Fractional photoconductivity glow curves of β-rhombohedral boron

Helmut Werheit and Frank Kummer
Experimental Physics, University Duisburg-Essen, D-47048 Duisburg, Germany
e-mail: helmut.werheit@uni-duisburg-essen.de and helmut.werheit@koeln.de

Abstract. The energy band structure of β-rhombohedral boron is characterized by multiple electron and hole traps in the band gap. Fractional photoconductivity glow experiments were performed between 170 and 360 K for obtaining further information on the various traps in this semiconductor. The results can easily be interpreted within the actual band scheme and confirm the previous assumption of a cascade-like recombination of optically excited electrons with an activation energy of about 0.12 eV. The result support the assumption of optically induced structural changes regarding the partly occupied sites B(13) and B(16) to B(20).

1. Introduction
Valuable information on trap parameters of semiconductors can be obtained from photoabsorption and photoconductivity glow experiments. In such experiments, at low temperatures free electron-hole pairs are generated with excitation energies exceeding the band gap. In the traps, which are localized states in the band gap, the excited free carriers are entrapped depending on the relation between capture and recombination cross section. Thermal reexcitation into the adjacent energy band is prevented by the low temperature. However, in this situation the trap depth could be determined by optical absorption experiments (“photoabsorption”) and optically excited conductivity (“photoconductivity”). Afterwards, reexcitation is systematically stimulated by continuously increasing the temperature. Depending on the number of released carriers and the process of subsequent interband recombination, the conductivity increases (“thermally stimulated current”). Simultaneously, the photoabsorption of trapped carriers decreases because of the decreasing occupation density of the traps. Sometimes, luminescence radiation from recombining electron-hole pairs can be obeyed as well. Such temperature dependent thermally stimulated photoabsorption, photoconductivity and luminescence experiments are called “glow curves”.

If there is one trap only, the typical photoconductivity glow curve is bell-shaped. The ascending branch at increasing temperatures is determined by the increasing number of mobile carriers thermally released from the trap, followed by a decreasing branch in consequence of the progressing exhaustion of the initially filled trap. The individual shape of the glow curve depends on activation energy, capture cross section, transition probability, retrapping and recombination factor. The parameters concerned can be more or less well estimated from series of measurements under modified conditions.

In more complex cases, where various traps occur, the associated glow curves overlap, and hence qualifying of individual trap parameters is complicated or even impossible. This problem is surmounted or at least reduced by fractional glow experiments (see [1-3]). In such methods the optically excited semiconductor is heated to a temperature, where largely emptying of the shallowest
trap is expected; this can be approximately assumed, when the first glow peak is reached. In the next step the sample is cooled down to the starting temperature again and the heating procedure is repeated until the next trap is emptied. This way, the different traps are emptied step by step, and the trap parameters can be derived largely separately.

In β-rhombohedral boron electron and hole traps affect the electronic properties decisively (see [4-9]). For additional and possibly particular information on the different traps and gap states respectively, fractional photoconductivity glow experiments were performed between 175 and 360 K.

2. Sample material and experimental setup
A prismatic sample (1.6×1.6×10.5 mm) was cut from a high-purity β-rhombohedral boron single crystal (Wacker Chemistry, Munich; claimed purity 99.9999% except carbon (typically 60 ppm)) roughly parallel to the crystallographic c-axis. The sample was etched to remove Beilby layers and surface contamination (for the method see [10]). On opposite side faces of the prismatic sample, a pair of ohmic contacts (0.1 mm platinum wires) was fixed by capacitor discharge in about 1.5 mm distance from the front surface, illuminated by a Xenon arc-lamp for optical excitation. The side faces were carefully shielded from light.

For realizing well-defined starting conditions, the sample was heated to about 350 K, and remained there for one hour for setting thermal equilibrium. After cooling down to the starting temperature 170 K in complete darkness, it was kept there for another hour. Hereafter the excitation by a two hours illumination with a Xenon arc-lamp took place for achieving completely filled electron traps. Then, in the first cycle of measurement a normal conductivity glow curve was recorded heating the sample to 350 K (heating rate, 5 K/min). In additional sequences of measurements, fractional glow curves were obtained after heating the sample from the starting point at 170 K to the temperature, at which the maximum of the preceding curve had occurred. After re-cooling again to 170 K the respective fractional glow curve was recorded.

3. Experimental results
In figure 1 the normal and three fractional glow curves are displayed compared with the dark current obtained at otherwise same conditions as described. For clarity, the curves of intermediate heating to 186, 198 and 213.4 K, respectively, each well coinciding with the red curve, are not displayed. After re-cooling to the starting point, the next cycle of fractional electrical conductivity was measured up to 350 K, and yielded the glow curves with afore partly emptied electron traps.

Figure 1. Normal dark conductivity (red) and fractional photoconduction (after optical excitation at 175 K and intermediate heating to 186 K (green), 198 K (blue), and 213.4 K (pink), respectively). Dark current (black) for reference (a, vs. T−1; b, vs. T−1/4)
Former investigations [11,12] showed that the electrical conductivity of \( \beta \)-rhombohedral boron follows Mott’s law of variable-range hopping at lower temperatures. Therefore, in figure 1b the data are accordingly re-plotted vs. \( T^{-1/4} \). The validity of Mott’s law is confirmed by the present data in a wide range of temperature. However, towards low temperatures a certain deviation occurs, apparently indicating a different conductivity mechanism. It cannot be excluded that this deviation is not real, indeed it is marginal for the evaluation of the fractional photoconduction as difference to the dark current.

4. Discussion

For visualizing the fractional photoconduction glow curves, the measured data after subtracting dark current are plotted in figure 2. Since thermal activation processes of carriers in the involved traps are expected, plotting vs. reciprocal \( T \) is chosen.

![Figure 2.](image)

**Figure 2.** Fractional photoconductivity glow curves obtained as difference between measured data and dark current

![Figure 3.](image)

**Figure 3.** Actual energy band scheme of \( \beta \)-rhombohedral boron (reproduced from [6,8]).

Above \( \sim 260 \) K the curves abruptly decrease. This is caused by the crossing between dark current and glow curves indicating that thermal equilibrium at higher temperatures depends on the antecedent at low temperatures, here with and without strong optical excitation at low temperatures as well. The
difference between dark current and glow curves at higher temperatures supports previous assumptions that the optical excitation of β-rhombohedral boron is correlated with structural relaxations. It seems natural attributing these interdependence with incompletely occupied sites B(13) and B(16) to B(20). In this context we point to the internal friction maxima at about 140 K and 230 K by Tsagareishvili et al (see [4] and references therein) indicating structural modifications in β-rhombohedral boron at such low temperatures even in thermal equilibrium as well.

The thermal activation energies within the fractional glow curves indicated in figure 2 are to be interpreted within the band scheme of β-rhombohedral boron (figure 3).

The activation energy of the glow curve for full optical excitation (red curve) seems to correspond to the distance between the valence band edge and the nearest defect state. This would indicate that the current is essentially represented by free holes generated by thermal excitation of valence electrons into adjacent localized gap states. Indeed must be conceded that beneath the range of measurement the slope could possibly be steeper. For all fractional glow curves representing the conductivity under the condition of partly emptied electron traps, the situation is uniform: The activation energy of the electrical conductivity represents the distance between occupied and unoccupied defect states beyond the valence band edge.

The consistent decrease of the glow curves towards higher temperatures is obviously determined by the recombination of trapped electrons. This process in the fractionated glow curves is thermally activated with the energy 0.11(2) eV, which well agrees with the activation energy 0.12 eV of cascade-like recombination of trapped electrons via the series of intrinsic electron trapping levels [5].

5. Conclusion

The fractional glow curves of β-rhombohedral boron can be consistently described within its actual energy band scheme (figure 3) and confirm the cascade-like recombination of electrons trapped in different levels below the conduction band.

Concordantly to previous investigations on photoabsorption and photoconduction, the present results confirm that the electronic thermal equilibrium at low temperatures is remarkably altered by optical excitation. We suppose a correlation with the partly occupied sites B(13) or B(16) to B(20) proved to be relevant for the gap states in β-rhombohedral boron. This could be in the way that the positions or occupancies of these atomic sites depend on specific conditions of the electronic surrounding in the structure, which is changed by the optical excitation. We take the internal friction maxima at low temperatures for supporting our thesis of easily realisable structural changes in β-rhombohedral boron, and suppose that in this respect the mentioned sites are very probable aspirants.

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