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Time-resolved hole transport in a-SiO_2†

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The transport of excess holes in amorphous SiO_2 is reported as a function of field and temperature, with an emphasis on the behavior at short times ($t \geq 10$ nsec) after the hole is introduced into the glass. The unusual features of the tranport for $t \gtrsim 10^{-5}$ seconds can be rationalized on the basis of the continuous-time random-walk model (CTRW) of Scher and Montroll. It is hypothesized that at short times the hole hops, perhaps as a small polaron, from one oxygen nonbonding orbital to one of the nearest-neighbor oxygen orbitals. The hole is eventually trapped at a structural defect and the transport continues as a tunneling from one defect to another, causing the unusual transport phenomena associated with the CTRW. The temperature dependence of the hole tranport is markedly non-Arrhenius below 200°K, which is consistent with the small-polaron model.

I. INTRODUCTION

It is now well established that holes in amorphous SiO_2 are mobile enough to drift significant distances in high electric fields.[1-5] However, the details of transport are much more complicated than one might expect from the hopping of a self-trapped hole[3-5] (cf. the simple case for a self-trapped electron is found in orthorhombic sulfur).[6]

It is apparent that there is a substantial dispersion in the transport history of the individual holes as they cross the thin layers of a-SiO_2, which results in a very wide range of transit times for holes across the films, even under conditions in which it can be shown experimentally that virtually all the holes have been swept through the oxide.[3-5] Dispersive transport has now been observed in a number of amorphous insulators, and the very distinctive experimental features have been rationalized in an elaborate theory, based on special random walks, by Scher and Montroll.[7] Boesch *et al.*[4] have shown that the continuous-time random-walk (CTRW) model as detailed by Scher and Montroll,[7] can describe the space-charge distribution in the oxide of a metal-oxide-semiconductor structure as the hole transport causes it to change. Their experimental method is limited to studying the charge transport to times longer than 10^{-4} sec, but the fit to the CTRW theory is fairly good. In this paper we would like to present high time resolution hole-transport data in an attempt to clarify some of the microscopic details of the hole transport.

The photocurrent data for times shorter than 10^{-6} sec provide evidence for two distinct types of transport for the holes. The hole is initially created by ionizing radiation at a random site in the SiO_2 lattice, and the transport initially takes place by the hopping of the hole, which is strongly localized in the nonbonding $2p$ orbitals of an oxygen, to a nearest-neighbor oxygen. The hopping rate is quite slow, and several features of the data suggest that the hole forms a small polaron by distorting the lattice positions of nearby ions. We call the hopping the "intrinsic" transport of the hole because it depends only on the short-range order which is common to all types of SiO_2 glass and crystal. The lifetime of the hole in the amorphous SiO_2 used in this study is less than 100 nsec at room temperature, because of a high concentration of structural defects which trap a hole which diffuses by the intrinsic mechanism to the vicinity of the defect. After the first trapping event for a given hole the transport takes place by the CTRW with its characteristic dispersion. Since the transport is dominated by the defect-controlled mechanism in all the types of a-SiO_2 studied thus far, much of this paper will be devoted to describing the experimental manifestations of the CTRW and how the data for our samples fit the theory, particularly for $t > 10^{-6}$ sec. Once the fit is established, the deviations from the predictions of the CTRW at short times will be employed to obtain the intrinsic hopping rates and the trapping lifetime of the holes.

The temperature dependence of both the intrinsic and defect-controlled hole transport has some very interesting features. Above 200 °K the transport is thermally activated and can be fit to a simple Arrhenius plot, but below 200 °K there is a dramatic decrease in the activation energy for hopping. Emin[8] has predicted that such a change in activation energy for intrinsic hopping is due to the transition from the dominance of multiphonon jump processes at high temperature to processes involving fewer phonons at low temperatures. Because of the high Debye temperature in SiO_2 (~ 600 °K), Emin predicts that the slope

change should occur at about 200 °K. The results reported here are the first confirmation of these ideas for injected carrier transport in an insulator.

II. EXPERIMENTAL

Many of the experimental details involved in obtaining the data reported here have been given elsewhere.[3,5,9] The a-SiO_2 was in the form of thin films grown on doped Si. The dry oxide refers to samples whose processing led to a thickness of 3700 Å. The wet oxide which is briefly mentioned is thicker (8600 Å). The x-ray pulse which creates the electron-hole pairs in the oxide has a halfwidth of 3 nsec. In a-SiO_2 the electron mobilities are so high that for the fields discussed here the electrons are swept out of the oxide within a few picoseconds after generation.[10] Thus, we are assuming that any current which flows after the x rays stop (about 6–10 nsec) is due to the motion of holes. The total amount of charge which flows during the x-ray pulse also gives us a calibration on the number of holes which are undergoing transport, and this number is corroborated by the magnitude of the delayed time charge which is always close to, but a few percent less than, the prompt charge. The primary data taken is the integral of the current vs time and since data is required over many decades in time, slightly different electronic gear is used for the different time regimes: (i) 10-nsec–to–10-μsec Tektronix 6045 probe (0.5-nsec risetime, 10^7-Ω input impedance) or Tektronix 7A12 amplifier; for the smaller signals a Biomation 8100 transient digitizer was used for signal averaging. The response of the probes and amplifiers were checked against known square-wave signals to make sure that the observed change, particularly at short times, was not due to the amplifier response to the large electron transport signal; (ii) 10 μsec to 1 msec, a Keithley 301 operational amplifier wired for unity gain. It has a risetime of 200 nsec and an input impedance of 10^{12} Ω which ensures that the current is being integrated completely; (iii) 1 msec to 100 sec, a Keithley 602 electrometer, battery powered which has very low noise and drift. Output was into a Fabritek (Nicolet) signal averager. Since the amount of charge flowing at the long times is small, care was taken to subtract out electronically the steady leakage currents, and to compare several samples for consistency. The charge versus log time over many decades was then plotted and fit to a smooth curve, which was then differentiated to yield $\log_{10}i$-vs-$\log_{10}t$ plots.

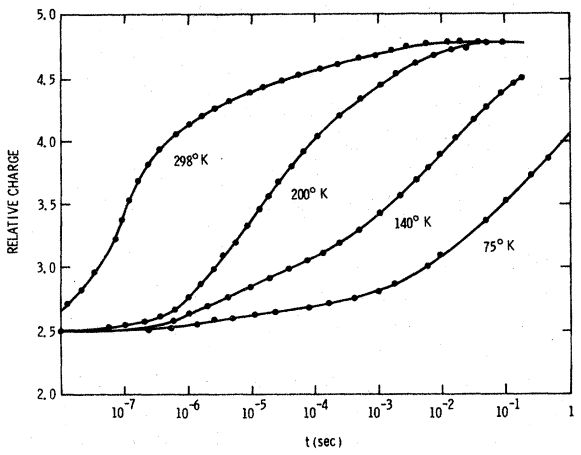

FIG. 1. Integrated current from the 3700-Å oxide as a function of log time at four different temperatures 298, 200, 140, and 75 °K. The data have been normalized to give the same yield, but the normalization factor was less than 10% in all cases. The applied field was 4.7×10^8V/m; similar data were generated for lower fields by applying the appropriate electronics for each time regime.

III. RESULTS

Figure 1 presents the integral of the current as a function of log time for the dry oxide at a very high electric field 4.7×10^8 V/m at four different temperatures. The data have been normalized to give the same value for the prompt charge due to electrons, but the actual temperature dependence of the electron-hole pair creation energy is quite weak, with only about an (8 ± 3)% increase in creation energy in going from 300 to 75 °K. The weak temperature dependence is expected at these high fields for a geminate recombination model even though at very low fields the creation energy should increase exponentially with inverse temperature.[11,12] At lower applied fields it is difficult to detect any delayed charge motion at 75 °K because of the dispersion (particularly in a thicker sample) which led to our earlier statement that no charge flowed at 75 °K.[3] Data similar to Fig. 1 were generated for each voltage and thickness, and the derivatives were taken so that the data could be presented as $\log_{10}i$–versus–log-time plots for analysis. The method for analyzing the data in terms of the CTRW model is given in the Appendix.

An important test for the applicability of CTRW model is the appearance of universality. Figure 2 gives the $\log_{10}i$ versus reduced time for three applied fields at 300 °K in the dry oxide. The value of α chosen for the best fit was 0.3 ± 0.1 and the fit is seen to be fairly good over many decades in time. The actual values of the t_τ are given in Fig. 2 and a further test of the applicability of the

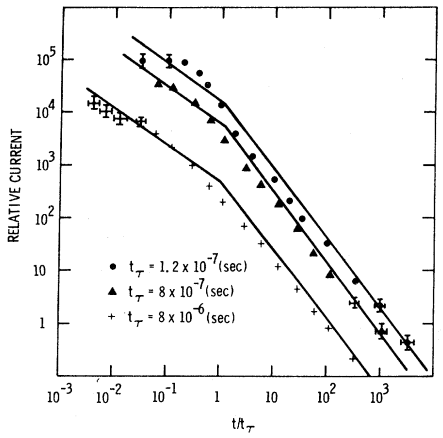

FIG. 2. Relative radiation-induced current vs reduced time showing universality as a function of the applied field. The actual characteristic time for each curve is given on the figure and corresponds to the applied fields: ●, 4.7×10^8 V/m; ▲, 2.7×10^8 V/m; and +, 1.35×10^8 V/m. The characteristic value of α which was chosen as the best fit for the data was $\alpha = 0.3$, which is reflected in the slopes of the lines on the graph. An α of 0.3 also implies that the characteristic time t_τ should vary like $t_\tau = E^{-3.3}$, which is also in good agreement with the data.

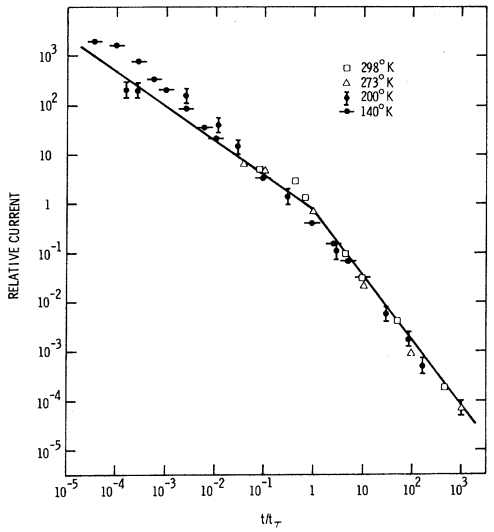

FIG. 3. Normalized log current vs log reduced time for several temperatures demonstrating the general universality of the transport with field and thickness held constant (4.7×10^8 V/m and 3700 Å). The deviations from the predicted curve ($\alpha = 0.3$) at short times are discussed in the text.

model is whether $t_\tau \propto E^{-1/\alpha}$ which would be $t_\tau \propto E^{-3}$ in this case. Again, the agreement is good for over a factor of 3.5 in field.

In determining the microscopic mechanism causing the dispersion in hopping times, it is important to know whether α is temperature dependent (as it is in a-Se)[13] or not. In Fig. 3 it is seen that within experimental error, the slope $(1+\alpha)$ at long times is independent of temperature, and thus universality also applies with temperature as the independent parameter.

The value $\alpha = 0.3$ (± 0.1) is found to fit the shape of the $\log_{10} i$-vs-$\log_{10} t$ curves and the field dependence of t_τ, and it also predicts a roughly cubic power dependence for thickness. At this time we only have two thicknesses at our disposal, and in spite of the fact that the thicker oxide is grown by the "wet" method and the thinner one by the "dry" method, the value of α which fits the data is close to 0.3 for both, as can be seen in Fig. 4. The data given are for the same voltage, so that Eq. (A1) predicts that the ratio of the t_τ should be about 300, which agrees with the observed value within experimental error. Thinner oxides prepared in a different laboratory displayed smaller values of α (0.15) and the t_τ are greater than would be expected from the data shown in Fig. 4,[4] which probably reflects a different defect structure resulting from different processing steps and the increased influence of the messy interfacial region in a thin oxide.

Unlike the strong field dependence of t_τ, the early time mobility of the holes is not field dependent in the range given in Fig. 5. The value of the mobility was taken from the peak current (or best fit to the curvature in data like Fig. 1) and the assumption that the number of holes undergoing transport is known from the size of the prompt

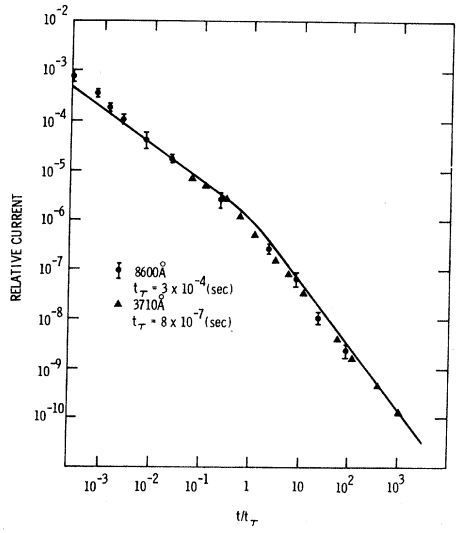

FIG. 4. Log current vs log reduced time for two different thickness oxides (3700 and 8600 Å) demonstrating universality with thickness. The voltage across each sample was 100 V and the theoretical curve is for $\alpha = 0.3$.

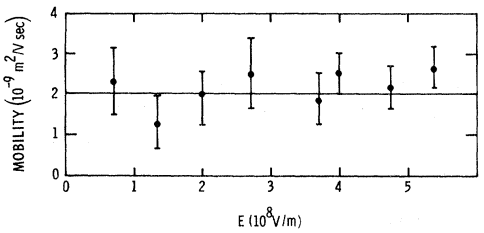

FIG. 5. Hole mobility at 300 °K taken from the highest current observed at early times, and calculated from the measured number of electrons swept out of the oxide, as a function of applied field. The error bars represent the difficulty in measuring the peak current (slope of curves like Fig. 1) and an average of three different oxide samples. The lack of a very strong field dependence of the mobility even at extremely high fields is apparent.

electron charge signal. It was not possible to obtain any data above 5.5×10^8 V/m because of destructive breakdown of the samples.

The temperature dependence of t_τ and μ are given in Fig. 6. Since t_τ is like a transit time for holes across the film, the mobility is plotted in terms of the transit time for all the carriers if no dispersion in the transport occurred, i.e., $d/\mu E$ (for the same d/E used to measure t_τ). The μ were determined as in Fig. 5 and are at 4.7×10^8 V/m. The solid lines are a fit to the higher-temperature data as an Arrhenius plot and the activation energies are 0.37 and 0.16 eV, respectively, for the t_τ and the prompt μ. The field independence of the prompt μ persists to the lower temperatures as in Fig. 5, but the error bars are larger because the magnitude of the current is decreasing with decreasing temperature.

IV. DISCUSSION

A. Physical basis for the CTRW model

A good fit to the CTRW model for the several criteria mentioned in Sec. II puts a strong set of constraints on any microscopic model of the hopping motion. Scher and Montroll[7] show that at least one plausible physical model can account for the wide distribution in site transition rates, of the correct shape to generate the observed data. The model involves tunneling of the carrier between sites that are randomly located in the lattice. Since the tunneling rate often varies exponentially with separation, a very wide distribution of site-to-site transition rates is possible. However, Silver and Dy[14] have shown that this is not a unique model, and that a similarly shaped distribution of transition rates can be generated by a distribution of trap depths. In this model the charge transport always occurs by the intrinsic mechanism so that the current at any given time is just proportional to the number of carriers which are not immobilized in a trap at that time (often called trap modulation of mobility). If the temperature dependence of the residence time of a carrier in a particular trap depends exponentially on the trap depth (typical Arrhenius behavior), then the value of α will tend to increase with increasing temperature. In the tunneling model the transition rates do not depend so much on the depth of the trap in energy as the distance between sites, and the temperature dependence of the transition rates depends on the mismatch in energy between sites. The sites with either long hopping times or short hopping times can have the same activation energy and α will be independent of temperature, even though t_τ is strongly activated by temperature. The temperature independence of α for the dispersive transport of holes in SiO_2 as seen in Fig. 3 favors the tunneling model, while in other materials, notably a-Se,[13] the temperature dependence of α favors the trap-modulated model of Silver.

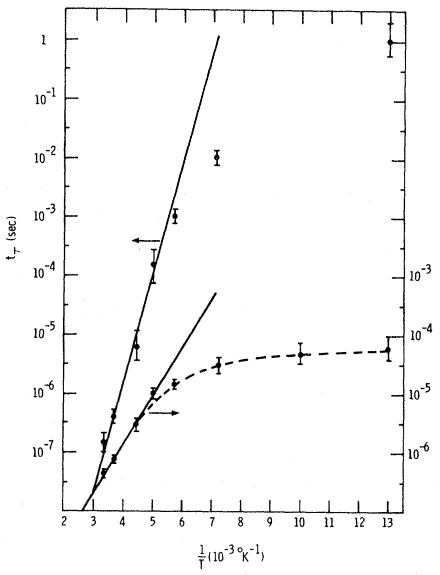

FIG. 6. Value of t_τ for the 3700-Å oxide at a thickness d of 3700 Å and a field of 4.7×10^8 V/m as a function of $1/T$ on the left-hand axis and the predicted transit time $(d/\mu E)$ from the same data using the magnitude of the early current to obtain the mobility μ (i.e., the time it would take to sweep all the holes out of the oxide if their drift velocity remained as high as measured at short times). The solid line in each case is an Arrhenius fit for the higher temperatures and yields the following analytic expressions: $t_\tau = 6\times10^{-14}\exp(+0.37\ \text{eV}/kT)$ sec, $d/\mu E = 6.6\times10^{-10}\exp(+0.16\ \text{eV}/kT)$ sec, $\mu = 1.2\times10^{-6}\times\exp(-0.16\ \text{eV}/kT)$ m^2/V sec.

B. "Intrinsic" mobility

The case for a good fit of the data to the CTRW model has been established in Sec. III, and the reason for going into such detail on the dispersive transport is to make a case for our hypothesis that for a short time after a hole is created it undergoes "intrinsic" transport and that deviations from the prediction of the CTRW model at short times allow us to measure the intrinsic mobility and its properties. The intrinsic mobility of the hole in SiO_2 might be defined as the mobility in a perfect single crystal with no structural defects (except those distortions due to phonons and polaron formation). Since the hole is created at a random place in the lattice by the x rays, the hole must diffuse by the intrinsic mechanism until it is trapped by one of the defects. Transport of the hole from then on is trap controlled by one of the dispersive mechanisms discussed above. In the rest of the discussion we examine the magnitude of the intrinsic mobility, the kinetics of the trapping of the holes, and the details of the hole transport including temperature and field dependence, and the close relationship in hole hopping rates between those reported here and the hole hopping in the A center in single-crystal quartz.

C. Magnitude of the mobility

The intrinsic mobility that we have measured by the high time resolution technique is very low, and the amount of charge transported by the holes in the first 10–50 nsec after excitation makes it clear that there is not a higher mobility state with a short lifetime. Intrinsic mobilities as low as observed are not unprecedented since electrons in single-crystal sulfur have a mobility of 6×10^{-4} cm^2/V sec at 295 °K, and no dispersive transport is seen.[6] It is also interesting that the activation energy for electrons in S and for holes in SiO_2 is the same, 0.16 eV, which is a reasonable size for a polaron binding energy. Band-structure calculations[15,16] for SiO_2 indicate that a very narrow band exists at the top of the valence band, which is suggestive of localization of the hole in the oxygen lone-pair ($2p$) orbital. But band-structure calculations cannot predict whether a small polaron will form, which involves a nuclear distortion in the vicinity of the hole (e.g., a change in the Si-O bond length which lowers the site energy with the hole present). Since the hole appears to hop to its nearest neighbor, sampling only short-range order, the role of the amorphous structure of the glass is not yet clear for the hole transport.[17-19]

D. Trapping kinetics

The low intrinsic mobility of the hole makes it reasonable to use a simple random-walk model to describe the trapping kinetics. In its simplest form the trapping rate will be given by[20]

$$k_1 = 4\pi D N_t R_t \,, \tag{1}$$

where D is the diffusion constant, related to the measured mobility by $D=\mu kT/e$, N_t is the concentration of trapping sites, and R_t is the radius of the trapping site.

The current versus time for this model is then the sum of the current due to carriers undergoing intrinsic drift and those participating in the CTRW

$$i = N_0 e\mu E(e^{-t/\tau}) + N_0 eE(1-e^{-t/\tau})At^{-0.7}\ \mathrm{A/cm^2}\,, \tag{2}$$

where τ is just $1/k_1$, N_0 is the concentration of carriers, and A is the constant which fits the data for $t \gg \tau$ (i.e., when virtually all carriers are undergoing CTRW). The lifetime was determined from the fit to the data at 200 °K, and was found to be 3×10^{-6} sec, and then τ was calculated for the other temperatures from the measured μ; Table I gives the calculated values. In Fig. 7 the fit of the model to the early time data is given for temperatures between 300 and 140 °K. The fit is quite good for the range 300–200 °K which is a factor of 50 in τ. At the higher temperatures the data becomes harder to interpret because the t_τ is not much longer than the trapping time τ, which means that a significant number of carriers are being swept to the interface before all of them are undergoing CTRW. This is a consequence of the higher activation energy for t_τ than for the intrinsic mobility as seen in Fig. 6. Below 200 °K the fit becomes increasingly poor because the in-

TABLE I. Mobility of the holes at short times at various temperatures (see also Fig. 8), along with the calculated lifetimes from Eq. (1) in the text. The experimental data were fit by Eq. (2) at 200 °K and the lifetimes at the other temperatures were then calculated from Eq. (1).

T (°K)	τ (sec)	μ (m^2/V sec)
298	7×10^{-8}	2×10^{-9}
273	1.5×10^{-7}	10^{-9}
230	6×10^{-7}	3×10^{-10}
200	3×10^{-6}	7×10^{-11}
175	6×10^{-6}	4×10^{-11}
140	1.5×10^{-5}	2×10^{-11}
100	4.2×10^{-5}	10^{-11}
75	6×10^{-5}	10^{-11}

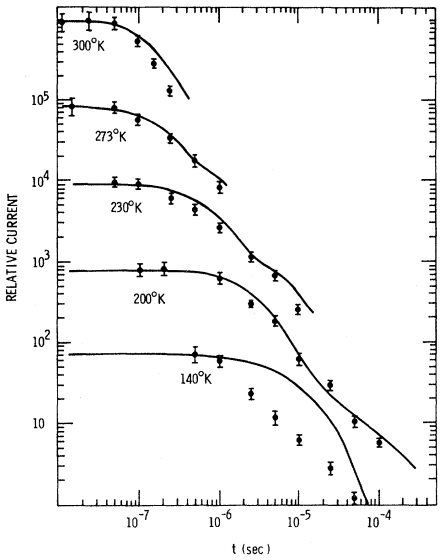

FIG. 7. Log current vs real time at short times only for the indicated temperatures. The field was 4.7×10^8 V/m. The relative currents have been arbitrarily adjusted to separate the data; the actual values of the early mobility as a function of temperature can be seen in Fig. 6. The solid curves were calculated from Eq. (1) in the text and the lifetimes employed are given in Table I.

trinsic current drops off too fast, i.e., the lifetime in the intrinsic state is not as long as it should be considering the measured mobility and Eq. (2). One can speculate that at the very low temperatures some shallow trapping unrelated to the CTRW is shortening the intrinsic lifetime as often happens in other low-mobility solids, like sulfur.[6]

From Eq. (1) one can get a rough idea of the density of traps necessary for lifetimes in Table I. The main assumption is the size of the trapping site R_t, but taking $R_t \sim 10$ Å, one finds that the trap density is about 3×10^{19} traps/cm^3. The average separation of the traps, if they are actually random, will be 20 Å.[20] A concentration of defects (such as nonbridging oxygens) this high is not unreasonable, and it is interesting to note that the average mean free path of excess electrons at low temperature is about 40 Å,[11] which means that the same defects which trap the low-mobility holes may be scattering the high-mobility electrons.

Other evidence which supports the intrinsic hopping model includes the following: (i) The hole mobility in single-crystal quartz is also very low although it has been difficult to get quantitative data because positive ions in single-crystal quartz have higher mobilities, at least in special directions.[9] It can be said with confidence, however, that the hole mobility in single-crystal quartz is not higher than 2×10^{-5} cm^2/V sec and may actually be lower. Preliminary results on the temperature dependence of the hole diffusion in single-crystal quartz to Al substitutionals show an activation energy of just over 0.2 eV, not much higher than reported here for the intrinsic mobilities. (ii) Ion-implantation studies have shown that structural damage (in contrast to the impurity ion itself) can create electron and hole traps, which confirms to some extent the notion that the lattice disorder can be the hole trap involved in the CTRW.[5] (iii) The fact that the activation energies for the intrinsic transport (0.16 eV) and the CTRW (0.37 eV) are so different suggests two unrelated transport processes, although some care must be taken since the activation energy in the CTRW model for t_τ (see Fig. 6) is larger than that for the CTRW current for $t<t_\tau$ by the factor $1/\alpha$ in the simple interpretation given in the Appendix. (iv) The data on oxides grown in different laboratories, in particular Boesch *et al.*,[4] give different values of α. Thus, the CTRW would seem to be a result of the particular defect structure of the sample.

E. Further considerations on hopping transport

One of the most interesting features of the data in Fig. 6 is the dramatic change in slope (decrease in activation energy) which occurs below 200 °K. In his detailed theoretical studies of the hopping rates of small polarons, Emin[8] has found that a general feature of the jump rates is that there is a large decrease in activation energy at lower temperatures. The physical basis of the phenomena is that phonon-assisted hopping processes become frozen out at low temperatures where fewer phonons are available. In the specific model that Emin considers in which the carrier interacts with a narrow band of optical frequencies, the change in slope occurs at about $\frac{1}{3}$ the Debye temperature, which is about 200 °K in SiO_2. This phenomenon was not observed for electrons in orthohombic sulfur,[6] because the data did not extend down to $\frac{1}{3}$ of the Debye temperature. Emin has applied the theory to the observed conductivity in amorphous semiconductors, but we believe that the results reported here are the first demonstration of the phenomenon for a wide band-gap insulator in which the hopping rates are measured directly in a transient experiment. A competing theory for the non-Arrhenius temperature dependence of conductivity in amorphous semiconductors is variable-range hopping, introduced by Mott.[21] In the variable-range model the non-Arrhenius temperature dependence of the hopping rate occurs because the average hop distance (or tunneling distance) becomes longer at low temperatures as

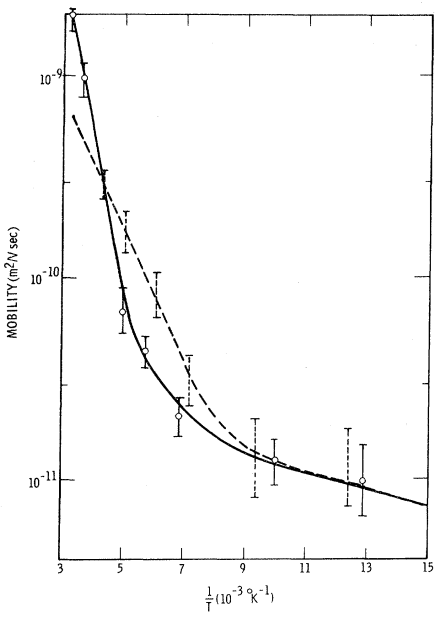

FIG. 8. Temperature dependence of the measured intrinsic hole mobility (solid line, the same data as in Fig. 6), compared with a mobility calculated from the measured hopping rate of holes between nearest neighbor oxygens in the "A" color center in quartz (dashed line).

carriers sample sites farther away that are more closely matched in energy. It is difficult to devise experiments that distinguish between the two models, but a reasonable hypothesis from our transport model would be that the non-Arrhenius temperature dependence of t_τ (see Fig. 6) which involves tunneling from defect to defect is due to variable range hopping, while the temperature dependence of the intrinsic polaron hopping is due to phonon-assisted hopping.

There is one independent measure of the hopping rates of holes in SiO_2 and that comes from the characteristics of the "A" color center in single-crystal quartz.[22] The "A" center consists of a hole trapped in the oxygen lone-pair orbital, but Coulombically bound to a substitutional Al^{+++} which is a negatively charged impurity site unless compensated by the hole (or an alkali-metal ion). The hole cannot hop away at 300 °K and below, but it does hop between inequivalent oxygen sites in the AlO_4 tetrahedron (the Al-O bond length to two of the oxygens is slightly shorter than the other two and is quite similar to the SiO_4 tetrahedron). This motion has been detected by the dielectric relaxation of the color center[23] and by EPR techniques[22] and the hopping rates and activation energies have a close relationship to the prompt mobility values reported here.

In Fig. 8 the mobility of holes at short times is plotted versus $1/T$ with a solid line (the same data was given in the form of a transit time in Fig. 6). The dashed curve gives the experimentally measured hopping rates for holes in the "A" center, converted to mobility by the simplist hopping theory: the hopping rate above 100 °K between inequivalent sites in the color center is given by $\nu = 3.3 \times 10^{10} \exp(-0.085\ \mathrm{eV}/kT)$ hop sec^{-1}. At 230 °K the hopping rate is 4.5×10^8 sec^{-1}, which can be translated to a hopping mobility by first calculating the diffusion constant for a random walker $D = \nu a^2/6$,[20] where a is the O-O distance (2.65 Å), and then using the Einstein relation to get the mobility from the diffusion constant: $D = \mu kT/e$. Both kinds of hopping show a drastic decrease in activation energy below 200 °K, so that in spite of the difference in apparent high-temperature activation energy, the hopping rates (directly proportional to the mobilities) are not more than a factor of 2 different at any temperature where both have been measured experimentally. Thus the evidence is very strong that the same hopping mechanism is involved in both cases with small differences probably due to the substitution of the Al^{+++} ion for the Si^{++++} ion. This result is not unexpected since the bonding is the same in both cases. The EPR[22] and dielectric relaxation[23] results show that the hole is localized in the nonbonding $2p$ oxygen orbitals. Those same orbitals make up the top of the valence band in the band-structure calculations, and this assignment receives experimental support from photoemission measurements.[16] The hopping motion occurs because of overlap between the nonbonding orbitals of one oxygen and its nearest neighbors, and both band-structure calculations and the photoemission results indicate that the overlap is comparatively weak (in band-structure language, a very narrow band at the top of the valence band). However, the band structure calculation does not tell us whether a small polaron forms or what other barrier to hopping exists, which causes the thermal activation of the hopping rate.

Since most of the measurements reported in this paper are made at what are considered very high electric fields (over 10^8 V/m), it is of interest to ask what effect the high fields have on the transport. In Fig. 5 it was shown that within experimental error, the mobility was independent of the field, which is equivalent to the carrier drift velocity being linear in the field. In the simplest type of hopping transport theory the mobility is given by[24]

$$\mu = 2a\nu_0 \left(\frac{1}{E} \sinh \frac{aE}{2kT}\right) \exp\left(\frac{-\Delta E}{kT}\right), \qquad (3)$$

which for $aE \ll kT$ (i.e., the energy gained in a

downfield jump less than kT), reduces to the familiar

$$\mu = (a^2/kT)\nu_0 \exp(-\Delta E/kT) , \quad (4)$$

which is independent of the field for low fields. However, at the highest fields imposed (5×10^8 V/m) and the shortest hop distance (2.65 Å), Eq. (3) is nonlinear with the mobility higher by at least a factor of 2, which would be outside experimental error. It should be noted that there are no data which support the high-field effect predicted in Eq. (3) and it has been criticized as being inapplicable at high fields, particularly because of its one-dimensional character. Emin[8] has performed a derivation of the field dependence of polaron mobility which is similar to Eq. (3) at low field but has an additional term which, in effect, cancels the sinh argument and predicts a field dependence of the mobility consistent with our data. His model actually predicts that at still higher fields the mobility should decrease.

V. CONCLUSIONS

Hole-transport data has been presented which has the unusual properties as a function of time, applied field and thickness which can be rationalized by the CTRW model of Scher and Montroll. The deviations from the predictions of the CTRW model at very short times after the creation of the holes are ascribed to the "intrinsic" hopping transport of the holes as it moves from one oxygen to the next. The measured hopping rates are almost the same as have been observed for nearest-neighbor oxygen hole hopping in the AlO_4 color center in quartz (measured by dielectric relaxation and EPR). It is hypothesized that the CTRW occurs in a-SiO_2 because the hole diffuses by the intrinsic process and becomes trapped at a structural defect and further transport is by tunneling from defect to defect. The temperature dependence of the intrinsic hole transport is markedly non-Arrhenius below 200 °K (i.e., there is a drastic decrease in activation energy) which corresponds to the predicted behavior of a small polaron. The temperature dependence of the CTRW transport is also markedly non-Arrhenius at low temperature, and can be understood in terms of the variable range tunneling model of Mott.

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APPENDIX. FITTING THE EXPERIMENTAL DATA TO THE CTRW MODEL

The CTRW model provides a method for calculating the current versus time in a pulse photoconductivity experiment as a function of the variables: applied field, thickness of the photoconductor, number of carriers undergoing transport, and temperature.[7] For a given material, the data at one temperature is fit with a single parameter α. The value of α is between zero and one and it characterizes the dispersion in hopping times between sites in the material. A small α implies a very wide distribution of hopping times and consequently a large dispersion in the current vs time profile, and a large α implies a narrow distribution of hopping times. An analytical calculation of the exact current versus time profiles for the variables given is complicated,[7] but a rough analysis of the data can be made as follows: (i) The current versus time after a δ-function creation of carriers at one side of the insulator consists of two parts, the short time where the current varies as $i = At^{-(1-\alpha)}$, and the long-time portion where the current drops faster with time $i = Bt^{-(1+\alpha)}$. The change in slope occurs at a characteristic time t_τ, which reflects the arrival of some of the carriers at the far electrode. The most convenient way to compare the data with the theory is to plot the log of current versus the log of time over many decades of both current and time, and then find the best fit for the slopes $1+\alpha$ and $1-\alpha$ and the time t_τ, where the slope changes. Having the sum of the early and late time slopes close to minus two (i.e., same α) is already a fairly rigorous test of the applicability of the model to the system under study, but a stronger test is found in changing the applied field and/or the thickness of the insulator. The prediction is that only t_τ should change and not the early and late slopes. This characteristic has been called universality[7] because the current-versus-time data can be plotted versus a reduced time t/t_τ, and data for all values of field and thickness should superimpose. The third test for the data is the functional dependence of t_τ on field E, and thickness d. Scher and Montroll[7] find that

$$t_\tau \propto (d/E)^{1/\alpha} , \quad (A1)$$

which predicts a very strong field dependence for small α.

The integral of the current (which is often measured experimentally) should go roughly as

$$q(t \le t_\tau) = (A/\alpha)t^{+\alpha}, \tag{A2}$$

$$q(t \ge t_\tau) = (B/\alpha)t_\tau^{-\alpha} - (B/\alpha)t^{-\alpha}. \tag{A3}$$

At $t = t_\tau$, $i = At_\tau^{-(1-\alpha)} = Bt_\tau^{-(1+\alpha)}$, thus

$$A = Bt_\tau^{-2\alpha}, \tag{A4}$$

and the total charge (which depends only on the number of carriers) is

$$Q(t \to \infty) = (2B/\alpha)t_\tau^{-\alpha}, \tag{A5}$$

and Eq. (2) can be rewritten

$$q(t \le t_\tau) = \tfrac{1}{2}Q(t/t_\tau)^\alpha. \tag{A6}$$

It is often asked whether the microscopic transition rates between sites are affected by the field, and the theory provides an easy way to test for this if the above criteria are met by the data. t_τ may be strongly field dependent as seen above in Eq. (A1), but at the same time if there is no field effect on the microscopic transition rates, then the early current will be just proportional to E. This can be easily seen by substituting Eq. (A1) into Eq. (A6).

The holes in all these experiments are created in the bulk of the insulator rather than at one surface, but there is not a very large difference in the predictions of the CTRW model for the two cases. At short times before a significant fraction of the carriers have been collected at the electrode, the predictions for bulk excitation and surface excitation are identical. The total amount of charge transported in the bulk case for the same number of carriers of one sign is just one-half the surface case so the long-term current is smaller, but the limiting slope of $1+\alpha$ is the same. Since the bulk excitation can be thought of as wiring a number of films of different thickness up to the thickness of the sample in parallel, the universality relations should be the same as for surface excitation. The t_τ observed in the bulk case is shorter than the t_τ would be if all the carriers started at one side of the film.[25]

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