1. Introduction

The diamond layers grown by chemical vapor deposition (CVD) have become recently the subject of extensive studies mainly due to their unique combination of thermal, mechanical, and optoelectronic properties. However, the polycrystalline nature of the CVD diamond layers is a bottleneck in the construction of diamond-based electronic devices. Another challenge is the presence of graphitic and nondiamond impurities co-deposited during the growth of diamond layers. On the other hand, the nondiamond impurities, occurring mainly at the grain boundaries, may introduce localized states in the energy gap, which result in modifying the electrical transport mechanism [1–4].

In this work we show results of measurements of the bulk electrical dc conductivity of the polycrystalline diamond layers grown at different deposition pressure. The RT conductivity measurements, current–voltage (I–V) characteristics obtained for three representative samples of the CVD diamond layers of different crystalline quality and different concentrations of nondiamond phase.

The variation of $\sigma_{300}$ conductivity and density of states at the Fermi level $N(E_F)$ are attributed to the chemically bonded H-atoms in the diamond structure.

2. Experimental

The diamond layers have been deposited on the $n$-type Si substrate using home-made HF CVD reactor described elsewhere [5]. The gases flow rates were controlled by calibrated mass flow meters. The tungsten filament temperature was measured by Optiris CT ratio 1M optical pyrometer while the substrate temperature was controlled by PtRh10-Pt thermocouple. The diamond synthesis was carried out using mixture of methanol (3 vol.%), hydrogen (97 vol.%) at the flow rate of 150 sccm (standard cubic centimeter per min). The all process parameters are summarized in Table I.

The scanning electron microscopy (SEM) microscope type JSM-820 was used to study the morphology of the obtained diamond layer. The Raman spectra were recorded using Renishaw InVia Raman spectrometer equipped with argon laser operating at 488 nm line using an excitation source. X-ray diffraction spectra were recorded by type Dron-4a X-ray diffractometer, working with a step of 0.05 degree.

3. Results and discussion

The SEM photos of morphologies of diamond layer deposited at different pressures are presented in Fig. 1.

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The estimated thicknesses of the layers were in the range from 10.2 to 10.6 \( \mu m \). As it is seen the obtained morphologies only slightly depend on the working gas pressure. The diamond layer synthesized at 20 mbar is characterized by microcrystalline grains exceeding 1 \( \mu m \) in size while the remaining diamond layers are composed of microcrystalline grains smaller than 1 \( \mu m \). It means that the working gas pressure has not an essential influence diamond layers morphologies.

Nevertheless, the SEM studies are in agreement with the Raman spectroscopy measurements (Fig. 2 and Table II). The presented Raman spectra of the diamond layers consist of sharp, narrow diamond peak at around 1332 cm\(^{-1}\) and broad G-band peaked at 1530–1560 cm\(^{-1}\) [6].

The Raman peaks (diamond and G-band) are superimposed on a broad luminescence background inclined at different angles. The numerical deconvolution of these spectra, according to the procedure described elsewhere [7] allows to estimate the following parameters of the Raman spectrum: FWHM of diamond line, \( sp^2/sp^3 \) ratio and slope \( m \) of photoluminescence background. The ratio of \( sp^2/sp^3 \) was calculated using formula given by McNamara et al. [7]. The obtained results are collected in Table II.

It is known that broad luminescence background arise from \( sp^2 \)-hybridized amorphous carbon admixture in diamond layers and its slope \( m \) can be used to determine the hydrogen content. The hydrogen content, associated with \( sp^2 \) carbon phase residing mainly on diamond grain boundaries, can be calculated from the normalized background slope \( m \) according to the empirically derived following equation [8]:

\[
H \ [\text{at.\%}] = 21.7 + 16.6 \log \left( \frac{m/I_G \ [\mu m]}{\mu m} \right),
\]

where \( m \) — slope of PL background of the Raman spectrum, \( I_G \) — integral intensity of the Raman G-band.

The slopes \( m \) and hydrogen concentrations in amorphous carbon phase admixture, which is small fraction of diamond layers, are collected in Table II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure [mbar]</th>
<th>FWHM [cm(^{-1})]</th>
<th>( sp^2/sp^3 ) [%]</th>
<th>( m ) [cm]</th>
<th>( H ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>20</td>
<td>7.2</td>
<td>0.30</td>
<td>1.9</td>
<td>7.5</td>
</tr>
<tr>
<td>Kf 230</td>
<td>60</td>
<td>7.5</td>
<td>0.49</td>
<td>7.1</td>
<td>11.6</td>
</tr>
<tr>
<td>Kf 217</td>
<td>100</td>
<td>8.8</td>
<td>0.53</td>
<td>10.2</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Results presented in Table II coincide with SEM images. Diamond films consisting of smaller microcrystalline grains show higher values of both the FWHM and the slope \( m \). In order to confirm the observation obtained from the Raman measurements the XRD diffraction was carried out. In Fig. 3 the main (111) and (220) peaks of each samples are presented. Unfortunately, XRD does not prove information on amorphous carbon admixture, which is a main problem in growing high quality diamond
films, but gives valuable information about diamond layers crystallinity.

The crystalline parameters i.e. the values of lattice spaces \( d \) and crystallite sizes \( D \) in \((111)\) direction were calculated from XRD spectra and are collected in Table III.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \Theta ) (deg)</th>
<th>( d ) (Å)</th>
<th>( D ) (nm)</th>
<th>( \Theta ) (deg)</th>
<th>( D ) (nm)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>43.98</td>
<td>2.0587</td>
<td>36.09</td>
<td>75.34</td>
<td>61.11</td>
<td>95.1</td>
</tr>
<tr>
<td>Kf 230</td>
<td>43.97</td>
<td>2.0594</td>
<td>30.16</td>
<td>75.35</td>
<td>56.30</td>
<td>84.0</td>
</tr>
<tr>
<td>Kf 217</td>
<td>44.04</td>
<td>2.0559</td>
<td>28.26</td>
<td>75.39</td>
<td>40.03</td>
<td>64.7</td>
</tr>
</tbody>
</table>

The XRD spectra show a single-phase crystalline diamond structure with noticeable differences in the intensities of the \((111), (220)\) diamond reflexes. As one can see, diamond deposited at 100 mbar is characterized by most intense \((220)\) reflex. Slightly shifted reflexes indicate on internal stress existing in diamond layer. In our case XRD spectra indicate on internal stress existing in diamond layer. In our case XRD spectra indicate on the (220) preferred orientation as it was determined by texture coefficient \( TC_{(hkl)} \) defined by the following formula [9, 10]:

\[
TC_{(hkl)} = \frac{I_{(hkl)}}{I_{(111)}} \sum_n I_{(hkl)}^n \frac{I_{(hkl)}}{I_{(hkl)}^0},
\]

where \( TC_{(hkl)} \) is the texture coefficient of the \((hkl)\) plane, \( I_{(hkl)} \) is intensity of the XRD peak corresponding to \((hkl)\) planes, and \( n \) is the number of preferred directions of growth (number of the diffraction peaks taken into account). \( I_{(hkl)}^0 \) denotes the intensity of the XRD peak reference of the randomly oriented crystallites and is assumed to be the same as the JCPDS-ICDD (or ASTM) powder diffraction files.

It should be noted that the Raman spectroscopy and XRD measurements clearly indicate on the differences between the samples, although their morphologies are very similar.

From the Raman and XRD measurements one can conclude that the studied diamond layers show noticeable differences in hydrogen concentration (slope \( m \) of background of the Raman spectra, \( G - \) band intensity) and in crystallites sizes \( D \) (XRD). It is well known that “as-grown” CVD polycrystalline diamond films exhibit \( p \)-type conductivity which can be removed by oxidation [11, 12]. Ballutaud et al. showed that the hydrogen concentration in polycrystalline diamond layer increases with increase of \( sp^2/sp^3 \) ratio, and increase with decrease of crystallite sizes [13] which is in agreement with our observations (see Tables II and III). According to Zhang et al. [14] chemically bonded hydrogen should govern the electrical properties of diamond layer. The \( I-V \) characteristics recorded for each sample in Au/n-Si/diamond/Au heterostructure configuration exhibit rectifying behavior (Fig. 4a).

As it is seen, each sample exhibits different rectifying properties of which depend on their structural properties. The analysis of \( I-V \) characteristic in forward direction (Fig. 4b) shows two different characters depending on the voltage regions. For the region of low voltages (< 0.7 V) the \( I-V \) characteristics show linear dependence of \( I \) vs. \( V \) as it shown in Fig. 5a. For higher voltages (> 0.7 V) the linear dependence is observed for the plot \( I \) vs. \( V^2 \), according to Eq. (3).

For higher voltages \( I-V \) forward current is controlled by space charge limited current (SCLC) mechanism and the dependence of \( I \) vs. \( V \) can be described by the following formula [15]:

\[
I = \frac{9}{8} \varepsilon \varepsilon_0 \theta \mu_0 \frac{V^2}{d^2},
\]

where \( \theta \) is the ratio of free to trapped charges at given temperature, \( \mu_0 \) — hole mobility, \( d \) - diamond layers thickness, \( \varepsilon \) — dielectric constant.

From the slope of the plots shown in Fig. 5a one can estimate the specific electric conductivity using the Ohm law. The estimated values of \( \sigma_{300} \) are collected in Table IV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \sigma_{300} ) (µS/cm)</th>
<th>( N(E_F) ) (nm(^{-3})meV(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>0.12</td>
<td>71</td>
</tr>
<tr>
<td>Kf 230</td>
<td>0.51</td>
<td>81</td>
</tr>
<tr>
<td>Kf 217</td>
<td>1.26</td>
<td>131</td>
</tr>
</tbody>
</table>
clearly suggest that acceptor states associated with chemically bonded hydrogen are mainly responsible for charge transport in undoped CVD diamond layers.

The exact nature of the hydrogen promoting shallow acceptor states remains still not fully explained and is worthy of further investigation.

Acknowledgments

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References