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On the diffusion of free carriers in β-rhombohedral boron

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Abstract

To determine the diffusion of untrapped carriers in β-rhombohedral boron, we constructed a feedback pico-ammeter based on pulse integration technique. This enabled measuring deviations from the bias in a $10^9\,\Omega$ sample in the order of 1 nA with 0.7 ms time resolution. For the first time, we obtained the drift velocity of optically generated untrapped electron–hole pairs $106(20)\,cm\,s^{-1}$ yielding for the band-determined diffusion coefficient $D = 12(4)\,cm^2\,s^{-1}$ and for the carrier mobility $\mu_{ambipolar} = 565(120)\,cm^2\,V^{-1}\,s^{-1}$. Fitting Fick's second law to the measured trap-determined dispersion of carriers yields the ambipolar diffusion coefficient $D^* = 0.043(14)$ and $0.28(10)\,cm^2\,s^{-1}$ at 260 and 340 K, respectively. The thermal activation energy of 0.18 eV agrees with the well-known trapping levels in β-rhombohedral boron.

Keywords: Boron; β-rhombohedral; Charge transport; Ambipolar diffusion; Carrier mobility

1. Introduction

Completing the idealized structure formula of β-rhombohedral boron ($(B_{12})_4(B_{28})_2B$ or $B_{84}(B_{10})_2B$) (see Ref. [1]) there are several additional atomic sites (B(16)–B(20)) with considerably reduced occupation densities leading to about 106.5 atoms per unit cell in total. The actual electronic band scheme [2–4] shows a gap of about 1.5 eV and numerous high-density gap states, which are at least partly correlated with structural defects [5]. The band gap is essentially determined by the Jahn–Teller splitting of the orbitals of the B_{12} icosahedron [6]. Charge transport by electrons and holes is usually determined by a superposition of band conduction and hopping processes. Depending on the actual conditions, one of these mechanisms can prevail. However, because of the extremely high trapping probability of electrons and holes the separation of band-type, that means untrapped free carriers failed till now. For example, in previously performed photoconductance (see Ref. [1] and references therein) [3,4,7] and drift experiments [8–11] the sensitivity was not sufficient to detect the very small contribution of untrapped free carriers. Object of the present work was a sufficiently sensitive equipment to close this gap.

2. Sample material and experimental setup

A prismatic sample ($1.6 \times 1.6 \times 10.5$ mm) was cut from a high-purity β-rhombohedral boron single crystal (Wacker, Munich; claimed purity 99.9999% except carbon (typically 60 ppm)) roughly parallel to the crystallographic c axis and immediately neighbored to the sample investigated in Ref. [11] and prepared according to [12]. On opposite places of the side faces of the prismatic sample, pairs of thin platinum wires (0.1 mm) were fixed by capacitor discharge as ohmic contacts.

After switching on, the radiation of a laser diode (Sharp LTO15MDO, $\lambda = 827$ nm, 30 mW) generated a time-independent concentration of electron–hole pairs at one end face of the prismatic sample within the penetration depth of 0.25 mm. The concentration gradient causes the ambipolar drift of electron–hole pairs thus increasing the local and time-dependent conductivity in the sample. As the optical excitation changed the dark current by less than 1%, the deviation from thermal equilibrium is negligible. The time-dependent conductivity was tapped at the ohmic probes mounted in different distances from the illuminated

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surface. A self-constructed feedback ammeter based on pulse integration measurements with the IC's INA116, IVC102 and OPA27 (Burr–Brown) and a digital storage oscilloscope (Tektronix 2430) as essential components allowed measuring photocurrents in the order of 10^{-9} A in a $10^{9}\,\Omega$ sample, with a time resolution of 0.7 ms. The principle of the method is as follows: After the equipment is initially triggered by the onset of the optical excitation, a capacitor is charged by an electric current passing the sample, whose conductance determines the charging process. In periods of 0.7 ms the capacitor is shortcut, and the charging process restarts. These cycles are stored in the oscilloscope, whose data are continuously transferred into a PC memory for evaluation. The sample temperature was controlled by a closed-cycle He cryostat and measured with a thermocouple fixed close to the sample. The basic circuit diagram (Fig. 1) allowed adjusting the bias before optical excitation. In the optimal setting, the arriving front of untrapped carriers changed the sign of the charging current of the capacitor (see Fig. 2).

The high density of traps and extremely long relaxation times of trapped carriers in β-rhombohedral boron ($\tau_{relax} \geqslant 2.5$ h at room temperature; see Refs. [1,11,13] and references therein) required careful precautions to realize thermal equilibrium: Before each measuring cycle, the sample was kept in complete darkness; at first for 6 h at 60 °C to empty the traps, then within about 2 h slowly cooled to the wanted temperature, where it finally remained for additional 14 h.

3. Results

Some examples of the steep front of drifting electron–hole pairs in 1.3 mm distance from the illuminated surface are displayed in Fig. 2. The front is obviously determined by untrapped electron–hole pairs. The derivative $\Delta I_{photo}/\Delta t$ obtained from the smoothed average of numerous spectra measured between 260 and 340 K and displayed in Fig. 3 is closely related to the spectra of classical time-of-flight measurements. The free carriers determining the sharp peak are followed by carriers delayed by trapping and multitrapping. The diagram yields the velocity $v_{drift} = 106(20)\,\mathrm{cm\,s^{-1}}$, and accordingly the ambipolar diffusion coefficient $D = xv = 14(3)\,\mathrm{cm^2\,s^{-1}}$. The Einstein

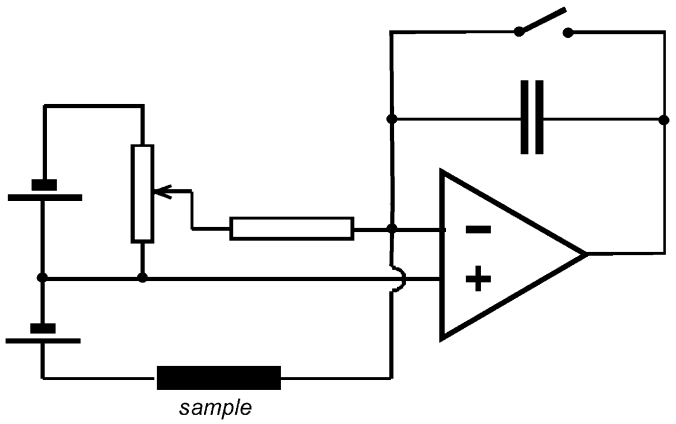

Fig. 1. Basic circuit diagram.

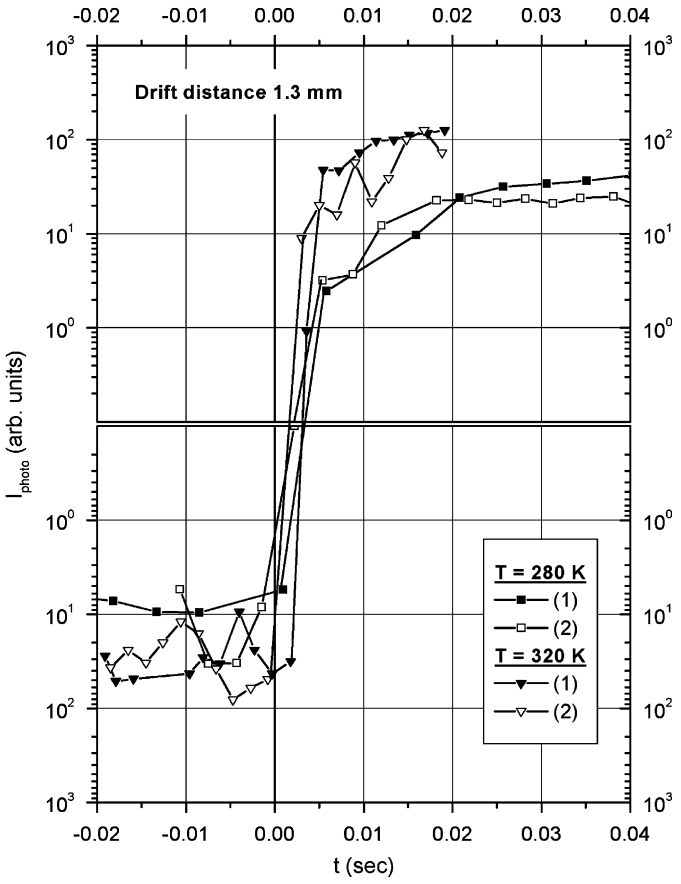

Fig. 2. Drift front of electron–hole pairs in 1.3 mm distance from the place of generation; photocurrent vs. time.

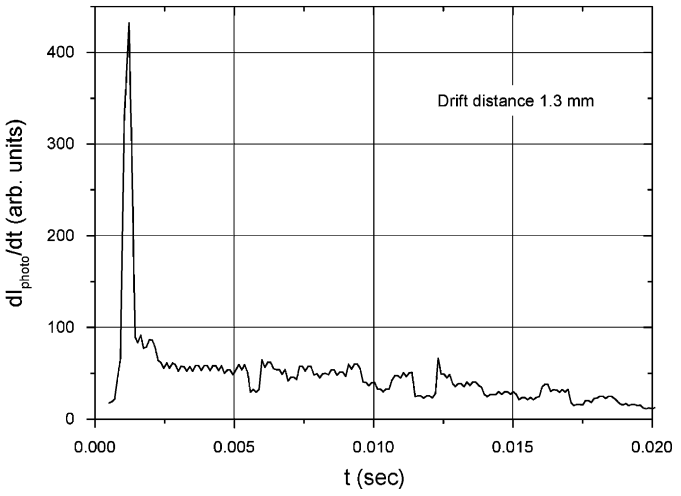

Fig. 3. Derivative of the average of numerous drift spectra measured at permanent optical excitation between 260 and 340 K. The result is closely related to the spectra of time-of-flight measurements, where electron–hole pairs are generated by pulsed optical excitation. The spectra obtained between 260 and 340 K were averaged because they agree within the accuracy of measurement.