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Electric field ionization of boron acceptors in single-crystalline diamond

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Vertical hole transport in single-crystalline diamond films with ohmic and Schottky contacts was studied at dc and pulsed electric fields up to ~ $5\cdot10^5$ V/cm. Conductivity mechanisms at different fields were identified. The concentrations of free carriers (holes) and acceptors were determined. The hole recombination time at boron acceptors has been estimated. The mechanisms of electric field ionization of boron acceptors are discussed.

Keywords: single-crystalline diamond, boron acceptors, electric field ionization.

1. Introduction

Boron is the dominant acceptor impurity in diamond which can be introduced in high concentration. Opposite to silicon and germanium, where boron ionization energies are 45 and 10 meV, respectively, the boron impurity in diamond has sufficiently high ionization energy ~370 meV, which makes problematic the usage of diamond for electronic applications [1]. Even at room temperature, only 1–2% of boron atoms are ionized, and the conductivity of the boron-doped diamond is rather small. To increase the conductivity, the elevated temperatures, or high boron concentration or high enough electric fields are needed. The scientific interest in boron ionization processes is connected with its relative similarity with hydrogen-like impurities in classical semiconductors Ge and Si. On the other hand, the high ionization energy of boron in diamond should give distinctive characteristic properties of high-field effects. In this report, the studies of conductivity of diamond weakly doped with boron at electric fields up to ~$5\cdot10^5$ V/cm are presented. The data of field ionization of boron acceptors in the diamond are given, as well.

2. Experimental

Basically, undoped diamond films of ~10 to 12 μm thicknesses were grown by chemical vapor deposition (CVD) on synthetic high-pressure high-temperature (HPHT) diamond substrates heavily doped with boron (~$2\cdot10^{19}$ cm^{-3}). The 3×3×0,3 mm substrate plates were cut in (100) crystallographic direction. The substrate surface layer damaged during polishing was removed by successive annealing at 1500 °C in a vacuum, dissolving the formed graphite in H_2SO_4 + $K_2Cr_2O_7$, and etching by 7 keV Ar^+ ion beam. Synthesis of epitaxial diamond films was performed by 2.45 GHz magnetron plasma in the high-purity methane and hydrogen mixture.

The contacts made of Ni–W alloy or Pt to form ohmic and Schottky contacts, respectively, were deposited by means of magnetron sputtering. In the case of Pt contact, the structure of m–i–p^+ type is formed as contact between

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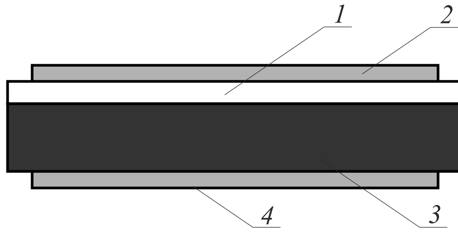

Fig. 1. Schematic view of the sample: *1* — homoepitaxial diamond film of 10 μm thickness, *2* — Pt- or Ni-W contact of 35 nm thickness, *3* — HPHT diamond substrate heavily doped with boron (10^{19} cm^{-3}) of 300 μm thickness, and *4* —metallic contact of 35 nm thickness.

undoped diamond *i*-layer and p^+ substrate should be ohmic. Contact areas were ~ 0.04 cm^2. Figure 1 schematically shows the cross-section of the samples used. Current–voltage (*I–V*) characteristics at low voltages (in particular, in the linear part of *I–V* curves for samples with ohmic contacts) were measured at the dc bias. To avoid Joule heating of samples at high voltages, the rectangular voltage pulses of 10 to 1000 μs duration and repetition frequencies of 1 to 100 Hz were used.

3. Results and discussion

The current–voltage characteristics of the diamond film with upper Schottky contact measured at dc and pulsed voltages are shown in Fig. 2. The dc *I–V* characteristics at different voltage polarities (curves *1*, *2*) are sharply asymmetrical because of the asymmetry of $m–i–p^+$ structure studied; the current at blocked Schottky contact (positively biased substrate) was ~ 3 orders of magnitude less than at the opposite polarity. The quadratic *I*(*V*) dependence in a wide voltage range is caused by the monopolar injection of holes. The *I–V* curves measured at pulsed voltage (curves *3*, *4*) differed cardinally from the dc characteristics. First, sample resistances in both polarities coincided in some voltage range. Second, there is the considerable voltage range (50 to 1500 mV) of linear *I*(*V*) dependence. This is the result of a shortening of the Schottky barrier by the pulsed voltage because of its capacitance so that the total voltage is applied to the high-resistance diamond *i*-layer. Note that the sample capacitance measured at 1 MHz frequency coincided practically with the geometric one and very weekly depended on voltage. It means that the contact depletion layer was much shorter than the *i*-diamond layer.

At higher voltages, the linear *I–V* dependence changed by square-law one corresponding to the monopolar injection. Naturally, the hole injection began at the lower voltage at a negatively biased substrate. The voltage of the transition from the linear to quadratic dependence gives the possibility to estimate the capture time of boron acceptors. The injection begins when the conditions $v\tau_M > L$ and/or $v\tau > L$ are fulfilled. Here $v = \mu E$ is the drift velocity of charge carriers, μ is their mobility, *E* is the electric field, τ_M and τ are times of dielectric relaxation and recombination, respectively, and *L* is the sample length. The first condition is not fulfilled in our case because of low concentration. So, we can use the second injection condition for recombination time to estimate. The recombination time for hole capture on boron acceptors turns out to have a reasonable value $\tau \sim 5\cdot10^{-9}$ s.

The data presented in the next Figs. 3, 4, 6–8 are for samples with the ohmic contacts. The plot shown in Fig. 3 is the current–voltage characteristic of the diamond film in a log–log scale. The *I–V* characteristics at low fields are linear, which makes it possible to estimate the concentrations of free carriers *p*. Using the mobility value of 2000 $cm^2/V\cdot s$ [2], we obtain $p \sim 10^8$ cm^{-3}. The concentration of active acceptor centers can be estimated from the recombination time value presented above by means of expression $1/\tau = \alpha(N_A - N_D)$, where N_A and N_D are acceptor and donor

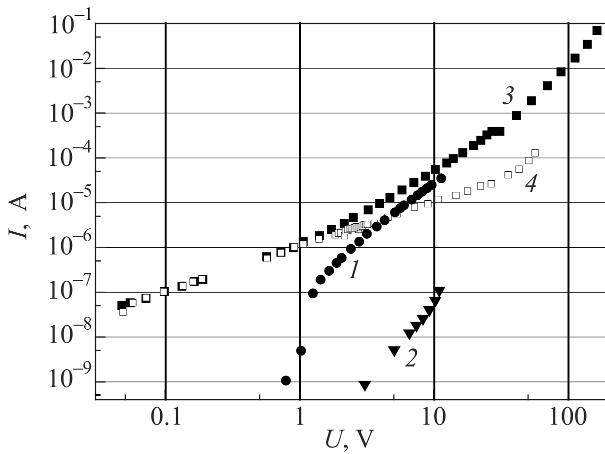

Fig. 2. I–V characterstics of 10 μm diamond film with the Schottky contact measured at different polarities of dc (*1*, *2*) and pulsed (*3*, *4*) voltages.

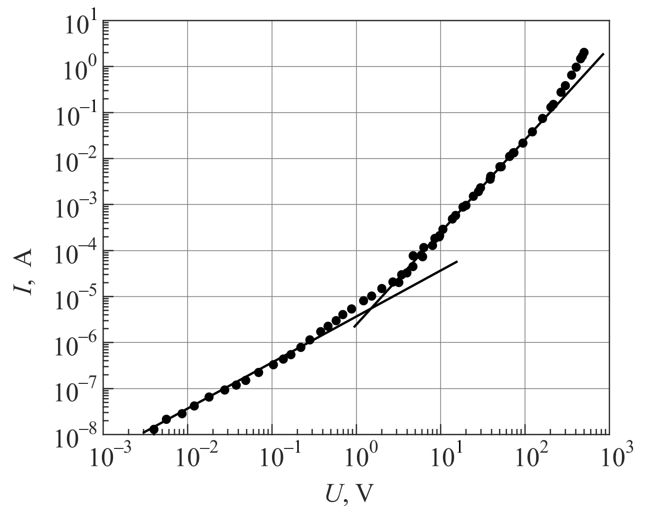

Fig. 3. Current-voltage characteristic of boron doped diamond with ohmic (Ni–W) contacts. Straight lines show linear and quadratic fittings. *T* = 300 K.

concentrations, respectively, $\alpha = sv_T$ is the capture coefficient for negative boron ions, s is the capture cross-section, $v_T = (3kT/m)^{1/2}$ is the average thermal velocity of charge carriers and m is the hole effective mass. Because there is high enough spreading in experimental values of hole capture cross-sections at boron ions [3–6] (approximately by an order of magnitude), we used here some average value of $s \approx 7\cdot10^{-13}$ cm^2. For m we used the effective mass of light holes ($m = 0.36m_0$) as they are excited mainly at thermionic emission [7]. Thus, $N_A - N_D = (s\tau)^{-1}(3kT/m)^{-1/2}$ and, for room temperature, we get $N_A - N_D \approx 2\cdot10^{13}$ cm^{-3}.

At fields larger than ~ 3 kV/cm, the I–V characteristics are quadratic (Fig. 3) caused in this case by the linear field dependence of a hole capture rate at ionized boron centers [7]. The similar field dependence was observed, e.g., at hole capture on boron acceptors in Si [8]. At higher fields (> 30 kV/cm), the field ionization of the boron acceptors was observed which was resulted in an exponential rise of current. The boron ionization is the result of Poole–Frenkel effect — the increase of thermionic emission of carriers from attractive impurities due to the lowering of the potential barrier of impurity by an external electric field [7]. Scheme of Poole–Frenkel effect is shown in Fig. 4. This is ascertained by fitting the experimental current–voltage characteristic by Frenkels formula $p \sim \exp\,[\varepsilon_{PF}/kT]$. Here ε is the elementary charge, E is the applied electric field, κ is the permittivity, k is Boltzmann's constant, T is the temperature, and $\varepsilon_{PF} = 2(e^3E/\kappa)^{1/2}$ is the Frenkel energy of the lowering of impurity barrier. Indeed, at fields exceeded 30 kV/cm, the drift velocity of charge carriers has to be saturated and the current density $j = epv_s$ (v_s is the saturated drift velocity) is proportional to the free carrier concentration. The square root field dependence of the logarithm of current at room temperature is shown in Fig. 5. The fit of this dependence by straight-line shows, indeed, that the ionization rate of the boron acceptors in a diamond increases exponentially with the square root of E in accordance with Frenkels theory [9].

The electric field ionization of shallow hydrogen-like impurities in Si and Ge is usually due to impact ionization, which becomes apparent, in particular, in the S-shaped form

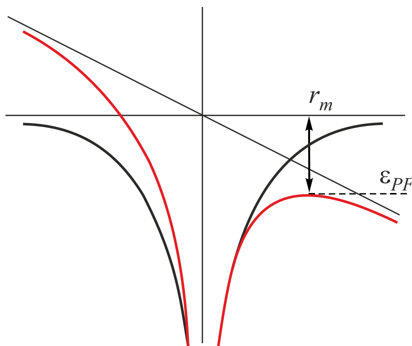

Fig. 4. The scheme of Poole–Frenkel effect. r_m is the position of the impurity potential maximum.

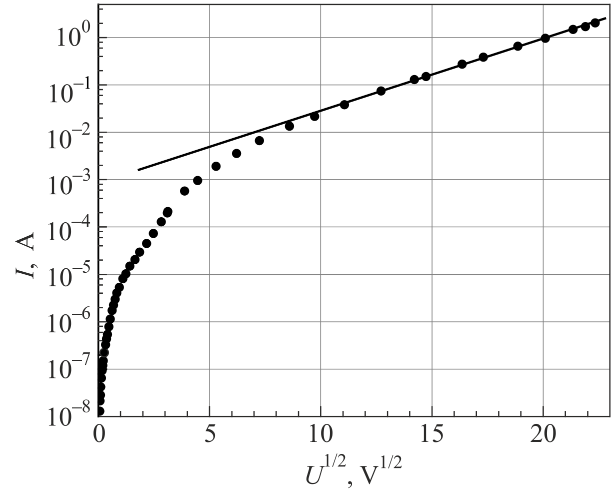

Fig. 5. I–V curves of boron doped diamond in log I–$U^{1/2}$ scale showing boron ionization through Poole–Frenkel effect.

of I–V curves. The origin of this S-shaped I–V characteristics is connected with excited states of impurities. As the result of impact ionization of the ground acceptor state,

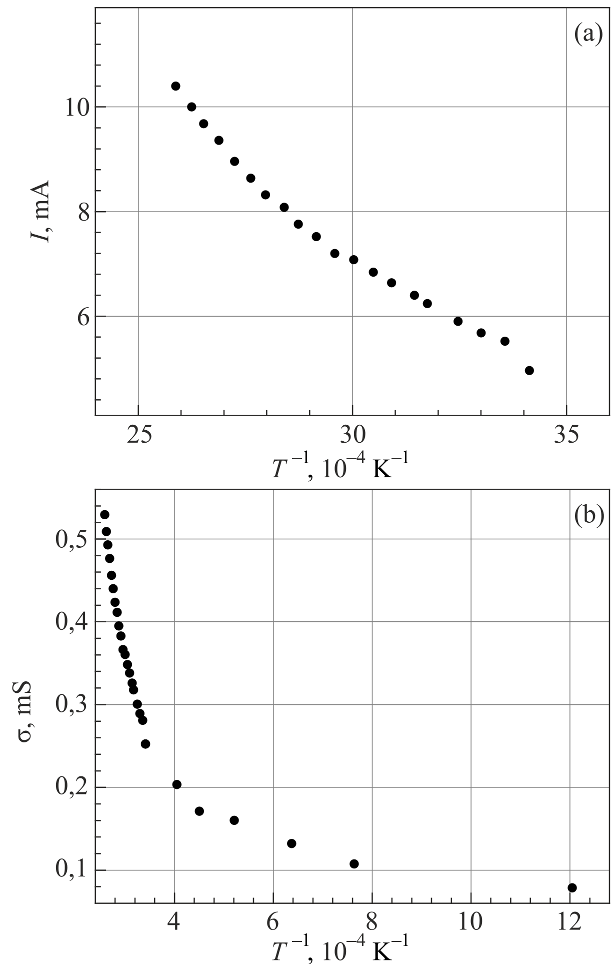

Fig. 6. (a) Temperature dependence of current in the range ~ 300–400 K. (b) Dependence of conductivity of 10 μm diamond film with ohmic contacts on temperature down to the liquid nitrogen one. E = 100 kV/cm.

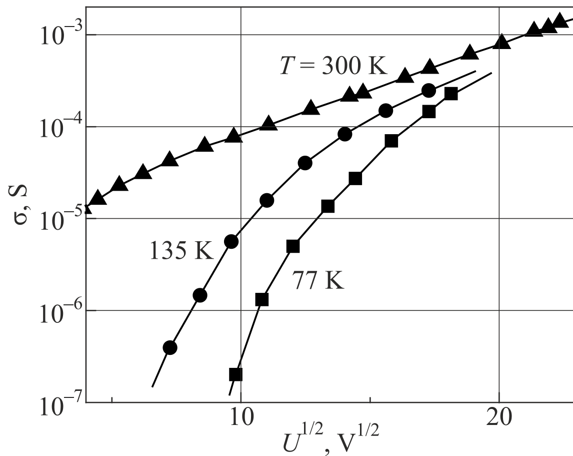

Fig. 7. Dependences of conductivity on voltage for 10 μm diamond film with Ni–W contacts at different temperatures.

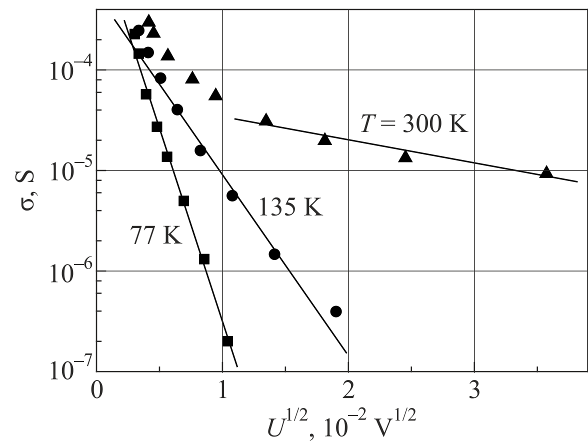

Fig. 8. Dependences of conductivity on voltage for diamond film in log (I/U)–U^{-1} scale showing boron ionization through direct tunneling.

these states are populated owing to the cascade mechanism of capture of carriers at attractive centers. The field of ionization of the excited states is considerably less than that for the ground state, resulting just in the *S*-shape of *I*–*V* curve (this model has been suggested in Ref. 10). In our case, the *I*–*V* curves are not *S*-shaped. The reason for this is also the Poole–Frenkel effect. At high fields sufficient for the impact ionization of boron ground state, the deepest excited state (~ 70 meV) is in the continuous spectrum (created so-called resonant state) because of large lowering of impurity potential. However, the *S*-shaped *I*–*V* curve has been observed in a heavily doped diamond [11].

Shown in Fig. 6 is the temperature dependence of high-field (100 kV/cm) conductivity. At the temperatures above room one, the current is proportional to exp $(\Delta\varepsilon/kT)$ [Fig. 6(a)]. At lowering the temperature, the conductivity should be frozen down into hopping one through impurity centers [12–14]. However, the hopping conductivity is extremely weak because of the small acceptor concentration and the large acceptor ionization energy (370 meV). So, the measurable conductivity can be only due to electric field ionization of acceptors at sufficiently high fields. The dependence of the conductivity on T below the room temperature down to that of liquid nitrogen is not exponential [Fig. 6(b)]; the most probable cause of this is the heating of holes by an electric field. The conductivity vs $U^{1/2}$ dependences at different T are shown in Fig. 7. The strong exponential rise of conductivity in the low-voltage region is supposed to be the result of direct tunneling of carriers from impurity centers into the continuum (Zener ionization). In this case, the dependence of the ionization rate should be the exponential function of the inverse electric field [7]. To prove this, we plotted the logarithm of conductivity versus $1/E$ (Fig. 8). A linear fit of this dependence evidences the predominance of the direct tunneling in boron acceptor ionization at low temperatures.

4. Conclusion

Vertical hole transport in single-crystalline diamond films doped with boron was studied at dc and pulsed electric fields up to $\sim 5\cdot 10^5$ V/cm. The *I*–*V* characteristics of diamond samples with Schottky contacts give the possibility to estimate the times of hole capture on boron acceptors. The impurity and free-carrier concentrations were estimated. The ionization of boron acceptors by high electric field above room temperature was shown to be due to Poole–Frenkel effect — enhancement of thermal emission of carriers in external electric fields. At low temperatures, it was possible to observe the field ionization owing to direct tunnel transitions of holes into the valence band from impurity centers (Zener ionization).

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Іонізація сильним електричним полем акцепторної домішки бору в монокристалічному алмазі

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У сильному електричному полі (~ $5\cdot10^5$ В/см) досліджено провідність епітаксійних алмазних плівок, які слабколеговані бором. Ідентифіковано механізми провідності в різних полях. Визначено концентрацію вільних носіїв (дірок). Оцінено час рекомбінації дірок на акцепторах бору. Обговорюються механізми іонізації акцепторів бору сильним електричним полем.

Ключові слова: монокристалічний алмаз, акцептори бору, іонізація електричним полем.