

# High hole mobility in boron delta-doped layers in diamond: why it is not achieved as yet and how it can be achieved

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The required parameters of nanometer boron  $\delta$ -doped layers in diamond for achieving high conductivity and hole mobility are calculated. The boron concentration in such layers has to be sufficient to achieve the insulator-metal phase transition, i.e. metallic conductivity. Then, it is demonstrated that taking into account valence band edge energy shift due to the presence of ionized boron atoms leads to the significant deepening of the potential well formed by the  $\delta$ -doped layer for holes. It results in much stronger hole confinement than it was expected before. Thus, it is predicted that a significant delocalization-induced increase of hole mobility can be achieved if metallic boron  $\delta$ -doped layer thickness is of order and smaller than 0.5 nm and compensation ratio does not exceed 42%.

**Keywords:**  $\delta$ -doped layers, nanostructures, diamond films chemically deposited from the vapor phase, hole mobility, insulator-metal phase transition.

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## 1. Introduction

The thin (on the order of a few nanometers thick) doped (usually with an acceptor admixture of boron) layers (so-called  $\delta$ -doped layers) in chemically deposited from the vapor phase (CVD) diamond have been obtained in many laboratories (see, for example, [1–10]). These layers are considered as a promising way to increase the mobility of charge carriers for various electronic applications, for example, to create high-frequency field-effect transistors based on the diamond CVD [11,12]. This increase is achieved due to the partial penetration of charge carriers enclosed in a potential well formed in the  $\delta$ -doped layer by parent ionized impurity atoms into the surrounding undoped diamond, i.e. their delocalization. As a result, the scattering of charge carriers on these atoms decreases, and the mobility increases.

$\delta$ -doped layers have long served to increase the mobility of charge carriers in conventional semiconductors [13]. But, unfortunately, for  $\delta$ -boron-doped layers in the diamond CVD, there was no increase in the mobility of holes due to their delocalization [14].

This article offers a possible answer to the question why the increase in hole mobility caused by delocalization has not yet been observed in  $\delta$ -doped layers in the diamond CVD. The article also suggests a possible way to achieve this increase. For this purpose, the next section discusses the results of measuring the mobility of holes in  $\delta$ -boron-doped layers in the diamond CVD and suggests a possible reason for the lack of an increase in this mobility due to delocalization. In Section 3 a method of numerical modeling of such layers is described. Its results are given in Section 4.

In Section 5 these results are confirmed by comparison with experimental data available in the literature. Further, a possible way to increase the mobility of holes due to their delocalization is proposed and confirmed by appropriate calculations.

## 2. Why is the increase in the mobility of holes caused by delocalization in boron-doped metal delta layers in the diamond CVD still not achieved?

All  $\delta$ -boron-doped layers in the diamond CVD described in the literature can be divided into two types: relatively weakly  $\delta$ -doped layers (with a concentration of boron atoms  $N_B < 5 \cdot 10^{20} \text{ cm}^{-3}$ ), in which the insulator-metal phase transition [15–19] does not occur at room temperature (non-metallic layers) and strongly  $\delta$ -doped layers ( $N_B > 5 \cdot 10^{20} \text{ cm}^{-3}$ ) in which this transition takes place (metal layers). In the first, there is a strong decrease in conductivity with a decrease in temperature, while the conductivity of the second practically does not depend on the temperature [14].

Non-metallic  $\delta$ -boron-doped layers, as a rule, cannot meet the needs of diamond CVD electronics. This is due to the fact that the ionization energy of individual boron atoms (the shallowest of the known doping impurities in diamond) is  $\sim 370 \text{ meV}$  [20], i.e. much more than the thermal energy at room temperature. Therefore, for  $\delta$ -doped layers with a low boron content at room and even elevated temperature, only a relatively small fraction of boron atoms is ionized and therefore supplies holes to the valence band ( $\sim 20\%$

according to calculations in [21] for  $\delta$ -doped layer 2 nm thick with a concentration of boron atoms  $5 \cdot 10^{18} \text{ cm}^{-3}$ , heated to 500 K). Despite the fact that  $\sim 95\%$  of these holes are located outside the  $\delta$ -doped layer and therefore have high mobility [21], its small thickness leads to a low concentration of valence band holes per unit of its area, insufficient to ensure high conductivity required for electronic applications. At the concentration of boron atoms in the  $\delta$ -doped layer  $> 5 \cdot 10^{19} \text{ cm}^{-3}$  (but still below the threshold of the insulator-metal phase transition  $5 \cdot 10^{20} \text{ cm}^{-3}$  at room temperature) the dominant conduction mechanism is the jumping of holes between localized states in the impurity zone [22]. Such a mechanism obviously cannot provide the high mobility of holes necessary for high-frequency electronics. This conclusion is confirmed by the experimental results of [23], where the mobility of holes was measured from 0.01 to  $0.1 \text{ cm}^2/(\text{V} \cdot \text{c})$ , and the results of the work [14], where for such layers, slightly greater, but still very low mobilities of holes were obtained,  $0.6\text{--}1 \text{ cm}^2/(\text{V} \cdot \text{c})$ .

Metal  $\delta$ -boron-doped layers provide sufficient conductivity for electronic applications and much greater mobility of holes than in the jump mode. This is due to the fact that all boron atoms in them are ionized and, consequently, supply holes to the valence band, where the mobility of holes is much greater than in the impurity zone. This conclusion is confirmed by the experimental results of [14], where the mobility of holes in metal  $\delta$ -boron-doped layers is measured, equal to  $3.6 \pm 0.85 \text{ cm}^2/(\text{V} \cdot \text{c})$ , i.e. more than 3 times greater than in non-metallic  $\delta$ -boron-doped layers in jump mode. But these values are still low. They are characteristic of the diamond CVD, strongly and uniformly doped with boron at a concentration of the latter  $5 \cdot 10^{20}\text{--}10^{21} \text{ cm}^{-3}$  (i.e., when the insulator-metal phase transition at room temperature has already occurred) [24], and do not increase with decreasing thickness of the  $\delta$ -doped layer up to 2 nm, so that the increase in hole mobility caused by delocalization is not observed [14].

A possible reason for this experimental fact is that the holes are bounded by a potential well associated with a  $\delta$ -boron-doped layer, even if its thickness is only 2 nm. This contradicts the numerical simulation in [25], where for a  $\delta$ -doped layer with a concentration of boron atoms  $5 \cdot 10^{20} \text{ cm}^{-3}$  and a thickness of 2 nm, a noticeable penetration of holes into the surrounding weakly (unintentionally) doped (with concentration of boron atoms  $10^{15} \text{ cm}^{-3}$ ) the diamond CVD is. The authors of this work calculated that even at zero temperature (when the delocalization effect is clearly weaker than at nonzero temperature)  $\sim 50\%$  of the holes are outside such a  $\delta$ -doped layer.

The reason for the discrepancy between the experiment and the theory probably lies in the fact that the study [25] did not take into account the dependence of the energy of the valence band edge on the concentration of ionized boron atoms. Meanwhile, it follows from the Pearson–Bardin formula [26–28] that the presence of ionized boron atoms increases this energy (at a fixed energy of the edge of the

conduction band, i.e. narrows the width of the band gap) by  $\alpha N_{B-}^{1/3}$ , where  $N_{B-}$  — concentration of ionized (negatively charged) boron atoms,  $\alpha \approx \frac{3e^2}{\epsilon} = 7.6 \cdot 10^{-8} \text{ eV} \cdot \text{cm}$  — semifenomenological constant,  $e$  — elementary charge,  $\epsilon \approx 5.7$  — static permittivity of diamond [20]. This increase in the energy of the valence band edge can be considered as a decrease in the ionization energy of the boron atom due to the presence of other ionized boron atoms compared to its value of 370 meV for an isolated boron atom given above.

Obviously, for a weakly (unintentionally) doped the diamond CVD surrounding a  $\delta$ -boron-doped layer, this correction is negligible (much smaller than thermal energy at room temperature) because of the very low concentration of boron atoms. But in the  $\delta$ -boron-doped layer itself (where the concentration of boron atoms  $N_B = 5 \cdot 10^{20} \text{ cm}^{-3}$ , i.e., high enough for an insulator-metal phase transition to occur and all boron atoms are ionized, so that  $N_{B-} = N_B$ ) this correction is  $\sim 0.6 \text{ eV}$  [29]. This value is more than 20 times higher than thermal energy at room temperature and is therefore very significant.

In fact, this correction leads to a significant deepening of the potential well formed by the  $\delta$ -boron-doped layer for holes. Therefore, the retention of holes there is much stronger, and their penetration into the surrounding weakly (unintentionally) doped diamond CVD is much weaker than predicted in [25]. This may be the reason why the experiments [14] did not measure the increase in the mobility of holes caused by delocalization for metal  $\delta$ -boron-doped layers even at their thickness 2 nm, whereas in numerical modeling conducted by the authors [14,25], this effect was predicted. Indeed, as the calculations show (see the following sections), this correction leads to a  $\delta$ -doped layer with a concentration of boron atoms  $5 \cdot 10^{20} \text{ cm}^{-3}$  and a thickness of 2 nm, embedded in weakly (unintentionally) doped diamond CVD with a concentration of boron atoms  $10^{15} \text{ cm}^{-3}$ , to the fact that at room temperature only 7% of holes are located outside the  $\delta$ -doped layer, unlike a much larger value, 50%, predicted in [25].

### 3. Method of modeling a boron-doped metal delta layer in the diamond CVD

To confirm this answer to the question put in the title, sec. 2, numerical simulation of metallic  $\delta$ -doped layers in CVD diamond has been carried out, taking into account the above-mentioned correction to the energy of the valence band edge due to the presence of ionized boron atoms. It is assumed that  $\delta$ -doped layers have infinitely sharp interface boundaries. This approximation is good for the experimentally achieved very high sharpness of boron doping of a CVD diamond of the order or even smaller than 1 nm decade<sup>-1</sup> [3,8,9,30] and is additionally confirmed by comparing the numerical results obtained on its basis with experimental data (see the next section).  $\delta$ -doped layers are embedded in a weakly (unintentionally)

doped CVD diamond with a low concentration of boron atoms  $10^{15} \text{ cm}^{-3}$ . The concentration of boron atoms inside the  $\delta$ -doped layers is  $N_B = 5 \cdot 10^{20} \text{ cm}^{-3}$ , i.e. above the threshold for the insulator-metal phase transition at room temperature. Therefore, all boron atoms there are assumed to be ionized, i.e.  $N_{B-} = N_B$ . Compensation is considered to be absent in the entire sample. The correction mentioned above to the energy of the edge of the valence band due to the presence of ionized boron atoms is not taken into account in the weakly (unintentionally) doped CVD diamond surrounding the  $\delta$ -doped layer, and is assumed to be equal to  $\alpha N_B^{1/3}$  inside the layer. The thicknesses  $\delta$ -doped layers were 2, 1 and 0.5 nm.

The energy profile of the valence band edge and the hole concentration distribution were found using the mean field theory in the Hartree approximation [31] by self-consistent solution of the system of Schrodinger and Poisson equations. It was found using the FreeWare program „1D Poisson“, developed by G. Snyder [32]. Its work is described in detail in the manual available on the same website [32], and verified by the author of this article by comparing its results with known examples.

Three doubly spin-degenerate hole subzones were taken into account: heavy holes (effective mass  $0.588m_e$ ,  $m_e$  — free electron mass), light holes (effective mass  $0.303m_e$ ) and spin-orbitally split holes (effective mass  $0.394m_e$ ) [33]. The spin-orbit splitting energy was assumed to be 6 meV [20].

We also note that at the considered concentration of boron atoms inside  $\delta$ -doped layers  $N_B = 5 \cdot 10^{20} \text{ cm}^{-3}$  and room temperature, an increase in the constant of crystal lattice of diamond due to doping, according to [34], is at maximum 0.05%. Therefore, the effect of this increase on the zone structure of doped diamond may not be taken into account.

#### 4. Simulation results

The results of the modeling of  $\delta$ -boron-doped layers in diamond CVD described above are shown in Fig. 1–3.

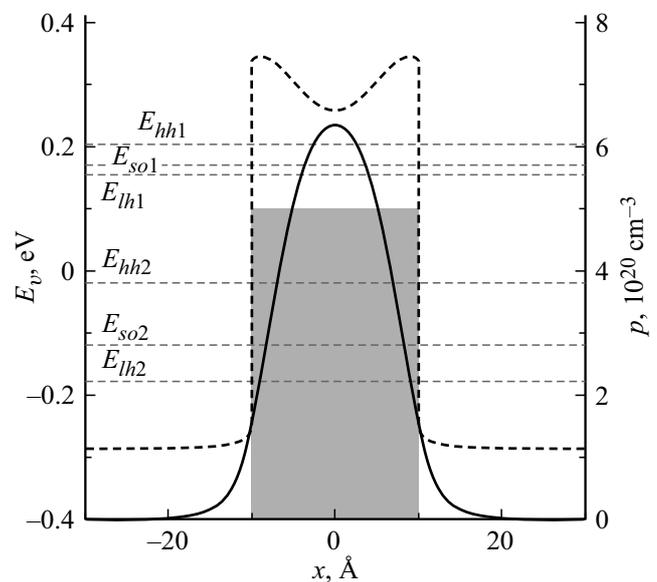
To interpret these results from the point of view of hole delocalization, we denote the total concentration of holes when  $\delta$ -doped layer is inserted into a weakly (unintentionally) doped diamond CVD by  $p$ , and the total concentration of holes when  $\delta$ -doped layer not entered into it, — via  $p_0$ . The latter is homogeneous and equal to  $4.7 \cdot 10^{13} \text{ cm}^{-3}$  for  $N_B = 10^{15} \text{ cm}^{-3}$ , as follows from the calculations. Then the degree of penetration of holes into the weakly (unintentionally) doped diamond CVD surrounding the  $\delta$ -doped layer will be the ratio of the number (per unit area) of holes of the valence band supplied by boron atoms of the  $\delta$ -doped layer and located outside this layer, i.e.,  $\int (p - p_0) dx$ , where the integral is taken over a weakly (unintentionally) doped diamond CVD surrounding the  $\delta$ -doped layer, to the total number (per unit area) of valence band holes supplied by boron atoms of  $\delta$ -doped layer, i.e. to  $\int (p - p_0) dx$ , where the integral is taken over

the entire thickness of the sample, including the  $\delta$ -doped layer. Calculations show that for the thickness of the  $\delta$ -doped layer 2 nm, this ratio is  $\sim 7\%$ , for 1 nm — 19%, and for 0.5 nm — 47%.

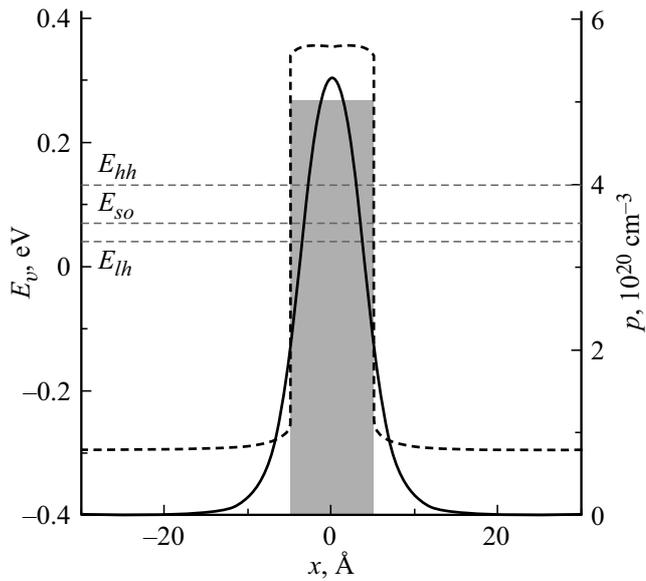
According to Fig. 1–3, only the  $\delta$ -boron-doped layer 2 nm thick has excited hole subzones. Calculations show that their population is  $1.23 \cdot 10^{12} \text{ cm}^{-2}$  (1.2% of the total number of valence band holes supplied by boron atoms of the  $\delta$ -doped layer, which is equal to  $\int (p - p_0) dx$ , where the integral is taken over the entire thickness of the sample, including  $\delta$ -doped layer) for the excited subzone of heavy holes,  $2.06 \cdot 10^{10} \text{ cm}^{-2}$  (0.02%) for the excited subzone of spin-orbitally split holes and  $1.71 \cdot 10^9 \text{ cm}^{-2}$  (0.002%) for the excited subzone of light holes. Despite the fact that the wave functions of these subzones have maxima at the boundaries of the  $\delta$ -doped layer and thereby provide a high degree of penetration of the holes of these subzones into the weakly (unintentionally) doped diamond surrounding the  $\delta$ -doped layer, a very low proportion of holes, contained in these subzones, makes their contribution to delocalization negligible.

#### 5. Discussion

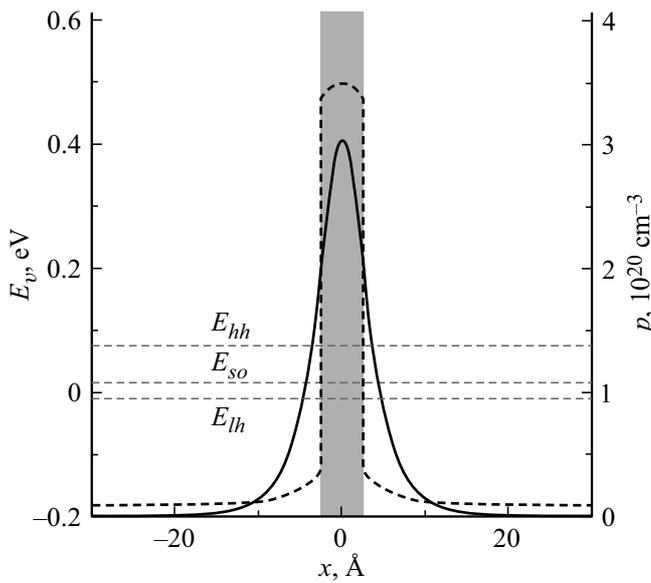
The results obtained above are confirmed by volt-farad [13] measurements [23,35] of hole concentration



**Figure 1.** The energy of the edge of the valence band  $E_v$  (bold dotted line, left scale), the energy of the edges of dimensionally quantized hole subzones of heavy ( $hh$ ), light ( $lh$ ) and spin-orbitally split ( $so$ ) holes (horizontal thin dashed lines, left scale) and total hole concentration  $p$  (bold solid line, right scale) for  $\delta$ -doped layer 2 nm thick and boron atom concentration  $N_B = 5 \cdot 10^{20} \text{ cm}^{-3}$  (gray rectangle) embedded in a weakly (unintentionally) doped diamond with  $N_B = 10^{15} \text{ cm}^{-3}$ , at room temperature. Compensation is assumed to be absent in the entire sample. All energies are counted from the level of chemical potential.



**Figure 2.** The same as in Fig. 1, but for a  $\delta$ -boron-doped layer 1 nm thick.



**Figure 3.** The same as in Fig. 1, but for a  $\delta$ -a boron-doped layer 0.5 nm thick.

distributions in metal  $\delta$ -boron-doped layers with the following parameters: boron atom concentration at peak  $N_B = 5 \cdot 10^{20} - 10^{21} \text{ cm}^{-3}$ , full width at half the maximum of the boron atom concentration profile 1 nm and its gradient  $\sim 0.9 - 1.2 \text{ nm decade}^{-1}$  on both sides of the peak. These measurements show that almost all holes are enclosed in a  $\delta$ -doped layer. This coincides with the results of numerical modeling of such a layer, showing that the concentration of holes at its boundaries drops by more than 2 times compared to its value in the center of the layer (see Fig. 2). Also, this coincidence justifies the approximation

used above of the infinitely sharp boundaries of the  $\delta$ -doped layer to describe the experimentally achieved sharpness of the doping profiles in such layers.

The values of hole delocalization calculated in the previous section, 7% for a layer with a thickness of 2 nm, 19% for a layer with a thickness of 1 nm and 47% for a layer with a thickness of 0.5 nm in Fig. 1–3, should be compared with the simulation results in the work [25], where, as mentioned earlier, the dependence of the energy of the valence band edge on the concentration of ionized boron atoms was not taken into account. Even at zero temperature, when, as mentioned above, the delocalization effect is clearly weaker than at nonzero temperature, the authors [25] obtained for  $\delta$ -doped layers with the same parameters as in Fig. 1–3, significantly higher values:  $\sim 50$ , 70 and 75%, respectively. Thus, neglecting the dependence of the valence band edge energy on the concentration of ionized boron atoms and, as a consequence, deepening the potential well formed by the  $\delta$ -doped layer for holes leads to a significant overestimation of the number of holes located outside the  $\delta$ -doped layer.

To clarify the effect of delocalization of holes in  $\delta$ -doped layers on their mobility, the latter was calculated taking into account only the contribution of scattering on ionized impurity atoms. To do this, the formulas obtained in [36] were used, considering the degeneracy of holes and the screening effect in the Lindhard approximation [31]. If we assume there is no compensation, this gives mobility 33, 36 and  $58 \text{ cm}^2/(\text{V} \cdot \text{c})$  for  $\delta$ -doped layers with a thickness of 2, 1 and 0.5 nm, respectively. For the first two layers, these values are close to  $\sim 30 \text{ cm}^2/(\text{V} \cdot \text{c})$ , i.e. to the mobility of holes determined by scattering on ionized impurity atoms in a diamond uniformly doped with boron at a concentration of the latter  $5 \cdot 10^{20} \text{ cm}^{-3}$  without compensation calculated by the Brooks–Herring formula [37]. Thus,  $\delta$ -boron-doped layers 2 and 1 nm thick do not show a noticeable increase in hole mobility compared to uniformly doped diamond with the same concentration of boron atoms. The reason for this is clear: as it was shown above, the holes are strongly localized in these layers and therefore their scattering on ionized boron atoms occurs in the same way as in the case of homogeneous doping. On the contrary, for a  $\delta$ -boron-doped layer 0.5 nm thick, the mobility of holes is  $\sim 2$  times higher than in a uniformly doped diamond with the same concentration of boron atoms. Thus, the delocalization of holes in this layer calculated above leads to a significant suppression of their scattering by ionized boron atoms compared to the case of homogeneous doping.

It should be repeated that in all the above calculations, compensation was assumed to be absent. This explains that the calculated mobility of holes at their homogeneous concentration of  $5 \cdot 10^{20} \text{ cm}^{-3}$  by  $\sim 10$  times exceeds the value  $3.6 \text{ cm}^2/(\text{V} \cdot \text{c})$ , measured in [14]. A simple analysis using the Brooks–Herring formula shows that at a homogeneous concentration of holes  $5 \cdot 10^{20} \text{ cm}^{-3}$ , the experimentally measured mobility of holes [14] is reproduced at

a compensation degree of 82%. Such high compensation certainly reduces the delocalization of holes for  $\delta$ -doped layer of a given thickness for the following reason.

For a fixed concentration of holes per unit area of the  $\delta$ -doped layer, necessary, for example, for the operation of a field-effect transistor based on such a layer, compensation increases the concentration of ionized boron atoms. This, according to the Pearson–Bardin formula above, deepens the potential well formed by the layer for holes. As a result, the edge energies of the populated hole subzones become farther from the edge of the well, and, consequently, their wave functions become more localized in the  $\delta$ -doped layer. Thus, compensation leads to a decrease in the delocalization of holes and, as a consequence, to the suppression of the increase in the mobility of holes in the  $\delta$ -doped layer compared to the case of homogeneous doping. Estimates show that the compensation-induced increase in the intervals between the edge energies of the subzones populated by holes and the edge of the potential well is significantly smaller than the values of these intervals for uncompensated samples with a compensation degree of  $< 42\%$ . Thus, only with such a relatively weak compensation, the values of delocalization of holes calculated above and, consequently, an increase in their mobility with a decrease in the thickness of the  $\delta$ -layer are preserved.

## 6. Conclusion

Thus, in order to achieve a significant increase in the mobility of holes in a  $\delta$ -boron-doped layer with a sufficiently high concentration of holes per unit area of the layer suitable for electronic applications at room temperature, it must have the following parameters. The concentration of boron atoms in it should be  $> 5 \cdot 10^{20} \text{ cm}^{-3}$  for the insulator-metal phase transition to take place, the degree of compensation should be  $< 42\%$ , and its thickness should be  $\lesssim 0.5 \text{ nm}$ . The physical reasons for this are clear: only for such  $\delta$ -layers almost all holes are located in the valence band, where their mobility is much greater than in the impurity zone, and a noticeable number of them inhabit the subzones located in energy near the edge of the potential well formed by  $\delta$ -doped layer. Due to weak localization of the wave functions of these subzones, the holes partially exit the  $\delta$ -doped layer, which provides an increase in their mobility. As far as the author of this article knows, such ultrathin metal weakly compensated  $\delta$ -doped boron layers in the diamond CVD have not yet been created, but modern nanotechnology is close to their implementation.

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## Conflict of interest

The author declares that he has no conflict of interest.

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