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Hot Electrons in SiO_2†

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The experimentally determined drift velocity of excess electrons in a-SiO_2 as a function of field is reported. Saturation of the velocity-field curve above 10^7 cm/sec provides evidence for phonon emission by significantly heated electrons. The data provide the first test of, and good agreement with, the Thornber and Feynman theory of electron energy loss in polar materials at high applied fields.

It was pointed out a few years ago by Thornber and Feynman[1] that the anomalously high electron energy loss in thin oxide films on cold cathodes might be due to emission of LO phonons. In this Letter I present the first direct evidence for "hot" electrons in a-SiO_2 in the form of the measured electron drift velocity as a function of field. The drift velocities are stable at fields up to at least 8×10^5 V/cm, which corresponds to a large energy loss of almost 10^{-2} eV/Å. I will also present evidence from pulse-x-ray-induced conductivity measurements on thin SiO_2 films that the drift velocity is stable up to fields of at least 5×10^6 V/cm. The electron drift velocity shows the onset of saturation with field around 8×10^6 cm/sec which can be understood if the energy loss is being dominated by the 0.15-eV LO phonon in SiO_2. However, the energy loss at lower drift velocities (i.e., the low-field mobility) is apparently dominated by the lower-energy LO phonon (0.06 eV) at room temperature because the electron is scattering off the thermal population of phonons rather than emitting phonons. A number of authors have recently discussed the possible effect of hot electrons on electrical phenomena found in thin SiO_2 films [i.e., metal-oxide-semiconductor (MOS) devices] and I will comment on the relevance of the data to the explanations offered.

The drift velocities were obtained by measurement of the transit time of electrons across specimens of Suprasil II fused quartz. The specimen thickness was varied from 0.02 to 0.1 cm. I have reported earlier on measurements of the low-field mobility and its temperature dependence with the data taken in a similar fashion.[2] The electrons are generated in the bulk of the SiO_2 by a 3-nsec pulse of x rays from a Febetron-706 electron-beam machine. Typical wave forms from this kind of experiment are given in Fig. 1, where the integral of the current is given. In Fig. 1(a) the field was held low enough so that very few electrons were swept out during the bulk lifetime of the carriers (in this case about 8 nsec). Figure 1(b) is for a higher field and the effect of the sweepout of electrons is easily seen. The sweepout time t_s was derived from data similar to Fig. 1 and the drift velocity is found from $v_d = d/t_s$, where d is the thickness and t_s is the transit time. To obtain an accuracy of ± 10% it was necessary to fit the experimental curves with simulated transits[2] involving the lifetime and shape of the x-ray pulse. The drift velocity as a function of field for several specimen thicknesses is given in Fig. 2. The sublinear dependence at high fields was checked by comparing the high-field traces with traces from thinner samples at lower fields where the transit times were identical (this is somewhat more accurate than unfolding the effect of the shape of the x-ray pulse). The high-field data were taken with the sample immersed in a special high-voltage chamber filled with Humble x-ray oil, and connected to a Del 120-kV dc power supply by 30 ft of high-voltage cable to prevent reflections. The upper voltage limit was due to arcing around the edge of the sample which, at these energy densities, destroys the sample.

The problem of the behavior of an excess electron in a polar insulator under the influence of an electric field has received a great deal of attention over the last thirty years. A survey of the

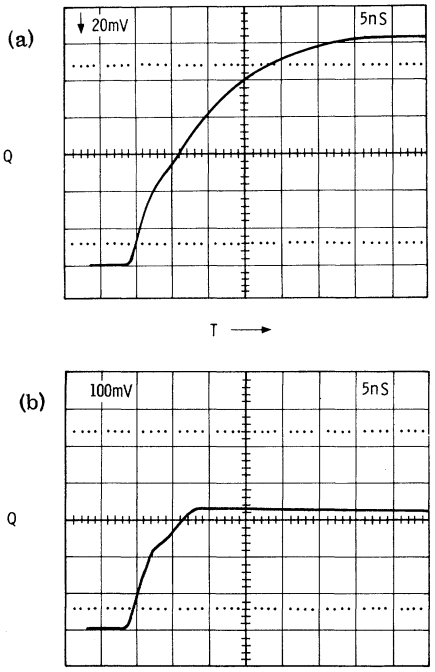

FIG. 1. The integral of the excess electron current in a 1-mm sample at two different applied fields; (a) 10^5 V/cm and (b) 5.5×10^5 V/cm. In (a), the transit time of the electrons across the sample is much larger than the electron lifetime ($t_s \sim 50$ nsec, while $\tau = 8$ nsec). In (b) the electron transit time is 10 ± 1 nsec, which yields an electron drift velocity of $(1\pm0.1)\times10^7$ cm/sec. The dose in the 3-nsec-wide x-ray pulse is about 0.1 rad (Si) and the 5 nsec/div sweep needed some correction for linearity by use of a crystal-stabilized oscillator to obtain the lifetime and transit-time values given above.

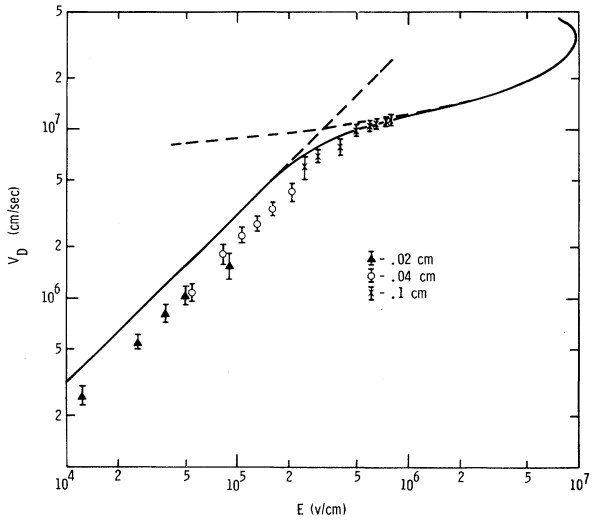

FIG. 2. The electron drift velocity as a function of the applied field for several thicknesses of Suprasil II fused quartz. The linearity is good up to about 2×10^5 V/cm, giving a low-field mobility of 21 ± 2 cm^2/V sec. The solid line in the low-field region is for a mobility of 32 cm^2/V sec, which is calculated from theory for the LO-phonon scattering of the electrons at 298°K (Ref. 6). The high-field curves give the predictions for the effect of phonon emission by hot electrons from the quantum mechanical calculation of TF (Ref. 1) and the classical calculation of Lynch (Ref. 6).

treatments has been given by O'Dywer[3] in his recent book on dielectrics and more detailed accounts for high-field effects in semiconductors have been given by Conwell[4] and Chynoweth.[5] The most complete and recent treatment, and the one that seems most germane to our results, is that of Thornber and Feynman[1] (hereafter TF), who calculate the energy loss as a function of field for an electron of arbitrary coupling to the lattice. The calculation is very complex, but the features of a fairly simple physical interpretation of drift velocity and energy loss are confirmed. It is assumed that SiO_2 is a sufficiently polar substance that the electron energy loss is dominated by polar scattering from the LO phonons and other scattering mechanisms, such as acoustic-mode scattering, are ignored. The dielectric dispersion of quartz (and fused quartz) is quite well known, so that it is reasonable to discuss the LO-mode scattering in terms of the importance of the individual modes, rather than treating the Debye temperature as an average mode for the material. Lynch[6] has presented such an analysis and finds that at room temperature and low fields the mobility is dominated by the 0.063-eV LO mode because it is much more populated than the 0.15-eV mode to which the electron is also strongly coupled. With application of Matthiessen's rule to the important modes and with use of the TF result for the low-field mobility for each mode, one arrives at a mobility of 32 cm^2/V sec at room temperature (a mobility of 50 cm^2/V sec is calculated for the 0.063-eV mode alone).[6] This low-field mobility is predicted to be quite temperature dependent because it follows the thermal population of LO phonons and over a limited range of temperature this was found to be true in Ref. 2. As the drift velocity of the electrons is increased by increasing the field, it is expected that at some point the energy loss will be dominated by phonon emission from hot electrons and the mobility will drop.

When the average kinetic energy of the drifting

electrons, defined as $\frac{1}{2}mv_d^2$, is greater than the highest-LO-mode energy, $\hbar\omega_l$, it is expected that the energy loss will be a decreasing function of velocity and thus no stable drift velocity in an electric field is possible (at least for the particular energy-loss mechanism of phonon emission). Thus the slope of the energy-loss versus velocity curve will change sign in the vicinity of $\frac{1}{2}mv_d^2 = \hbar\omega_l$. The applied field required for this velocity, of course, depends on the details of the calculation, and is often considered the ultimate dielectric strength of the material, since an electron introduced into the insulator above the critical field will be accelerated to sufficient energy to cause impact ionization and thus a rapid drop in the resistance of the material.[6]

The most prominent feature of the measured drift velocities is the linearity (i.e., constant mobility) to very high energy loss, almost 3×10^{-3} eV/Å. Most semiconductors show marked deviations from linearity at much lower fields and drift velocities because of the dominance of acoustic-phonon emission.[4] The TF theory tackles the problem of calculating the energy loss when the mean free path becomes very short (a few angstroms) as it must for the drift velocity to be stable at high fields. The drift velocities and energy losses for excess electrons in SiO_2 can be understood almost quantitatively with the TF model in which the electron interacts with the known LO modes only.

The solid line in Fig. 2 is composed of two parts. The low-field line is for a mobility of 32 cm^2/V sec, which is found by using the TF theory and summing over the losses for all the LO modes.[6] The curved portion is interpolated from Fig. 1 of Ref. 1 for $\beta = 6$ and $\alpha = 1.3$ (where β is the ratio of the mode energy to the temperature and α is the Fröhlich coupling constant) which approximates the action of the 0.15-eV phonon only. Lynch[6] has made a classical energy-loss calculation for electrons in SiO_2 which takes into account the full dielectric dispersion and is almost identical in shape to the TF curve for high fields. At lower fields (and kinetic energies) the classical model predicts very little interaction of the electron with the lattice as the almost horizontal dashed line in Fig. 2 indicates.

The low-field mobility is about 30% lower than predicted from LO-phonon scattering, which, aside from inadequacies of the theory, could arise from the following: (1) An effective mass greater than 1 is certainly expected for a polaron, but the band structure which would be required for a very accurate description of the electron mobility is not available yet.[7] (2) The amorphous structure of the specimen has a still unspecified effect on the transport. The low-temperature mobility saturates at about 40 cm^2/V sec which suggests that scattering by the disorder should be added to the LO-phonon scattering in calculating the 300°K mobility. At very high fields the mean free path for phonon emission becomes very short and thus one might expect that the fit to theory would be better since other scattering mechanisms would become relatively less important than at lower fields. (3) Other energy-loss mechanisms have been neglected, including acoustic-mode scattering[5] and impurity scattering, which would lower the mobility. But, on the whole, the agreement seems quite good (in comparison to other systems where transport properties have been calculated)[3] if one considers the electron interacting with the LO phonons only.

In further support of the model, we have taken charge-transport data on thin SiO_2 films (3700 Å) grown on Si at fields up to 5×10^6 V/cm. The electron transit times could not be resolved (they would only be a few picoseconds), but the total charge transported could be measured (and separated from the hole charge transport which is much slower) and no charge multiplication could be observed even at the highest field.[8] This is strong evidence that the drift velocity is still in the stable region as predicted by the theory, and that the distribution of electron kinetic energies is not broad enough to include a significant number of electrons accelerated to the bandgap energy, 9 eV.

Recently several high-field experiments on MOS structures have been performed in which the interpretation of the results depends on the behavior of hot electrons in the SiO_2 layer. Weinberg, Johnson, and Lampert[9] determined that electrons were the dominant carrier in the oxide and found that even at 10^7 V/cm, an average electron cannot have as much as 2 eV kinetic energy because of the lack of the expected charge multiplication of such electrons entering the Si layer. This is consistent with the hypothesis given here; that electrons accelerated to 0.15 eV are very likely to emit a LO phonon and that this loss mechanism can stabilize the electron average velocity up to 10^7 V/cm. The recent data on trap filling and ionization of DiMaria, Feigl, and Butler[10] are more difficult to understand on the basis of the present data. They fill a 2.5-eV trap in the SiO_2 (which they have purposely introduced)

with photoemitted electrons and, on the basis of the observed trap filling and depopulating kinetics, propose that at fields as low as 5×10^5 V/cm some excess electrons have sufficient kinetic energy to ionize an occupied trap. Our data clearly show that the average electron at the highest fields has less than 0.15 eV energy, but of course there will be a distribution of electrons with higher kinetic energies the shape of which is not predicted by the TF theory. There is also the possibility as suggested by both DiMaria, Feigl, and Butler[10] and TF[1] that electrons which have much more than 0.15 eV upon injection will be in the unstable part of the energy-loss versus energy curve and will be accelerated by the field until some other energy-loss mechanism drops them into the stable part of the curve. Evidence for impact ionization by hot electrons in the oxide layer has been obtained in the switching studies of Shatzkes, Av-Ron, and Anderson,[11] but only for fields over 10^7 V/cm which can be maintained by the space charge of the low-mobility holes.[12]

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Differences in Charge Transfer between Surface and Bulk Species in Tetrathiafulvalene-Tetracyanoquinodimethane

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The charge-transfer complex tetrathiafulvalene-tetracyanoquinodimethane has been studied by x-ray-photoelectron spectroscopy at both normal and grazing electron take-off angles. Changes in the N_{1s} and S_{2p} spectra with angle show that a discrete layer exists at the surface of the a-b plane. Essentially zero electron transfer takes place in this layer versus $\sim 0.8\pm0.2$ in the bulk. The surface layer is ca. 1 to 5 layers of complex thick and appears to be intrinsic to "good" organic conductors.

Unusual multiplet structure in the N_{1s} and S_{2p} core-electron spectra of the charge-transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) has been reported.[1-3] Both discrete intrinsic energy-loss phenomena[1] and chemical shifts due to neutral and singly charged molecules coexisting in the solid on the time scale of bond vibrations[2] have been mentioned as possible causes of the structure. To date, however, neither explanation has been demonstrated and, consequently, conclusions based on core-level or valence-band photoemission spectra concerning the amount of charge transfer and the localization of conducting electrons in solid TTF-TCNQ are open to question.

We find from grazing-angle[4,5] x-ray-photoelectron spectroscopy (ESCA) that the core-level multiplet structure is due to a discrete layer of