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Transient Effects in Chalcogenide Glasses

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Significant field effects have been reported in chalcogenide glasses, despite the pinning of the Fermi energy by valence alternation pairs. It is shown that the existence of a potential barrier between the two neutral defect centers is responsible for this, but the field effect should decay away with time. It is predicted that the relaxation times are temperature activated, and the activation energies can be used to determine the density of localized states in the gap. New experimental data are reported which demonstrate all of these effects.

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Recent progress in understanding the unique properties of chalcogenide glasses was spurred by the suggestion of Anderson[1] that electrons in states near the Fermi energy E_F are characterized by a negative effective correlation energy, U_{eff}. Street and Mott[2] proposed that this negative U_{eff} is associated with electrons localized on well-defined defect centers. Kastner, Adler, and Fritzsche[3] showed how these concepts follow naturally from the electronic structure of chalcogen atoms, and identified the local nature of the resulting charged defect centers. Adler and Yoffa[4] demonstrated how a negative U_{eff} strongly pins E_F even when the charge density is varied, a result which indicates the absence of a significant steady-state field effect, as we now show.

We assume that a single type of valence alternation pair (VAP)[3] has a creation energy sufficiently smaller than that of any other defect so that it is the origin of the vast majority of the localized states in the gap of the chalcogenide glass. The positively charged center then acts like an ionized donor while the negatively charged center acts like an ionized acceptor. We take the zero of energy as that of the ionized donor. Let T_0 be the energy of the neutral donor and T_0+W the energy of the neutral acceptor. (Note that W can be positive or negative, depending on which neutral center has the lower total energy.) But the ionized acceptor must have energy $2T_0-U$, where U is the magnitude of U_{eff}. The average occupation of the states in the gap is then given by[4]

$$\bar{n}=2\{\exp[-(T_0-\mu)/kT]+\exp[-(T_0+W-\mu)/kT]+\exp[-(2T_0-U-2\mu)/kT]\}/Z, \tag{1}$$

where μ is the electrochemical potential and Z is the grand partition function. When a potential φ is applied, the trapped charge, given by $\rho_T = N(\bar{n} - 1)$, where N is the density of VAP's, is then

$$\rho_T = N \tanh[(E_\mathrm{F} - \mu_0 - q\varphi)/kT], \qquad (2)$$

where $\mu_0 \equiv T_0 - \frac{1}{2}U$ is the Fermi energy at equilibrium. In Eq. (2), we have assumed that the free charge is negligible compared to N.

The negative correlation energy arises from the fact that neutral donors and acceptors can interconvert by either the breaking or the formation of a bond.[3] This implies that their two concentrations must be in thermal equilibrium, i.e.,

$$N_D{}^0 = e^{W/kT} N_A{}^0, \qquad (3)$$

a relation which directly leads to the pinning of E_F. For example, if E_F is increased by an applied potential, the initial effect is to fill some of the ionized donors and ionize some of the neutral acceptors. But this leads to an imbalance in Eq. (3), so that neutral donors convert to neutral acceptors and then ionized acceptors, ultimately returning E_F to its original position. During the time necessary to interconvert the neutral centers, transient behavior in the field effect is observable.

We first derive the field-effect characteristics at equilibrium by integrating Poisson's equation and inserting typical values for the parameters. We find that the field-effect mobility is

$$\mu_\mathrm{eff} \simeq \mu_p p_0 / N, \qquad (4)$$

where μ_p is the free-hole mobility and p_0 is the equilibrium free-hole concentration. Since $p_0/N \sim 10^{-9}$, the field effect should not be experimentally observable. Of course, this is a direct consequence of the Fermi-energy pinning expressed by Eqs. (2) and (3). However, this prediction is not in agreement with previously reported field-effect measurements. Marshall and Owen,[5] Mahan and Bube,[6] and Radjy and Green[7] have all reported much larger field effects for arsenic telluride glasses, although Radjy and Green found that the effect decays away with time. These experimental results are in disagreement not only with the magnitude of the prediction of Eq. (4), but also with the temperature dependence. Equation (4) requires the field-effect mobility to have the same temperature dependence as the conductivity, while in all reported measurements the field effect always has a much lower activation energy. In addition to these problems, the temperature dependence observed by Marshall and Owen[5] is inconsistent with that of Mahan and Bube.[6]

We have performed an extensive study of the field effect in a well-characterized[8] chalcogenide glass, $\mathrm{Te_{39}As_{36}Si_{17}Ge_7P_1}$. The change in source-to-drain current as a function of gate voltage at several temperatures for a linear ramp applied at the gate is shown in Fig. 1. However, when a gate voltage step was applied, the response was found to be transient, as is evident from Fig. 2.

It is the main purpose of this Letter to show that the transient field effect is a natural consequence of the VAP model, provided that a potential barrier exists between the two neutral defect centers. Vanderbilt and Joannopoulos (VJ)[9] find

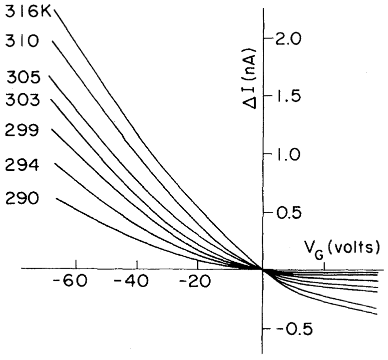
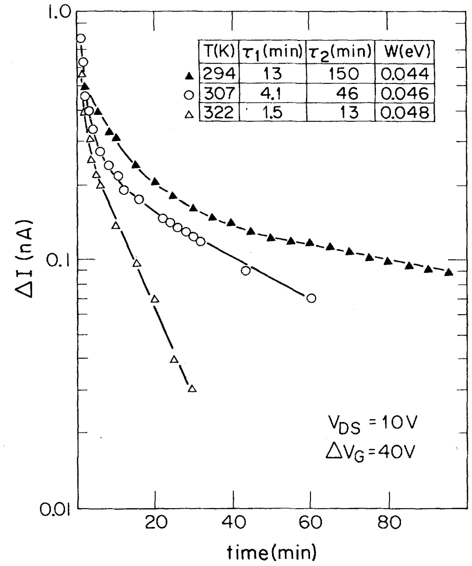


FIG. 1. Change in source-to-drain current as a function of gate voltage at several temperatures.



	T(K)	τ_1(min)	τ_2(min)	W(eV)
▲	294	13	150	0.044
○	307	4.1	46	0.046
△	322	1.5	13	0.048

FIG. 2. Transient current decay at several temperatures. The table shows the values of the parameters τ_1 and τ_2 and the inferred value of W (see text).

no such barrier in pure Se, a system much simpler than the one presently under investigation. However, since no field effect is observable in Se or even As_2Se_3, there is no experimental evidence for the existence of a barrier in these cases. On the other hand, this is not the case for As-Te alloys. The VJ calculation indicates that π bonding lowers the total energy of C_1^0 relative to C_3^0 in Se. In Te, a larger atom than Se, π-bonding effects are significantly smaller, and a barrier between, e.g., a C_3^0 and a P_2^0 center could well exist. If the barrier is sufficiently high, it could lead to a bottleneck in the equilibration kinetics, which, as we shall show, explains all of the diverse behavior in field-effect experiments in chalcogenide glasses.

In our model, a defect can exist in any one of four states, but not all states are connected by a single-step process. Rather the transitions occur via the sequence $N_D^+ \leftrightarrow N_D^0 \leftrightarrow N_A^0 \leftrightarrow N_A^-$. We can write rate equations for all six of these processes in terms of phenomenological time constants. By using the constancy of total defects and recognizing that the relaxation time, τ, for the structural relaxation, $N_D^0 \to N_A^0$, should be the longest time in the problem, we arrive at the time rate of change of the trapped charge density, ρ_T:

$$(d/dt)\{\rho_T - [\tfrac{1}{2}\alpha_A(e^{-\beta\varphi}-1) - \tfrac{1}{2}\alpha_D(e^{\beta\varphi}-1)]N\} = (2\alpha_A\tau^{-1}\cosh\beta\varphi)(-N\tanh\beta\varphi - \rho_T), \tag{5}$$

where $\alpha_A \equiv 2\exp[-(W+U/2)/kT]$ and $\alpha_D \equiv 2\exp(-U/2kT)$. In the steady state, Eq. (5) gives the same result obtained from an equilibrium analysis [see Eq. (2)]. However, for times small compared to τ,

$$\rho_T = \rho_0(\varphi) = \tfrac{1}{2}\alpha_A N(e^{-\beta\varphi}-1) - \tfrac{1}{2}\alpha_D N(e^{\beta\varphi}-1).$$

This is the trapped-charge density that would arise from $\frac{1}{2}N$ acceptors located at an energy $W + \frac{1}{2}U$ below E_F and $\frac{1}{2}N$ donors located at an energy $\frac{1}{2}U$ above E_F, provided that they are *uncoupled*. This conclusion is consistent with all reported field-effect results on chalcogenide glasses.

At intermediate times,[10] the field-effect current initially decays exponentially with a time constant of $\tau/2$. At long times, however, the rate of decay increases to $\tau\alpha_D/2\alpha_A$. We can understand the physical origin of these results by considering the sequence of events in a transient-field-effect experiment. Initially, free holes flood the space-charge region and are quickly trapped by the negatively charged acceptors. This leads to an imbalance of neutral acceptors and they decay to neutral donors with a time constant, $\tau/2$. These effects increase ρ_T, thus causing a decrease in the screening length, which in turn requires the emission of holes in the bulk which then move towards the gate. This last process occurs in two steps. As the potential collapses, some positively charged donors emit their holes, leading to excess neutral donors, which convert to acceptors with a time constant $\tau\alpha_D/2\alpha_A$. The resulting neutral acceptors quickly emit another hole and become negatively charged.

Since the ratio of the decay times is $2\exp(-W/kT)$, the results in Fig. 2 can be used to obtain W. The table in the inset of that figure shows that W is essentially independent of temperature, as it should be. Furthermore, these results explain the disagreement in the temperature behavior reported in previous experiments. It can be seen from Fig. 2 that the initial current always increases with temperature, but because the transient decays faster at higher temperatures, ΔI appears to decrease with increasing temperatures after a few minutes. This accounts for the anomalous behavior reported by Mahan and Bube.[6]

The activation energy of the transconductance, g_m, shows that $\frac{1}{2}U - W = 0.25 \pm 0.05$ eV. The data of Fig. 2 indicate that $W = 0.043 \pm 0.02$ eV. Thus $U = 0.59 \pm 0.14$ eV. Furthermore, from the ratio of the bulk current, I_B, to g_m, we can estimate that $N \simeq 10^{20}$ cm^{-3}. The effective one-electron

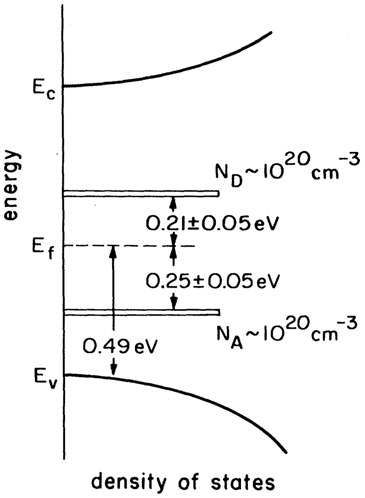


FIG. 3. Effective one-electron density of states at equilibrium obtained from the transient analysis.

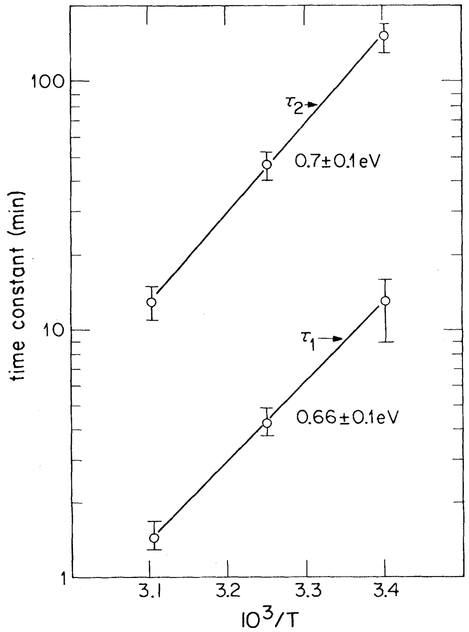


FIG. 4. Initial decay time constant, τ_1, and final decay time constant, τ_2, as functions of the temperature.

density of states at equilibrium is sketched in Fig. 3.

Finally, we must discuss the origin of the bottleneck. If a potential barrier exists between the two neutral defects, both τ_1 and τ_2 must be thermally activated. Figure 4 shows that this is indeed the case, the acceptor-to-donor decay rate being given by $\tau^{-1} = (2\times 10^8\ \text{sec}^{-1})\exp[(-0.65\ \text{eV})/kT]$. The pre-exponential factor is quite low; however, since it is extremely sensitive to small errors in the activation energy, we expect that it is actually considerably larger. The main point is that it is the large potential barrier which controls the kinetics at room temperature. We should note that an explanation of the bottleneck invoking the excitation of a neutral center is not a convincing alternative to the model presented here because it does not reproduce the shape of the curves shown in Fig. 1. In addition, we observe *two* distinct delay times, as is evident from Fig. 2, a result which follows from our model in a natural way but would be very difficult to understand from the alternative possibility.

In conclusion, we have shown that the existence of a single VAP with a negative U_{eff} is consistent with the wide variation in field-effect observations reported for chalcogenide glasses. The presence of a potential barrier between the two neutral defect centers controls the kinetics of equilibration in experiments dealing with field effect or photoconductivity. In such cases, the density of states appears to be a function of time. However, a careful analysis of the decay can be used to obtain the density of VAP's, the energies of the defect centers, and the magnitude of the effective correlation energy.

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