Anomalous high capacitance of $\beta$-rhombohedral boron induced by structural defects

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Abstract. Capacitance and dielectric loss tangent measurements have been carried out for $\beta$-rhombohedral boron within the frequency range $10^2 - 10^4$ Hz and temperature interval $77 - 373$ K. Different specimens were studied: high-purity macrocrystals, vapor-liquid-grown faceted crystals, zone-melted single crystals, and crucible-melted polycrystals. Within the whole ranges of measurements, the capacitance of all samples was 10-60 times larger than their geometric capacitance. Temperature dependences of the capacitance reveal two-level step-like behavior. Location of levels is independent from the applied electric field frequency, but at higher frequencies, the capacitance steps shift to lower temperatures. For all frequencies, an abrupt rise in capacitance takes place at one and same temperature ~ 290 K. At low temperature, dielectric losses are negligible, but they increase towards the room temperature. At ~ 290 K (i.e., simultaneously with the abrupt rise in capacitance) their value abruptly falls down. Dielectric properties of $\beta$-rhombohedral boron are discussed on the basis of generalized barrier model of the heterogeneous semiconductor within its three-layer version. Planar defects like twins and stacking faults characteristic for real crystals are assumed to produce local elastic stresses sufficient for the local lowering in conductivity due to the piezoresistive effect. Consequently, layers adjacent to the planar defects should represent low-conducting inclusions in the relatively high-conducting matrix. In addition, the lesser-conducting barrier layers should appear at their boundaries. Effect at ~ 290 K seems to be related with a symmetry-restoring phase transition driven by the occupation patterns of certain atomic sites in $\beta$-rhombohedral crystalline boron lattice.

1. Introduction

Semiconductor can be considered as a dielectric with variable conductivity. When the changes in conductivity are heterogeneous, material reveals unusual dielectric properties such as “giant” capacitance. They may be useful in electronics, e.g., for making electrical elements with high capacitance. In recent years, perovskites and some related complex materials have attracted much attention due to their extremely high dielectric constants at low frequencies, which are unchanged over the wide temperature ranges [1-10]. Similar effect is known for a long time in elemental boron. Here we return to this interesting problem aiming to present new experimental results on $\beta$-rhombohedral
boron (below, β-B), namely “giant” capacitance, and discuss them on the basis of a model of the heterogeneous semiconductor.

β-B is semiconductor, real samples of which quite often are characterized by the “giant” values of capacitance \( C \): they noticeably exceed the geometric value \( C_0 \) calculated from the specimen form and static dielectric constant \( \varepsilon : C_0 = \varepsilon_\delta \varepsilon S / d \). Here \( S \) is the area of electrodes and \( d \) is the distance between them. Effective (apparent) dielectric constant \( \varepsilon_{eff} \) can be recalculated from the measured low-frequency capacitance using similar formula \( C = \varepsilon_\delta \varepsilon_{eff} S / d \). Thus, the ratio of effective dielectric constant and real one is defined by the ratio of measured and geometric capacitances of a sample, \( \varepsilon_{eff} / \varepsilon = C / C_0 \). To the best our knowledge, there are no recent studies devoted to the low-frequency dielectric properties of boron. As for the early data, summarizing them one can mark two main features: (1) polarizing dielectric losses in this material are small, and hence its dielectric constant weakly depends on the frequency of applied electric field; in any case, it is of the order of 10; (2) as a rule, a measured low-frequency capacitance is “giant”, exceeding the value calculated from the sample geometry.

2. Experiment

Four types of samples were studied in the present work:

No. 1 – pure macrocrystalline material obtained by vacuum deposition of boron on boron filament with subsequent zone melting. It contains \( \leq 30 \) ppm carbon and has room-temperature resistivity \( \sim 2 \cdot 10^7 \) \( \Omega \cdot \text{cm} \).

No. 2 – faceted single crystals grown by vapor–liquid crystallization inside the voids nucleated in boron melt. In such a material foreign atoms are manly segregated at the planar defects, and their single-crystalline matrix contains significantly less impurities than crucible-melted polycrystals (see below No. 4). This assumption, based on the structural features, is supported by the room-temperature resistivity value \( \sim 8 \cdot 10^6 \) \( \Omega \cdot \text{cm} \), which significantly exceeds that for the crucible-melted samples.

No. 3 – zone-melted single-crystal specimens with purity 99.99 % and room-temperature resistivity \( \sim 2 \cdot 10^6 \) \( \Omega \cdot \text{cm} \).

No. 4 – polycrystals melted in crucible with purity 99.95 % and room-temperature resistivity \( \sim 4 \cdot 10^5 \) \( \Omega \cdot \text{cm} \).

Figure 1. Electron-microscopic image of polysynthetic twin packet in β-rhombohedral boron single crystal.
X-ray diffraction confirms that all samples have the \( \beta \)-rhombohedral structure. Stacking faults and twinned layers are observed by electron diffraction. The image of the polysynthetic twin packet in \( \beta \)-rhombohedral boron single crystal presented in figure 1 is typical for all investigated samples. It is not easy to measure the planar defect concentrations. Even if they are assumed equal in specimens of various origins, they should be distinguished by orientations of the defect planes. Planar defects in pure \( \beta \)-B single crystals prefer \{101\} planes of the elemental rhombohedron faces. However, impurities accumulated at the planar defects may randomize their orientations to some extent.

Prismatic specimens were cut out from rods by a diamond saw. Their surfaces were mechanically polished using boron carbide powders and then the formed amorphous surface layers were etched in boiling nitric acid solution. Tail-end surface cleaning was made using solution containing alkaline potassium before flushing with distilled water. Such treatment excludes any interface capacitance. The pairs of symmetrical layer-electrodes were formed by the vacuum sputtering of silver onto the opposite flat surfaces of the tested specimens.

Dielectric parameters were measured within the frequency range \( \omega / 2\pi = 10^2 \sim 10^4 \) Hz (\( \omega \) is the cyclic frequency) in the temperature range between boiling points of nitrogen and water \( T = 77 \sim 373 \) K. Electrical oscillations were excited applying a low-frequency generator. Temperature of a tested sample was estimated by a thermocouple, soldered end of which was placed inside a similar sample placed nearby in the same chamber.

The capacitance parameters are summarized in table 1. Geometric capacitances are specified in the second column. They were calculated taking the \( \beta \)-B static dielectric constant as \( \varepsilon = 8.0 \). In the whole frequency and temperature ranges, the measured values of capacitance for all samples were \“giant\”, i.e., significantly exceeding corresponding geometric capacitances, \( C / C_0 \sim 10 \sim 60 \).

**Table 1.** Measured capacitance parameters of \( \beta \)-rhombohedral boron samples.

| Sample | \( C_0 \), pF | \( C_{1+2} / C_0 \) | \( C_1 / C_0 \) | \( C_1 / C_{1+2} \) | \( p_2 / p_1 \) |
|--------|---------------|-----------------|----------------|----------------|----------------|
| No. 1  | 1.0           | 15              | 43             | 2.9            | 1.9            |
| No. 2  | 1.5           | 16              | 34             | 2.1            | 1.1            |
| No. 3  | 2.4           | 10              | 23             | 2.3            | 1.3            |
| No. 4  | 1.1           | 20              | 58             | 2.9            | 1.9            |

Frequency and temperature dependences of the dielectric properties of purer crystals (samples No. 1 and No. 2) are shown in figures 2 and 3. In the low-temperature region, capacitance practically does not depend on the temperature and has certain constant value \( C_1 \). With increasing temperature, it rapidly decreases to the new value \( C_{1+2} \), and further, right up to \( \sim 290 \) K, again does not change. At this point, capacitance suddenly comes back to the former value \( C_1 \), and at higher temperatures also remains constant. As for the dielectric loss tangent \( \tan \delta \), it is small in the whole low-temperature region and does not depend on temperature. Losses start to increase only near the room temperature, and the sudden increase in \( C \) at \( \sim 290 \) K is accompanied by the same-type reduction in \( \tan \delta \) value. In the temperature ranges where the dielectric parameters of the samples are constant, they are frequency independent as well. Locations of the features on \( C - T \) and \( \tan \delta - T \) curves also do not depend on \( \omega \): at any frequency they are observed at \( \sim 290 \) K. On the contrary, with increase in frequency the
regions of decrease in capacitance are displaced towards low temperatures (they can even fall outside the measurements range), and dielectric losses, which depend on temperature only near the room temperature and above, weaken.

![Graph 1](image1.png)

![Graph 2](image2.png)

**Figure 2.** Temperature dependences of capacitance (1) and dielectric loss tangent (2) for pure macrocrystalline $\beta$-rhombohedral boron measured at frequencies $2 \times 10^2$ (white circles) and $5 \times 10^3$ Hz (black circles).
Figure 3. Temperature dependences of capacitance (1) and dielectric loss tangent (2) for faceted single-crystalline β-rhombohedral boron measured at frequencies $1 \cdot 10^3$ (white squares) and $1 \cdot 10^4$ Hz (black squares).

In samples with lesser purity (No. 3 and No. 4), dielectric losses are stronger. In general, their temperature characteristics are similar to the described above. However, curves for the given
frequency were only partially reproducible. Within the measurement errors, capacitance values \( C_i \) and \( C_{i+2} \), and temperature of jumps \( \sim 290 \text{ K} \) are the same. However, neither measured values of \( \tan \delta \) nor regions of decrease in capacitance are reproducible.

3. Discussion

In general, heterogeneity is known to be a rationale for any abnormal change in measured values of dielectric or other electrophysical parameters of a material [11].

Results of the present measurements, together with earlier empirical data on the dielectric properties of \( \beta \)-B real crystals, can be explained within a model of the crystalline semiconductor heterogeneous by the conductivity. Indeed, temperature dependence of the capacitance of such semiconductor should be a step-like function with levels determined by the sum (in the specimen thickness) of layers with relatively low conductivity within given temperature region, because they are “short-circuited” by the relatively high-conductive layers; and these levels may significantly exceed the geometric capacitance. As for the temperature dependence of dielectric losses in heterogeneous semiconductor, it should follow that of the specimen conductivity averaged in some way (for efficient numerical simulation of the alternating current conduction in heterogeneous materials see, for example, [12]). All semiconductors, including \( \beta \)-B, reveal monotonous growth in their ohmic conductivity with temperature. Correspondingly, dielectric losses should reveal a general growth trend. However, inside the inhomogeneous specimen, between two adjacent layers with different ohmic conductivities, a barrier-layer with non-ohmic conductivity can be formed with an unusual temperature dependence of the conductivity.

There are many different physical mechanisms causing heterogeneous conductivity related with chemical impurities and structural defects in semiconductors, like the heterogeneous doping, impurities segregation at the grain boundaries in polycrystalline specimens, formation of complexes of impurity atoms with radiation defects in irradiated material (see [13]), etc. There is a strong evidence for heterogeneity effects in some single-crystalline and chemically pure semiconductors. Apparently, in such cases the layers with different conductivities can be formed only due to piezoresistance effect induced by the local elastic stresses, which are related with twins and stacking faults existing in real single crystals. Indeed, elastic textures, such as twin and anti-phase boundaries, can generate electronic heterogeneity in materials with strong electron-phonon coupling [14]. Note that such coupling is characteristic for \( \beta \)-B.

To answer a question, what kind of heterogeneity is responsible for unusual dielectric properties of \( \beta \)-B, we should pay attention to the fact that the high capacitances are measured not only for contaminated polycrystals, but also for pure single crystals. Therefore, the models, based on significant concentration of impurities and/or grain boundaries between fine crystallites, have to be excluded. On the one hand, even pure single crystals of \( \beta \)-B can include twinned layers and stacking faults, which are capable to combine into micro-twins; and metallographic analysis of the fracture faces in zone-melted boron reveals accumulation of high residual stresses in twinning planes. On the other hand, \( \beta \)-B exhibits piezoresistance, which can lead to the local changes in conductivity of the stressed layers adjacent to planar structural defects and to the increase in the electrical resistance of \( \beta \)-B single crystal due to the internal stresses during the plastic deformations. Correlation was found [15] between heat-treatment modifications in mechanical and electric properties of samples, which reveals influence of stresses on the \( \beta \)-B conductivity.

For estimation of the internal pressure value \( p \) in stressed layers adjacent to twinning planes in \( \beta \)-B crystals, we can use its elastic parameters, e.g., Young modulus \( E = 4.58 \cdot 10^{11} \text{ Pa} \) [16]: \( p \sim 10^{12} \text{ Pa} \). Piezoresistance coefficient \( \Pi \) of \( \beta \)-B single crystal for uniaxial deformation is known to be \( \Pi \sim 10^{-9} \text{ Pa} \) [17]. Then, we obtain \( \Pi p \sim 10^{3} \gg 1 \). Thus, the conductivity within the stressed layers will be smaller by few orders of magnitude than in the rest of crystalline \( \beta \)-B. Note that
piezoresistance effect in $\beta$-B can reflect two possible effects causing heterogeneity by the conductivity: changes in hopping mobility of the localized charge carriers and/or in concentration of the localization centers controlling hopping conductivity. As for the thickness $d$ of the stressed layers including twinning planes in $\beta$-B crystals, it can be estimated using the lattice constant value $a = 10.15 \text{Å}$ [18]. For example, for the sample No. 4, presence of the low-conductive layers with thickness $d \sim 10 \text{Å}$ increases capacitance by $C_i / C_0 \sim 60$ times. Then, at least one planar defect should exist approximately on every $60 \times 10 \text{Å} = 600 \text{Å}$ of the specimen thickness. The obtained value is reasonable for linear density of such defects in $\beta$-B.

Presence in our $C - T$ characteristics of only two different horizontal levels $C_i$ and $C_{i+2}$ placed noticeably higher than $C_0$ level shows that for describing the low-frequency dielectric properties of the tested $\beta$-B samples it is sufficient to consider only two kinds of low-conductivity layers. They can be treated within a simple barrier model of the heterogeneous semiconductor, according to which in a crystal there are ohmic inclusions with relatively lower conductivity together with adjacent barrier layers. At low temperatures, probably, only low-conductive stressed ohmic layers contribute to the capacitance. If their sum in the sample thickness is $p_1$, then we get $C_0 / C_1 = p_1$. Upon temperature increase, when conductivity of the barrier layers decreases, those two start to affect the measured capacitance. If the sum of the barrier layers is $p_2$, we get $C_0 / C_{i+2} = p_1 + p_2$. Suggested sequence of “actuations” of ohmic and barrier layers follows from the fact that averaged ohmic conductivity of $\beta$-B always increases with temperature. The fact that values $C_i / C_0$ and $C_{i+2} / C_0$ for samples of various origins vary noticeably is not unexpected, because these ratios are determined by the concentration and orientation of planar defects. Meanwhile, the ratio $C_i / C_{i+2} = 1 + p_2 / p_1$ of two levels of capacitance expressed by the ratio $p_2 / p_1$ is constant to some extent. The given result is one more argument in favor of the barrier model accepted for $\beta$-B, which suggests correlation between sums of the low-conductive layers of two kinds.

Analysing obtained differences in $C / C_0$ ratios between tested samples, we should take into account that maximal effect of the relatively low-conductive thin planar inclusions on the sample capacitance takes place when inclusions are perpendicular to the applied bias, while they have almost no effect being parallel to the field. In case of randomly oriented inclusions, only layer projection on plane perpendicular to the applied electric field acts effectively. On the other hand, measured ratio $C / C_0$ increases as the sum of low-conductive layers decreases. Thus, higher values are expected in polycrystalline samples with random orientations of the planar defects regarding the applied bias. Such conclusion of the proposed theory agrees well with experimental data showing general trend that ratios $C / C_0$ of the single-crystal samples No. 2 and 3 are smaller compared with those of macro- and polycrystalline samples No. 1 and 4.

As it was mentioned, there are no recent studies devoted to the “giant” capacitance of the real $\beta$-B crystals. There are few new experimental studies [19-21] of other related properties, like the time-dependent photoconductivity of pure and carbon-doped $\beta$-B, as well as the correlation between electronic properties and structural defects in $\beta$-B, which could be helpful in explaining our results. According to them, in $\beta$-B the influence of structural defects on the electronic properties is much stronger than in common semiconductors. Conductivity of the pure $\beta$-B is controlled by the centres of carrier localization related to the point structural defects, preferably certain vacancies, high concentrations of which are characteristic for the real structure of $\beta$-B. At $\sim 380 \text{K}$ and probably at lower temperatures slow structural relaxations, e.g., diffusion of certain interstitial atoms into energetically more favourable vacant sites, should take place. It influences electrical conductivity causing statistical fluctuations (stochastic precipitous jumps) and is responsible for some structural hysteresis effects in $\beta$-B crystals. Besides, carbon donor-states in the $\beta$-B band gap were identified,
which can affect time-dependent conductivity at the sufficient concentrations of carbon. Consequently, irreproducibility of some dielectric parameters of the unrefined $\beta$-B crystals No. 3 and 4 can be considered as a result of the transient conductivity characteristic for $\beta$-B.

In the proposed model, abrupt capacitance recovery at temperature ~ 290 K, which is independent of the applied electric field frequency and is accompanied by the jump in dielectric losses, specifies elimination of conditions for existence of the low-conductive barrier layers. This effect can not be connected with displacements of the trace impurities segregated on planar defects as it is found not only in contaminated polycrystals, but also in purest macrocrystalline material with conductivity controlled by the intrinsic point defects. The reason seems to be related to the above-mentioned structural relaxations in $\beta$-B. The most reliable explanation can be based on a moderate-temperature structural transition recently predicted [22] in $\beta$-phase of boron. Using density functional theory methods and an extensive search of the configuration space, a unique, energy-minimizing pattern of occupied and vacant sites was found that could be stable at low temperatures and break $\beta$-rhombohedral symmetry. However, alternative configurations are close in energy, allowing the entropy of partial occupancy to stabilize the $\beta$-rhombohedral structure through a phase transition. The strong heat capacity peak around ~ 300 K revealing intrinsic phase transition is only a crude estimate (because of several approximations made) and difficult to observe experimentally (because of slow atomic diffusion at this temperature). Nevertheless, the closeness of the transition temperature with ~ 290 K measured for abrupt changes in dielectric properties does not seem accidental. However, without detailed comparative analysis of the fine microstructures characteristic for $\beta$-B matrix and stressed inclusions, it is impossible to imagine how such transition promotes sample homogeneity by the concentration of hopping carriers.

4. Conclusions

Summarizing investigations carried out on temperature and frequency dependences of the dielectric properties of $\beta$-rhombohedral boron, we come to conclusion that the principal cause of the measured “giant” low-frequency capacitance of this semiconductor is propensity of its crystalline structure to form planar defects, namely twins. In the adjacent regions, twinning boundaries generate stresses causing piezoresistance, which is sufficient to form inclusions in form of thin layers with noticeably reduced conductivity. Besides, barrier layers arise at the borders of such layers with the matrix; those layers could have sufficiently low conductivity. Such heterogeneity of the conductivity in real $\beta$-rhombohedral boron crystals means an opportunity of electric charge accumulation not only on the sample interfaces with electrodes, but also in the bulk – at borders between areas with relatively low and relatively high conductivities. As a result, effective thickness of the equivalent capacitor decreases and the measured value of capacitance increases in comparison with the geometric one.

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