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Transient Photocurrent Studies on Amorphous and β-Rhombohedral Boron

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Carrier transport properties in amorphous and β-rhombohedral boron were studied by the time of flight method. The activation energy for holes in β-rhombohedral boron was estimated to be 240 meV. This activation energy corresponds to the depth of hole traps originating from B_{12}, that is, the intrinsic acceptor level. Dispersive (non-Gaussian) transient photocurrents were observed both for electrons and holes in amorphous boron. The activation energy for electrons and holes were estimated to be about 20 and 85 meV, respectively. The average hopping distance of holes was evaluated from the electric field dependence of the photocurrent to be 11 Å. These activation energies and hopping distances are small compared with those of other amorphous semiconductors. The results suggest that the excited carriers propagate by hopping between localized states within a certain narrow band.

INTRODUCTION

Icosahedral clusters and their arrangement are the characteristic features of boron-rich solids. Their unique electrical properties are assumed to be characterized by these clusters (1). Although boron-rich solids have the ability to be used as electronic material, their electronic properties have not yet been fully understood. To measure the fundamental properties in detail and clarify their relation to the structure is not only of basic but also of practical interest.

The time of flight (TOF) experiment is a powerful technique for measuring electron and hole transport properties in solids, and is extensively used to measure the drift mobility in amorphous solids (2). The advantage is the direct observation of unipolar carrier propagation. In the present paper, we report results of amorphous and β-rhombohedral boron.

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EXPERIMENTAL PROCEDURE

Amorphous boron films with thicknesses from 1.2 to 1.6 μm were deposited on *p*-type and *n*-type single-crystal silicon wafers by an electron-beam evaporation technique; the pressure during the evaporation was about 10^{-6} Torr, and the deposition rate was 2 Å/sec. The purity of raw material is 99.9%. Substrate temperatures were 200, 300, and 350°C. The thicknesses of the films were estimated from interference patterns in optical transmission spectra of films deposited on a quartz substrate. An ultrathin Au layer with 3 mm^2 area was sputtered on the sample as a semitransparent electrode. Single crystal β-rhombohedral boron (5N) produced by Eagle-Picher Inc. has been mechanically polished to a thickness of 100 μm. A thin mica film was used to block carrier injection.

A block diagram of the setup is shown in Fig. 1. The samples were mounted in a variable-temperature cryostat in vacuum. Carriers were created at the sample surface near the semitransparent electrode by a single shot of a nitrogen-laser pumped dye-laser (3.10 eV). Their time of flight to the interface with the c-Si substrate was measured with a pulsed bias applied between the Au electrodes and the c-Si substrate. The acquisition of the data was done using a 1 GHz bandwidth digital oscilloscope in conjunction with a personal computer for storage and analysis of the transient wave forms. For β-rhombohedral boron, the transient currents were averaged over several signals in order to improve the signal-to-noise ratio.

RESULTS

Amorphous Boron

We observed dispersive (non-Gaussian) transient currents (2) for amorphous boron films. It is characterized by a significant and asymmetric broadening of carrier packet due to the disorder of the solids.

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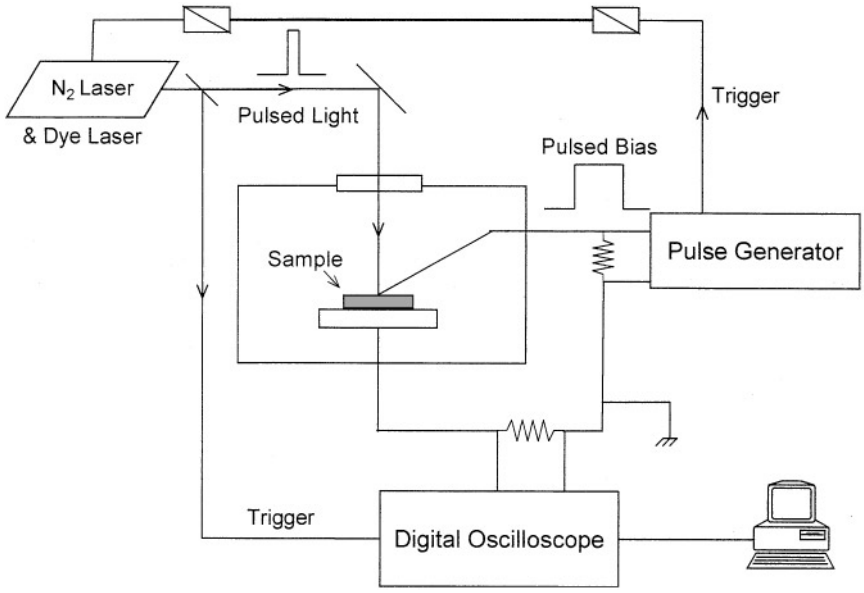

FIG. 1. Block diagram of the setup for TOF measurement.

As shown in Fig. 2, the current decays with time as

$$i(t) \propto \begin{cases} t^{-(1-\alpha_i)}: & t < t_T \\ t^{-(1+\alpha_f)}: & t > t_T, \end{cases} \quad [1]$$

where α_i and α_f are dispersive parameters at short and long time, respectively. α is a parameter related to the microscopic details of the transport process and therefore is a measure of the local disorder. α decreases as disorder increases. A plot of $\log i$ versus $\log t$ has tangents of slope $-(1-\alpha_i)$ and $-(1+\alpha_f)$, respectively. The transit time (t_T), which approximately characterizes the time when the leading edge of the carriers reaches the absorbing substrate, is defined by the intersection of the tangents. The drift mobility was calculated according to

$$\mu_d = \frac{L}{t_T F}, \quad [2]$$

where L is the film thickness and F is the applied electric field.

The temperature dependence of the drift mobility for electron and hole at an electric field of 2.8×10^4 V/cm in the temperature range from 100 to 300 K is shown in Fig. 3. The electric field dependence of the transit time measured at 290 K for hole in the film prepared with a substrate temperature of 200°C shown in Fig. 4 can be fitted by a straight line for high electric fields in the $\log t_T$ versus F plot.

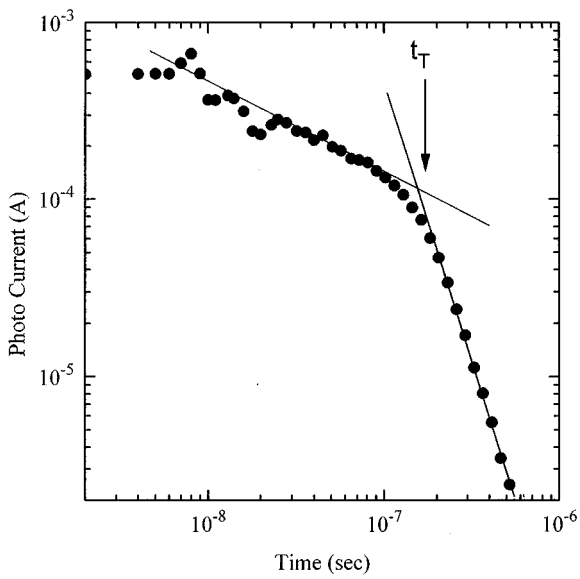

FIG. 2. Typical hole transient current observed at 200 K for an amorphous boron film prepared with a substrate temperature of 350°C. The arrow indicates the transit time (t_T).

β-Rhombohedral Boron

Transient hole photocurrents in β-rhombohedral boron were measured for an electric field of 1.8×10^4 V/cm in the temperature range from 280 to 350 K. The drift mobility of the excess holes was calculated according to Eq. [2]. The temperature dependence of the drift mobility is thermally activated as shown in Fig. 5. Werheit *et al.* have performed

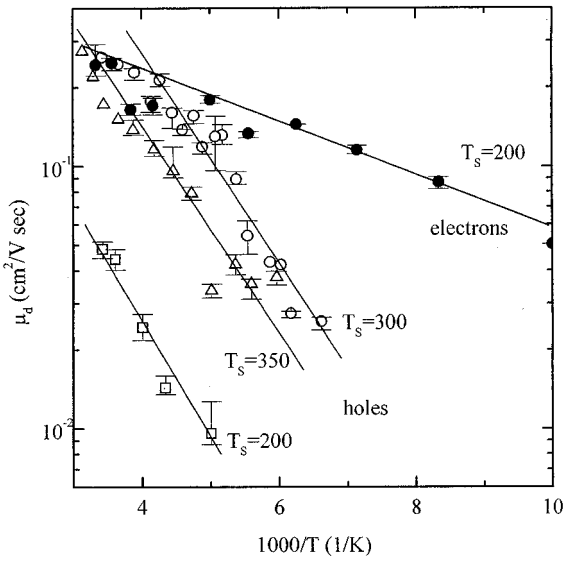

FIG. 3. Temperature dependence of the drift mobility in amorphous boron films prepared with different substrate temperatures (T_S) (solid circles, electrons; open symbols, holes).

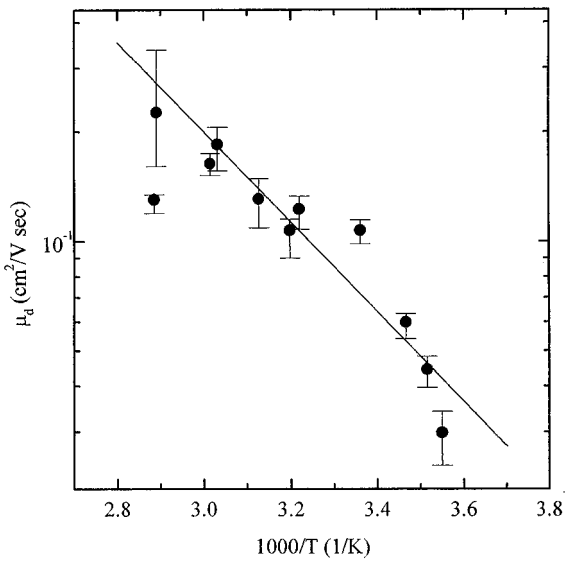

FIG. 5. Temperature dependence of the hole drift mobility for β-rhombohedral boron.

drift experiments on optically excited holes at room temperature and obtained the drift mobility for hole of 0.076 cm^2/V sec (3). The drift mobilities obtained in the present study roughly equal to the previous reported value.

DISCUSSION

Amorphous Boron

Figure 3 shows that the temperature dependence of the drift mobility for $F = 2.8 \times 10^4$ V/cm is thermal activation type with activation energies for electrons and holes of about 20 and 85 meV, respectively. These values are rather small compared with those of other amorphous semiconductors, e.g., 170 meV for a-Si:H (4), 400 meV for boron doped a-Si:H (5), 280 meV for a-Se (6), and 600 meV for a-As_2Se_3 (7).

Transport mechanism, i.e., multiple-trapping or thermally activated hopping transport, can be determined by the electric field dependence. For multiple-trapping (8),

$$t_T \propto F^{-1/\alpha_i}, \qquad [3]$$

and for thermally activated hopping (9),

$$t_T \propto \exp\left(\frac{\Delta E_0}{kT}\right) \exp\left(-\frac{e\rho F}{2\alpha_i kT}\right), \qquad [4]$$

apply for the field dependence. In Eq. [4], ΔE_0 is the activation energy at $F = 0$, and ρ is the average distance between nearest-neighbor hopping sites. The data for high electric fields in Fig. 4 can be interpreted not by Eq. [3] but by Eq. [4]. From the field dependence of the transit time, the average hopping distance is estimated to be 11 Å with $T = 290$ K and $\alpha_i = 0.4$. This hopping distance is short compared with those of other amorphous semiconductors (40 Å for a-Si:H (10), 48 Å for a-As_2Se_3 (7) and is roughly the same as the rhombohedral lattice constant of β-rhombohedral boron (10.143 Å) (11) which corresponds to twice the distance between B_{12} clusters. The B_{12} cluster is the basic structural unit in amorphous boron as well. This shows that the photoexcited holes transport between the B_{12} clusters

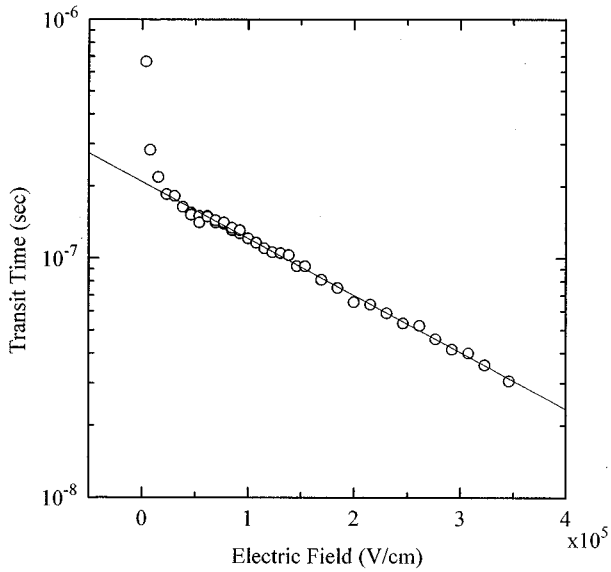

FIG. 4. Electric field dependence of the transit time for an amorphous boron film prepared with a substrate temperature of 200°C.

by thermally activated hopping. The activation energy at $F = 0$, ΔE_0, was calculated to be 89 meV.

For amorphous boron, the activation energy is small and the hopping length is short compared with those in typical amorphous semiconductors. This indicates that the hopping transport occurs in localized states with rather large density. On the other hand, the optical gap of amorphous boron is about 1 eV smaller than that of β-rhombohedral boron (12), and the difference is considerably larger than in the case of typical amorphous semiconductors. If we assume that all of the tail states in amorphous boron are localized and act as trap levels for photoexcited carriers, it is hard to explain such small activation energies observed in amorphous boron films by the TOF. It may be possible to understand that the behavior arises from the following situation: photoexcited carrier propagates by hopping between localized states within a certain narrow band. Other measurements by which the mobility gap and gap states distribution are determined must be carried out.

β-Rhombohedral Boron

From the temperature dependence of the drift mobility shown in Fig. 5, the activation energy 240 meV was estimated. It is known from optical measurements that β-rhombohedral boron has an intrinsic acceptor level lying about 0.2 eV above the valence band (1). This activation energy for holes is assumed to correspond to the energy difference between the top of the valence band and the acceptor level due to an intraicosahedral orbital split-off valence band. Thus we consider that the photoexcited holes propagate through β-rhombohedral boron by multiple trapping at the acceptor level (that is B_{12}) and thermal reexcitation into the valence band.

CONCLUSION

The activation energy of the drift mobility in the β-rhombohedral boron corresponds to the energy between the valence band and the intrinsic acceptor level originating from the B_{12} cluster. In the amorphous boron, we estimated the activation energies of electron and hole and found that these energies are small in comparison with the decrease of the optical gap. We do not have enough results to determine a suitable model which explain the behavior. Therefore, the experiments by which the mobility gap can be estimated are now in progress and will clarify the transport mechanism and gap states distribution in amorphous boron together with the present results.

ACKNOWLEDGMENTS

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