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On possible new methods for δ-layer synthesis of the diamond transistor

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Abstract: An upper estimate of the activation barrier E_a, overcome by boron atom during its adsorption on singular face of unalloyed diamond, has been obtained using quantum chemistry methods. This process is connected with the formation of boron-doped δ-layer in the unalloyed diamond, which is an integral part of the diamond transistor. The estimate of E_a was found to be approximately 6–7 eV. It is correspondent by the order of magnitude with floating electrode potential drop relative to stationary low-temperature plasma at electronic temperature above ~ 1 eV. Meanwhile, in the existing high-frequency plasma-enhanced CVD (MWCVD) technology used to create boron-doped δ-layers, the source of the δ-layer growth is high-energy boron ions with energies of hundreds of eV (and even units of keV) which enter the substrate from MW plasma. This energy that the ions acquire at the near-electrode voltage drop is clearly excessive and leads both to excessively high depth of ion penetration into the diamond and to large dispersion of this depth. This reduces the quality of the δ-layer and the transistor efficiency as a whole. At the same time, specificity of high-frequency plasma, created in the MW-resonator for the diamond growth, allows plasma modes and diamond growth both with large (units of keV) and small (units of eV) near-electrode voltage drops. This paper considers the possibility of switching between these two modes. The high-drop mode realizes the rapid growth of unalloyed diamond and the low-drop mode – high quality δ-layer.

Keywords: diamond transistor; doping δ-layer in diamond; chemical vapor deposition; quantum-chemical simulation.

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О возможных новых методах синтеза δ-слоя алмазного транзистора

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Аннотация: Методами квантовой химии получена верхняя оценка активационного барьера E_a, преодолеваемого атомом бора при его адсорбции на сингулярной грани нелегированного алмаза. Этот процесс связан с формированием дырочного δ-слоя, легированного бором в толще нелегированного алмаза и являющегося неотъемлемой частью алмазного транзистора. Найденная оценка величины E_a составила примерно 6…7 эВ. Она соответствует по порядку величины плавающему приэлектродному падению потенциала электрода-подложки относительно стационарной низкотемпературной плазмы при электронной температуре свыше ~ 1 эВ. Между тем в существующей технологии CVD, усиленного высокочастотной плазмой (MWCVD) и используемого для создания легированных бором δ-слоев, источником роста δ-слоя являются высокоэнергетичные ионы бора с энергией в сотни эВ (и даже единицы кэВ), поступающие на подложку из высокочастотной плазмы. Столь высокая энергия ионов бора, набираемая ими на приэлектродном падении напряжения, явно избыточна и приводит как к чрезмерно большой глубине проникновения ионов в алмаз, так и большому разбросу этой глубины. Это снижает качество δ-слоя и эффективность транзистора как целого. Специфика высокочастотной плазмы, создаваемой в СВЧрезонаторе для роста алмаза, допускает реализацию режимов работы установки и роста алмаза как с большими (единицы кэВ), так и малыми (единицы эВ) приэлектродными падениями напряжения. В работе рассматривается возможность переключения между этими двумя режимами. Режим с большим падением реализует быстрый рост нелегированного алмаза, режим с малым падением – δ-слой высокого качества.

Ключевые слова: алмазный транзистор; легирующий δ-слой в алмазе; химическое осаждение из газовой фазы; квантовохимическое моделирование.

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1. Introduction

Diamond is a material that is exceptional in its electronic, thermal, and mechanical characteristics; many prospects are associated with it in extreme, power, microwave electronics, acoustoelectronics [1–5], as well as high technologies that are not directly related to electronics [6].

With regard to the central element of electronics – the transistor – diamond has an advantage over traditional silicon in a situation where the scattering of charge carriers is small, and the concentration of the carriers themselves, which determines the magnitude of the current, is high. Such a combination of properties is realized in doped δ-layers, where the source of carriers is a thin and sharply defined doped layer with a volume impurity concentration of 10^{20} cm^{-3}, and the current is transferred in the near-layer region of carrier tunneling from the layer to undoped diamond; in the open state, the carried current can then have a very high linear density. Boron is the only impurity available when working with diamond and allowing a relatively high degree of activation at moderate temperatures [7, 8]. Another possibility for creating a δ-layer is an H-terminated layer, where univalent atomic hydrogen, like boron, acts as an acceptor impurity located at a depth of ~1 nm from the diamond surface [9, 10]. The technology for manufacturing such a hydrogen δ-layer can be considered to be fully developed, but the temperature stability of the layer leaves much to be desired, and further we will discuss only the δ-channel created by boron atoms.

The key physical requirement for such a doped δ-layer in the thickness of undoped diamond is, as already mentioned above, its minimum possible thickness; ideally, the layer should be monatomic. When a layer is grown by the MWCVD method (microwave chemical vapor deposition – chemical deposition stimulated by microwave plasma), an impurity (boron) atom arrives at the doping stage from the plasma to the electrode – a substrate of undoped diamond (which will be referred below as a substrate) in the form B^+ ion accelerated by the near-electrode voltage drop near the substrate (hereinafter, near the electrode drop) and transferring its charge to the substrate. Then the necessary condition for the monoatomicity of the resulting layer is that all B^+ ions entering the layer surface must have a minimum energy sufficient for their adsorption on the substrate, or a slightly higher energy. When the ion energy is too high (for example, hundreds of eV), binding with the substrate is certainly achieved, however, the depth and spread of depths of the distribution of boron atoms in diamond turn out to be large, no less than (5–10) nm [1−4]. This increases the gate voltage required to turn off the transistor or even makes complete blocking impossible [7−8]. Nevertheless, in the existing technology for both processes, i.e. doping and growth of undoped diamond in a plasma microwave cavity, the same vibrational mode (TM mode) [11] is formed, which is fundamentally aimed at the fastest possible growth of diamond. At the same time, the situation with the formation of the δ-layer and the structure as a whole is somewhat similar to the situation in the main method of synthesizing artificial diamonds in general – synthesis at high pressure and temperature. The method works effectively (albeit with significant limitations), but its theory and the possibility of fundamentally developing the results missing.

The approach associated with the “soft” doping proposed below, when the near-electrode drop and the activation energy E_a in the adsorption reaction of the doping atom on the diamond surface correspond to each other, obviously requires knowledge of such an energy and then the search for appropriate technical means. However, it was not possible to find out the value of E_a from the literature data.

The purpose of the paper is to calculate the value of E_a, substantiate the plasma resonator TE mode as optimal for ensuring the supply of doping boron atoms with an energy slightly higher than E_a to the substrate, and a preliminary assessment of the possibility of dynamic rearrangement of the discharge, which provides the necessary stages of growth of diamond and the doping layer of boron atoms. The following issues were also considered:

– how the boron adatom is fixed on unalloyed diamond at the topochemical level of description;

– how much energy E_a decreases on the beveled surface of undoped diamond compared to the necessary adsorption energy of the boron atom on the singular face of the diamond (for example, the (111) plane); this question is relevant if E_a in the reaction of the boron atom adsorption on the singular face of the substrate is too high;

– a preliminary assessment of the compatibility of the TE mode, which is natural for the stage of creating a boron-doped δ-layer in diamond, with the TM mode, which is traditional for layer-by-layer growth of undoped CVD diamond using the MWCVD technique.

2. Quantum-chemical simulation of the boron adsorption on the hydrogenated diamond surface

The analysis of the problems of quantum chemical modeling listed above is presented in the appendix. Here the formulation of the calculation and its results will be considered. Since the gas medium of diamond growth in the MWCVD-method includes predominantly hydrogen with a small admixture of a carbon carrier (usually methane) and a small admixture of boron (at the doping stage), the initial configuration upon the boron atom adsorption on the diamond substrate is the (100) or (111) plane covered with a layer of hydrogen atoms H. This surface includes a boron atom (i.e. a B^+ ion accelerated by an electrode drop and then transferring its charge to the surface), associated with three hydrogen atoms located on the interface carbon atoms (Fig. 1).

The meaning of the adsorption reaction of a boron atom (as an elementary act of growth of the future δ-layer) on a specific interface carbon atom is the separation of one of three hydrogen atoms from the diamond surface and the transition of a boron atom to its place.

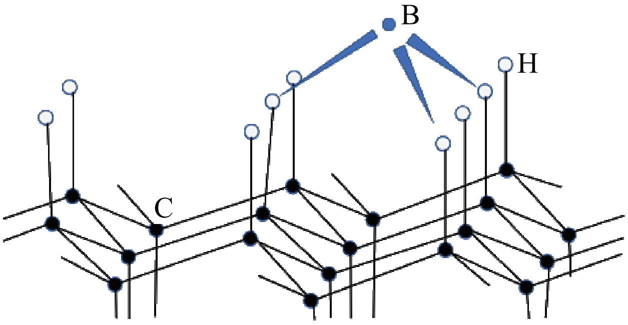

Fig. 1. The initial steady-state of the system in the boron atom adsorption reaction on the diamond surface (111): B atom is bound to three H coordination centres (simulation in HyperChem); C atoms are black circles, hydrogen atoms are white, a B atom is blue

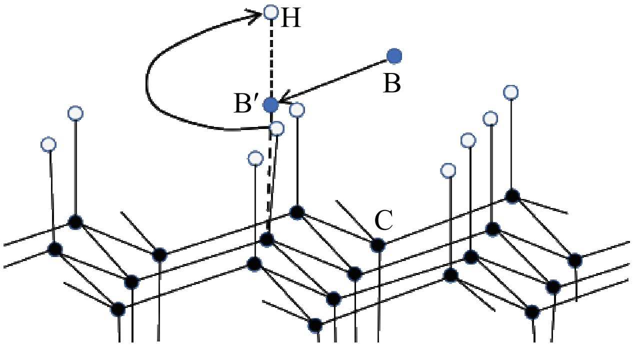

Fig. 2. Adsorption of the boron atom onto the carbon C atom of the diamond surface (111). (The boron atom pushes out one of the three hydrogen atoms and moves into its place; the pushed atom H lines up at the end of the chain C–B–H. The trajectory of the "B" atom movement to its new position is shown by a straight arrow $\mathrm{B} \to \mathrm{B}'$; the position on this arrow plays the role of a reaction coordinate when modelling the transition state. The trajectory of the atom "H" is shown by an arc, the newly formed bonds in the final state are shown by dotted lines)

The hydrogen atom detached from the substrate moves to the end of the C−B−H chain providing an increase in the total binding energy (Fig. 2). In this case, the distance of the B atom on its trajectory from the initial position of the atom can be chosen as the reaction coordinate r_B.

Both of the configurations described above, initial and final, are indeed stationary, i.e. they appear in the calculation as minima of the binding energy of the system. The gain in binding energy upon passing from the initial configuration to the final one is about 0.6 eV. The reaction activation barrier E_a, defined as the maximum in the dependence of the binding energy on the reaction coordinate, is estimated from above by the value of 6–7 eV (Fig. 3).

The section of the change curve in the binding energy of the system $E(r_\mathrm{B})$ in Fig. 3 at $r_\mathrm{B} \geq 1.2$ nm, where $E(r_\mathrm{B})$ decreases to a level below both the initial and final stationary states, is apparently associated with an extremely rough calculation scheme.

The obtained estimate of the E_a value is consistent with the standard value of the floating potential (1) of the electrode-substrate $\varphi_{\mathrm{flow}}^{(\mathrm{stat})}$ relative to the plasma calculated for the stationary low-temperature low-pressure plasma (i.e. plasma which origin is not related to microwave) [12].

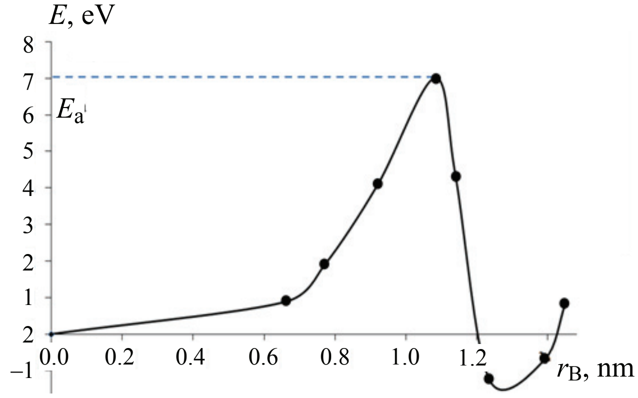

Fig. 3. The change in the binding energy of the system with relation to the initial configuration energy in Fig. 1 and further along the reaction coordinate r_B counted from the B atom's initial position

Such a potential is calculated from the condition that the electron current $\frac{1}{4} n_0 \sqrt{\frac{8T_e}{\pi m}} \exp\left(\frac{-\varphi_{\text{flow}}^{(\text{stat})}}{T_e}\right)$ to the substrate is equal to the Bohm current of ions $n(\varphi_B) v_B$ that have passed without collisions of the potential drop $\varphi_B = T_e/2$ from a formally unperturbed plasma with a concentration n_0 to the point where quasi-neutrality is still preserved [12]:

$$n(\varphi_B) v_B = \gamma n_0 \sqrt{\frac{T_e}{M}}. \qquad (1)$$

In expression (1) $n(\varphi_B) = \gamma n_0$ the plasma concentration at a point with the potential φ_B, $\gamma = \exp(-1/2)$, the value $v_B = (2\varphi_B/M)^{1/2} = (T_e/M)^{1/2}$ is the ballistic (Bohm) velocity of the ion at the point φ_B. Then the potential $\varphi_{\text{flow}}^{(\text{stat})}$ is

$$\varphi_{\text{flow}}^{(\text{stat})} \approx (T_e/2)\ln(M/2\pi m) \approx 6.5T_e. \qquad (2)$$

This value, as mentioned above, corresponds to the calculated activation barrier E_a at an electron temperature of ≥ 1 eV and an ion mass M equal to the proton mass. The latter assumption is based on the fact that the main gas-phase component (both during doping and in the growth mode of undoped diamond) is hydrogen.

The value $\varphi_{\text{flow}}^{(\text{stat})}$ in (2) refers to the stationary plasma. When the plasma is formed by an electromagnetic microwave field, which is the most effective means of stimulating the growth of diamond [2, 3], a near-electrode voltage drop close to $\varphi_{\text{flow}}^{(\text{stat})}$ occurs if the electric microwave field strength lines are parallel to the diamond substrate and have little effect on the formation of the structure of the near-electrode layer. This situation is realized if the substrate is placed in the microwave resonator perpendicular to the resonator walls and one or another TE mode is excited in the resonator [13], for example, TE_{11n}, as in Fig. 4. In such a mode, there is no alternating electric field perpendicular to the substrate, and the equations describing the near-electrode layer do not differ in any way from those in the case of the stationary plasma. The electron temperature realized in such a vibrational mode is discussed below.

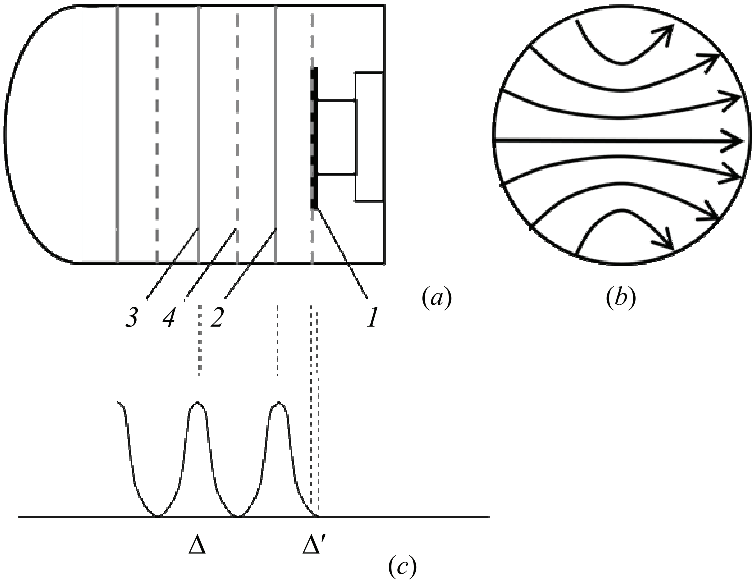

Fig. 4. Characteristic surfaces and placing of the growth substrate in TE_{11n} mode: *a* – planes of electric field oscillations parallel to the substrate *1*; *2* and *3* are antinodes; *4* – nodes; details of power input device from the waveguide are not shown; *b* – electric field oscillation in the antinode planes *2*, *3* and planes similar with them; *c* – electric field oscillation amplitude along the resonator axis; Δ is the distance between nodes (antinodes), Δ′ is the substrate shift relative to the plane of nodes. (To save space, the resonator circuit is rotated by 90°. In fact, the resonator is placed vertically)

An additional condition for placing the substrate plane in the TE mode in the nodal planes of the amplitude of the electric field oscillations parallel to the substrate (similar to planes *1* and *4* in Fig. 4*a*) makes it possible to exclude the effect of this alternating field component on the formation of the near-electrode drop as well.

It is these arrangements and growth modes that can be considered optimal for growing the δ-layer. The comparison of the described conditions with those in the alternative TM mode is discussed in section *3*.

3. The growth of diamond and doped δ-layers on the substrate inside the plasma microwave resonator

As mentioned above, the rapid growth of undoped diamond is best achieved in a unit with plasma high-frequency stimulation of CVD growth [2, 3] (MWCVD).

The schematic diagram of a rather typical unit of this type, a plasma resonator on a waveguide path [5], is shown in Fig. 5. The direct synthesis of diamond occurs on the substrate placed inside the bell jar reactor [5].

The type of oscillations in the resonator is set primarily by the fact that during the growth of undoped diamond, plasma should have a high concentration of the “building material” of such growth – ionized dissociation products of the gas-phase hydrocarbon carrier of carbon (mainly CH_3^+ ions and CH_3^* radicals [2, 5]), as well as high electron and gas temperatures.

This condition is realized in a mode when the electric field strength lines are orthogonal to the side walls of the resonator and, at the same time, to the substrate located across the resonator (Figs. 5 and 6). In a prismatic resonator, such modes can be TM_{11n} modes, and in a cylindrical resonator, TM_{01n} modes, and the substrate should be in the region of the antinode of the electric field [14, 15].

When the resonator operates with the TM mode, the electrons oscillate along the direction of the vector product $[\boldsymbol{E} \times \boldsymbol{H}]$ of the strengths of the electric and magnetic fields, i.e. in a straight line and parallel to the generatrix of the waveguide. Therefore, it is the TM mode that is optimal for the rapid growth of layers of unalloyed diamond both before and after the growth of the δ-layer; the record growth rate is currently considered to be 1 monolayer per second. The order of parameter values obtained using the TM_{012} mode in [15] is: plasma density is up to several units $\times 10^{11}$ см$^{-3}$, maximum electron temperature is up to $(1.7–1.9)\cdot 10^4$ K (1.5–1.7 eV), maximum gas temperature is up to 2000 K [15].

The calculated picture of the amplitude of the electric field strength for the TM_{012} mode, taking into account the presence of plasma in the resonator and the resonator excitation device [15], is shown in Fig. 6. Areas of dense field lines of the electric microwave field appear as dark spots, several of these field lines are added to the original illustration in Fig. 6.

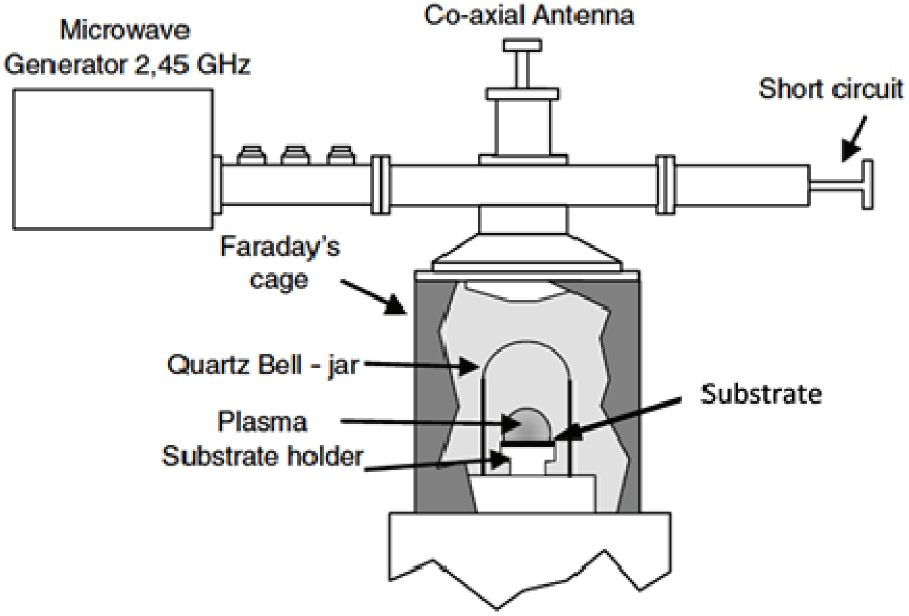

Fig. 5. Schematic diagram of the bell jar reactor used for diamond growth in the MWCVD process [5]

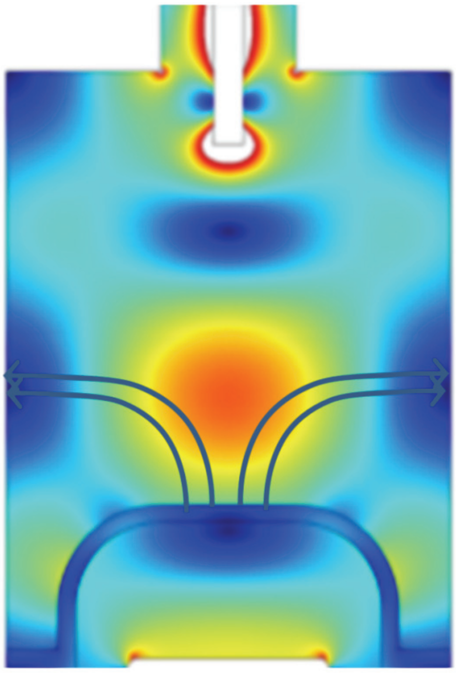

Fig. 6. The structure of the electric field amplitude in the resonator mode TM_{012} with presence of plasma, the resonator excitation element and the bell jar, calculated in [15]

On the contrary, when the TE mode is excited, the motion of electrons along the circle in the cross section of the resonator dominates. In this case, the plasma ionization and its heating occur to a lesser extent than upon excitation of the DM mode. The maximum calculated electron temperature now does not exceed $(0.8–1.1)\cdot 10^4$ K (1 eV), the plasma concentration at the same pressure (below 10^{-2} Torr) is also an order of magnitude lower than when operating in the TM mode [12].

Although the temperature of 1 eV, which is almost the limit for the TE mode, is the minimum for fulfilling relation (2), the necessary activation energy of 6–7 eV compared with it is also sharply overestimated, which has been also obtained on the singular diamond face (where the activation barriers of all potential reactions are maximum). On the other hand, the independence of the near-electrode drop from the details of the microwave discharge is a clear advantage of using the TE mode.

In an alternative situation of the TM resonator mode (Fig. 6), the time-averaged near-electrode potential drop near the substrate $\varphi_{\text{flow}}^{(\text{MW})}$, on the contrary, is extremely variable, many times exceeds T_e temperature and can reach hundreds of volts or even units of kilovolts (the “MW” sign indicates the microwave field as the source of existence of the plasma, the “flow” icon indicates that the potential of the substrate relative to the plasma is floating, i.e. the electron and ion currents are equal). This result was established back in the 1970s when studying a high-frequency capacitive discharge CCP (conductively coupled plasma) [16–19]. For example, it was shown in [16] that in the zero current mode between the plasma and each of the electrodes (considered identical), a time-averaged near-electrode potential drop $\varphi_{\text{flow}}^{(\text{MW})}$ of the order

$$\varphi_{\text{flow}}^{(\text{MW})} \sim \varphi^{(\text{MW})}/\pi - \varphi_{\text{flow}}^{(\text{stat})}, \tag{3}$$

the second term is generally neglected. Thus, $\varphi_{\text{flow}}^{(\text{MW})}$ is only π times less than the amplitude of microwave oscillations in the plasma reaching kV. This result was then refined for various special cases. In particular, in [17, 18], a semi-analytical dependence $\varphi_{\text{flow}}^{(\text{MW})}$ on plasma parameters and microwave power and frequency given independently. In [19], the plasma parameters for the CCP case, including $\varphi_{\text{flow}}^{(\text{MW})}$, were calculated depending on the external microwave parameters in a self-consistent way, although with strong simplifications.

The reason for such large near-electrode drops in microwave discharges is as follows. In a wide range of plasma parameters, the frequency of oscillations supplied to the resonator consists, as a rule, in the range $\omega_{pe} >> \omega >> \omega_{pi}$ between the electron and ion plasma frequencies. At an oscillation frequency of 2.4 GHz, this condition is valid for plasma concentrations from 10^{10} to 10^{14} cm^{-3}, and at a frequency of 13.75 MHz, at a sufficiently low concentration $n \le 4\cdot 10^9$ cm^{-3}. In this case, the ions cannot oscillate with the oscillation frequency in the resonator, and the ion current to the substrate can be considered as a stationary Bohm current according to formula (2).

On the contrary, the electron current is qualitatively different from the current to the electrode formed by the fast part of the Maxwellian distribution of electrons proportional $\exp\left(-\varphi_{\text{flow}}^{(\text{stat})}/T_e\right)$ in the stationary plasma. This current is formed by electrons that find themselves at the boundary of the near-electrode layer in the desired phase of the microwave voltage and have time to reach the substrate gaining energy from the microwave field (or managing to use the energy already accumulated).

At microwave power $P = 45$ W, introduced into the plasma resonator with a cross section $S_\perp = 5$ cm, and frequency of 13.75 MHz, the amplitude of potential oscillations in the microwave field $\varphi^{(\mathrm{MW})}$, which is included in expression (2), is expressed through the electric field strength $E[\mathrm{V \cdot cm^{-1}}] = 19.4\left(P[\mathrm{W}]/S_{\perp}[\mathrm{cm}^2]\right)^{1/2}$ [20], and is $\varphi^{(\mathrm{MW})} \approx 5.0$ kV. The near-electrode drop has the same order.

At energies of B^{+} ions corresponding to such a near-electrode drop and bombarding the substrate during δ-doping, the ions go inside the nominally undoped diamond to a depth of tens of layers. This follows both from the experience of growing δ-layers in diamond [7, 21] and from estimates of characteristic activation barriers in the reaction of the passage of various atoms through the graphene layer [22]. A relatively acceptable narrowness of the δ-layer can then be ensured by a short-term and carefully controlled supply of a gas-phase boron carrier to the discharge. Such an organization of the CVD process, which preserves the same type of oscillations in the resonator both during the growth of undoped diamond and the δ-layer, is used in all, even the most advanced, variants of growing δ-layers, for example, in [23].

At the same time, from our point of view, an approach, which ensures a high growth rate of undoped diamond above and below the δ-layer and does not sacrifice its quality, is possible. The approach consists in switching oscillations in the resonator from the TM_{01n} mode to one of the TE modes for the period of growing the δ-layer and then switching back. When operating in the TE mode, the near-electrode potential drop is approximately described by formula (1). Then, if the energy of boron ions generated in the plasma, falling on the boundary of the near-electrode layer and then on the substrate, is minimally sufficient for their adsorption. The roughness of the conditional boundary of the resulting δ-layer is determined only by the natural roughness of the growing diamond surface.

The sequence of actions during the transition from the growth of the undoped substrate to the growth of the δ-layer can be as follows. Immediately before the switchover, the supply of the gas-phase carbon carrier is stopped. After switching, the supply of the carrier is resumed, but the gas-phase source of boron is added to the gas flow. In this case, the growth of diamond layers and the annealing of already formed layers in hydrogen slow down sharply (according to estimates made in [15], up to tens of monolayers per hour, as in early versions of the MWCVD-method).

At the same time, due to the sharp deceleration of crystal growth in the TE mode, the required doping time can be chosen quite accurately. The subsequent shutdown of the dopant supply after such a time does not degrade the quality of the layer and at the same time allows to gradually clean the chamber from impurities. This factor provides an additional advantage over the standard technology, in which the impurity still circulates in vortex gas flows over the substrate for some time even after the impurity source is turned off.

It should be noted that as the ensemble of boron adatoms transforms into a single δ-layer with high electrical conductivity, the substrate becomes a source of an additional boundary condition for the fields $\boldsymbol{E}$ and $\boldsymbol{H}$ in the resonator. In particular, the condition $\boldsymbol{E}_{\mathrm{t}} = 0$ on the tangential (t) component of the electric field, which identifies the substrate with an ideal conductor, could turn off the TE mode. However, this should not happen; firstly, due to the finite conductivity of the δ-layer, and secondly, due to the existence of a gap between the substrate and the side walls of the resonator. This circumstance allows for the second, in addition to switching the $\mathrm{TM} \rightarrow \mathrm{TE}$ modes, the possibility to exclude the electric microwave field perpendicular to the substrate for the time of growth of the δ-layer. It is sufficient to move the substrate from the plane of the antinodes of the TM_{01n} mode to one of the nodal planes, where the component of the vector $\boldsymbol{E}$ perpendicular to the substrate is close to zero (for example, in Fig. 6, to the horizontal plane passing through the center of the bright yellow spot in the center of the figure; however, it is necessary to take into account that the spot itself must move when the substrate is displaced).

However, in the case of the transition to the TE mode, the movement of the substrate into the region of nodes, which is common for both variants of changing the diamond growth mode, imposes lower requirements on the movement accuracy. An error in the position of the substrate can change the amplitude of oscillations in the resonator, but not the magnitude of the near-electrode potential drop near the substrate. In the case of the TM mode, the error Δ' in the position of the substrate relative to the position of the nodal plane (for example, planes *1* or *4* in Fig. 4*a*, *b*; Δ is the distance between the antinode planes, the parameter Δ' is shown in Fig. 4*c*) should lead to the appearance near the substrate of non-zero amplitude of potential oscillations of order

$$\varphi^{(\mathrm{MW})}(\Delta') = \frac{\varphi^{(\mathrm{MW})}_{\max}}{2}\left(1 - \cos\frac{2\pi\Delta'}{\Delta}\right) \approx \varphi^{(\mathrm{MW})}_{\max}\left(\frac{\pi\Delta'}{\Delta}\right)^2,$$

where $\varphi_{\max}^{(\mathrm{MW})}$ is the value $\varphi^{(\mathrm{MW})}$ at the antinode. At $\Delta'/\Delta \sim 0.1$, the ratio $\varphi^{(\mathrm{MW})}\big/\varphi_{\max}^{(\mathrm{MW})}$ is also approximately 0.1, and the amplitude of microwave potential oscillations $\varphi^{(\mathrm{MW})}$ is at least several hundred eV. Fluctuations in the amplitude of the near-electrode drop of this order should degrade the layer quality and can only be acceptable if the alternative solution turns out to be too complicated.

A separate work will be devoted to the discussion of technical possibility to implement switching of the resonator operation modes.

4. Conclusion

As a result of modeling, the activation energy E_a for the adsorption reaction of boron atoms on the diamond surface (substrate) which is not volumetrically doped, but terminated by hydrogen, was estimated using semi-empirical methods of quantum chemistry. Carrying out such reactions is a necessary element in the formation of the δ-layer of the diamond transistor. The value of the upper boundary of E_a was 6–7 eV (and, all the more, it should be less on the surface beveled relative to the singular face of diamond (111) considered in the simulation). This E_a value does not exceed the floating potential of the electrode calculated for the substrate using the standard formula of the theory of stationary low-pressure plasma $\varphi_{\mathrm{flow}}^{(\mathrm{stat})} \sim$ $\sim (T_e/2)\ln(M/2\pi m) \approx 6.5T_e$, if the electron temperature in the plasma is not lower than $T_e \sim 1$ eV. The same formula and similar requirement can also be provided in the plasma microwave resonator introduced into the TE vibrational mode (for example, the TE_{11n} mode, $n > 1$) and placing the substrate perpendicular to the cavity resonator axis in one of the nodal planes of the TE mode. Switching the resonator from the TE mode to the TM mode with the simultaneous exclusion of the dopant from the composition of the gas mixture and then the reverse switching makes it possible to ensure the rapid growth of undoped diamond within the same unit. In this case, it is possible to fulfil the characteristics of the diamond δ-layer, which are higher than those of the diamond δ-layers obtained at present.

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6. Conflict of interests

The authors declare no financial or other conflicts.

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Supplementary Material

The calculation of activation barrier of boron adsorption on hydrogenated undoped diamond substrate (singular face (111))

The process of gas-phase alloying is switched on after a long-term growth of unalloyed diamond from a gaseous mixture with hydrogen. Therefore, the surface of unalloyed diamond can be considered fully hydrogenated.

The complexity of the problem from the quantum chemical (QC) point of view is due to the fact that when a boron atom or ion is adsorbed on a carbon atom of the substrate, boron replaces the hydrogen atom connected to this C atom earlier. Therefore, the transition state must take into account the excess of the formal valency of the hydrogen atom in the state when this atom is connected to both boron B and carbon C at the same time. In our analysis, we used a fairly simple HyperChem KX software package and limited ourselves to the AM1 semi-empirical method (in the future, it is planned to carry out calculations in various versions of the density functional method, which are not implemented very efficiently in HyperChem). Previously, we successfully used the HyperChem package to analyze the conditions that determine the predominant nucleation of diamond (rather than graphite) under conditions of a sharp increase in temperature [24, 25].

The diamond cluster, simulating the already grown layer of unalloyed diamond, included two (111) bilayers; a total of 60–65 carbon atoms and 44–50 hydrogen saturating the dangling valencies of carbon atoms at the edges. Unfortunately, HyperChem did not have the means to combine the excess of the formal valence and the calculation of the transition state. Nevertheless, it was possible to obtain an upper bound for the required activation barrier E_a by solving the problem partially by hand.

First of all, it has been found that there is an initial (Fig. 1) and a more favorable final configuration of the system (Fig. 2), which describe boron adsorption as the formation of a B–C chemical bond (more precisely, the C−B′−H chain presented in Fig. 2). In the initial configuration, the boron atom is located above the center of the diamond double hexagonal cell (Fig. 1) interacting with three hydrogen atoms. When adsorbed on the interface C atom of the diamond lattice, the boron atom displaces one of these hydrogen atoms, and it either appears above it (Fig. 2) or combines with one of the other nearest H atoms. In the first case (C−B′−H configuration), the binding energy of the system turns out to be higher in absolute value by 0.57 eV; in the second case, it is approximately the same as in the initial state.

Thus, the passage of a boron atom through the hydrogen layer is an energetically favorable process, and it remains only to correctly determine the activation energy on the reaction trajectory between Fig. 1 and 2. The role of the reaction coordinate r_B in the transition from the initial configuration to the final position of the boron atom B (Fig. 2): $B \rightarrow B'$. For each r_B, the real position of the displaced H atom and a certain number of atoms closest to it must conditionally correspond to the minimum energy of the system.

However, partial optimization of the configuration of atoms at a fixed position of the boron atom with respect to the unperturbed diamond lattice turned out to be impossible using all QC methods without exception. This reflects both the limitations of the package and the fact that the minimax problem is correct only in the presence of a semi-infinite lattice. Otherwise, the substrate, like a large molecule, simply moves away from the adatoms. Therefore, at each step of the movement, we conditionally optimized the system by the simplest method from the arsenal of the HyperChem package – the MM molecular mechanics method. In this case, a set of additional bonds of the boron atom and the displaced H atom with their nearest environment is constructed in the Arbitrary valence mode of arbitrary valence. The need for such an additional construction is due to the fact that in the MM method an atom interacts only with those neighboring atoms with which it is formally connected by a chemical bond, i.e. by a connecting line.

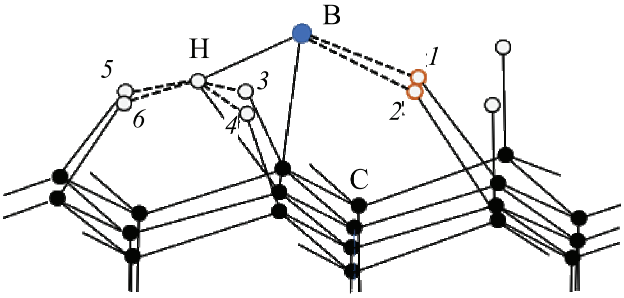

Fig. 7. The boron atom B in some intermediate position on the reaction trajectory. (Additional bonds introduced in the arbitrary valence mode to reveal the response of the system are indicated by dashed lines)

Such bonds should exist at least from the following positions (Fig. 7): between the boron atom B and hydrogen atoms *1*, *2*, between the B atom and the nearest C atom (to which it should join), and also between the displaced H atom and the set of *3* – *6* hydrogen atoms closest to it, with which it must interact along its exit trajectory. All the atoms and bonds taken into account during the optimization are highlighted in Fig. 7 with a light fill, with the exception of the “dark” boron atom; the considered links are marked with a dotted line.

To estimate the binding energy of the system at each step of the displacement of the B atom, the adopted set of additional constructions was chosen as the minimum, but ultimately turned out to be sufficient. After partial optimization by means of MM for the selected set of hydrogen atoms, additional bonds were removed, and the energy of the system was determined by the semi-empirical AM1 method without optimization (there was no longer any arbitrary valency in this final calculation).

It is obvious that the resulting configuration is far from the optimal, hypothetically existing in the AM1 method, it can correspond to one of the huge variety of fundamentally possible configurations for a given reaction coordinate. For such a non-optimized energy (for each reaction coordinate r_B), the dependence of the binding energy of the system on r_B was constructed, and the maximum was determined on it. It exceeds the actual, unknown activation energy, but it can be used for the upper estimate of the required energy of B^+ ions adsorbed on the diamond surface (Fig. 3). For several diamond configurations, arrays (r_B, $E_a(r_B)$) of 10–15 points were built (in different arrays, the size of the original diamond and the diamond polytype, i.e. cubic or hexagonal diamond varied); the value of the activation energy in all cases was 5.5–7 eV.

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