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Localized gap states in amorphous semiconductors estimated by dielectric relaxation

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Low-frequency dielectric relaxation of amorphous Te_xSe_{1-x} and As_2Se_3 has been measured. Dielectric dispersion was found in $\omega \simeq 0.1$–500 Hz for Te_xSe_{1-x} and $\omega \simeq 0.1$ Hz for As_2Se_3 at 293 K, where ω is the angular frequency. The activation energies for dispersion were smaller than that for electrical conduction in contrast with oxide glasses. To account for the data, a model is proposed. The dielectric loss is caused by hopping of trapped holes between localized centers through tail states. From this model the hole-trap levels and its density are estimated. It is suggested that measurements of low-frequency dielectric relaxation find broad application in the estimation of deep localized states in amorphous semiconductors.

I. INTRODUCTION

Through studies on dielectric relaxation phenomena in several types of oxide glasses,[1,2] dielectric dispersion is observed in a low-frequency range between 0.1 and 1000 Hz and the activation energy for dielectric relaxation is nearly equal to that for electrical conduction. Both the dielectric loss and the electrical conduction have been considered to be caused by some type of ionic diffusion.[2]

Usually dc and ac conduction at a high frequency in chalcogenide glass semiconductors are known to have electronic properties,[3-5] but there have been few studies on electrical conduction at low frequencies (dielectric properties).

This paper presents an investigation on dielectric properties in amorphous As_2Se_3 and Te_xSe_{1-x}. The choice of these systems was based on the following considerations: amorphous As_2Se_3 is known to be a relatively well-ordered "amorphous" material[6] and a considerable amount of information has been accumulated about this material. Components of amorphous Te-Se system are isomorphous and the phase diagram is simple. In this system, there is evidence for a change in the drift mobility correlated with Te impurity states.[7] If the charge carriers are localized, ac techniques are often employed to prove their behavior.[4,5,8,9] Here measurements of dielectric relaxation are made by using an absorption-current method.[2,10] By introducing a digital memory and a printer, as shown in Fig. 1, dielectric loss and relaxation time are quantitatively determined accurately.

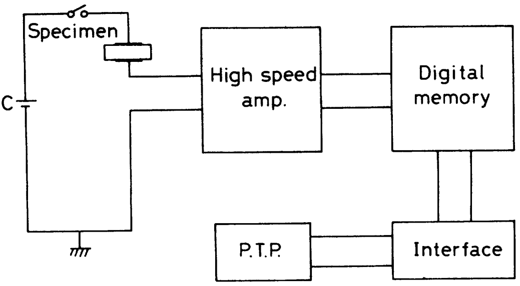

FIG. 1. Block diagram for absorption-current measurement. PTP is the tape printer for the computer.

Dielectric dispersion was found in a low-freqquency $\omega \simeq 0.1$ Hz for As_2Se_3 and $\omega \simeq 0.1$–500 Hz for Te_xSe_{1-x} at 293 K. The activation energies for dispersion were smaller than that for electrical conduction.[10-12] This low-frequency dielectric relaxation can be interpreted by hopping of trapped holes between deep localized centers through tail states. We can estimate the hole trap levels and its density in terms of the model proposed. The same centers have been observed in the hole drift mobility[13,14] and proposed on the photoluminescence[15] in amorphous As_2Se_3 and As_2S_3.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

Materials used were $Te_{15}Se_{85}$, $Te_{25}Se_{75}$, $Te_{35}Se_{65}$, and As_2Se_3. In $Te_x Se_{1-x}$ system, each of these materials was sealed off in a quartz ampoule at 1×10^{-6} Torr, heated at 650 °C for 10 h, and then heated at 450 °C for 5 h. The melt was then quenched in ice water. In As_2Se_3, polycrystalline As_2Se_3 was heated at 650 °C for 15 h and was slowly quenched in air.

Disk-shaped samples 10 mm in diameter were cut off from an ingot and surfaces were mirror-polished. Gold was evaporated onto the sample and was used as electrodes for measurements of dielectric relaxation.

B. Dielectric relaxation measurement

Complex dielectric constant was estimated by using the absorption-current method as shown in Fig. 1. By introducing a digital memory and a printer, highly sensitive detection of absorption current was obtained.

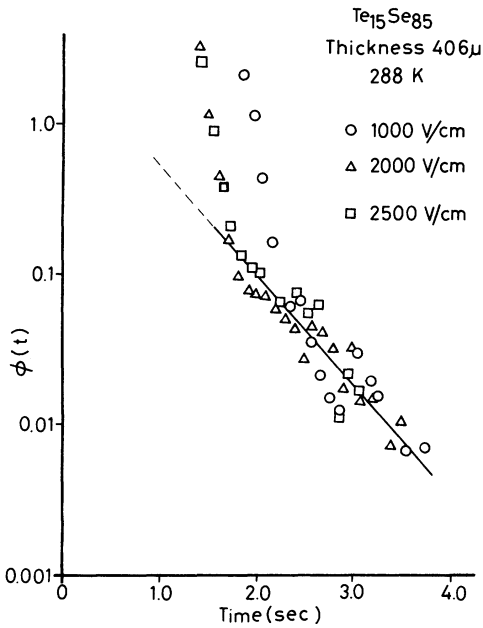

FIG. 2. Dependence of the after-effect function $\phi(t)$ on the electric field in $Te_{15}Se_{85}$.

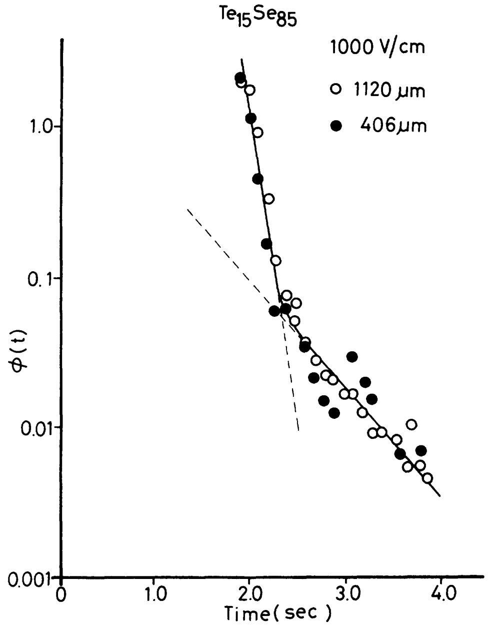

FIG. 3. After-effect functions $\phi(t)$ on $Te_{15}Se_{85}$ for 406 and 1120 μm in thickness under the electric field of 10^3 V/cm.

The complex dielectric constant, $\epsilon(\omega)=\epsilon'(\omega)+i\epsilon''(\omega)$ (ω: angular frequency), is expressed in terms of the absorption current $I(t)$ (t: time):

$$\epsilon'(\omega)=\epsilon'_\infty+\int_0^\infty [I(t)/C_0V]\cos\omega t\,dt\ , \tag{1}$$

$$\epsilon''(\omega)=\int_0^\infty [I(t)/C_0V]\sin\omega t\,dt\ , \tag{2}$$

where C_0 is the geometric capacitance of the sample, V the applied voltage, and ϵ'_∞ the high-frequency dielectric constant. When the after-effect function, $\phi(t)=I(t)/C_0V$ is written approximately as[16]

$$\phi(t)=\sum_j \beta_j \exp(-\alpha_j t)\ , \tag{3}$$

where α_j and β_j are constant, then $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are represented by

$$\epsilon'(\omega)=\epsilon'_\infty+\sum_j \alpha_j\beta_j/(\omega^2+\alpha_j^2)\ , \tag{4}$$

$$\epsilon''(\omega)=\sum_j \omega\beta_j/(\omega^2+\alpha_j^2)\ , \tag{5}$$

respectively. The average relaxation time $\langle\tau_m\rangle$ is defined by the reciprocal of peak frequency ω_m on the loss curve $\epsilon''(\omega)$.

III. RESULTS AND DISCUSSION

A. Dielectric loss

Figure 2 shows dependence of the after-effect function $\phi(t)$ on the electric field in $Te_{15}Se_{85}$. Curves of $\phi(t)$ have a fast component and a slow one. Traces of fast components are qualitative because they include the rise time of a high-speed amplifier. Slow components, from which we obtain the low-frequency dielectric relaxation, are reduced to one curve. This means that the dielectric relaxation is independent of the electric field measured.

Figure 3 shows $\phi(t)$ curves on $Te_{15}Se_{85}$ for 406 and 1120 μm in thickness under the electric field of 10^3 V/cm. It is apparent that the after-effect function $\phi(t)$ is independent of the thickness of the samples, indicating that the absorption current observed is a bulk effect rather than a surface effect.

Results for $Te_{15}Se_{85}$ mentioned above were similar to that for $Te_{25}Se_{75}$, $Te_{35}Se_{65}$, and As_2Se_3. Thus it was confirmed that the low-frequency dielectric relaxation in all samples is a bulk effect and is independent of the electric field measured.

As $\phi(t)$ is approximately represented by

$$\phi(t)=\beta_0\exp(-\alpha_0 t)\ , \tag{3'}$$

as shown in Figs. 2 and 3, the dielectric loss $\epsilon''(\omega)$ obtained is close to the Debye-type single relaxation.

Figure 4 shows the temperature dependence of $\langle\tau_m\rangle=\alpha_0^{-1}$ for the samples No. 1($Te_{15}Se_{85}$), No. 2($Te_{25}Se_{75}$), and No. 3($Te_{35}Se_{65}$). Figure 5 shows that for No. 4(As_2Se_3). Average relaxation time $\langle\tau_m\rangle$ decreases with increasing ambient temperature T and is expressed by

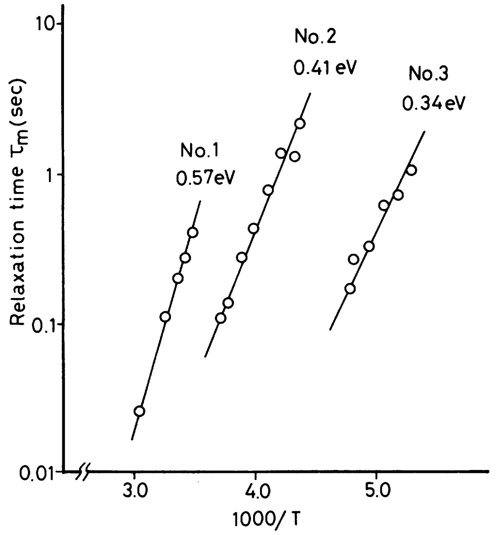

FIG. 4. Temperature dependence of the average relaxation time $\langle\tau_m\rangle$ for the samples No. 1 ($Te_{15}Se_{85}$), No. 2 ($Te_{25}Se_{75}$) and No. 3 ($Te_{35}Se_{65}$).

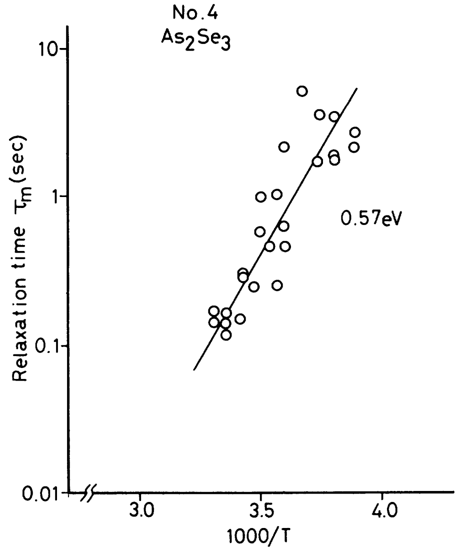

FIG. 5. Temperature dependence of the average relaxation time $\langle\tau_m\rangle$ for No. 4 (As_2Se_3).

$$\langle\tau_m\rangle = \tau_0 \exp(E_r/kT) , \qquad (6)$$

where τ_0 is a constant, k the Boltzmann constant, and E_r the activation energy for dielectric relaxation. Values of E_r and other electrical parameters are tabulated in Table I. E_r is smaller than the activation energy for dc conduction, while both values are almost equal to those of oxide glasses.[1,2]

B. Dielectric relaxation mechanism

Conduction process in chalcogenide glasses is known to be dominated by hole carriers[5] and hole drift velocity is controlled by traps.[13,14] For the case of trap-controlled ac conduction, carriers are thermally excited from traps into extended states or tail states and subsequently retrapped. This would lead to a single relaxation time for a single localized level.

The dielectric relaxation in this study is likely to be dominated by the mechanism stated above. In this case the electronic relaxation time of carriers released from traps is given by[17]

$$\tau = \nu_0^{-1} P(R) \exp(W/kT) , \qquad (7)$$

where ν_0 is a factor of the phonon spectrum, $P(R)$ the overlap term of the localized wave function, and W the energy difference between the localized and the extended states or the tail states. By putting $\tau = \langle\tau_m\rangle$ at 293 K and $W = E_r$, the values of $\nu_0^{-1}P(R)$ for Nos. 1, 2, 3, and 4 are estimated to be 5×10^{-11}, 3×10^{-9}, 1×10^{-9}, and 4×10^{-11}, respectively. If the conduction is by hopping in tail states as Nagels *et al.*[18] and Street,[15] then the dielectric relaxation is caused by the classical hopping of holes between trapped states and tail states as shown in the model of Fig. 6. The relaxation mechanism proposed is related to Pike's model,[9] in which a thermally activated dielectric loss has been predicted at much lower frequencies.

C. Evaluation of localized hole density

If localized holes distribute randomly with average spherical separation R, the energy difference between two sites is eRE, where E is the external electric field. Through the difference between the jumping probability of two sites is taken into consideration, the dielectric increment $\Delta\epsilon'$

TABLE I. Electrical and dielectric parameters in Te-Se and As_2Se_3.

	Resistivity at 298 K(Ω cm)	Dielectric constant	Activation energy (eV) Electrical conductivity ΔE	Dielectric relaxation E_r
No. 1($Te_{15}Se_{85}$)	2.2×10^{13}	11.5	0.87	0.57
No. 2($Te_{25}Se_{75}$)	2.0×10^{10}	11.4	0.80	0.41
No. 3($Te_{35}Se_{65}$)	6.6×10^{8}	11.9	0.64	0.34
No. 4(As_2Se_3)	1.2×10^{12}	11.0	0.92	0.57

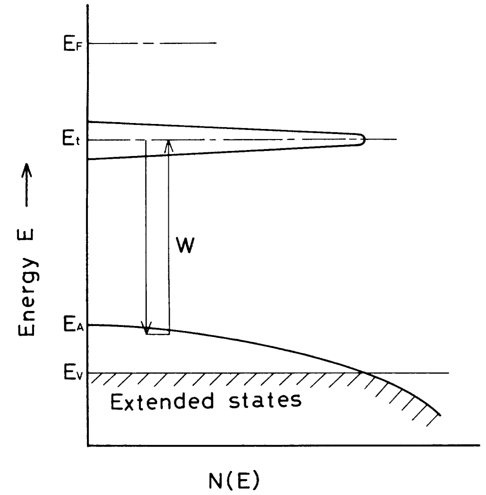

FIG. 6. Model for the classical hopping of holes at low frequencies in chalcogenide glasses. E_v denote the top of the extended valence states (mobility edge) and the band tailing extends about 0.1 eV to E_A. W is the thermally activated hopping energy of holes.

is given by

$$\Delta\epsilon' = \epsilon_s' - \epsilon_\infty' = n(eR)^2/4\epsilon_0 kT , \qquad (8)$$

where n is the number of localized holes, ϵ_s' is the static permittivity, and ϵ_0 the free-space permittivity. This formula is derived by a method similar to that of Fröhlich.[19] Correlation between the localized carrier number n and the localized density of states N_t is written by

$$n = N_t \exp[-(E_F - W - 0.1)/kT] , \qquad (9)$$

where the width of the tail states is assumed to be 0.1 eV as shown in Fig. 6. Let Eq. (9) substitute into Eq. (8), and assuming $nR^3 = 1$,[20] then the dielectric increment $\Delta\epsilon'$ is written by

$$\Delta\epsilon' = e^2 N_t^{1/3} \exp[-(E_F - W - 0.1)/3kT]/4\epsilon_0 kT , \qquad (10)$$

where E_F is defined by the activation energy for dc conduction.[3,5]

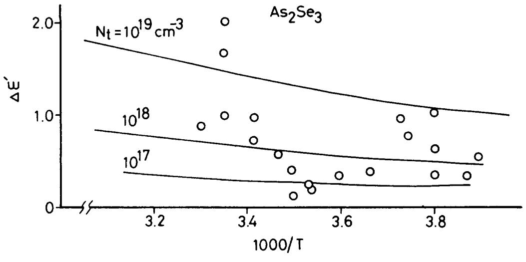

FIG. 7. Relationship between the dielectric increment $\Delta\epsilon'$ and the temperature in As_2Se_3. Solid lines are theoretical curves for $N_t = 10^{17}$, 10^{18} and 10^{19} cm^{-3}, respectively.

Figure 7 shows the temperature dependence of the dielectric increment $\Delta\epsilon'$ in As_2Se_3, where the solid lines are theoretical curves obtained by Eq. (10). From the figure, N_t is estimated to be the order of 10^{18} cm^{-3}.

In Table II the values of the localized state density and its energy level which is measured from the top of the extended valence states E_v, deduced from various experiments, are summarized. Here N_t for hole drift mobility have been estimated by assuming the conduction in tail states.[15] All the experiments are consistent with $N_t = 10^{16-18}$ cm^{-3} in As_2Se_3, suggesting that the localized gap center in this study are the same centers determined by various experiments.[13-15,21,22] These centers have been considered to originate from the simple structural defect according to Street and Mott.[23] In Te_xSe_{1-x} system, N_t was estimated to be of the order of 10^{18-21} cm^{-3}. The density of gap centers in Te_xSe_{1-x} is relatively higher than that for As_2Se_3.

IV. SUMMARY

From the measurement of the low-frequency dielectric relaxation of amorphous Te_xSe_{1-x} and

TABLE II. Values of localized state density and its energy level estimated from various experiments. Here the energy level of 0.56 eV for the hole drift mobility is only taken into consideration in three discrete sets of trapping centers in a Ref. 14.

	Dielectric relaxation		Hole drift mobility[a,b]		Photoluminescence[c]		Induced ESR[d]	TSC[e]
	E_t(eV) + W + 0.1	N_t(cm^{-3})	E_t(eV)	N_t(cm^{-3})	E_t(eV)	N_t(cm^{-3})	N_t(cm^{-3})	E_t(eV)
No. 1($Te_{15}Se_{85}$)	0.67	10^{18}–10^{19}						
No. 2($Te_{25}Se_{75}$)	0.51	10^{21}						
No. 3($Te_{35}Se_{65}$)	0.44	10^{18}						
No. 4(As_2Se_3)	0.67	10^{17}–10^{18}	0.53[a] 0.56[b]	10^{17}–10^{18} 10^{17}–10^{18}	0.55	10^{17}–10^{18}	10^{16}–10^{18}	0.40

[a] Reference 13.
[b] Reference 14.
[c] Reference 15.
[d] Reference 22.
[e] Reference 23.

As_2Se_3, the following results and conclusions were obtained:

(a) Dielectric dispersion was observed in a low-frequency $\omega \simeq 0.1$–500 Hz for Te_xSe_{1-x} and $\omega \simeq 0.1$ Hz for As_2Se_3 at 293 K. Their activation energies were smaller than that for electrical conduction in contrast with oxide glasses.

(b) Low-frequency dielectric relaxation was interpreted by the hopping of trapped holes between deep localized centers through tail states. From this model we obtained energy levels and densities of the deep localized states (hole trap) in Te_xSe_{1-x} and As_2Se_3.

(c) The centers observed are thought to be the same as those measured by other techniques. It has been considered that the simple structural defect in chalcogenide glasses causes these centers according to Street and Mott.

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