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Temperature Dependence of Hole Transport in Vitreous Selenium

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Hole drift in vacuum-evaporated films of vitreous selenium was measured as a function of temperature (+35 to −130 °C) and applied electric field using a time-of-flight technique. Below −70 °C, a region not previously examined, the inverse hole transit time becomes a nonlinear function of the applied field. Therefore, a unique hole-drift mobility *cannot* be defined. In addition, the transient current below −70 °C shows increasing dispersion (normally characteristic of spatial spreading in the sheet of holes) with decreasing temperature. It is suggested that these effects are caused by an electric-field- and temperature-dependent release rate from shallow traps. Above −70 °C, well-defined electric-field-independent hole-drift mobilities are observed, and the values are in excellent agreement with previously reported results.

INTRODUCTION

Hole-drift mobilities in evaporated films of amorphous selenium have been measured by Spear[1] using electron-beam excitation and by Hartke[2] using a fast light pulse. Both Hartke and Spear reported a thermally activated hole mobility with an activation energy of 0.13–0.14 eV, which they attributed to a shallow trapping mechanism. This result was reexamined by Grunwald and Blakney[3] who found that the measured activation energy depended on the sample preparation and that the hole mobility obeyed the simple exponential law only at low temperatures (200–260 °K).

In this paper, hole-mobility measurements have been extended down to −130 °C. Our high-temperature measurements confirm the results of Grunwald and Blakney. Below −70 °C (a region not previously examined) we find a radically different type of behavior in the hole-transport properties; most of the experimental results reported here are concentrated in this range. In this region, an electric-field-independent mobility *cannot* be defined. The plot of inverse hole-transit time versus applied voltage is no longer a straight line and the nonlinearity in this plot increases as the temperature decreases. In addition, the dispersion or spreading of the sheet of holes as they drift through the sample is also considerably increased compared to the high-temperature case. Results of this type are quite interesting and suggest an electric-field-dependent release rate in a shallow trap-controlled mobility model. Similar results have been reported for poly N-vinyl carbazole [4,5] (PVK) and for vitreous films of As-Se alloys[6-8] at room temperature.

EXPERIMENTAL PROCEDURE

Amorphous selenium films ranging in thickness from 22 to 51 μ and 1 cm diam were prepared by vacuum evaporation onto Kel-F[9] substrates held at 55 °C. The evaporation was performed from an open boat held at 280 °C at a pressure of approximately 5×10^{-5} Torr. A gold electrode was evaporated on the substrate before the selenium was put down, and a semitransparent gold electrode was evaporated on top of the selenium film to complete the sandwich structure. The Kel-F substrate, a transparent insulating plastic, has a thermal-expansion coefficient that allows low-temperature measurements without cracking the selenium film. The details of the experimental arrangement for measuring drift mobility have been described elsewhere[10]; the most important features are summarized below.

A fast pulse (either a 50-nsec Kerr-cell-modulated flash or a 0.5-μsec flash from a General Radio Strobotac) of strongly absorbed light was used to generate a thin sheet of charge near the illuminated surface. With the illuminated surface positive, free holes will drift in the applied field and induce a charge across the electrodes. This induced surface charge can be detected either as a change in voltage across the sample or as a conduction current, depending upon the magnitude of the *RC* time constant of the total circuit.

At high temperatures, where the mobility is high (≈ 0.1 cm^2/V sec) and the transit time is short (< 2 μsec), one is constrained to using the 50-nsec Kerr-cell flash in order to keep the duration of the light flash short compared to the transit time. Because of sensitivity and signal-to-noise problems, only voltage changes can be detected. For the intermediate region, where transit times are of the order of 2–200 μsec, it is possible to use the higher intensity of the 0.5-μsec strobe flash and make either a current- or voltage-mode measurement depending upon the load resistor selected. At the lowest temperatures, where transit times are longer than 200 μsec, only the current mode is convenient because of the difficulty of achieving the very long *RC* times necessary in the voltage mode. In all cases, the total charge injected was kept small compared to the charge on the electrodes so that any perturbation in the applied field due to the injected charge could be neglected.

Figure 1 shows an oscilloscope trace in the intermediate region where both the voltage- and current-mode measurements could be made. These traces are for hole transport at – 95 °C in a 38-μ Se sample at an applied field of 5.8×10^4 V/cm. The transit time may be clearly seen in the current trace by its rapid drop at approximately 55 μsec after the light flash; however, this time is not well defined in the voltage trace. It is interesting to compare this voltage trace with that obtained at + 15 °C for the same sample as shown in Fig. 2. The applied voltage was reduced by more than a factor of 10, but the transit mark is still much more sharply defined than in Fig. 1. At high temperatures, where current-mode measurements cannot be made, the voltage trace exhibits a well-defined decrease in slope which is a measure of the transit time. In general, as the temperature was decreased, dispersive effects increased. The rapid drop in current became less distinct and a greater fraction of the total charge flowed after the transit time. For example, in Fig. 1 (– 95 °C) approximately 40% of the total charge flowed after the transit time, while in Fig. 2 (+ 15 °C) that fraction is reduced to about 10%. However, in all cases, the transit time was defined by a clearly defined drop in current or, at higher temperatures, from a sharp leveling off of the voltage trace. By using this method of determining the transit time, the results are independent of bulk trapping effects. Reasons for increased dispersion in the current trace at the lower temperature will be discussed later.

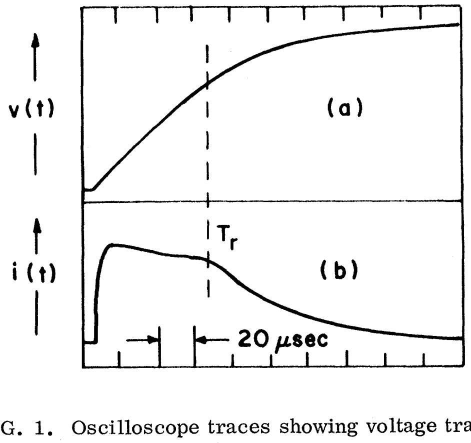

FIG. 1. Oscilloscope traces showing voltage transient (a) and current transient (b) for a 38-μ vitreous selenium sample at – 95 °C with 220 V applied (5.8×10^4 V/cm). The rapid drop in current at 55 μsec indicates the transit time of the injected holes.

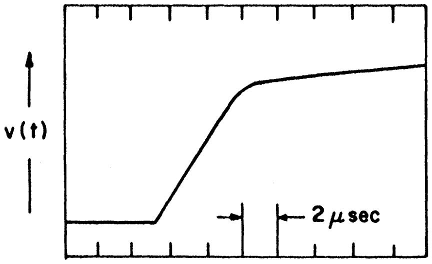

FIG. 2. Oscilloscope trace showing voltage transient at + 15 °C for a 38-μ selenium sample with 20 V applied (5.3×10^3 V/cm). The transit time for this high-temperature trace is well defined by the sharp leveling off of the voltage pulse.

EXPERIMENTAL RESULTS

The hole transit time (defined above) was measured as a function of voltage and temperature for five samples ranging from 22 to 51 μ in thickness. The results of these measurements are summarized below.

For temperatures higher than – 70 °C, a hole-drift mobility could be defined from a plot of $(T_r)^{-1}$ versus V, where T_r is the measured transit time and V is the applied voltage. Figure 3 shows typical results for several temperatures ranging from – 4 to – 48 °C, for the 38-μ sample. At temperatures higher than – 25 °C, plots of $(T_r)^{-1}$ versus

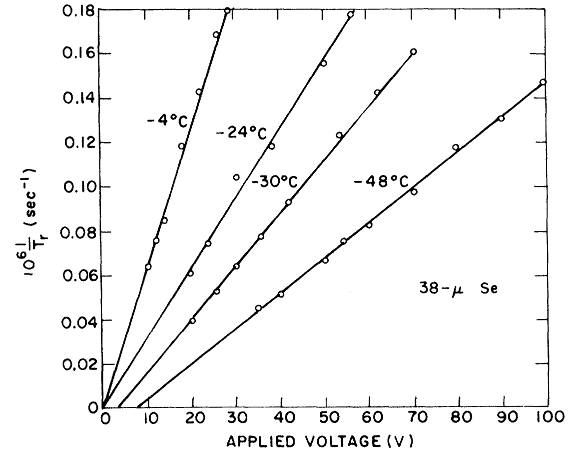

FIG. 3. Inverse transit time of injected holes versus applied voltage for a 38-μ film for four different temperatures. Hole-drift mobilities ranging from 9.4×10^{-2} cm^2/V sec at – 4 °C to 2.3×10^{-2} cm^2/V sec at – 48 °C can be calculated from the slope of these lines.

V pass through the origin. At temperatures between − 25 and − 70 °C the curves are still linear, but the applied potential appears to be reduced by an amount determined from the nonzero intercept. This offset voltage was first noticed by Spear[1] and reexamined and subsequently explained by Scharfe and Tabak[11] in terms of a bulk space-charge distribution. The hole-drift mobility can be obtained directly from the slope of the curves in Fig. 3, and, for the data shown, varies from 9.4×10^{-2} cm^2/V sec at − 4 °C to 2.3×10^{-2} cm^2/V sec at − 48 °C.

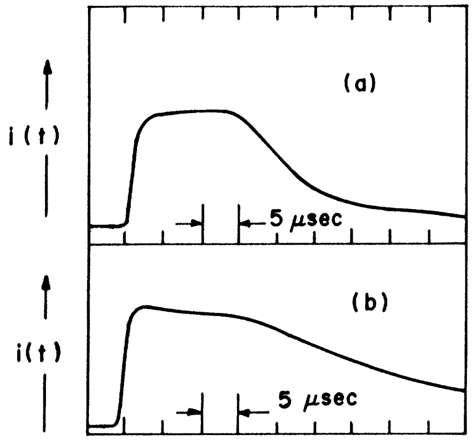

FIG. 5. Comparison of two current traces for a 50-μ Se film: (a) − 52 °C with 140 V applied (2.8×10^4 V/cm), and (b) − 89 °C at 700 V applied (1.4×10^5 V/cm). Note that at roughly the same transit time, the lower-temperature trace shows much more dispersion, even though the applied field is a factor of 5 higher.

Below − 70 °C, an entirely different result is obtained. A plot of inverse transit time versus applied voltage for a 50-μ Se sample at − 93 °C is shown in Fig. 4. These data were obtained from well-defined transit times measured in a current-mode measurement similar to the lower trace in Fig. 1. The curvature in these data is unmistakable and means that a field-independent mobility cannot be defined even though well-defined transit times exist. The current traces, taken where curvature exists in the $(T_r)^{-1}$-versus-V plot, also show much more dispersion than those where a field-independent mobility can be defined. The two traces in Fig. 5 illustrate these differences. The transit times are approximately equal (the time scale is 5 μsec/division for both traces), but because of the difference in mobility the low-temperature trace is taken at a much higher applied field. In view of these unusual but interesting effects, it is understandable why previous measurements were restricted to temperatures greater than − 70 °C. The lower limit of our measurements was − 130 °C, fixed by the lowest temperature at which a transit time could be determined.

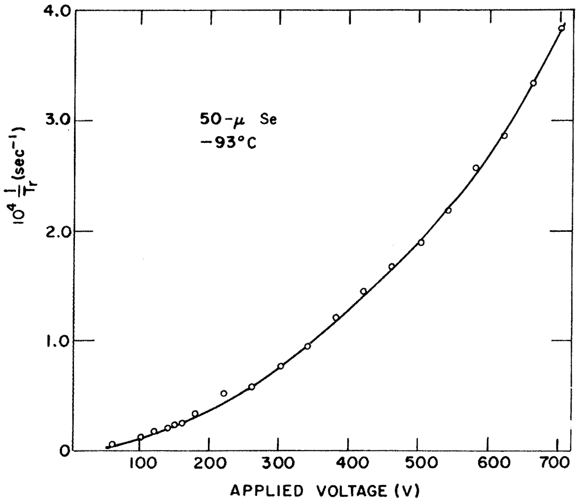

FIG. 4. Plot of inverse transit time versus applied voltage for a 50-μ Se film at − 93 °C. The curvature in this plot does not allow a field-independent mobility to be defined.

The results of the hole-drift mobility measurements from + 35 to − 70 °C on several samples are presented in Fig. 6. Also included for comparison are data from the results of Spear[1] and Hartke.[2] At 20 °C, the maximum spread in hole-drift mobility among five samples was 0.13–0.17 cm^2/V sec. This compares with the values of 0.13–0.14 cm^2/V sec found by Spear[1] and also by Hartke[2] and the values of 0.11–0.12 cm^2/V sec found by Grunwald and Blakney.[3] The agreement between different samples and with previous workers is excellent; the main source of error is probably due to inaccuracies in the thickness measurement. These measurements tend to confirm the results of Grunwald and Blakney,[3] i.e., the hole mobility deviates from a simple exponential dependence above − 10 °C. Between − 10 and − 70 °C, a straight-line portion can be drawn that gives an activation energy of 0.23 eV.

Below − 70 °C a simple electric-field-independent hole mobility cannot be defined; hence, it is impossible to specify the behavior at a given temperature by a single number. Because of the curvature in the $(T_r)^{-1}$-versus-V plot, it is more convenient to present the results on a $\log_{10}(T_r)^{-1}$-versus-$\log_{10} V$ plot for different temperatures as shown in Fig. 7 for a 38-μ sample. In terms of a power law $(T_r)^{-1} \propto V^n$, the exponent n increases from 1.3 at − 73 °C to 2.0 at −115 °C. Note that the temperature dependence of $(T_r)^{-1}$ becomes stronger at lower applied fields. The temperature dependence is ap-

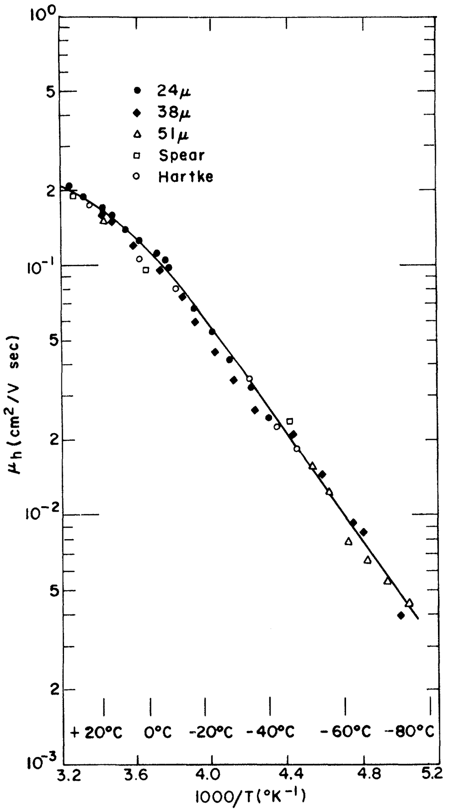

FIG. 6. Temperature dependence of the hole-drift mobility for the 24-, 38- and 51-μ amorphous selenium films and values from the results of Spear and Hartke (Refs. 1 and 2). The straight-line portion at the lower temperatures gives an activation energy of 0.23 eV; the data for temperatures higher than – 10 °C show distinct curvature.

proximately exponential, and an activation energy can be defined as a function of the applied field. From the data in Fig. 7, one can calculate an activation energy of 0.23 ± 0.02 eV at 80 V (2.1×10^4 V/cm), decreasing to 0.16 ± 0.02 eV at 300 V (1.3×10^5 V/cm). It is obvious that a unique activation energy cannot be defined. A mobility arbitrarily defined from a transit time at a given field is found to be thermally activated, but the activation energy is a decreasing function of the applied field.

DISCUSSION

The hole-transport results have generally[1-3] been explained in terms of a shallow trap-controlled drift mobility. The physical picture is that of holes being trapped and thermally released during the course of a transit across the sample. Experimentally, one determines the sum of the drift time and the total time of localization. If the time spent in the trap is much greater than the time the hole is free, then the drift mobility can be written

$$\mu_h = \mu_0 \tau_f / \tau_r \quad ,$$

where τ_f is the mean free time of a hole in the valence band, τ_r is the localization time of a trapped hole, and μ_0 is the microscopic mobility.

The thermal activation of the drift mobility is contained in the term τ_r in the shallow trap-controlled mobility model. In the temperature range above – 70 °C this picture fits quite well. Below – 70 °C the apparent drift mobility becomes electric field dependent and the dispersion or spreading of the hole sheet increases. The release time at these lower temperatures may become electric-field dependent in a way which depends on how the potential barrier of the trap is modified by the applied electric field. As the temperature is lowered the electric field has a stronger effect on the thermal release, since the barrier-lowering effect would be in proportion to $(kT)^{-1}$. The spreading of the hole sheet can arise from nonuniformities in the electric field causing the release time to be a function of position. Increased deep trapping and release after the transit time would also produce increased dispersion. This becomes more probable as the temperature is lowered because of the decreasing hole range.[3]

An alternative to this model is that of intermolecular hopping-type transport,[12] where the hole moves from one center to the next without activation into the valence band. This alternative explanation for the high-temperature results is not

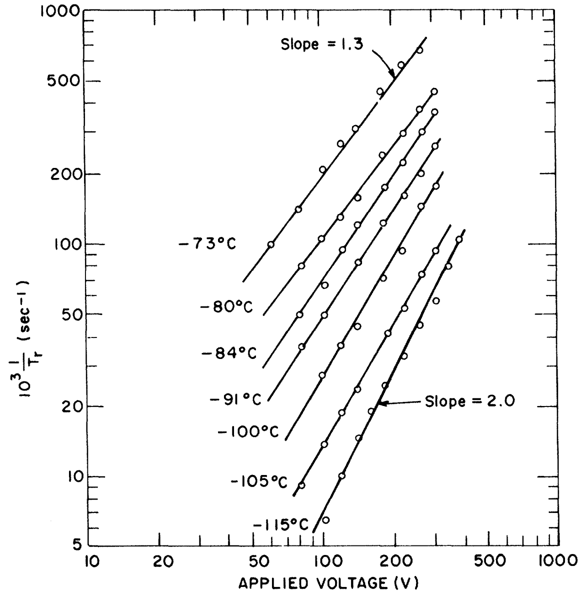

FIG. 7. Inverse transit time versus applied voltage on a log-log scale for the 38-μ amorphous selenium film at several temperatures.

supported by the recent results of Dolezalek and Spear[13] where the hole-drift mobility at room temperature is insensitive to hydrostatic pressure up to 5 kbar. However, it is possible that at lower temperatures hopping through localized states may be the transport mechanism. In this model holes do not communicate with the valence band but rather jump from one localized state to the next, with the release time being much larger than the time-of-flight between states. Such a model has been described in detail by Pai[4] and has been used with some success in explaining similar field-dependent mobilities for hole transport in PVK, and by Scharfe[7] in vitreous films of As_2Se_3. However, only in amorphous selenium can one observe a continuous transition from a shallow trap-controlled mobility at high temperatures to an anomalous electric-field-dependent mobility at low temperatures. If this anomalous region were due to a hopping-type transport, one would expect to see a significant decrease in the activation energy with decreasing temperature; otherwise, the activation energy associated with the high-temperature region would dominate. In fact, the activation energy at the lowest field where transits can be observed is 0.23 eV, the same value obtained in the − 10 to − 70 °C region. This smooth transition implies that the release rate is being determined by a function of the form

$$\tau_r = f\{[\phi_A - g(E,\ T)]/kT\} \quad ,$$

where ϕ_A is the high-temperature activation energy (≈ 0.23 eV) and $g(E,\ T)$ represents the electric field and temperature modulation of the potential barrier.

In summary, for temperatures above − 70 °C, well-defined electric-field-independent mobilities are observed. As a function of temperature, the hole-drift mobility in this region shows a deviation from a simple exponential dependence confirming the results of Grunwald and Blakney.[3] Below − 70 °C, the apparent hole mobility as calculated from well-defined transit times exhibits an anomalous electric-field dependence. It is suggested that this behavior is caused by an electric-field modulation of the localization time of the trapped holes.

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Energy Levels of the F_A Center

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An approximate expression which describes the effects of finite ion size on the *F*-center energy levels is developed and investigated. It is used in a study of the F_A-center energy levels; the impurity-induced changes in the ion-size correction, ionic displacements, and polarization are treated as perturbations on the *F*-center energy levels. We find that the splitting of the *F*-center excited state results mainly from the difference in the ion-size correction for the impurity and host cations, and that the approximate *F*-center excited-state wave functions used here concentrate too much charge at the impurity site.

I. F_A CENTER

The F_A center[1] in the alkali halides consists of an *F* center, an electron bound to an anion vacancy, modified by the presence of an impurity alkali ion of smaller size which substitutionally replaces a cation on a nearest-neighbor site to the vacancy. The introduction of this impurity ion reduces the