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OPTICAL DLTS MEASUREMENTS OF LOCALIZED STATES IN AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

M. Okuda, H. Naito, H. Nakayama and T. Nakau

Department of Electronics, University of Osaka Prefecture, Mozu, Sakai, Osaka, Japan 591

Abstract.- New combined optical/thermal method (optical DLTS) for the investigation of gap states is presented. The concentration and energy distribution of the gap states have been studied. The optical DLTS signal $S(T)$ vs. temperature is calculated from the photoconductivity decay $I(t,T)$. The effective levels and density of states for amorphous Se and As$_2$Se$_3$ films were obtained.

Introduction.- Recently, there has been a considerable interest in determining the concentration and energy distribution of states in the gap of amorphous chalcogenide semiconductors. The techniques for obtaining such information have been the field effect method (1), C-V method (2), photo-capacitance method (3), and DLTS (4-6).

However, it is difficult to obtain the gap states of chalcogenide semiconductors (Se, As$_2$Se$_3$), because their resistivity is much larger than $10^{15}$ ohm-cm and formation of the p-n junction or Schottky barrier is impossible. A simple method to characterize deep levels in high-resistivity GaAs was reported for the transient photocurrent analysis (optical DLTS) (7).

It is the purpose of the present paper that we apply this optical DLTS method to the high resistivity chalcogenide materials, and investigate the concentration and energy levels of gap states by the optical DLTS analysis. Moreover, we present an approximation method applied to the optical DLTS method, since the photocurrent decay of the chalcogenide is not given by the equation of $\exp(-At)$ (8).

Experimental.- Figure 1 shows the schematic diagram of the experiment. Electron-hole pairs can be generated by using a monochromatic light (100 $\mu$W/cm$^2$). In high-resistivity chalcogenide materials, carriers cannot be easily injected by electrical means. So, in the optical DLTS method, they are optically generated in

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Fig.1 Schematic diagram.
Detrapping of carriers is investigated by transient current measurements with various temperatures.

Results and Discussion.

Figure 2 shows the decay curves measured at 8 temperatures between 254 K and 293 K after the end of the illumination for 10 sec. In high temperature region, the decay of photocurrent is fast. In low temperature region, the residual photocurrent becomes to decrease more slowly as temperature is lowered. In intermediate temperature region, the residual photocurrent at the initial stage is rather slow.

When the chalcogenide contains several kinds of traps, the photo-transient current consists of several exponential terms with various time constants, as shown in Fig. 2. However, a relation derived for materials containing one kind of traps is often used for the DLTS analysis, even if several kinds of them are present in the materials.

In order to investigate in which cases the assumption of independence of the trap centers hold we derive a equation for the time constants of the transient curve in materials containing m kinds of traps. For simplicity, we consider only p-type photoconductivity under illumination (about 100 µW/cm²). In such case, the basic equations for the transient current after switching off the illumination may be written as

$$\frac{dp}{dt} = -Rp - \sum_{i=1}^{m} N_{ti} w_{i} p + \sum_{i=1}^{m} r_{i} p_{ti}$$

(1)

$$\frac{dp_{ti}}{dt} = N_{ti} w_{i} p + r_{i} p_{ti}$$

(2)

where p and $p_{ti}$ are non-equilibrium densities of holes in the valence band and the i-th trap level; $w_{i}$ and $r_{i}$ are probabilities of trapping and emission of a hole by the trap level, respectively. $N_{ti}$ is the density of these traps and R is the recombination rate of the conduction holes.

The solution of eqs. (1) and (2) gives the photocurrent decay,

$$I(t, T) = \sum_{i=1}^{m} I_{i}(0, T) \exp(-a_{i} t)$$

(3)

where t is the time measured with 2 traps (m=2).
from switching off the illumination, T is the absolute temperature, \( a_i \) is the thermal emission rate of hole from the trapping levels, and \( I_i(0,T) \) is the initial photocurrent.

For an example of two trapping levels \((m=2)\), the decay curve of photocurrent is shown in Fig. 3, and the decay region is separated in region 1 and 2.

In region 1, \( I(t,T) = I_1(0,T)\exp(-a_1t), \quad t < t_0 \) \( (4) \)

in region 2, \( I(t,T) = I_2(0,T)\exp(-a_2t). \quad t > t_0 \) \( (5) \)

In each region, the normalized DLTS signal \( S(T) \) is defined as

\[
S(T) = \frac{[I(t_1,T)-I(t_2,T)]/I(0,T)}{\Delta I(T)/I(0,T)} = \exp(-t_1/\tau_1)[1-\exp(-\Delta t/\tau_1)],
\]

where, \( \tau_1 = 1/a_i \), and \( \Delta t = t_2 - t_1 \). The relationship between \( \tau_{\text{max}} \) and \( t_1, t_2 \) is simply determined by differentiating \( S(T) \) with respect \( \tau \) and setting the result equal to zero. The desired expression is then

\[
\tau_{\text{max}} = (t_2-t_1)/\ln(t_2/t_1).
\]

Thus, the emission rate corresponding to the maximum observed in an optical DLTS thermal scanning is a precisely defined quantity and can be used along with the temperature corresponding to the maximum in constructing a semilog activation energy plot.

At the maximum of the optical DLTS signal, one can determine the temperature and calculate \( \tau_{\text{max}} \) from eq. (7) to get one point of \( \ln(a_i) \) vs. \( 1000/T \) plot. Other points can be similarly obtained from other measurements made with different gate settings, and thus different values of \( \tau_{\text{max}} \) and different peak positions.

Figure 4 shows typical DLTS spectra with four different rate windows in region 2 (Fig. 3). The two kinds of traps in the amorphous Se sample are labeled A and B. The emission rates with various temperatures can be calculated from the \( t_1 \) and \( t_2 \) values by using eq. (7).

Fig. 4 Optical DLTS spectra for hole traps in amorphous Se.
The resulting data points are shown in Fig. 5. Two traps have activation energies measured from the valence band of 1.0 and 1.2 eV, respectively. For the amorphous As$_2$Se$_3$ film, we obtained one level (0.6 eV).

If the decay is governed by thermal release of holes trapped above the quasi-Fermi level, a Fermi level analysis can be applied to the data of Fig. 4 (9). The decay time $\tau$ for the photoconductivity is interpreted as the time required for the emptying of trapped holes lying within $kT$ above the steady-state Fermi level. Then,

$$\tau = \tau_0 [1 + N_{ti}/p], \quad (8)$$

where $\tau_0$ is the hole lifetime, and $N_{ti}/kT$ is the density of trapped holes within $kT$ above the steady-state Fermi level. If $N_{ti} > p$,

$$N_{ti} = f\tau, \quad (9)$$

where $f = p/\tau_0$ is the photoexcitation rate per unit volume for the steady-state photoexcitation preceding the decay.

When we use the data for the hole density $p=10^{14}$ cm$^{-3}$, the hole lifetime $\tau_0=30$ ns, and the decay time of photocurrent $\tau=2$ sec, the density of states can be obtained as $N_{ti}=6.6\times10^{18}$ cm$^{-3}$. This value coincides with the density of states obtained from ac conductivity measurements.

**Conclusion.**—The optical DLTS method was applied to the high resistivity chalcogenide materials, and investigated the concentration and energy levels of gap states. The concentration of gap states was calculated by the Fermi level analysis, using the data of optical DLTS. These values of density coincide with the results from ac conductivity measurements.