: SEM, AFM, spektroskopii Ramana i Elektronowego Rezonansu Spinowego (ESR). Przeprowadzono dyskusję wyników, wskazując na korelację pomiędzy wynikami emisji polowej a koncentracją centrów paramagnetycznych oraz widmami ramanowskimi badanych warstw diamentowych. Zaobserwowano znaczną poprawę właściwości emisyjnych heterostruktur, w których warstwa diamentowa domieszkowana została azotem. Dla układów z niedomieszkowanymi warstwami diamentowymi wartość natężenia pola włączeniowego wynosiła około 10 V/μm, zaś dla domieszkowanych azotem warstw diamentowych wartość ta równa jest 3 V/μm. Różnice w wartościach pola włączeniowego dla odpowiednich układów wynikają prawdopodobnie z różnej zawartości materii grafito-podobnej w badanych warstwach diamentowych. Warstwy domieszkowane azotem są silnie zdefektowane i zawierają znaczną ilość materii grafitopodobnej.