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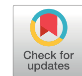

Yu.N. Novikov[a,*], V.A. Gritsenko[a,b,c]

[a] Rzhanov Institute of Semiconductor Physics SBRAS, 13 Lavrentiev aven., 630090 Novosibirsk, Russia
[b] Novosibirsk National Research University, 2 Pirogov str., 630090 Novosibirsk, Russia
[c] Novosibirsk State Technical University, 20 Marx aven., 630073 Novosibirsk, Russia

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ABSTRACT

The charge transport mechanism in thick film (~ 100 nm) amorphous boron nitride (a-BN) was studied experimentally and theoretically. Applying the experiments on the injection of minor carriers of n- and p-type silicon, the contribution of electrons and holes to the a-BN conductivity in the Si/BN/Al structure was determined. It was established that electrons and holes contribute to the a-BN conductivity, i.e. the a-BN conductivity is two-band. In a broad range of electric fields and temperatures, the charge transport in a-BN is satisfactorily described in the framework of the multiphonon trap ionization theory with thermal W_T = 1.0 eV and optical *Wopt* = 2.0 eV trap ionization energies, respectively.

1. Introduction

Boron nitride (BN) is a binary compound of boron and nitrogen. There are the following main structure modifications experimentally found of BN: a – amorphous [1–3], h - hexagonal, c-cubic, w-wurtzite and r-rhombohedral [4]. In addition to this, the existence of about a dozen allotropic modifications of BN was theoretically predicted [4]. The hexagonal modification of the BN lattice is closest to graphene (lattice difference ~ 1.8%). Amorphous boron nitride (a-BN) has a bandgap of ~ 4.5 −5 eV [1,2]. The a-BN films attract attention due to their thermal and mechanical properties, chemical stability and a large bandgap value [1]. Amorphous BN films can be grown on different substrates and have good interfaces with Si, SiO_2, Al_2O_3, metals, and two-dimensional materials, such as MoS_2 and graphene [1]. The breakdown voltages in a-BN thin films [1] considerably exceed the breakdown voltages in h-BN [5].

To use a-BN in microelectronics, it is necessary to know the charge transport mechanism in it. In most dielectrics, the charge transport is accomplished using traps. Many researchers use the Frenkel effect when describing the charge transport in various boron nitride (h-NB, c-BN) modifications [6,7]. However, in some cases, when interpreting experiments on the charge transport in dielectrics, for example, Si_3N_4, Al_2O_3, using the Frenkel effect, it is necessary to use, in agreement with the experiment, a nonphysically small frequency factor value $\nu 10^6$-10^9 s^{-1} in the calculations [8,9]. In the original Frenkel paper, the frequency factor magnitude was estimated as $\nu \approx 10^{15}$ s^{-1} [10].

The objective of the present paper is the experimental study of the charge transport in a-BN and the determination of: firstly, the type of carriers involved in the charge transport; secondly, the trap ionization mechanism (the quantitative comparison of experiment data with the Frenkel effect and the multiphonon trap ionization theory).

2. Methods

The metal-insulator-semiconductor (MIS) structures were prepared for electrophysical measurements. Thick boron nitride films (d_{BN}~100 nm) were synthesized on a Si substrate with a conductivity of about 7 Ω•cm. Amorphous BN was obtained using a borazin pyrolysis ($B_3N_3H_6$) at T = 400–600 °C. A metal (Al) contact with the area of $5{\cdot}10^{-3}$ cm^2 was deposited through a mask in vacuum at 10^{-5} Torr. To determine the type of conductivity, a-BN films were grown on n- and p-type Si substrates. The refractive index was measured by a laser ellipsometer at the wavelength of 6328 A and it equaled 2. To determine the charge transport mechanism in a-BN, the I-V characteristics for various temperatures in MIS structures for n-Si substrate at a positive potential on Al were measured.

Here we consider two trap ionization models: Frenkel effect (Fig. 1(a)) [10], along with the thermally assisted tunneling (TAT) [8,9] and the multiphonon mechanism (Fig. 1(b)) [8,9,11]. The rate of trap ionization P_F in the Frenkel model is given by [10]:

$$P_F = \nu \exp\left(-\frac{W_t - \beta\sqrt{F}}{kT}\right), \quad \beta = \sqrt{\frac{e^3}{\pi\varepsilon_\infty\varepsilon_o}}, \tag{1}$$

here W_t is the trap energy, F = U/d_{BN} is the electric field, U is the

* Corresponding author.
E-mail address: nov@isp.nsc.ru (Y.N. Novikov).

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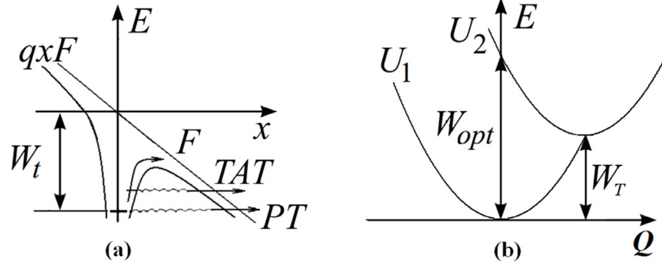

Fig. 1. Energy diagrams for two trap ionization mechanisms: (a) the Frenkel effect with the TAT marked as: *F*- Frenkel effect, TAT- thermally assisted tunneling, PT – pure tunneling, W_t - coulomb trap energy, (b) multi-phonon ionization mechanism; U_1 - trap potential energy filled with an electron, U_2 - empty trap potential energy, *Q* - configuration coordinate, W_T and W_{opt} are the thermal and optical trap ionization energies, respectively.

voltage,$\beta$is the Frenkel constant, $\varepsilon_\infty = 4$ is the high-frequency a-BN dielectric constant, ε_0 is the electric constant, *e* is the electron charge, *k* is the Boltzmann constant, *T* is the temperature, ν is the frequency factor value.

For the TAT, the trap ionization probability for the Coulomb potential is given as [8]:

$$P_{TAT} = \frac{\nu}{kT}\int_0^{W_t-\beta\sqrt{F}} dW \exp\left(-\frac{W}{kT} - \frac{2}{\hbar}\int_{x_1}^{x_2} dx\sqrt{2m^*(eV(x) - W)}\right), \tag{2}$$

$$V(x) = W_t - \frac{e}{4\pi\varepsilon_\infty\varepsilon_0 x} - Fx,$$

here *W* is the excited energy level, $m^*$is the tunnel effective mass, values x_1, $x_2$are classical turning points

$$x_{1,2} = \frac{1}{2}\frac{W_t - W}{eF}\left(1 \mp \left(1 - \frac{eF}{\pi\varepsilon_0\varepsilon_\infty(W_t - W)^2}\right)^{1/2}\right) \tag{3}$$

The electron tunneling, treated here by the semi-classical approximation and the integral over *x*, can be expressed with elliptic integrals.

The rate of trap ionization by the Frenkel mechanism, taking into account the TAT, was calculated using the formula [8]:

$$P_{F,TAT} = P_F + P_{TAT} \tag{4}$$

To describe the charge transport experiments in a-BN, the multi-phonon trap ionization theory was also used, and it showed a good agreement with the experiment for the charge transport [8,9]. In the framework of this model [11], rate of trap ionization is given by the expression:

$$P_{MP} = \sum_{n=-\infty}^{+\infty} \exp\left[\frac{nW_{ph}}{2kT} - S\coth\frac{W_{ph}}{2kT}\right] I_n\left(\frac{S}{\sinh(W_{ph}/2kT)}\right) P_i(W_T + nW_{ph}),$$

$$P_i(W) = \frac{eF}{2\sqrt{2m^*W}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m}}{\hbar eF}W^{3/2}\right), \quad S = \frac{W_{opt} - W_T}{W_T},$$

$$F = U/d_{BN}, \tag{5}$$

where *In* is Bessel modified function, W_T and W_{opt} are the thermal and optical trap ionization energies, respectively, W_{ph} is the phonon energy. The electric current density (*J*) for two models is calculated by the expression [12]:

$$J = eN^{2/3}P \tag{6}$$

where *P*- rate of trap ionization Formula (4) or (5) and *N* – trap concentration in the a-BN.

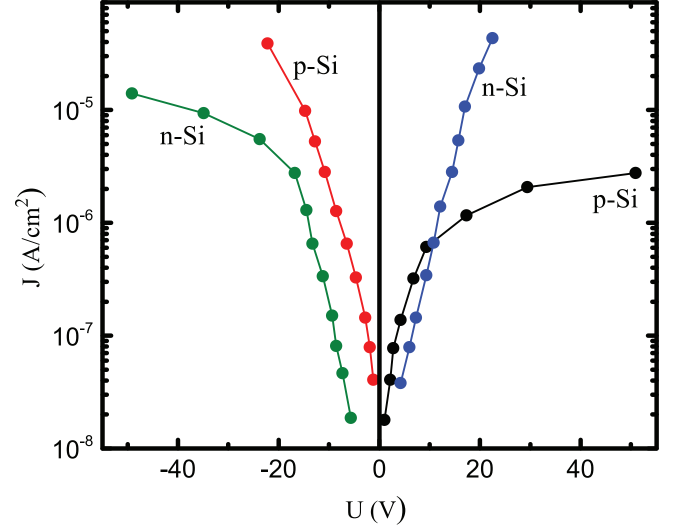

Fig. 2. Experimental I-V characteristics for the MIS-structure with a-BN (100 nm) films on n- and p- Si substrates at different polarities on Al ($T = 300$ K).

3. Results and discussion

Experiments were performed to demonstrate the two-band charge transport mechanism in a-BN. In Fig. 2 are the current–voltage (I-V) characteristics measured on MIS structures for n- and p-type substrates in the depletion and in accumulation modes ($T = 300$ K).

In the accumulation mode with a negative potential on Al (p-Si) and a positive potential on Al (n-Si), an exponential increase in the electrical current with an applied voltage was observed. The conductivity, in this case, is carried out by the major carriers injected from the Si substrate into a-BN. At the positive potential on Al in the MIS-structure (p-Si), the charge transport in a-BN is carried out by electrons, i.e. minority carriers. At a negative potential on Al, the conductivity in the MIS-structure (n-Si) is carried out by holes. In the depletion mode on n- and p-types of substrates, the current saturation in Fig. 2 was observed at two polarity types. The voltage, at which saturation begins to be observed, corresponds to the formation of non-equilibrium depletion near the Si/BN interface. In this layer, a limited generation of minority carriers occurs, and it leads to the current saturation in the I-V characteristic. This experiment shows that the conductivity in a-BN is limited by the bulk mechanisms and has a two-band character, i.e. it can be carried out by both electrons and holes.

The experimental I-V characteristics (circles) and their calculation using the Frenkel effect with TAT in a-BN (solid lines) are shown in Fig. 3. The calculation was performed for the following trap parameters: W_t=1.3 eV, $N = 9{\cdot}10^{18}$ cm^{-3}, $\nu = 4.3{\cdot}10^{11}$ s^{-1} and m^*=0.3m_o (m_0 – free electron mass). For high temperatures ($T = 460$ - 520 K), in the region of weak fields $<10^6$ V/cm ($U < 10$ V), a good agreement of the experiment with the calculation is observed (Fig. 3). At lower temperatures, the agreement with the experiment becomes worse. The calculation predicts that, for electric fields $>10^6$ V/cm ($U > 10$ V), the effects associated with the electron tunneling through the potential barrier created by the trap should be most pronounced. In this connection, the calculation predicts a higher electric current value for electric fields $> 10^6$ V/cm than in the experiment. In addition, the frequency factor value used in the calculations was $4.3{\cdot}10^{11}$ s^{-1}, which is by four orders of magnitude less than the frequency factor value ($\nu = W_t/h \approx 10^{14}$ s^{-1}) estimated in the original work by Frenkel [10]. Thus, the Frenkel effect, taking into account the TAT, describes the experiments on the charge transport in a-BN for high temperatures, but the frequency factor value used in the calculations is non-physically small. Earlier, a small frequency factor value was obtained at describing

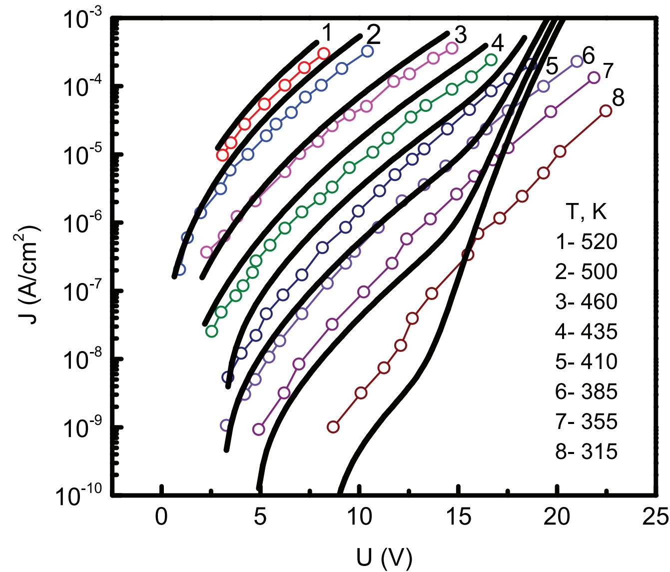

Fig. 3. Experimental I-V characteristics (circles) for the MIS-structure with a-BN films on n-Si substrates at different temperatures at a positive potential on Al and the calculated one using the Frenkel effect with TAT (solid lines). Trap parameters: W_t=1.3 eV, $\nu = 4.3{\cdot}10^{11}$ s^{-1}, m^*=0.3m_o, $N = 9{\cdot}10^{18}$ cm^{-3}.

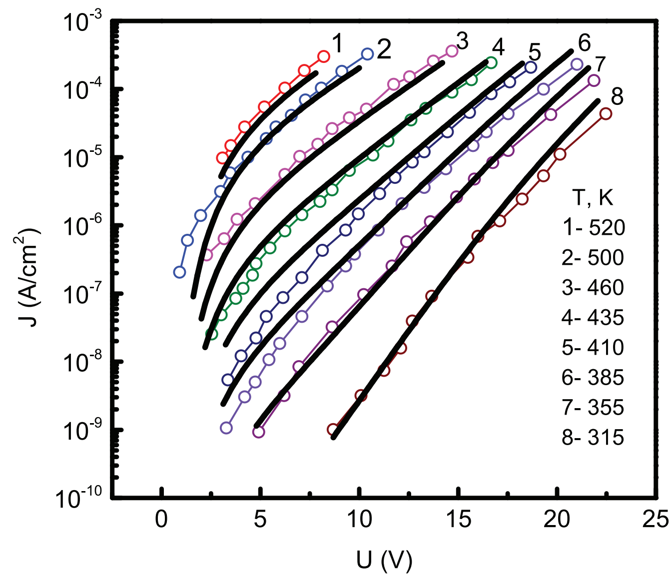

Fig. 4. Experimental I-V characteristics (circles) for the MIS-structure with a-BN films on n-Si substrates at different temperatures at a positive potential on Al and the calculated one using the multiphonon trap ionization mechanism (solid lines). Trap parameters: W_T=1.0 eV, W_{opt}=2.0 eV, W_{ph}=0.06 eV, $m^* = 0.3m_o$, $N = 2.5{\cdot}10^{18}$ cm^{-3}.

the charge transport in SiN_x [8] and Al_2O_3 [9].

The experimental I-V characteristics (circles) and their calculation using the multiphonon trap ionization mechanism in a-BN (solid lines) are shown in Fig. 4. The calculation showed a satisfactory agreement with the experiment in the entire range of voltages and temperatures. The following trap parameters were used in the calculations: W_T=1.0 eV, W_{opt}=2.0 eV, W_{ph}=0.06 eV, m^*=0.3m_o and $N = 2.5{\cdot}10^{18}$ cm^{-3}.

The pre-exponential factor value $4{\cdot}10^{13}$ s^{-1} calculated by the formula $\nu = eF/2\sqrt{2m^*W_{opt}}$ is in a good agreement with the order of the pre-exponential factor values obtained in various dielectrics [8,9]. In the present paper, $W_{opt}/W_T = 2$. The same ratio (or close to this) for W_{opt} and W_T, when applying the multiphonon ionization theory to describe the charge transport, was obtained in other dielectrics: Si_3N_4, Al_2O_3 and $Hf_{0.5}Zr_{0.5}O_2$ [8,9,12]. In all these materials, the charge transport is described using deep traps ($W_T \geq 1$ eV). To describe these experiments, in a wide range of electric fields and temperatures, the most convenient initial location of U_1 and U_2 is shown in Fig. 1(b), i.e. the minimum of U_2 lies on U_1, which corresponds to the condition $W_{opt}/W_T = 2$. With a positive potential on Al (taking into account that on n-Si substrates), the main contribution to the a-BN conductivity should be made by electrons (Fig. 2). Bulk amorphous boron nitride is characterized by predominantly sp^2 bonding [1,3], as in h-BN. However, in particular, in [13] the composition and structure of a-BN films deposited from borazin pyrolysis are reported. This technology is close to the technology of preparing a-BN in this work. It was shown [13] that the a-BN films consist of the mixtures of poorly crystalline h-BN and c-BN. In the work Ref. 14, it was shown that the nitrogen vacancy (three-boron center) in h-BN is a trap for an electron with energy of ~ 1 eV, which coincides with the thermal energy obtained in this work.

4. Conclusion

To sum it up, in a wide range of electric fields and temperatures, the charge transport in a-BN films was studied experimentally and theoretically. It was shown that the charge transport in a-BN is two-band, i.e. carried out by both electrons and holes. The multiphonon trap ionization theory satisfactorily describes the experimental I-V characteristics with following trap parameters: W_T=1.0 eV, W_{opt}=2.0 eV, W_{ph}=0.06 eV, m^*=0.3m_o and $N = 2.5{\cdot}10^{18}$ cm^{-3}.

CRediT authorship contribution statement

Yu.N. Novikov: Conceptualization, Data curation, Methodology, Investigation, Writing - original draft, Writing - review & editing. **V.A. Gritsenko:** Conceptualization, Data curation, Methodology, Investigation, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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