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Modulated Photocurrent Measurements on Pure and V-Doped β-Rhombohedral Boron

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The modulated photocurrent method has been applied to pure and vanadium (V)-doped β-rhombohedral boron (β-B) with the goal of investigating the difference in the distribution of electronic states in the band gap between them. Excitation light intensity dependence of the amplitude and phase shift of photocurrent shows that V-doped β-B has a much larger trapping states density for photoexcited carriers than pure β-B. With increasing temperature, the amplitude increases and decreases for pure and V-doped β-B, respectively, indicating that the conduction mechanism for photoexcited carrier is completely different between the two samples. The unusual negative temperature dependence for V-doped β-B is similar to that for Al–Pd–Re quasicrystal and the change of dependence from positive to negative is consistent with the approach to aluminum-based icosahedral quasicrystals in atomic structure and in transport properties by V-doping to β-B. The modulated frequency dependence of the amplitude and phase shift cannot be explained by the usual photoconduction processes, which are indicating that the gap states distribution and photoconduction processes in these materials are complicated. © 2000 Academic Press

Key Words: **modulated photocurrent; β-rhombohedral boron; V–B alloys; metal–insulator transition; density of gap states.**

INTRODUCTION

β-Rhombohedral boron (β-B) is a semiconductor with about 1.5 eV band gap energy (1) and one of the modifications of pure boron, which is stable at high temperature. This solid has been reported to have slightly distorted B_{12} icosahedral clusters, which cause the existence of acceptor level at 0.2 eV above the valence band (2). It has also been reported that there are six electron-trapping levels below the conduction band (1,3).

Doping vanadium (V) into β-rhombohedral boron brings in a metallic transport behavior such as increase in electrical conductivity and no appreciable temperature dependence of it (4). This transition has been explained by the hybridization between the states of β-B and the 3*d* states of the V atom. Among several dopant elements, V atoms most preferentially occupy the A_1 site, which is one of three main doping sites for β-B. The A_1 site is the vacant site in the second shell of multiple shell structures of β-B, which corresponds to a part of dodecahedral site in the second shell of the Frank-Kasper-type aluminum-based icosahedral approximant crystal and quasicrystal (5). Therefore, by V-doping, the atomic structure of β-B approaches that of the aluminum-based quasicrystal, and not only dc electrical conductivity mentioned above but also optical conductivity of the former shows similar behavior to that of the latter.

Up to now, we have performed modulated photocurrent (MPC) measurements for β-B and amorphous boron (6), for YB_{66} (7), and for Al–Pd–Re icosahedral quasicrystal (6,8) to investigate their electronic states and interrelation between them. In this study, we have applied the MPC measurements for polycrystalline V 1.18%-doped β-B. In spite of the metallic property of the sample, the MPC signal was successfully measured because of high sensitivity of the method. In this paper, we report the results of the MPC measurements for V-doped β-B, together with those for pure β-B, and discuss the difference in the distribution of electronic states in the band gap between them.

EXPERIMENTAL PROCEDURES

A single crystal of β-rhombohedral boron (5N) produced by Eagle-Picher Inc. was mechanically polished with diamond paste (finest grade 0.25 μm) for the measurements. A bulk sample of $V_{1.18}B_{105}$ was produced according to the procedures described in Ref. (4). The sample was cut into a disk and thinned by mechanical polishing to about 100 μm. Gold electrodes with 0.5 and 1-mm spacings were sputtered onto the both samples, respectively. Ohmic behavior was confirmed for these specimens by measuring I–V character.

A block diagram of the setup is shown in Fig. 1. The sample surface between the two gold electrodes with about

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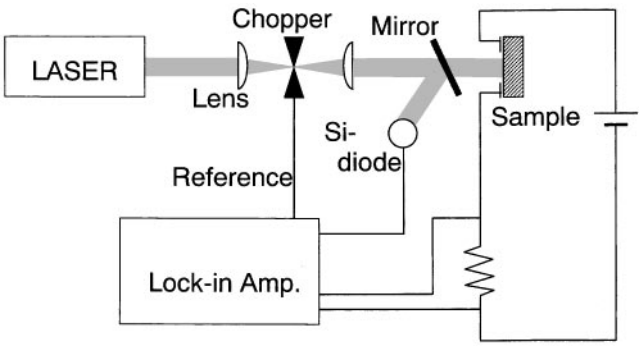


FIG. 1. Block diagram of setup for modulated photocurrent measurements.

1 mm spacing was illuminated by mechanically chopped light from an Ar-ion laser (2.5 eV and 1 mW–1 W) while applying a DC bias voltage of 10 V and 100 mV for Pure β-B and V-doped β-B, respectively, between the two electrodes. For precise modulation, incident light beam was focused on the blade plane of the mechanical chopper. The lock-in amplifier detected the induced photocurrent synchronized with chopping frequency as the potential difference across a series resistance. This configuration enables simultaneous measurements of amplitude and phase shift of photocurrent. Since the measured phase shift also includes a phase shift due to instrumentation delay time, the actual phase shift was obtained by subtracting the phase shift of the excitation light measured by a fast-response Si diode with a response time of 1 ns, from that measured for the sample.

The measurements were done successfully from low frequency to high frequency after preillumination of various periods from 5 min to 1 h. Essentially the same results were obtained from the different periods of preillumination.

RESULTS AND DISCUSSION

Figure 2a shows the excitation light intensity dependence of amplitude and phase shift of the modulated photocurrent measured at 200 K for pure β-B. The following facts should be noted. (i) The amplitude is almost proportional to the light intensity in the whole range up to 1 W. (ii) The phase shift is almost constant up to about 10 mW and then decreases with increasing light intensity. The linear dependence of the amplitude on the light intensity indicates that the

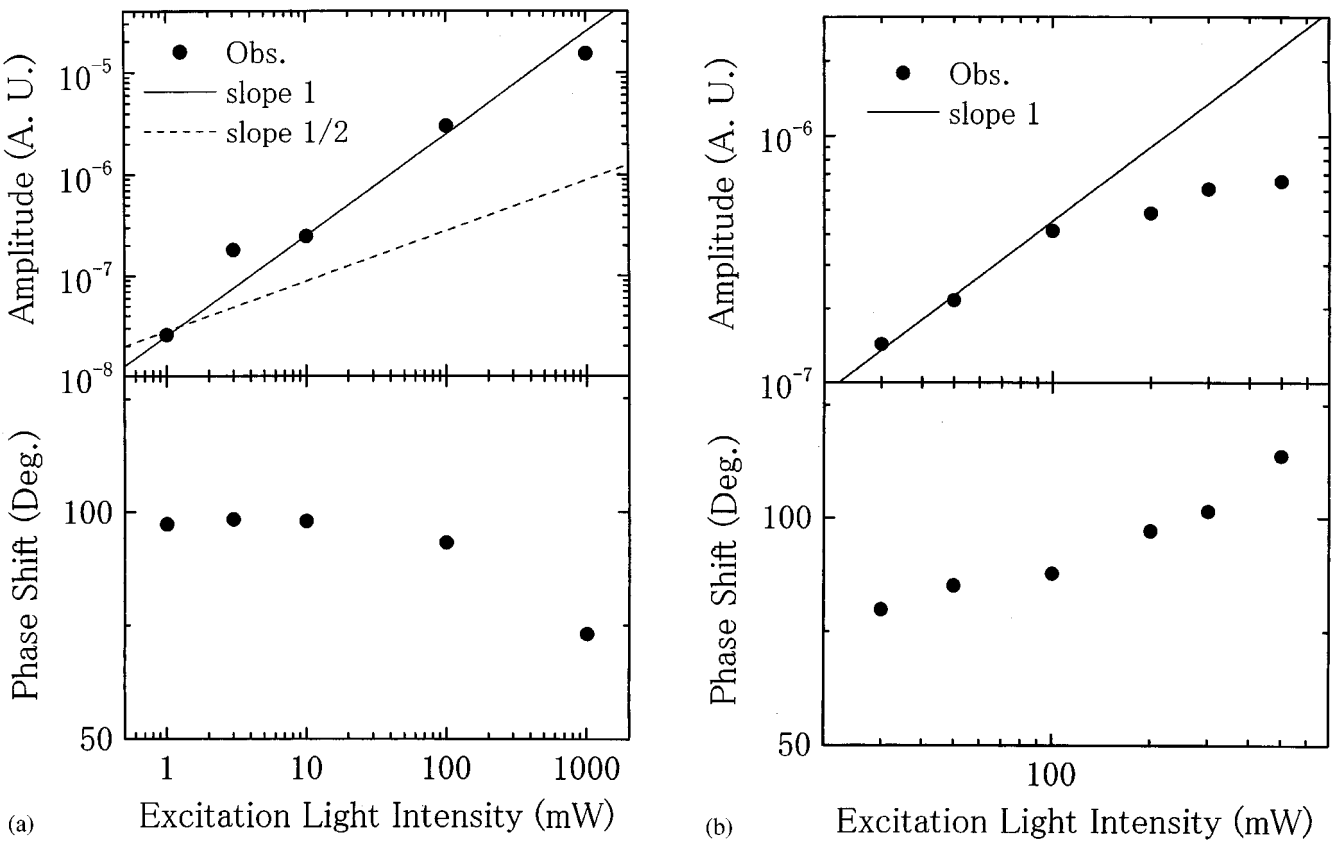


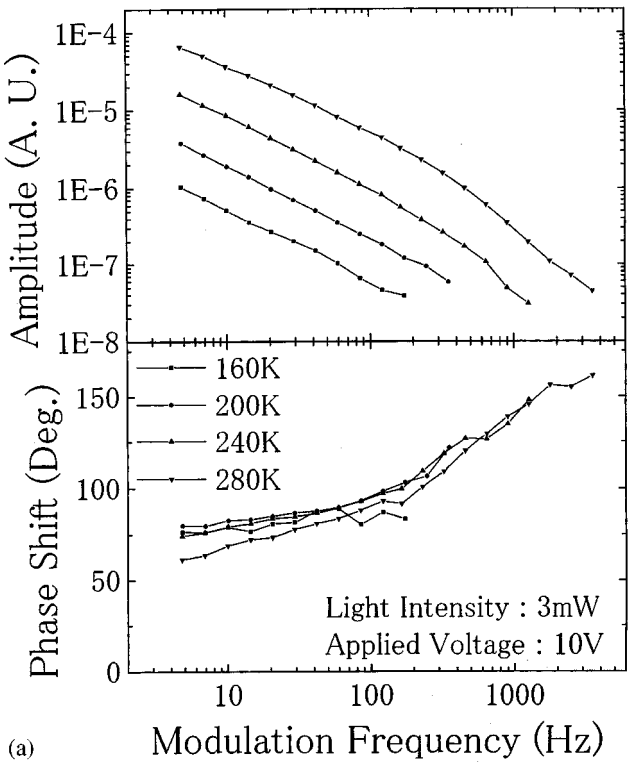
FIG. 2. Excitation light intensity dependence of the amplitude and the phase shift of modulated photocurrent for pure β-boron (a) and for V-doped β-B (b) at 200 K at 121 Hz.

recombination process of excited carriers is monomolecular. In general, the phase shift of photocurrent is constant against the light intensity when the density of excited carrier is sufficiently small compared with that of trapping states for the carrier in the band gap. With increasing light intensity, the density of excited carrier becomes comparable to that of the trapping states and then the phase shift starts decreasing because the trapping process becomes less effective to the phase shift. These behaviors are actually observed in the light intensity dependence of the phase shift in Fig. 2a.

In Fig. 2b, the results for V-doped β-B are presented, where we can see behaviours qualitatively different from those for pure β-B. The amplitude shows a linear relation to the light intensity only up to about 100 mW, above which it deviates downward from the linear relation. This fact suggests that the recombination process of excited carriers changes from a monomolecular process to a bimolecular one at about 100 mW. The phase shift gradually increases with increasing light intensity. The origin of this unusual behavior is not clear at present.

Figures 3a and 3b show the modulation frequency dependence of the amplitude and the phase shift of the photocurrent at various temperatures for pure β-B and V-doped β-B, respectively. The measurements were done for pure β-B and for V-doped β-B using the light intensity of 3 and 100 mW, respectively, for which we can assume monomolecular process in both samples. The temperature dependence of the amplitude is opposite for the two samples; the amplitude for pure β-B increases with increasing temperature, just like conventional semiconductors, while that for V-doped β-B decreases with increasing temperature. In general, conventional semiconductors show a positive temperature dependence of the amplitude because the release rate of the trapped carrier; i.e., carrier density contributes to the photocurrent increases with increasing temperature. The negative temperature dependence of the amplitude in V-doped β-B implies that the photoconduction mechanism in this sample is different from that in conventional semiconductors. This unusual behavior can be realized when the temperature dependence is not associated with the change in the density of the carrier but with that in the mobility of the carrier; if the carrier density does not change very much and the mobility decreases with increasing temperature due to increase in the scattering rate of carrier by phonon, negative temperature dependence of the amplitude results. This situation may actually be realized in V-doped β-B.

In both samples, the phase shift is considerably larger than that in conventional semiconductors, indicating the existence of high-density gap states and complicated photoconduction process. The modulation frequency dependence of phase shift is qualitatively different between the two samples; the phase shift in pure β-B increases monotonically



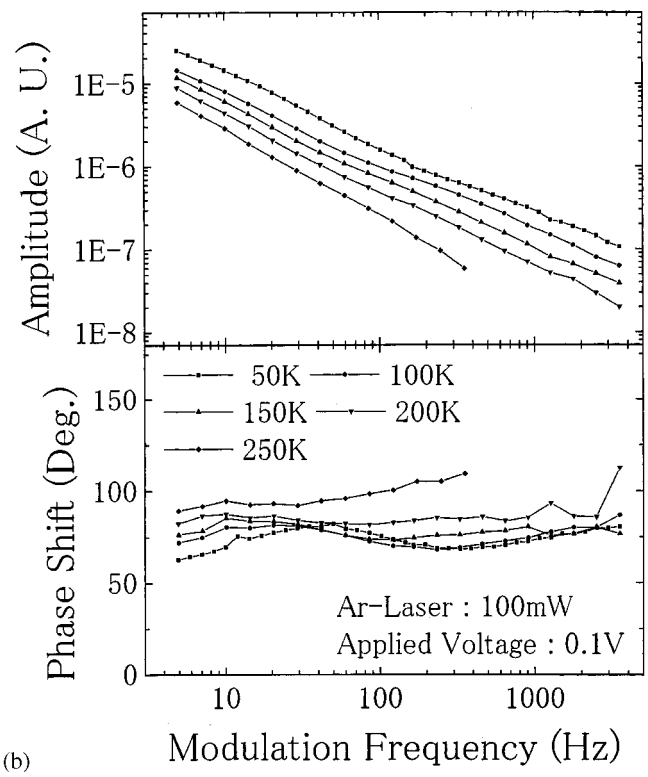


FIG. 3. Modulation frequency dependence of the amplitude and the phase shift for pure (a) and V-doped (b) β-boron. Detailed measurement conditions are indicated in the figure.

while that in V-doped β-B shows two humps in the measured frequency region.

The negative temperature dependence of amplitude shown in Fig. 3b for V-doped β-B is also observed for Al–Pd–Re icosahedral quasicrystal (8). The change from positive to negative temperature dependence by V-doping to β-B is considered to be consistent with the approach to aluminum-based icosahedral quasicrystals in atomic structure and in transport properties. As for Al–Pd–Re icosahedral quasicrystal, the amplitude of photocurrent is almost proportional to the light intensity and the phase shift is almost constant in the whole range up to 1 W of Ar-ion laser at 150 K. This behavior may correspond to that of Fig. 2b below 100 mW for V-doped β-B. The phase shift for Al–Pd–Re is also considerably large, though its modulation frequency dependence is much simpler than those of two samples in this paper.

We attempted an analysis of the data for V-doped β-B according to a model proposed by Oheda for conventional semiconductors (9). Now, we have the experimental data of phase shift ϕ_j and amplitude I_j as a function of modulation frequency ω_j $(j = 1, 2, \ldots, N)$. In the model, I_j is given by

$$I_j = \frac{\tau_{RO} C}{\left\{\left[1 + kT \sum_{s=2}^{j} \ln\left(\frac{\omega_s}{\omega_{s-1}}\right) A(E_j)\right]^2 + \left[\omega_j \tau_{RO} + \frac{\pi kT}{2} A(E_j)\right]^2\right\}^{1/2}},$$

where

$$A(E_j) = \tau_{RO} v \sigma M(E_j).$$

Here, τ_{RO} is an apparent recombination time, v the thermal velocity, σ a capture cross section for an electron, $M(E_j)$ a density of states at energy E, C a constant, and kT has the usual meaning. The function $A(E_j)$ is calculated for in stepwise manner from the experimantal data of ϕ_j measured at 50 K (Fig. 3b) according to the equations:

$$A(E_1) = \frac{2}{\pi kT}(\tan \phi_1 - \omega_1 \tau_{RO}),$$

$$A(E_j) = \frac{2}{\pi kT}\left\{\left[1 + kT \sum_{s=2}^{j} \ln\frac{\omega_s}{\omega_{s-1}} \times A(E_{s-1})\right] \tan \phi_j - \omega_j \tau_{RO}\right\}.$$

Figure 4 presents the experimental data of I_j, together with the result of calculation. The calculation does not reproduce the experimental data. We attempted the calculations using various τ_{RO} ranging from 10^{-12} to 10^{-1} s. All the calculations fail to reproduce the experimental data, indicating that this model cannot be applied to the present sample. Models for explaining the photoconduction phenomena on these materials are now being constructed.

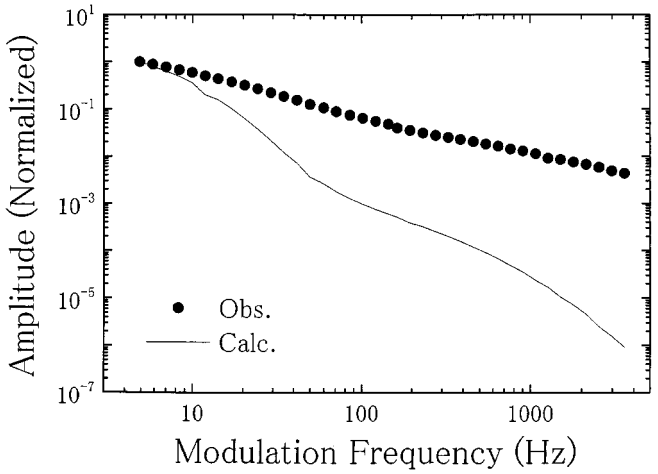


FIG. 4. The amplitude data of photocurrent for V-doped β-B at 50 K, together with the calculated curve using $\tau_{RO} = 1 \times 10^{-8}$ s.

CONCLUSIONS

The modulated photocurrent method has been applied to pure and V-doped β-rhombohedral boron. From the excitation light intensity dependence of modulated photocurrent, it has been considered that V-doped β-B has a higher density of gap states than pure β-B. The analysis of either sample by conventional model failed, which means that the photoconduction processes in these materials are not as simple as in usual semiconductors and indicates the complicated distribution of gap states. These features have also been seen in the large value of phase shift. The difference between two samples appeared in the temperature dependence of amplitude, positive for pure β-B and negative for V-doped one, and the modulation frequency dependence of phase shift; phase shift in pure β-B increased while that in V-doped β-B showed two humps in the measured frequency region. The former is considered to be consistent with the approach to aluminum-based icosahedral quasicrystals in atomic structure and in transport properties by V-doping to β-B.

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