Charge generation from band-gap states in amorphous selenium films

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Band-gap states have been detected in amorphous selenium films by the observation of dark currents. These currents are a function of the selenium thickness, time, electric field E, and temperature. By studying the dependence on film thickness, the dark current due to bulk generation of charge is separated from the surface contribution. Subtracting the surface current from the measured dark currents permits the study of the remaining bulk contribution. The bulk dark current depends exponentially on $E^{1/2}$, consistent with the Poole-Frenkel effect. The time and temperature dependence reveal that the states involved are located 0.7–1.0 eV from the valence-band edge with a density of states of approximately 10^{14} cm^{-3}.

I. INTRODUCTION

While there is now evidence[1] that a band gap may actually exist in amorphous semiconductors lacking long-range order, there remain questions concerning the density of states in the band gap. It has been suggested, based on theoretical considerations, that density-of-state tails should extend from the conduction and valence bands into this energy region, with the states having an associated reduced mobility. However, while there is still disagreement among groups studying amorphous Ge and Si,[1–3] some groups have found the optical absorption edge of the amorphous films to be as sharp as the crystalline material. Donovan *et al.*[3] observed, in amorphous Ge, the band-gap absorption coefficient to be less than 10 cm^{-1}, which they associate with a band-gap density of states of less than 10^{18} cm^{-3} corresponding to less than 1.6×10^{18} cm^{-3} eV^{-1} with an 0.6-eV band gap. Among the chalcogenide semiconductors, band-gap states in amorphous As_2Se_3 have been probed by thermally stimulated currents,[4] dark currents,[5] and optical quenching of photoluminescence.[6] The results of these three independent measurement techniques suggests relatively low-density (10^{16}-cm^{-3}), discrete states in the band gap.

This work is concerned with band-gap states in amorphous selenium films. Experimental evidence is presented, based on the observation of dark currents, that there are relatively few discrete states of very low density (10^{14} cm^{-3}) located 0.7–1.0 eV from the valence band.[7]

Such a low value for the density of states in an evaporated amorphous material may at first seem surprising. However, the fact that amorphous selenium films can be used as the photoconductor in the xerographic process places definite limitations on the properties of these films.[8,9] If the density of deep-hole capture states were large, carriers would be trapped in transit across the films, shutting off the ability to re-image the photoconductor; if the density of hole generation centers was large, the latent electrostatic image on the surface of the film would decay before it could be developed into a real image. Assuming the capture time constant is long (or the generation time constant is short) compared to the time for the xerographic process (~1 sec), a lower limit on the sensitivity of the xerographic process to band-gap states can be obtained by setting the product of the total number of volume states and the film thickness equal to a normal surface charge density. Selenium films are normally charged to ~15 V/μm which requires ~5×10^{11} cm^{-2} surface charges. This is equivalent to 5×10^{13} cm^{-3} band-gap states in a 100-μm-thick film.

Band-gap states in amorphous selenium films are observed directly in this work by the study of dark currents.[5] The configuration of the experiment is sometimes called a xerographic discharge experiment: the upper surface of the film, evaporated into an oxidized aluminum substrate, is uniformly charged (by a corona device).[8,9] The resulting electrostatic potential is observed to decrease with time in the dark; the rate of change of potential is proportional to the currents flowing in the capacitor structure. It is demonstrated that these currents are due to bulk-generated holes by varying the film thickness. The study of the time and temperature dependence of the current due to these thermally generated holes measures the energy and density of the hole-generation centers.

II. THEORETICAL CONSIDERATIONS

The experiment is schematically shown in Fig. 1. With the aluminum substrate grounded, the top surface of the film is positively charged to a surface charge density σ. At least initially, the potential V above the film (measured with an electrostatic voltmeter) is given by

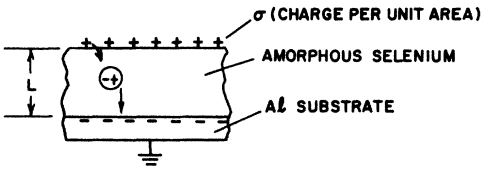

FIG. 1. Schematic diagram of the experiment. The free surface of the selenium film is charged positive. Two possible mechanisms for the observed time dependence of the resulting electrostatic potential are (1) surface injection (2) bulk hole generation.

$$V=(\sigma/\epsilon_0)\,L/K, \tag{1}$$

where K is the dielectric constant of the film ($K=6.3$ for Se). It is observed, in the dark, that V decreases with time.

It must be first established that the moving charges, which are responsible for the observed time dependence of V, are electronic and not ionic. As evidence, we note that after dark currents are generated for a long time the selenium film can be completely photodischarged with highly absorbed light in times which are small compared to the ionic transit time. Any ionic charge responsible for dark currents which have made only partial transit to the substrate would not be neutralized by the highly absorbed light, making it impossible to fully discharge the photoconductor.

It can also be established that the electronic charges are holes and not electrons. If these films are charged negative (instead of positive), they discharge very slowly in the light (on the order of days). Since electron-hole pairs are certainly generated by the light (films which were charged positive photodischarged normally), it must be that electrons cannot transverse the sample. This may be attributed to the presence of chlorine in these films, which is known to behave as a deep electron trap.[9,10]

We are therefore led to two possible sources for the dark currents (see Fig. 1): surface injection of holes and bulk generation of holes. Since the transit time of holes is small compared to the time scale of these experiments ($L/\mu E\sim 20$ μsec with $\mu=0.13$ cm^2/V sec,[11,12] $L=100$ μm, and $E=5$ V/μm), the analysis of dark currents becomes an elementary capacitor problem. The current I, capacitance C, and the rate of change of the potential dV/dt are related by $dV/dt=I/C$ which can be rewritten

$$\frac{dE}{dt}=\frac{q}{K\epsilon_0}\left(J_s+\frac{g_B L}{2}\right), \tag{2}$$

where E is the electric field, V/L, and the large parentheses contain the two possible sources of current flow

J_s = surface generation rate (cm^{-2} sec^{-1})

and

g_B = bulk generation rate (cm^{-3} sec^{-1}),

and q is the electronic charge. The bulk current is reduced by $\frac{1}{2}$ because the negative charge does not move, as argued above. Varying the film thickness permits separation of the bulk and surface components of the dark currents. As our primary interest is with the bulk generation of holes, attention is now focused on this process.

The density of states can be determined from the time dependence of g_B. Let there be N_i initially neutral states at energy E_i from the valence band and an associated time constant τ_i for release of the holes from these states into the valence band:

$$\tau_i^{-1}=f(E)\,\nu\,e^{-E_i/kT}, \tag{3}$$

where ν is a frequency factor and $f(E)$ is the electric field dependence of τ_i^{-1} discussed below. The fact that g_B is observed to decrease in time suggests that the number of filled traps per unit volume N, is being depleted (the Fermi level, initially below E_i, moves towards the conduction band):

$$\frac{dN}{dt}=-\frac{N}{\tau_i} \tag{4}$$

assuming first-order kinetics. This gives

$$N=N_i\,e^{-t/\tau_i} \tag{5}$$

and

$$g_B=(N_i/\tau_i)\,e^{-t/\tau_i}. \tag{6}$$

If there is more than one state involved in the dark decay process, a sum is appropriate

$$g_B=\sum_i \frac{N_i}{\tau_i}e^{-t/\tau_i}. \tag{7}$$

The application of an electric field will tend to reduce the trap energy of the bulk states. The Poole-Frenkel effect[13] describes this process for a Coulombic center (a more extensive calculation has been done by Onsager[14]), which predicts the barrier is lowered by U,

$$e^{-E_i/kT}\rightarrow e^{-(E_i-U)/kT}, \tag{8}$$

where

$$U=\beta E^{1/2} \tag{9}$$

and

$$\beta=(q^3/\pi K\epsilon_0)^{1/2}. \tag{10}$$

This gives $f(E)=e^{U/kT}$. For selenium at room temperature, $\beta/kT=1.2\times10^{-3}$ (m/V)$^{1/2}$. At a time in which the contribution from one state is predominant

$$g_B=(N_i/\tau_i)\,e^{-t/\tau_i} \tag{11}$$

and

$$t \ll \tau_i, \tag{12}$$

$$g_B \sim N_i/\tau_i = N_i f(E)\,\nu\, e^{-E_i/kT}$$

$$= N_i\,\nu \exp[-(E_i - \beta\sqrt{E})/kT]. \tag{13}$$

A straight line should be obtained by plotting g_B semilogarithmically versus the square root of the electric field and versus the inverse of the absolute temperature. The slope of the latter gives the energy of the state.

III. EXPERIMENTAL PROCEDURE

The selenium films are uniformly charged positive by translating them past an air corona device called a corotron.[8,9] (Ions are produced by applying a high potential to a thin wire, thereby causing air breakdown.) The film is then translated to a position over the probe of an electrostatic voltmeter (Monroe, Model 410B) by 0.5 sec (the zero of time is taken at the moment of charging), and the output is monitored by a Brush Mark 280 recorder. Use of an electrostatic voltmeter eliminated the problem of leakage currents sometimes observed with capacitive charge measuring devices. The output of the electrostatic voltmeter is filtered and differentiated with appropriate operational amplifier circuits. This is also recorded.

The films were vacuum evaporated from semi-batch-distilled Se from Canadian Copper Ltd. onto a previously oxidized aluminum plate held at 59 °C at a pressure of 3×10^{-6} Torr to thickness ranging from 23 to 220 μm. The same procedure was used in fabricating selenium for the drift mobility measurements of Tabak and Warter,[11] Pai and Ing[12] and others.[15,16] The aluminum is usually oxidized before the selenium evaporation to prevent injection of electrons at the Al-Se interface (another surface component of the dark currents); because the only component of the current from which information on the properties of the selenium film is obtained was the one that scaled with the film thickness, the detailed properties of the aluminum-oxide–selenium interface can be ignored here. The purity of the films was determined by spark analysis for metals and neutron activation for Cl. The results were approximately 1.3-ppm Cl, ~1-ppm Fe, and trace amounts of Si and Cu (< 0.1 ppm). The maximum possible concentration of other impurities is the sensitivity of the spark test which, except for Te (100 ppm), is on the order of 1 ppm or less.

The films had been cycled many times before these measurements were made. The films showed no evidence of crystallinity (by the Debye-Scherrer technique) and exhibited very long shelf life; the measurements reported here and preliminary measurements made a year earlier are in complete agreement. The upper surface of the selenium films were washed with nigrosine, a chemical which reduces surface injection.[9] This was done because the bulk contribution is of greater interest. (The effect of the nigrosine was not independently checked.) Finally, some evidence of persistent photoconductivity was observed: when exposed to room lights, the dark currents measured immediately afterwards were increased over the rested value. To avoid these effects the selenium films were discharged with uv light from a fluorescent lamp (GE 68 TS) and dark rested 6 h between every measurement.

IV. RESULTS

In Fig. 2 are shown the measured time dependence of the electric field E and dE/dt for a 100-μm-thick film at room temperature. Both E and dE/dt decrease with time.

The separation of the dark currents into surface and bulk components is accomplished in two steps. First, at a time, say 10 sec, E and dE/dt are noted. For this 100-μm plate, $E \sim 10$ V/μm and dE/dt ~0.015 V/μm sec. This is plotted in Fig. 3. This was repeated for various thickness plates, 23–220 μm, and electric fields 1–16 V/μm. From the curves of Fig. 3, dE/dt versus film thickness is plotted with E as a parameter (Fig. 4). These data can now be compared with the Eq. (2). The intercept is related to the surface component of the dark current; the slope is related to the bulk component.

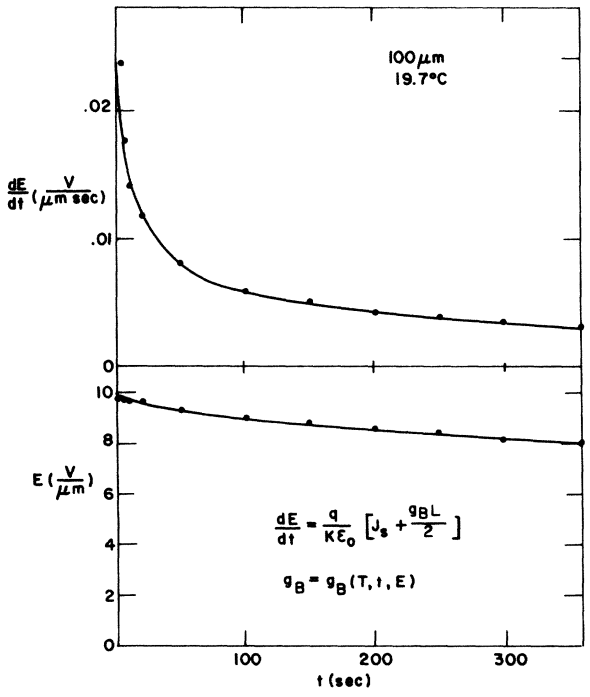

FIG. 2. Time dependence of the electric field E and dE/dt for a 100-μm-thick film at room temperature.

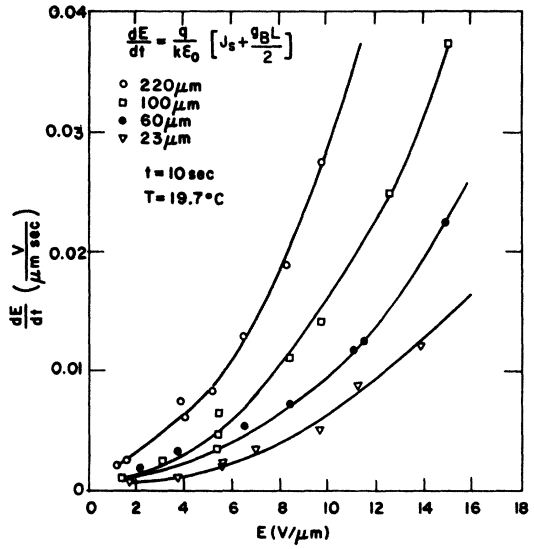

FIG. 3. Dependence of the dark current (proportional to dE/dt) on the electric field E and the selenium film thickness.

Clearly, a bulk component contributes to the observed dark current, and it depends on the magnitude of the electric field. The intercept suggests the existence of a surface component; however, it is possible that the intercept could be due to a non-

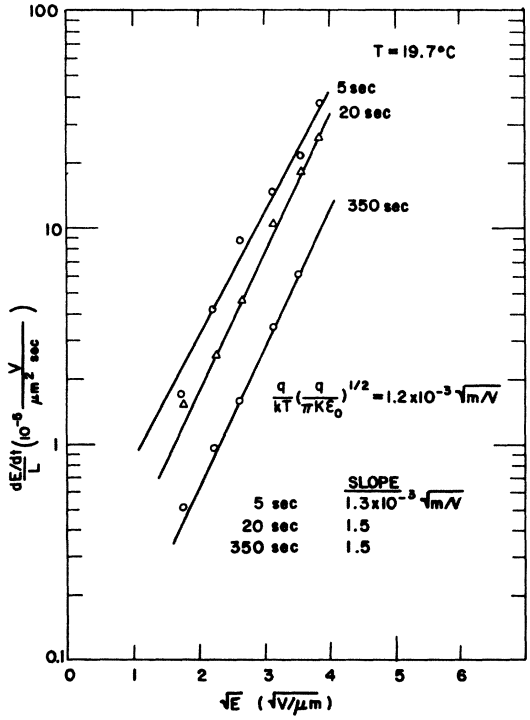

FIG. 5. Dependence of the bulk component of the dark current on the electric field. The straight line and magnitude of the slope are consistent with the Poole-Frenkel effect.

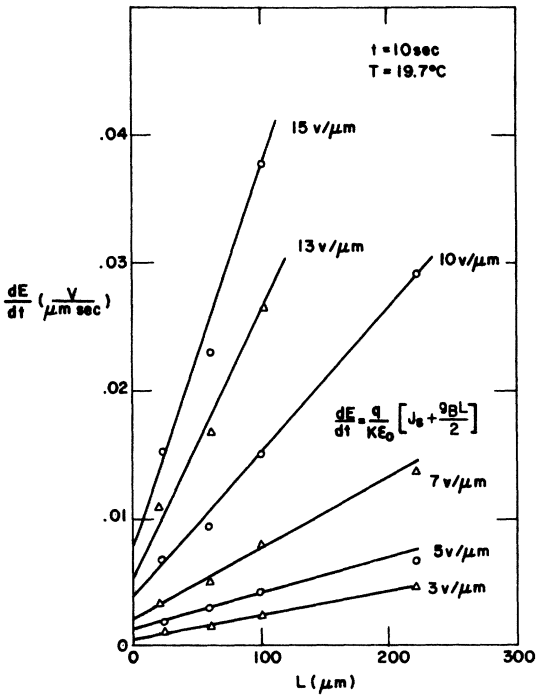

FIG. 4. Replotting the data of Fig. 3, showing the dark current's dependence on film thickness with the electric field as a parameter. Note that there is a bulk component to the current and it depends on the electric field.

uniform distribution of bulk states. Therefore, the dependence of the intercept on electric field is associated with the bulk generation's electric field dependence or an electric-field-dependent surface generation.

We now focus attention on the bulk component of the dark currents. The observed electric field dependence may be due to the Poole-Frenkel effect which predicts barrier height reduction by a term proportional to the $\sqrt{E}$ [Eq. (9)]. In Fig. 5 the bulk component of the dark current versus $\sqrt{E}$ is plotted semilogarithmically as suggested by Eq. (13) taken from data similar to Fig. 4 (at several times). Within the experimental error, the data can be fit by straight lines and the observed slope is in excellent agreement with the predicted value.

We return now to the data of Fig. 2, dE/dt versus time for a 100-μm plate at an initial field of approximately 10 V/μm. This is plotted semilogarithmically in Fig. 6 as suggested by Eq. (7). To consider the significance of dE/dt, it would be better if E, the electric field, were fixed. That can now be accomplished since we have shown that the dependence of this bulk dark current is exponential in $\sqrt{E}$ (triangles in Fig. 6). Finally, the surface component is subtracted, which is the intercept in earlier data. This step introduces the greatest experimental error. Note that the final

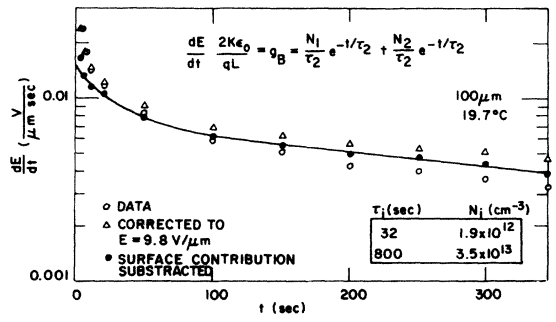

FIG. 6. Replotting and corrections to the data of Fig. 2. The open circles are the data, the triangles include corrections to a constant electric field (the initial field at zero time), and the open circles include corrections for the surface component. These data can be fit with two terms, physically representing two discrete state in the band gap.

curve, the closed circles, is clearly not representable by one straight line. Hence, more than one bulk state contributes to the dark decay.

Shown in Fig. 6, is a best fit for *two* states with the parameters obtained from the fit listed. (The slope of each line gives τ_i; the intercept is N_i.) The two states have time constants 32 and 800 sec and densities of 1.9×10^{12} cm^{-3} and 3.5×10^{13} cm^{-3}, respectively.

The energy of these states can be determined by measuring the dark currents as a function of temperature. Shown in Fig. 7, are data from three of the samples at $t=10$ sec. The data can be fit approximately by straight lines. The slope of the lines corresponds to an energy of 0.6 eV. Subtracting the Poole-Frenkel term gives the energy of the state to be 0.7 ± 0.05 eV. At 350 sec (see Fig. 8), the energy obtained in this manner is approximately 0.8 ± 0.05 eV. A simple consistency check on these results is the ratio of the time constants ($\tau_1/\tau_2=\frac{800}{32}=25$) should be determined by the ratio of the energies of the states for a constant frequency factor [see Eq. (3)] ($e^{(E_1-E_2)/kT}=e^{0.1/0.025}=e^4=54$), which gives acceptable agreement.

In an effort to identify higher states, the dark decay of one plate was monitored for two weeks. A third time constant of 200 h was found, which corresponds to an energy of approximately 0.97 eV assuming the same frequency factor for the states. The state density was 7×10^{13} cm^{-3}, but confidence in the values for this much deeper hole generation states is not as high as for the other two states.

V. DISCUSSION

Three discrete states at energies 0.7 and 0.8 and 0.97 eV from the valence band with total densities of 1.9×10^{12}, 3.5×10^{13}, and 7×10^{13} cm^{-3},

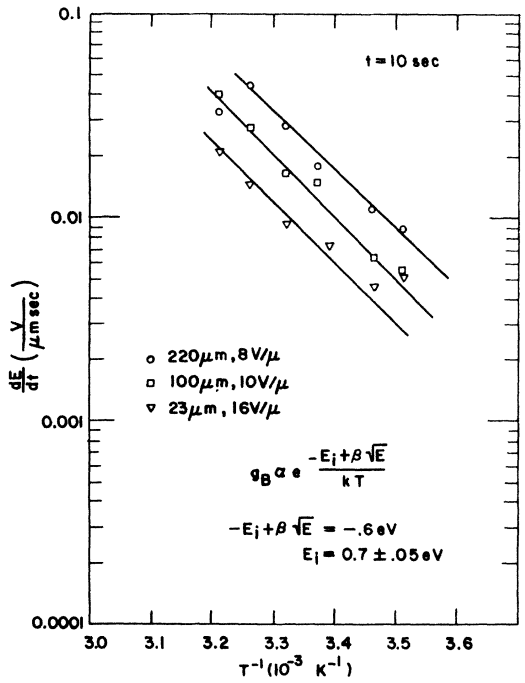

FIG. 7. Temperature dependence of the dark current reveals the energy of the state. The state predominant at $t=10$ sec is at an energy of 0.7 eV.

respectively, adequately describe the thermally generated, field assisted, bulk hole contribution to the dark currents. These states are placed on

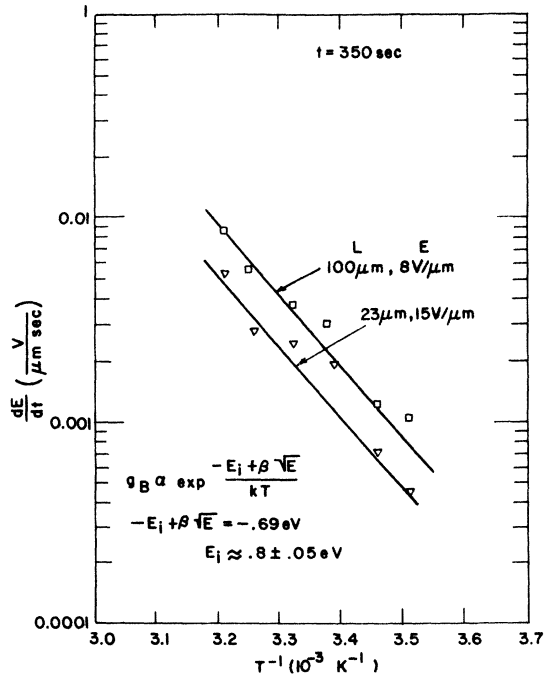

FIG. 8. Temperature dependence at 350 sec. The energy of the state is 0.8 eV.

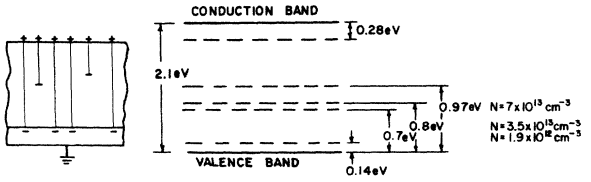

FIG. 9. State energies and densities are placed on a band diagram which includes the two states observed by drift mobility measurements (0.14 and 0.25 eV from the band edges).

a band diagram in Fig. 9, which includes the two shallow states identified by drift mobility experiments.[11,12]

A space and energy schematic diagram of this experiment is shown in Figs. 10(a) and 10(b). The charging process places positive charge on the top surface of the photoconductor [Fig. 10(a)]. Due to the temperature and the electric field, holes are released from attractive Coulombic centers into the valence band. Some field lines now terminate on the trapped negative charge in the bulk, producing a decrease in the observed surface potential V. On applying light, the generated electron-hole pairs are separated by the field; the electrons neutralize the positive charge on the surface, the holes neutralize the negative bulk charge and negative charge on the back electrode.

No statements regarding the density of states outside of this energy region (0.7–1.0 eV from the valence band) is possible from these experiments: states lower in energy would generate holes too fast to be observed by this experiment, and states above 1.0 eV are, similarly, too slow. This work does not prove that only three discrete states exist: a minimum of two states were required to curve fit the time dependence data. However, it has been demonstrated that there are $\sim 10^{14}$-cm^{-3} states in this energy region (0.7–1.0 eV) which can contribute to the dark currents. It is also clear, since the source of these states has not been identified, that 10^{14} cm^{-3} represents an upper bound for the density of intrinsic states. This number is consistent with limits placed on the density of band-gap states by photoemission measurements.[16] The determination of these state energies and densities was made with no assumed parameters and no assumptions were made concerning the nature of the electrodes.

This experiment directly measures the number of *neutral* states in the band gap which can emit a hole into the valence band. This is to a good approximation equal to the total state density because the number of free carriers available to neutralize ionized centers in the dark in this insulating material is negligible ($N \sim 10^6$ cm^{-3}, using $N = \sigma/e\mu_{\text{microscopic}}$, with $\sigma = 10^{-13}\ \Omega^{-1}\,\text{cm}^{-1}$ and $\mu_{\text{microscopic}} = 10$ cm^2/V sec).

Band-gap states in amorphous selenium films have been observed before. Aside from shallow states (0.14 eV from the valence band and 0.28 eV from the conduction band, which have been identified by drift mobility measurements[11]) deep hole capture centers can be observed by the measurements of space-charge-limited currents (SCLC). From the shape of the current-voltage curve, the distribution of states is deduced; from the temperature dependence or an assumed microscopic mobility, the density and energy of the states can be calculated. Lanyon and Spear[17] interpreted their data as indicating 9×10^{13}-cm^{-3} hole traps, 0.79 eV from the valence band. Later Lanyon[18] published SCLC data interpreted in terms of an exponential distribution of states $N(E) = N_0 e^{-E/\Delta}$, where $N_0 = 10^{20}$ cm^{-3} eV^{-1} and $\Delta = 0.067$ eV. Hartke[19] claims that below 1 eV above the valence there exists a band of width greater than 0.15 eV with a total state density of $1.5\text{–}9.0\times10^{14}$ cm^{-3}. Vautier *et al.*[20] fit their data with states 0.74 eV from the valence band with a width of 0.25 eV and a total density of 1.25×10^{14} cm^{-3}. We note the good agreement among the SCLC results of Lanyon and Spear, Hartke and Vautier *et al.* Pfister and Lakatos,[15] who did not vary temperature in their SCLC measurements, also support the conclusion that the band gap of selenium is essentially trap free. They found the ratio Θ_p of free to trapped holes is 6.3×10^{-7}. This is consistent with a hole-trap state density $N_t = 10^{14}$ cm^{-3} in 0.1 eV located at $E_t - E_v = 0.8$ eV:

$$\Theta_p = (N_v/N_t)\, e^{-(E_t - E_v)/kT} \sim 3\times10^{-7} \tag{14}$$

for the density of states in the valence band[21] $N_v = 2.6\times10^{22}$ eV^{-1} cm^{-3}. Pfister and Lakatos also demonstrated conclusively that hole currents were

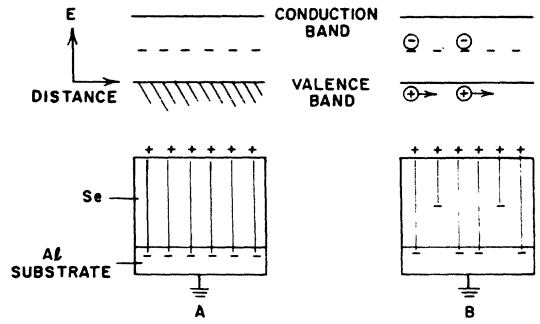

FIG. 10. Schematic space and energy diagram of the dark-current measurement. The charging process places positive charges on the top surface of the photoconductor. Due to temperature and the electric field, holes are released from attractive Coulombic centers into the valence band.

flowing in these experiments by generating the SCLC with highly absorbed uv light.

It is noted that the energy and density of states determined by SCLC and those reported here coincide. One must, however, be cautious in identifying these states as being the same. With the Pfister-Lakatos work, there can be no doubt that SCLC measurements detect hole capture centers; the dark current measurements, as argued above, detect hole generation centers. An initially neutral state becomes positive (in SCLC measurements) and negative (in the dark current measurements). For these measurements to be associated with the same state, the energy difference between the two charge states must be within ± 0.05 eV, the experimental error of the measurements. A second possible explanation[22] is that the states near 0.8 eV are partially ionized and compensated by even deeper trapped holes. Then hole capture occurs into the partially ionized states (the SCLC measurements) and hole generation occurs from the neutral centers. In this case the sum of the states determined by dark currents and SCLC measurements equals the total state density (still $\sim 10^{14}$ cm^{-3}).

Another possibility, that the model for the bulk dark current may not be correct, was also considered and rejected: perhaps during the initial charging, some holes were injected into the bulk and trapped, not an unexpected phenomena.[23] Then the dark currents would be due to the release of holes from hole capture centers and the states would behave as the states observed by SCLC (during these dark current measurements a positively charged state would release hole into the valence band). This however, must be rejected because (i) the observed Poole-Frenkel effect suggests holes are emitted from Coulombic centers and (ii) a bulk positive space charge would produce a residual potential when the film is photodischarged with highly absorbed light. Light-discharge experiments with (4000 ± 100)-Å photons showed no evidence for any residual potential.

It has been argued that there are relatively low density, discrete states in amorphous selenium which have been observed independently by two techniques. The nature of these states, whether they are intrinsic (due to the amorphous nature of the material) or extrinsic (due to impurities), has not been determined. Towards this end, it would be useful to repeat these measurements under conditions in which impurity concentrations (especially As) and substrate temperature during evaporation are varied.

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