Non-annealed ohmic contacts with reduced resistance to *p*- and *n*-type epitaxial layers of diamond and their thermal stability

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The possibility of decreasing the resistivity of ohmic contact to *p*- and *n*-type diamond epitaxial layers by using heavily boron- and phosphorus-alloyed layers, variation of different materials for metallization and annealing of contacts has been investigated. Two types of ohmic contacts have been studied: Ti/Mo/Au and Ti/Pt/Au. The use of platinum as a diffusion barrier in a three-layer system made it possible to reduce the specific contact resistance to *p*-type diamond by an order of magnitude compared to molybdenum to $2.7 \cdot 10^{-6}\,\Omega \cdot \mathrm{cm}^2$, which maintains stability during high-temperature annealing. A specific resistance of ohmic contacts to *n*-type diamond of $0.02\,\Omega \cdot \mathrm{cm}^2$ has been achieved. The current-voltage characteristic of the resulting contacts is linear.

Keywords: epitaxial layers of diamond, boron, phosphorus, ohmic contacts.

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1. Introduction

Diamond has long attracted attention as a material for high-power semiconductor devices operating at elevated temperatures. This interest stems from its wide band gap (5.4 eV), high thermal conductivity ($22\,\mathrm{W} \cdot \mathrm{cm}^{-1} \cdot \mathrm{K}^{-1}$ at room temperature), and very high breakdown field ($10^7\,\mathrm{V} \cdot \mathrm{cm}^{-1}$) [1,2]. The formation of ohmic contacts to *p*- and *n*-type diamond remaining stable at high operating temperatures is crucial for the advancement of diamond electronics, and the issue of contact resistance reduction still remains relevant. In the case of classical $\mathrm{A^{III}B^{V}}$ semiconductors and nitrides (GaN, AlN), an ohmic contact is formed with metals with their electronic work function (Φ_m) being lower than electron affinity energy X_s of an *n*-type semiconductor or Φ_m being greater than the sum of X_s and band gap E_g of an *p*-type semiconductor. There are no metals with electronic work functions satisfying these inequalities for *n*- or *p*-type diamond, and a potential barrier is always present. Therefore, special techniques are used in the fabrication of low-resistance ohmic contacts to diamond to make this potential barrier narrower and lower. The barrier width is reduced by heavy doping of diamond in the subcontact region. As a result of doping, the potential barrier at the metal–diamond interface becomes noticeably narrower and tunnel-transparent for carriers [3–7]. Specifically, the contact resistance on *p*-type diamond decreases from $10^{-4}\,\Omega \cdot \mathrm{cm}^2$ to $2 \cdot 10^{-6}\,\Omega \cdot \mathrm{cm}^2$ as the concentration of boron atoms increases from $10^{18}\,\mathrm{cm}^{-3}$ to $3 \cdot 10^{20}\,\mathrm{cm}^{-3}$ [8]. To reduce the barrier height, the chemical composition of diamond near the contact is altered (a narrow-band subcontact layer is created). Carbide-forming metals [9–14] (Ti, Mo, Ta, W), which allow one to reduce the barrier height to 0.4–0.6 eV [11,15,16], are used for this purpose. The mechanism of current flow through the barrier is of a thermal-field nature in this case.

However, these approaches were inadequate to form a reliable contact with low resistance to phosphorus-doped *n*-type diamond. Owing to the high density of surface states, the Fermi level at the metal/*n*-type diamond interface is pinned ~ 4.3 eV below the bottom of the conduction band, which makes it difficult to adjust the barrier height. In the first studies, research teams opted for reducing the barrier width by increasing the level of diamond doping with phosphorus. Increasing the concentration of phosphorus atoms, the authors of [17,18] managed to reduce ρ_c of an ohmic contact to *n*-type diamond to just $\sim 10^{-3}\,\Omega \cdot \mathrm{cm}^2$. However, these results could not be reproduced in later studies. In addition, the current–voltage characteristics between different contacts of a TLM line were nonlinear in these experiments, and this distorted the data processing results. It should be noted that, in contrast to boron doping of CVD diamond, the synthesis of *n*-type semiconductor CVD diamond with a high concentration of phosphorus atoms remains poorly studied. The main obstacle to fabrication of diamond layers with electronic conductivity is the high activation energy of dopant impurity (the lowest one is 0.57 eV for phosphorus), which makes it difficult to maintain a sufficient concentration of conduction electrons in a crystal. It is known from literature that the high degree of donor compensation is another problem arising in phosphorus doping of diamond. It became clear that other ways to fabricate an ohmic

contact to *n*-type diamond need to be explored in order to achieve $\rho_c \sim 10^{-5}\,\Omega\cdot\mathrm{cm}^2$ for *n*-type diamond. The same research group has later attempted [19] to produce ohmic contacts on *n*-type diamond with a pre-graphitized surface, but the obtained contact resistance was as high as $\rho_c = 0.9\,\Omega\cdot\mathrm{cm}^2$.

Preliminary catalytic etching under a Ni mask in the contact region followed by selective growth of *n*-type diamond in these regions was used in [20] to raise the phosphorus doping level for diamond with the (100) orientation. It was proposed in [21] that a layer of nanocrystalline diamond (NCD) doped heavily with nitrogen should first be applied to the surface of doped diamond, and only then should Ti-Pt-Au ohmic contacts to NCD be fabricated.

The issue of finding reliable low-resistance contacts to *n*- and *p*-type diamond remaining stable at elevated temperatures is still relevant. The aim of the present study is to probe the options for reducing the contact resistance: form diamond regions doped heavily with phosphorus and boron, use two types of metals as ohmic contacts (Ti/Mo/Au and Ti/Pt/Au), and study the effect of annealing on contacts.

2. Experiment procedure

Epitaxial layers of diamond doped with phosphorus (P13) and boron (S61) were grown by chemical vapor deposition (CVD) on HPHT (high pressure high temperature) diamond substrates with the (111) and (001) orientations, respectively, in a CVD reactor of a new type [22]. This reactor has the following key features: the use of a laminar vortex-free gas flow and a system for quick adjustment of the gas mixture composition.

Three-layer ohmic contacts of two types (Ti/Mo/Au and Ti/Pt/Au) with layer thicknesses of 20/30/100 nm were formed to P13 and S61 diamond layers. An AMOD setup was used to deposit individual metal layers by electron-beam evaporation. The contacts were ohmic without additional thermal annealing. When the needed experiments were completed, metals were removed completely in a boiling mixture of nitric and hydrochloric acids ($HNO_3 : HCl/1 : 3$).

CVCs were recorded using a Keithley SCS 4200 system; the values of specific and contact resistances were determined by the transmission line method (TLM). The distribution profiles of boron and phosphorus atoms in the studied structures were obtained by secondary-ion mass spectrometry (SIMS) using a TOF.SIMS-5 setup.

3. Results and discussion

An epitaxial diamond layer 220 nm in thickness with a boron atom concentration of $2\cdot10^{21}\,\mathrm{cm}^{-3}$ was grown on the S61 diamond substrate to form an ohmic contact to *p*-type diamond. A regime of epitaxial growth of phosphorus-doped diamond with a concentration of phosphorus atoms up to $3\cdot10^{20}\,\mathrm{cm}^{-3}$ (P13) was found. In our earlier studies, we have failed to achieve such a high level of phosphorus doping of diamond [23]. SIMS concentration profiles of boron and phosphorus atoms in the studied structures are presented in Figure 1.

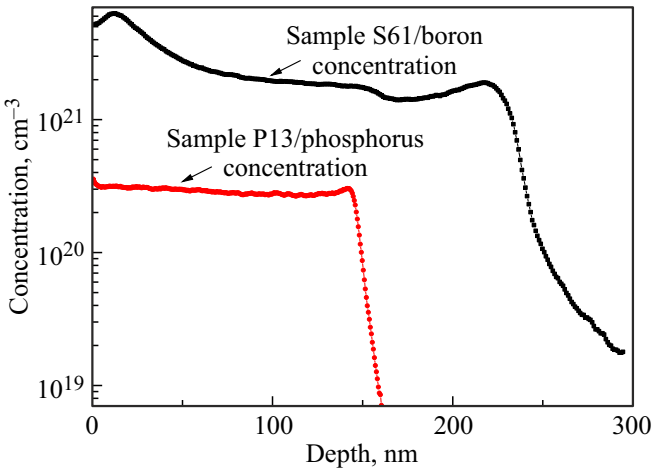

Figure 1. Distributions of phosphorus atoms in the P13 structure and boron atoms in the S61 structure (SIMS).

3.1. Ohmic contact to *p*-type diamond

In our previous studies into the formation of ohmic contacts to boron-doped diamond layers, we used a Ti/Mo/Au multilayer metal system [24]. In the present study, two types of contacts (Ti/Mo/Au and Ti/Pt/Au) were fabricated and examined. A metal mask for etching of mesa structures was formed in accordance with the chosen phototemplate. Following the mesa structure etching and mask removal, ohmic contacts to the p^+-diamond layer were fabricated. The diagram of formation of mesa structures and ohmic contacts is presented in Figure 3: Ti/Pt/Au metallization is on the left half of the diamond surface (TLM3, TLM4), while Ti/Mo/Au is on the right half (TLM1, TLM2).

Figure 2 shows the results of measurement of the contact resistance in a TLM line for two types of contact metallization.

The data in Figure 2 reveal a fine linear dependence of resistance on the distance between adjacent contact pads in the TLM line for both Ti/Mo/Au and Ti/Pt/Au contacts. The results of TLM measurements demonstrated an order-of-magnitude reduction in contact resistance due to the use of platinum instead of molybdenum as a diffusion barrier in the three-layer metal structure. The specific contact resistance was $\rho_c = 1.2\cdot10^{-5}\,\Omega\cdot\mathrm{cm}^2$ for Ti/Mo/Au and $\rho^c = 2.7\cdot10^{-6}\,\Omega\cdot\mathrm{cm}^2$ for Ti/Pt/Au. The CVCs of both ohmic contacts were linear and did not require additional thermal annealing. We have found no published reports of such a strong difference between contact resistances corresponding to different metals. This may be attributed to the fact that the potential barrier at the p^+-diamond–Ti/Pt/Au interface is lower than at the p^+-diamond–Ti/Mo/Au interface. Inequality $\Phi_m > E_g + X_s$ needs to be satisfied for a

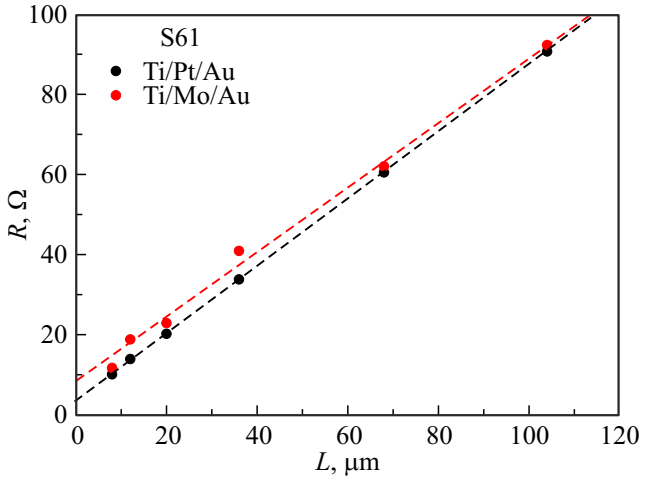

Figure 2. Total resistance between two adjacent Ti/Mo/Au and Ti/Pt/Au contacts as a function of distance between the contact pads in a TLM line.

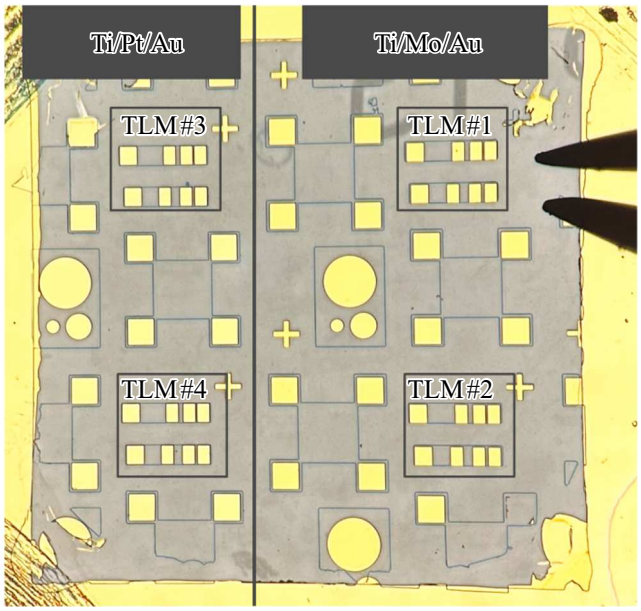

Figure 3. Photographic image of the diamond structure with metal contacts applied to test cells. The diamond sample is 3×3 mm in size.

potential barrier at the p^+-diamond–Me interface to vanish. Since the right-hand side of this inequality for diamond is 6.8 eV, it is not satisfied for any of the metals, and a barrier is always present. However, Φ_m for Pt (5.5 eV) is higher than the one for Mo (4.21 eV), and the inequality with Pt is closer to being satisfied.

3.2. Ohmic contact to *n*-type diamond

Mesa structures on diamond doped with phosphorus atoms were formed in a similar fashion (Figure 3). Figure 4 presents the total resistance between two adjacent Ti/Pt/Au contacts as a function of distance between the contact pads in a TLM line. A fine linear relation between resistance and distance is evident. The dotted line represents the least-squares fit. The inset in Figure 4 shows the CVCs corresponding to different distances between metal/phosphorus-doped diamond contacts at room temperature.

Similar measurements were performed for Ti/Mo/Au contacts. The CVCs of Ti/Mo/Au and Ti/Pt/Au contacts remain linear within a wide range of applied voltages, which is indicative of high quality of the obtained ohmic contacts. The specific contact resistance was $\rho_c = 5.4 \cdot 10^{-2}\,\Omega \cdot \mathrm{cm}^2$ for Ti/Mo/Au and $\rho_c = 8 \cdot 10^{-2}\,\Omega \cdot \mathrm{cm}^2$ for Ti/Pt/Au.

According to the results of TLM measurements, the variation of contact resistance and specific resistance induced by the choice of a specific metal was insignificant for n^+-diamond. The best contact resistance to diamond doped with phosphorus at the level of $3 \cdot 10^{20}\,\mathrm{cm}^{-3}$ was $\rho_c = 5.4 \cdot 10^{-2}\,\Omega \cdot \mathrm{cm}^2$ for Ti/Mo/Au without annealing. Using the same Ti/Mo/Au ohmic contact system, we have previously achieved $\rho_c = 2.3 \cdot 10^{-1}\,\Omega \cdot \mathrm{cm}^2$ for sample P6 at a phosphorus atom concentration of $2.5 \cdot 10^{20}\,\mathrm{cm}^{-3}$ [23]. It is evident that the concentration of phosphorus atoms in the diamond subcontact layer has a strong influence on the contact resistance reduction. According to the simple theory of metal/*n*-type semiconductor contacts, contact resistance $\rho_c \sim \exp(\varphi_b/N_\mathrm{D}^{1/2})$ varies exponentially with coefficient $\varphi_b/N_\mathrm{D}^{1/2}$, where φ_b is the Schottky barrier height and N_D is the donor concentration. The value of ρ_c in sample P13 was reduced by a factor of 4 relative to P6 due to an increase in N_D, which, in turn, led to narrowing of the barrier.

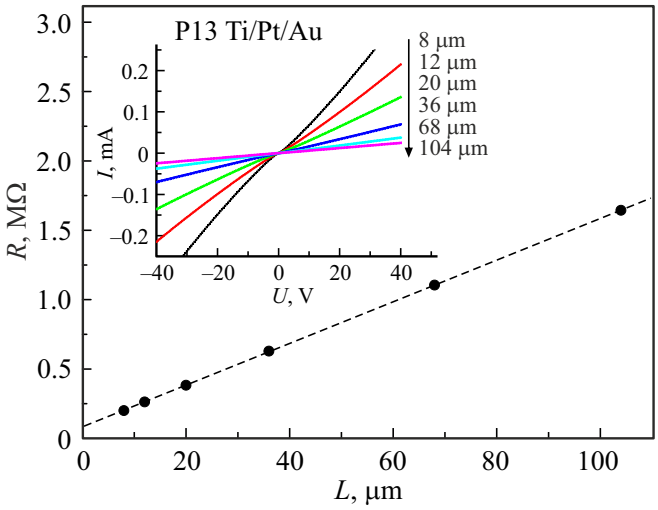

Figure 4. Total resistance between two adjacent contacts as a function of distance between the contact pads in a TLM line. The inset shows the CVCs between two adjacent contact pads corresponding to different distances between the metal/n^+-diamond contacts at room temperature. (A color version of the figure is provided in the online version of the paper).

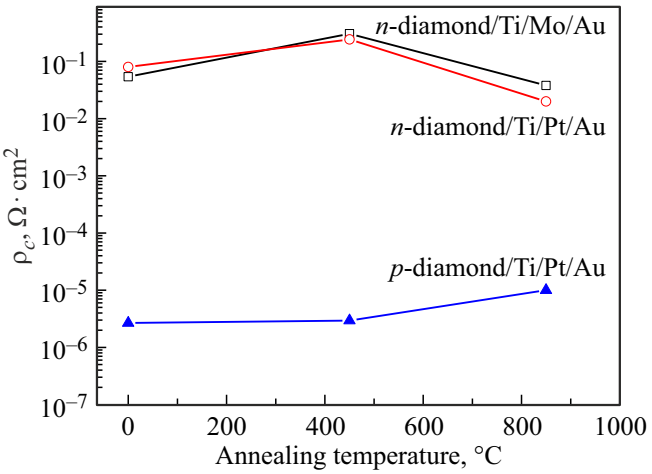

Figure 5. Dependence of the Ti/Mo/Au and Ti/Pt/Au contact resistance on annealing temperature.

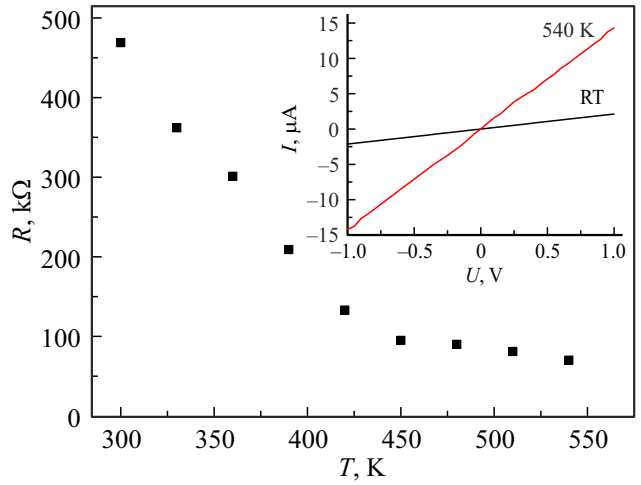

Figure 6. Temperature dependence of the total resistance between two adjacent Ti/Pt/Au contacts in a Hall cross on sample P13 annealed at 850°C. The CVCs of Ti/Pt/Au contacts at room temperature and 540 K are shown in the inset.

3.3. Effect of annealing at 450 and 850°C on the properties of contacts to *p*- and *n*-type diamond

The effect of annealing of metal contacts on the electrical properties of metal/p^+- and n^+-diamond contacts was examined: ρ_c was measured for Ti/Mo/Au and Ti/Pt/Au contacts after 5 min of annealing in argon atmosphere at different temperatures. The ρ_c values for two types of metals on p^+- and n^+-diamond before and after consecutive anneals at 450 and 850°C are shown in Figure 5.

The produced contacts on p^+- and n^+-diamond withstood two consecutive anneals of 450 and 850°C without degrading; their CVCs remained linear in a TLM line. This is indicative of high thermal stability of the obtained contacts.

In the case of p^+-diamond, high-temperature annealing had virtually no effect on ρ_c, and the semiconductor resistance also remained unchanged after annealing.

In the case of n^+-diamond, annealing at 450°C had a slightly negative influence on ρ_c for both metal types, and subsequent annealing at 850°C resulted in a 4-fold ρ_c reduction relative to the ρ_c value determined prior to annealing. We attribute the reduction in contact resistance to the formation of a titanium carbide layer at the metal/diamond interface, which may lower additionally the potential barrier. In addition, annealing at 850°C resulted in a 4–5-fold reduction in the resistance of the semiconductor itself: according to the results of Hall measurements, $\rho_{s/s}$ dropped from 12.8 to 2.8 Ω · cm. The CVCs of contacts in Hall crosses retained their linear properties after annealing.

Figure 6 presents the temperature dependence of the total resistance between two adjacent Ti/Pt/Au contacts in a Hall cross on sample P13 annealed at 850°C. The temperature dependence is of a semiconductor nature: the resistance decreases with increasing temperature. The contacts have linear CVCs at elevated temperatures (540 K).

4. Conclusion

The techniques for fabrication of two types of ohmic contacts (Ti/Mo/Au and Ti/Pt/Au) to epitaxial layers of *p*- and *n*-type diamond were compared. The obtained contacts did not require additional thermal annealing; their CVCs were linear in a TLM line. As far as we know, this has never been reported earlier in literature. In the case of *p*-type layers, the use of platinum instead of molybdenum as a diffusion barrier in a three-layer system made it possible to reduce the specific contact resistance by an order of magnitude to $\rho_c = 2.7 \cdot 10^{-6}\,\Omega \cdot \mathrm{cm}^2$ (for an epitaxial diamond layer with a boron concentration of $2 \cdot 10^{21}\,\mathrm{cm}^{-3}$). In the case of *n*-type diamond, the change of metal contact layers led to a less pronounced variation of contact resistance. This resistance was reduced to $\rho_c = 5.4 \cdot 10^{-2}\,\Omega \cdot \mathrm{cm}^2$ through the use of a diamond layer doped heavily with phosphorus in the subcontact region. The produced contacts on p^+- and n^+-diamond withstood two consecutive anneals of 450 and 850°C without degrading; their CVCs remained linear in a TLM line. This is indicative of high thermal stability of the obtained contacts.

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resulted in a 4–5-fold reduction in the resistance of the semiconductor itself.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Koizumi, C. Nebel, M. Nesladek. *Physics and Applications of CVD Diamond* (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008).
[2] S. Koizumi, H. Umezawa, J. Pernot. *Power Electronics Device Applications of Diamond Semiconductors*. Woodhead Publishing Series in Electronic and Optical Materials (2018).
[3] T.V. Blank, Yu.A. Goldberg. Semicnd., **41** (11), 1281 (2007).
[4] J.F. Prins. J. Phys. D: Appl. Phys., **22**, 1562 (1989).
[5] R. Kalish. Appl. Surf. Sci., **117/118**, 558 (1997).
[6] V. Venkatesan, D.M. Malta, K. Das, A.M. Belu. J. Appl. Phys., **74** (2), 1179 (1993).
[7] J.C. Pinero, M.P. Villar, D. Araujo, J. Montserrat, B. Antunez, P. Godignon. Phys. Status Solidi A, **214** (11), 1700230 (1-7) (2017). DOI: 10.1002/pssa.201700230
[8] Y.G. Chen, M. Ogura, S. Yamasaki, H. Okushi. Diamond Relat. Mater., **13** (11–12), 2121 (2004).
[9] T. Tachibana, B.E. Williams, J.T. Glass. Phys. Rev. B, **45** (20), 11975 (1992).
[10] J. Nakanishi, A. Otsuki, T. Oku, O. Ishiwata, M. Murakami. J. Appl. Phys., **76** (4), 2293 (1994).
[11] M. Yokoba, Y. Koide, A. Otsuki, F. Ako, T. Oku, M. Murakami. J. Appl. Phys., **81** (10), 6815 (1997).
[12] P.E. Viljoen, E.S. Lambers, P.H. Holloway. J. Vac. Sci. Technol. B, **12** (5), 2997 (1994). DOI: 10.1116/1.587549.
[13] K.L. Moazed, J.R. Zeidler, M.J. Taylor. J. Appl. Phys., **68** (5), 2246 (1990).
[14] Y. Chen, M. Ogura, S. Yamasaki, H. Okushi. Semicond. Sci. Technol., (20), 860 (2005). DOI:10.1088/0268-1242/20/8/041
[15] S. Kono, T. Teraji, H. Kodama, K. Ichikawa, S. Ohnishi, A. Sawabe. Diamond Relat. Mater., (60), 117 (2015). http://dx.doi.org/10.1016/j.diamond.2015.10.028
[16] D. Zhao, F.N. Li, Z.C. Liu, X.D. Chen, Y.F. Wang, G.Q. Shao, T.F. Zhu, M.H. Zhang, J.W. Zhang, J.J. Wang, W. Wang, H.X. Wang. Appl. Surf. Sci., **443**, 361 (2018). https://doi.org/10.1016/j.apsusc.2018.03.015
[17] H. Kato, H. Umezawa, N. Tokuda, D. Takeuchi, H. Okushi, S. Yamasaki. Appl. Phys. Lett., **93**, 202103 (2008). doi: 10.1063/1.3005639
[18] H. Kato, D. Takeuchi, N. Tokuda, H. Umezawa, H. Okushi, S. Yamasaki. Diamond Relat. Mater., **18**, 782 (2009).
[19] T. Matsumoto, H. Kato, N. Tokuda, T. Makino, M. Ogura, D. Takeuchi, H. Okushi, S. Yamasaki. Phys. Status Solidi RRL, **8** (2), 137 (2014). DOI 10.1002/pssr.201308252
[20] Nephi Temahuki, Rémi Gillet, Vincent Sallet, François Jomard. Physica Status Solidi A, **214** (11), 1700466 (2017).
[21] Patent Application Publication CONTACT STRUCTURES FOR N-TYPE DIAMOND, United States, Koeck et al. Pub. No.: US 2020/0343344 A1 Oct. 29 (2020).
[22] A.L. Vikharev, A.M. Gorbachev, M.A. Lobaev, A.B. Muchnikov, D.B. Radishev, V.A. Isaev, V.V. Chernov, S.A. Bogdanov, M.N. Drozdov, J.E. Butler. Phys. Status Solidi RRL, **10** (4), 324 (2016). DOI: 10.1002/pssr.201510453
[23] E.A. Arkhipova, M.N. Drozdov, S.A. Kraev, O.I. Khrykin, M.A. Lobaev, A.L. Vikharev, A.M. Gorbachev, S.A. Bogdanov, V.A. Isaev, A.V. Kudrin. Trudy XXVII Mezhdunarodnogo simpoziuma „Nanofizika i nanoelektronika,“ **2**, 526 (2023). (in Russian).
[24] E.A. Arkhipova, E.V. Demidov, M.N. Drozdov, S.A. Kraev, V.I. Shashkin, M.A. Lobaev, A.L. Vikharev, A.M. Gorbachev, D.B. Radishchev, V.A. Isaev, S.A. Bogdanov. Semiconductors, **53** (10), 1348 (2019).

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