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Electrical properties and Mott parameters of polycrystalline diamond films synthesized by HF CVD method from hydrogen/methanol gas mixture

AGNIESZKA BANASZAK-PIECHOWSKA[1], KAZIMIERZ FABISIAK[1], ELŻBIETA STARYGA[2], KAZIMIERZ PAPROCKI[1,*]

[1]Institute of Physics, Kazimierz Wielki University, Powstańców Wielkopolskich 2, 85-090 Bydgoszcz, Poland
[2]Institute of Physics, Technical University of Łódź, Wólczańska 219, 93-005 Łódź, Poland

The influence of diamond crystallinity and preferred orientation on electronic conductivity of synthetic diamond films grown by hot filament chemical vapor deposition (HFCVD) was investigated. The CVD diamond films of different morphologies and crystallite sizes varying from 36 nm to 67 nm, measured in $\langle 2\ 2\ 0\rangle$ direction were considered. The charge transport mechanism in the diamond samples was studied using temperature dependent DC conductivity measurements. The obtained results showed that in the temperature range of 90 K to 300 K charge transport is realized via Variable Range Hopping (VRH, $m = 1/4$) mechanism. Using VRH model, the Mott parameters were evaluated i.e. density of states at Fermi level $N(E_F)$ (0.22×10^{15} $eV^{-1}\cdot cm^{-3}$ to 1.7×10^{15} $eV^{-1}\cdot cm^{-3}$), hopping energy W (43.5 meV to 142.3 meV) and average hopping distance R (1.49×10^{-5}cm to 2.56×10^{-5}cm). It was shown that above mentioned parameters strongly depend on diamond film preferential orientation.

Keywords: *CVD diamond films; electrical conductivity; hopping conduction.*

1. Introduction

In recent years, diamond films have become a subject of intense research due to their exceptional mechanical, chemical, optical and electrical properties. The main reason that attracts researchers and scientists to these materials is also the possibility to modify their properties even after the deposition process, for example, by termination of their surfaces.

It is well known that the CVD polycrystalline diamond films may contain high concentration of defects which generate localized states (tail states) inside the energy gap of diamond. These localized states are associated with sp^2 hybridized carbon clusters (situated mainly at diamond grain boundaries) and sp^3 dangling bonds, a portion of which can be saturated by hydrogen atoms. It was already shown that hydrogen concentration in CVD diamond films depends on both sp^2/sp^3 hybridized C–C bonds and crystallite sizes as well [1].

The concentration of these states depends also upon the sp^2 hybridized carbon clusters and chemisorbed hydrogen atom concentration.

The localized (tail) states act as the charge carrier trapping centers creating also the space charge in the films. The defect states, associated with the dangling bonds, act as recombination centers and affect the lifetime of the charge carries [2, 3].

The both types of states, localized tail states and defect states, govern the electrical properties of the polycrystalline CVD diamond films.

Thus, the electrical properties of the polycrystalline diamond thin films depend on the electronic structures and the density of states inside the energy band gap of the diamond film.

The sp^3 bonding (hybridization) of carbon atoms gives rise to bonding (σ) and anti-bonding (σ^*) states, which respectively form

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[*]E-mail: paprocki@ukw.edu.pl

the conduction and valence bands separated by a wide band gap. The weak π-bonding between the sp^2 hybridized carbon atoms forms the bonding (π) and anti-bonding (π^*) states which lie inside the energy gap. Due to amorphous structures, these π-π^* energy states are spread into the band gap region called the band tail states [4].

It is already known that diamond surface terminated by hydrogen exhibits a high p-type conductivity, while diamond in bulk remains insulating [5, 6]. Kawarada et al. [7] attributed conducting mechanism to the hydrogen atoms terminating diamond surface which can modify surface energy states. It is possible that hydrogen atoms diffuse into the subsurface region of the diamond films giving contributions to the high surface conductivity, as it has been reported by Hayashi et al. [8] and Hoffman et al. [9]. The role of the hydrogen atoms and their influence on the electrical conductivity of diamond films is the subject of intense research but the conduction mechanism of hydrogen-terminated diamond film still requires explanation.

In the published literature one can find only few articles dedicated to the study of electrical transport mechanism in the undoped microcrystalline diamond films. For example Gan et al. [10] reported results of systematic study of the changes in the structural and electrical characteristics of nominally undoped diamond films using co-deposited samples with different thicknesses, de Oliveira et al. [11] investigated the influence of B doping level on the electronic conductivity and resistivity properties of microcrystalline diamond films grown by HFCVD method. Contribution of hopping mechanism to electrical conductivity was studied also by a Russian group using impedance spectroscopy [12].

The dark conduction properties of polycrystalline CVD diamond after ion implantation and subsequent annealing were investigated by Trajkov et al. [13]. The obtained results were consistent with the model developed by Baskin et al. [14].

The present study is focused on DC electrical characterization of (HFCVD) diamond, performed at different temperatures i.e. I-V-T characteristics performed on diamond films having similar thicknesses.

It is crucial to select an appropriate thickness since the electrical and microstructural properties of CVD diamond are thickness dependent because of the columnar structure of the films. The crystallite sizes and preferred orientation of diamond films studied in this work were determined on the basis of XRD spectra.

The study of diamond film properties is important for further optimizing and control diamond film fabrication technology. The dependence of electrical conductivity upon the temperature gives valuable information about the structural defects and the localized states in polycrystalline CVD diamond films and provides essential information about the conduction mechanism in CVD diamond layers.

2. Experimental

The microcrystalline diamond films (MCD) were grown using HFCVD (Hot Filament CVD) system employing the gas mixture of H_2/CH_3OH with the flow rate ratio of 100 sccm (standard cubic centimeter per minute). The parameters of the synthesis process of the diamond films are listed in Table 1.

Before starting the CVD diamond growth process, the n-type (1 1 1) Si substrate was mechanically polished (10 min) with a diamond paste (0.2 μm grain size) and then it was placed for 30 min in ultrasonic bath containing nano/micro-diamond powders dispersed in methanol. Finally, after the mechanical treatment, the substrate was ultrasonically cleaned for 5 min in alcohol and acetone.

The morphological and structural properties of synthesized polycrystalline diamond films were characterized using XRD (DRON4 with CuKα radiation) and scanning electron microscope (SEM, JSM-820).

The electrical characteristics were measured in the heterostructure configuration i.e. the gold contacts were evaporated on the surface of the diamond

Table 1. Technological parameters of the studied layers.

Sample	(a) MCD-2.3	(b) MCD-2.5	(c) MCD-2.7
Methanol concentration	2.3 vol.%	2.5 vol.%	2.7 vol.%
Filament temperature		2300 K*	
Substrate		(1 1 1) n-type Si	
Substrate temperature		1010 K**	
Gas flow rate		100 sccm	
Total gas pressure		0.9 Pa	
Growth time		4 h	

*measured using pyrometer, ** measured using thermocouple

film and the backside of n-type Si substrate. Such contacts were chosen because, according to Rodrigues [15], Kawarada [16] and Ye et al. [17], the gold/diamond contacts are nearly ohmic. The measurements were performed in temperature range of 90 K to 300 K using Keithley type 6485 Picoammeter.

3. Results and discussion

3.1. SEM and XRD measurements

Fig. 1 shows the SEM pictures of the morphologies and the corresponding diffraction patterns for diamond samples studied within present work.

As it is observed in Fig. 1, the surface morphologies of the diamond are not very different. Apparently, a typical microcrystalline character of the diamond film is observed. The film surfaces are rather rough, with a pyramidal morphology dominated by clearly faceted crystals, whose size reaches 0.3 μm to 1.8 μm, together with many smaller grains interspersed between the larger grains. The careful analysis of the picture presented in Fig. 1a (MCD-2.3) indicates that this diamond film has slightly bigger crystallites in comparison with others shown in Fig. 1b and Fig. 1c.

However, the structure of the diamond films investigated by XRD diffraction indicates essential differences. The XRD patterns of these films clearly show the reflections from the planes (1 1 1), (2 2 0), (3 1 1) and (3 3 1). The preferred orientation of crystallites in the films was quantitatively evaluated from X-ray diffraction spectra (Fig. 1) using texture coefficient, $T_{C(hkl)}$ [18, 19]. The most pronounced reflections are reflections from (2 2 0) planes. The results of detailed analysis of XRD spectra are summarized in Table 2. The crystallite sizes were calculated for (2 2 0) reflection, as the most pronounced reflection, and for comparison for (1 1 1) reflection as the least intense reflection.

The results of XRD analysis show that even a small increase of methanol concentration in working gas causes essential changes in crystalline structure (the crystallite sizes) and also has an influence on preferential growth direction and, in consequence, should also have influence on the other physical properties of the diamond films.

3.2. DC-conductivity

Fig. 2 presents the I-V-T characteristics of Au/diamond/n-Si/Au heterojunction measured in the voltage range of −5 V to +5 V at different temperatures. This device shows straightening properties and has a temperature dependent DC conductivity that increases with the increase in temperature, indicating semiconducting behavior.

The information about the transport mechanism through the polycrystalline diamond film may be obtained from the analysis of the forward part of J-V characteristics at different temperatures.

Fig. 3 shows the examples of J-V characteristics in the forward direction of Au/diamond/n-Si/Au heterojunction recorded at three different temperatures.

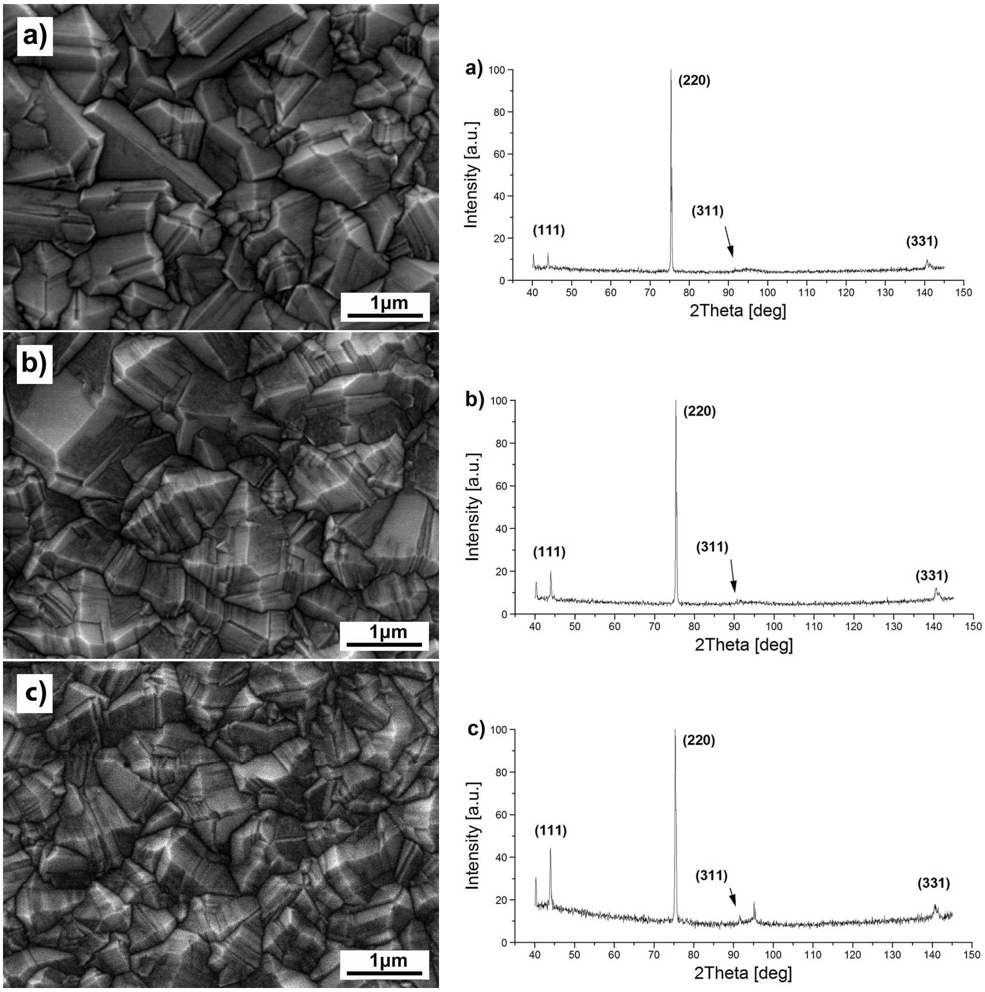

Fig. 1. SEM pictures and the corresponding normalized XRD patterns of investigated films (a) MCD-2.3, (b) MCD-2.5 and (c) MCD-2.7.

Table 2. The crystalline parameters of diamond films.

Sample	L(1 1 1) [nm]	L(2 2 0) [nm]	$T_{C(111)}$ [%]	$T_{C(220)}$ [%]	$T_{C(311)}$ [%]	$T_{C(331)}$ [%]
a) MCD-2.3	36	67	1.4	84.3	3.0	11.3
b) MCD-2.5	34	56	2.5	81.1	2.4	14.1
c) MCD-2.7	25	36	4.9	73.2	6.4	15.4

*The mean size L is the size of ordered domains and may be smaller than the grain size shown in Fig. 1.

As observed from this figure, there are two distinct regions in these characteristics: at low voltages, the slopes of ln(J) versus ln(V) plots are approximately equal to unity, while, at higher voltages above well-defined transition voltage (V_x), the slopes are approximately twice higher or more. These plots are typical of ohmic conduction for voltages below V_x.

The current density as a function of voltage at a given temperature is given by the following formula [20]:

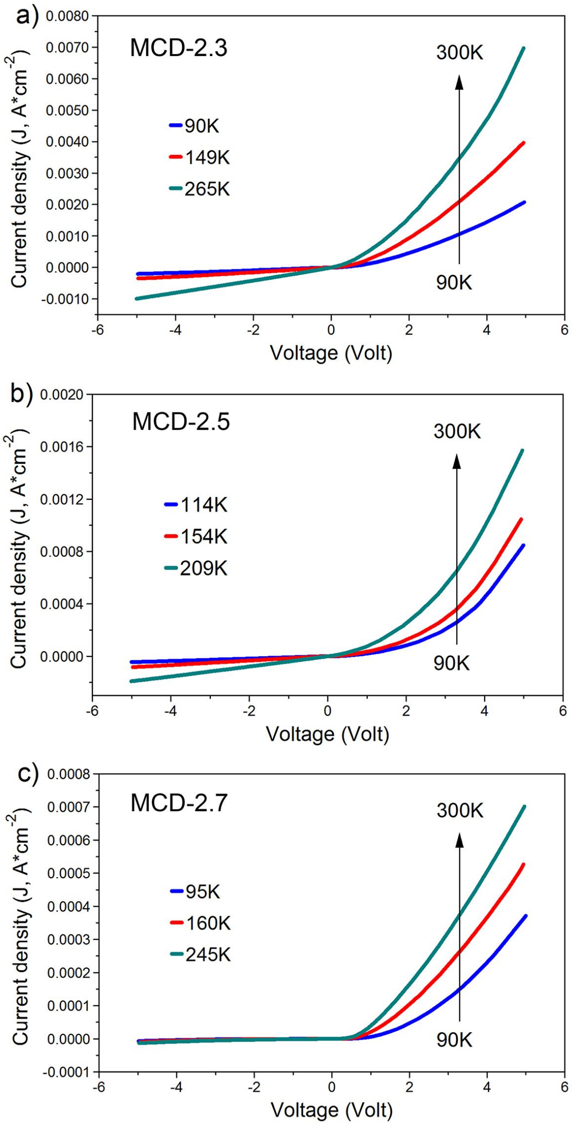

Fig. 2. I-V-T characteristics of investigated samples: (a) MCD-2.3, (b) MCD-2.5, (c) MCD-2.7.

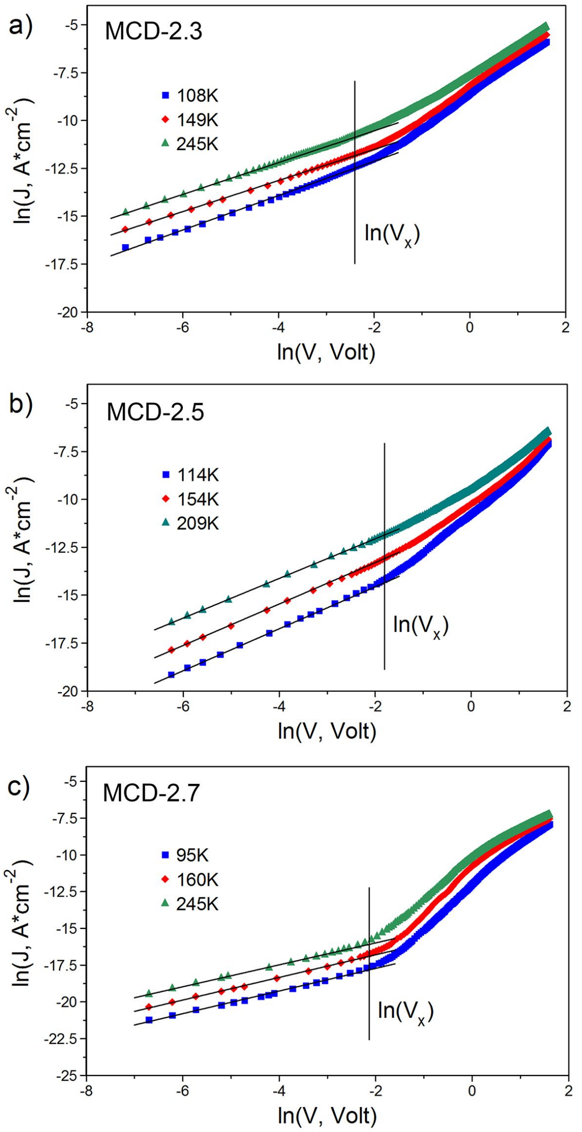

Fig. 3. The J-V characteristics in the forward direction of Au/diamond/n-Si/Au recorded at different temperatures for the samples: (a) MCD-2.3, (b) MCD-2.5, (c) MCD-2.7.

$$J = \sigma\frac{V}{d} + \frac{9}{8}\varepsilon\theta\mu_p\frac{V^2}{d^3} \tag{1}$$

where: μ_p is the mobility of dominant charge carriers, d is the thickness of CVD diamond film, ϵ is the permittivity taken as 5.04×10^{-11} F/m. The quantity θ is the ratio of free to trapped charges. The conductivity σ is described by formula [20]:

$$\sigma = q\mu_p N_v exp\left[-\frac{E_F}{kT}\right] \tag{2}$$

where: q is electric charge, E_F is the position of the Fermi energy level.

The first term of equation 1 describes the ohmic part (below V_x) of I-V characteristics which was used in present work for estimation of σ values for each temperature. For applied voltage greater than V_x, the slopes of ln(J) and ln(V) show that the forward biased current is SCLC (Space Charge Limited Current) controlled by a single dominating trap level and is described by second part of equation 1. The dependence of ln(σ) vs. 1/T is shown in Fig. 4a.

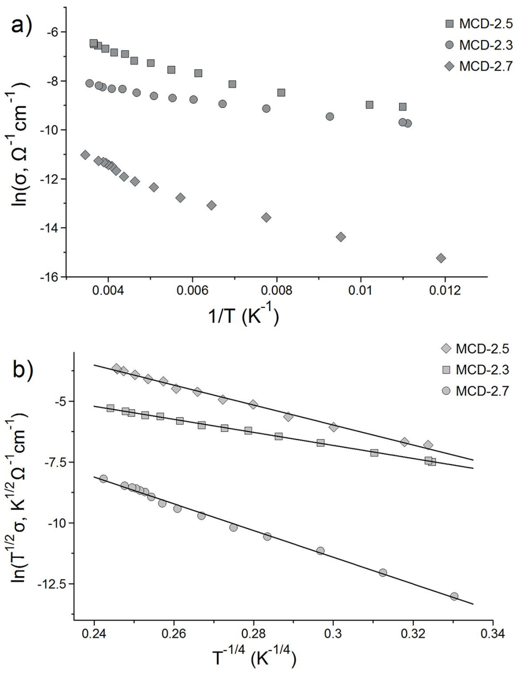

Fig. 4. The dependence of: (a) ln(σ) vs. T^{-1} for diamond films, (b) the dependence of ln($\sigma T^{1/2}$) vs. $T^{-1/4}$ for diamond films.

From the analysis of Fig. 4 it is evident that no fragment of the data follows a linear dependence, as expected for an activated process, indicating that the conduction in this temperature range is not thermally activated.

The data do, however, fit very well (Fig. 4b) the σ(T) dependence predicted by Godet [21, 22] for conductivity due to carriers hopping between energy levels within band-tails, present in amorphous semiconductors.

It was already observed that even in B-doped polycrystalline diamond films, the conduction mechanism is VRH (Variable Range Hopping) type mechanism in the temperature range below RT [11, 23].

At low temperatures, the hopping takes place within a few kT in vicinity of the Fermi level via localized states of density of N(E_F) given by formula [19, 20]:

$$N(E_F) = 2.12 \cdot 10^9 \cdot \sigma_{00}^3 \cdot T_0^{\frac{1}{2}} \quad \left[eV^{-1} \cdot cm^{-3}\right] \quad (3)$$

where σ_{00} and T_0 are constants estimated from the slope and intersection of linear fitting of the results shown in Fig. 4.

For a given temperature, the hopping distance R and hopping energy W can be calculated using following formulas:

$$R = \left[\frac{9}{8\pi\alpha kTN(E_F)}\right]^{\frac{1}{4}} \quad (4)$$

and:

$$W = \frac{3}{4\pi R^3 N(N_F)} \quad (5)$$

where α is the measure of the extent of localized function given by the formula:

$$\alpha = 22.52 \cdot \sigma_{00} \cdot T_0^{\frac{1}{2}} \quad \left[cm^{-1}\right] \quad (6)$$

The values of α, N(E_F), R, W and αR were calculated and listed in Table 3.

From a quick analysis of the obtained data in Table 2, it can be observed that the estimated Mott parameters depend on crystalline structure i.e. crystallite sizes and their preferred orientation in diamond films and are described by the texture coefficients T_C.

According to Mott model of variable range hopping conduction, the value of the hopping energy (W) and the value of the product (αR) must have values greater than (kT) and unity respectively [24, 25]. The results in Table 2 are in good agreement with Mott model because those conditions are satisfied.

A few reports exist that discuss different mechanisms to explain the electrical conduction properties of microcrystalline diamond films. Landstrass et al. [26] proposed that the conduction transition they observed at temperatures above RT was caused by the movement of hydrogen and other defects from electrically active deep levels to non-active sites during annealing. Mori et al. [27] suggested the existence of a surface conductive layer combined with chemical absorption and oxidation.

Table 3. The estimated Mott parameters of CVD diamond films.

Sample	α [cm^{-1}]	N(E$_F$) [eV^{-1}·cm^{-3}]	R [cm]	W [meV]
a) MCD-2.3	1.68×10^5	1.66×10^{15}	1.49×10^{-5}	43.5
b) MCD-2.5	2.01×10^5	7.14×10^{14}	1.76×10^{-5}	60.7
c) MCD-2.7	1.47×10^5	2.21×10^{14}	2.56×10^{-5}	142.3

Werner et al. [28] presented space charge limited currents as origins for the nonlinear increase of the conduction with temperature.

Spectroscopic impedance study of nanocrystalline diamond films performed by Ye et al. [17] and by Paprocki et al. [29] identified the grain interior and grain boundary contributions to the electrical conductivity of the diamond films. At temperatures below 250 °C they observed a single semicircular response of the Cole-Cole plots attributed to the diamond grain interior. A secondary semicircular response appeared above 250 °C and can be ascribed to the contribution from intergrain boundaries.

The obtained values of average hopping distance and small hopping energy W (Table 3) indicate that the conduction takes place by hopping between localized states in diamond grain interior which is in agreement with the earlier observation [17, 30, 31].

4. Conclusions

The polycrystalline diamond films deposited on polished n-type Si (1 1 1) substrates have been synthesized by HFCVD using alcohol and hydrogen.

SEM and XRD measurements confirmed that we have obtained diamond films having ⟨2 2 0⟩ preferred orientation and characterized by grain sizes in the range of 36 nm to 67 nm in ⟨2 2 0⟩ direction.

During DC conductivity investigation it was established that in low electric fields, when the temperature is less than 300 K, charge transport occurs through non-activated hopping, which has been confirmed by the small values of activation energies.

In the considered temperature range, the electrical charge transport occurs by variable range hopping mechanism via localized states near Fermi energy level which is the dominant mechanism. The obtained electrical characteristics in this temperature region have been successfully analyzed using Mott VRH model. The density of localized states near the Fermi level N(E$_F$) shows decreasing tendency, i.e. decreases with decreasing texture coefficient $T_{C(220)}$, reaching the values of 1.7×10^{15} eV^{-1}·cm^{-3} for $T_{C(220)} = 84$ % and the value of 2.2×10^{14} eV^{-1}· cm^{-3} for $T_{C(220)} = 73$ %. The average hopping energy W reaches the values in the range of 43.5 meV to 142.3 meV and depends on crystallite sizes, i.e. increases with decreasing crystallite average sizes.

The data from Table 2 show that the Mott conditions, i.e. $W > kT$ and $\alpha R > 1$ are fulfilled, indicating that the obtained results obey Mott law and are in agreement with variable hopping conduction mechanism in the studied temperature range.

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