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Investigation of the effect of hydrogen content on the conductivity of nanocrystalline diamond films

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The results are presented for investigation of electrical conductivity of nanocrystalline diamond (NCD) films with thickness of 0.5−0.6 microns grown on silicon Si(100) substrates by the CVD method using methane−hydrogen and methane−hydrogen−oxygen mixtures. By the method of heating in vacuum with using hydrogen analyzer AB-1, the concentration of hydrogen in the studied films was determined and the relationship between the content of hydrogen in the NCD film and its conductivity was estimated. It has been shown that high−temperature processing in vacuum at the temperature of 600°C leads to desorption of hydrogen from the films and to a significant increase in their resistance.

Keywords: nanocrystalline diamond, thin diamond films, electrical properties of films, hydrogen content.

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The interest to studying nanocrystalline diamond (NCD) films grown by the CVD method is to a high extent caused by a wide field of their application [1]. Such films possess high thermal conductivity, chemical and radiation resistance, high emission characteristics, ability to be doped, and, therefore, they are of interest in creating microelectronic devices, microelectromechanical structures (MEMS) and protective coatings [2–5]. Doped NCD films having essential conductivity and growing in gas mixtures after adding nitrogen or boron or phosphorous are being intensely investigated; the investigation results are vastly presented in literature [2–5]. At the same time, highly resistant undoped NCD films are less studied. These films are of great interest since they may be used as dielectric layers in high−frequency MEMS switches [6]. Such films with controllable leakage current can, for instance, eliminate the problem of charging that exists in devices with oxide dielectric layers used in high−frequency capacitive switches. Undoped NCD films may possess good insulation properties, high thermal conductivity, and resistivity close to the silicon dioxide film resistivity that is of about $10^{14}\,\Omega\cdot$cm [7].

Our work [8] has shown that electrical characteristics of undoped NCD films are strongly affected by the synthesis conditions and gas mixture composition that essentially govern the crystallite sizes and share of the non-diamond phase (sp^2) in the film. In their nature, an NCD film is nothing else but a defective diamond whose conductivity depends on both the number of defects and ionizable sites directly in the crystallites and the presence of non-diamond carbon at the crystallite boundaries. It is known that it is possible to essentially reduce the non-diamond carbon percent in the film and, hence, the film electrical conductivity, by properly selecting the CVD synthesis conditions [8]. At the same time, if hydrogen−methane mixture is used, hydrogen penetrating inside the NCD film can also enable retention of the electrical conductivity of the deposited film. The goal of this work is to estimate the hydrogen content in high−resistivity thin undoped NCD films grown under the same conditions as in [8] and also to investigate the hydrogen influence on the conductivity of such films. From literature there are known examples of determining the hydrogen concentration in films by the method of elastic recoil detection [9] that is quite laborious. In this work, we applied a simple technique for determining the hydrogen concentration in the films, which involves a commercial hydrogen analyzer AB-1.

For studying, there were prepared samples of NCD films deposited on silicon substrates Si (100) $20\times20\times0.5$ mm in size with a layer of detonation nanodiamond particles of 5 nm sizes preliminary applied on the substrates in an ultrasonic bath; this layer played a role of the nucleation centers. Density of the diamond nucleation centers reached the value of $10^{12}\,\text{cm}^{-2}$, which initiated formation of a coalescent uniform NCD film already at the thicknesses of ~ 100 nm. The films were grown from the gas phase in the microwave discharge plasma according to the procedure described in [8]. Three different compositions of the gas mixture were used in the experiments: hydrogen-methane mixtures with two different methane contents (8% and 0.5%) and a mixture of hydrogen, methane and oxygen. These mixtures allowed obtaining different films and estimating the effect of the crystallite sizes and

Table 1. Modes of the NCD films deposition

Samples	Composition of the gas mixture $H_2/CH_4/O_2$, sccm	Temperature of the substrate, °C	Power, kW	Pressure, Torr	Thickness of the film, nm
1 and 1*A*	200/16/0 (CH_4/H_2=8%)	710	2.2	35	560
2 and 2*A*	400/2/0 (CH_4/H_2=0.5%)	720	4.0	37	580
3 and 3*A*	400/2/0.4 (CH_4/H_2 = 0.5%, O_2/H_2=0.1%)	720	2.25	35	560

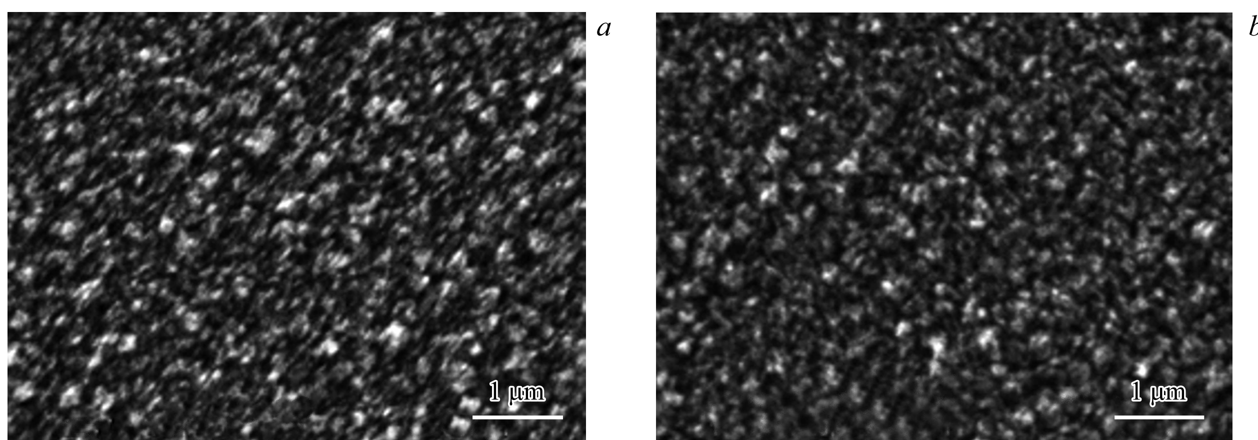

Figure 1. Surface microstructure of the NCD film grown in the CH_4/H_2 = 8% mixture prior to (sample 1) (*a*) and after (sample 1*A*) (*b*) annealing in the vacuum oven.

non−diamond phase content between them on the hydrogen embedding ability. As some of the experiments show [10], adding of oxygen into the gas mixture suppresses the hydrogen embeddability into the nanocrystalline diamond film. The realized conditions and parameters of the NCD film deposition modes are listed in Table 1. Each mode involved NCD film deposition for two samples simultaneously; one of the samples was further subjected to high−temperature processing in vacuum. Samples listed in Table 1 which are marked with letter *A* were annealed in vacuum (10^{-5} Torr) at high temperature (600°C) for an hour. The studies showed that in this case neither the film morphology nor Raman spectra underwent essential changes. Fig. 1 presents microphotos of the surface of an NCD film deposited in the hydrogen−methane mixture at CH_4/H_2 = 8% prior to and after annealing in a vacuum oven.

Hydrogen content in the samples under study was determined with mass-spectrometric hydrogen analyzer AB-1 at two extraction temperatures (T_1 = 350°C and T_2 = 700°C) according to the procedure described in [11]. It was found out that all the hydrogen was extracted at the temperature of 700°C from the silicon substrate free of NCD film (a reference sample), and its total content did not exceed 0.3 ppm. In experiments with NCD films on silicon substrates, the hydrogen content was typically considerably higher than this value. In addition, it is possible to assume that all the hydrogen is being removed from the silicon substrates during deposition of diamond films at the deposition temperature exceeding 700°C and, hence, does not contribute to measurements on NCD-films. As the reference for calibrating analyzer AB-1, state standard samples of new−generation aluminum alloys were used [12]. Table 2 lists the measurements of the hydrogen content in the samples prior to and after annealing.

Table 2 presents concentrations (Q_1 and Q_2) of hydrogen emitted from the studied sample at temperatures T_1 and T_2, respectively, and also the total amount (ΣQ) of H_2 emitted at two extraction temperatures. Table 2 shows that vacuum heating of the samples to 600°C led to significant decrease in the H_2 content in NCD films, which manifested itself in lower values of Q_1 for annealed films (marked with letter *A*). The H_2 content in non-annealed samples decreased with increasing temperature ($Q_1 > Q_2$). The amount of hydrogen embedded into an NCD film depended on the methane concentration in the mixture; besides, it decreased essentially if oxygen was added to the mixture. Thus, high-temperature processing of films grown with oxygen caused almost no changes in its content in the film.

Table 2. Measurements of hydrogen content in the NCD film

Sample	Annealing in vacuum	T_1,°C	Q_1, ppm	T_2, °C	Q_2, ppm	ΣQ, ppm
1	–	350	0.454	700	0.321	0.775
1*A*	600°C	350	0.042	700	0.115	0.157
2	–	350	0.476	700	0.233	0.709
2*A*	600°C	350	0.023	700	0.067	0.09
3	–	350	0.03	700	0.112	0.142
3*A*	600°C	350	0.043	700	0.1	0.143

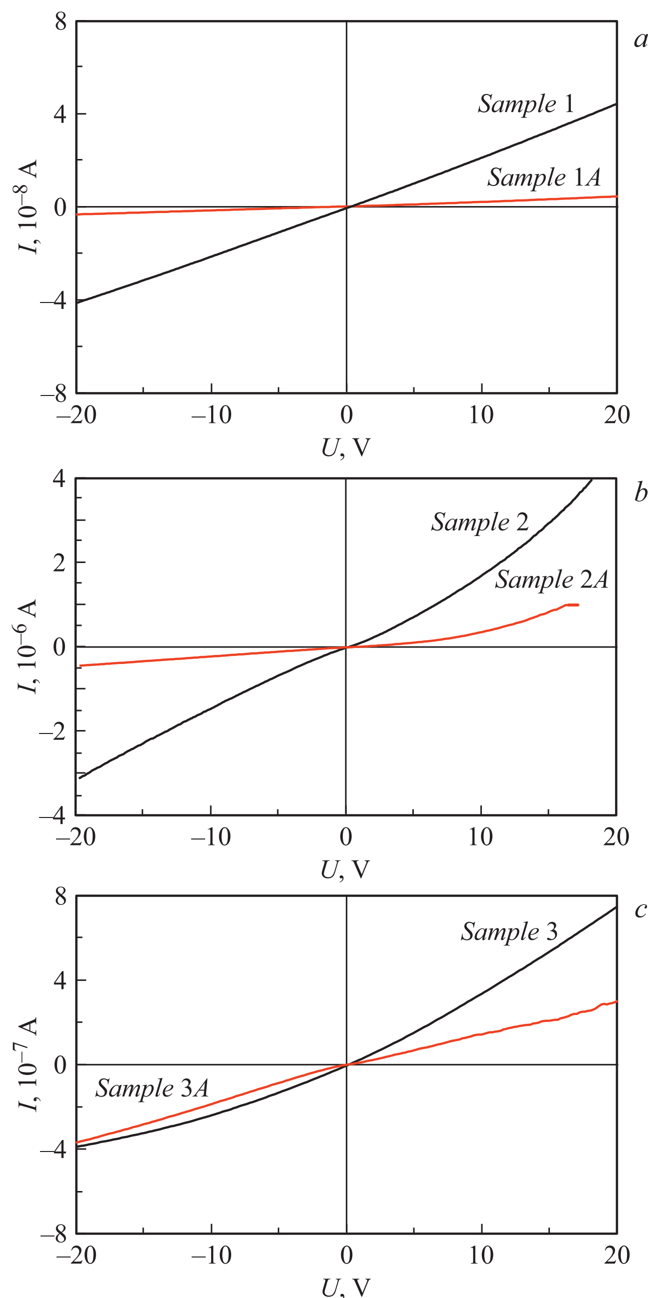

Figure 2. *a* — samples 1 and 1*A* ($CH_4/H_2 = 8\%$); *b* — samples 2 and 2*A* ($CH_4/H_2 = 0.5\%$); *c* — samples 3 and 3*A* ($CH_4/H_2 = 0.5\%$, $O_2/H_2 = 0.1\%$).

Notice also that, as shown in [11], hydrogen contained in diamond films is concentrated mainly on interfaces between crystallites. This was evidenced by relatively low measurements of the hydrogen binding energy in the film as compared to the C–H or C–C binding energy in the diamond structure. Therefore, the experimentally obtained H_2 concentration in the film was somewhat higher in the samples with higher content of the sp^2 phase (see values of ΣQ for samples 1 and 2).

At the next stage, resistance of the grown NCD films was measured prior to and after their thermal processing. The film resistance was measured by the two-probe method based on analyzing JV characteristics obtained with JV measuring device KEYSIGT B2901A in the range of ± 20 V. The measurements were performed according to the scheme „film surface contact–NCD film–conductive Si substrate (*n*–type) with an indium contact" described in details in [8]. JV characteristics of all the studied samples possessed typically a quasi-symmetric shape with a linear (ohmic) part in the given voltage range. Notice that symmetricity and linearity of the characteristics shape in a quite broad voltage range evidence for the ohmic nature of the contacts. JV characteristics of the studied samples prior to and after their high–temperature processing in vacuum at 600°C are demonstrated in Fig. 2.

The presented figures show that high–temperature processing results in essential increase in the NCD film resistance. For instance, the film resistance obtained from the JV characteristic slope increased in transition from sample 1 to sample 1*A* from $R_1 = (2-3) \cdot 10^8\,\Omega$ to $R_{1A} = (4-5) \cdot 10^9\,\Omega$. The respective change for sample 2 was from $R_2 = 6 \cdot 10^6\,\Omega$ to $R_{2A} = 2.3 \cdot 10^7\,\Omega$, that for sample 3 was from $R_3 = 3.8 \cdot 10^7\,\Omega$ to $R_{3A} = 6.5 \cdot 10^7\,\Omega$. These data correlate well with measurements of the hydrogen content in the films (Table 2), namely, a decrease in the hydrogen content in the film due to high–temperature annealing is accompanied by a decrease in the film conductivity. Notice also that addition of oxygen to the hydrogen–methane mixture led to a decrease in the H_2 content in the NCD film and, hence, to an increase in the film resistance. Because of a lower H_2 content in such a film, its resistance variation due to annealing was not so significant (Fig. 2, *c*). Such an oxygen influence may be qualitatively explained by modification of the

plasma−chemical processes in plasma, emergence of O and OH radicals that participate in graphite etching (along with hydrogen atoms) and react with carbon radicals CH and CH_2 with reducing the concentration of radicals responsible for embedding hydrogen into the film [13].

Thus, the paper demonstrates direct determination of the hydrogen concentration in NCD films by using conventional commercial equipment. It has been shown that hydrogen embedded in an NCD film during its growth essentially affects the film electrical properties, namely, increases its electrical conductivity. The hydrogen concentration in films grown in the hydrogen−methane mixture increases with the methane content and, hence, with the percent of the non−diamond phase in the films. High−temperature processing in vacuum promotes the hydrogen extraction from the films and, hence, an increase in their resistance. Adding a small amount of oxygen into the gas mixture leads to suppression of the hydrogen embedment into the film and allows obtaining high resistances without subjecting the film to high−temperature processing. The experiments have shown that it is possible to obtain undoped NCD films with different insulation characteristics by properly selecting the modes of film growth and post−growth processing.

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Conflict of interests

The authors declare that they have no conflict of interests.

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