Hot-Electron Transport in Polymeric Dielectrics

P. Pfluger, H. R. Zeller, and J. Bernasconi
Brown-Boveri Research Center, CH-5405 Baden, Switzerland
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An internal photoemission experiment which yields the energy-dependent momentum- and energy-loss rates of hot electrons is designed. The results on solid hydrocarbon films are analyzed in terms of the appropriate Boltzmann equation. Band mobilities are obtained for hot electrons. Their energy-loss rate has a maximum at the LO phonon energy associated with the C–H stretching mode.

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Thermalized carriers at the bottom of the conduction band in large band-gap insulators can be studied by classical transport experiments (e.g., drift-mobility and photocurrent measurements) in macroscopic specimen. Unless the phonons which control hot-electron ($E_{\rm kin} >> kT$) scattering are thermally populated, the extrapolation from $E_{\rm kin} \sim kT$ data to hot-electron transport is not possible. As a result, hot-electron scattering in polymeric insulators is only poorly understood, although it plays a crucial role in various areas.

Hot-electron processes are particularly important in the field of dielectric breakdown. In good polymeric insulators, intrinsic breakdown is reached at electric fields of the order of 5 MV/cm.[1] For impact ionization across the energy gap ($E_I \sim 10$ eV), one is therefore led to mean free paths of ~ 50 Å, or to mobilities in the 50 $\rm cm^2/V\cdot s$ range. This is at odds with drift-mobility experiments which yield $\mu = 10^{-4}$–10^{-11} $\rm cm^2/V\cdot s$ in polyethylenes (PE),[2] and even with the highest mobilities of ~ 1 $\rm cm^2/V\cdot s$ observed in high-quality alkane single crystals.[3] Hot electrons also play an essential role for the injection of space charge into polymeric insulators in regions with a strongly inhomogeneous electric field.[4] As will be shown in a forthcoming publication,[5] the injection of hot-carrier space charge is an essential element in the growth of dielectric discharge trees and in dielectric aging.

In order to establish the crucial quantity that describes the transport properties of hot electrons in high electric fields, we consider the energy and momentum conservation for a charged particle of effective mass m^*, moving in an insulator under the action of an electric field F:

$$\dot{E} = -\gamma_u(E)E + evF, \tag{1a}$$

$$\dot{n} = -\gamma_p(e)m^*v + eF. \tag{1b}$$

Here v denotes the velocity of the particle, and we have introduced the energy- and momentum-loss rates $\gamma_u(E)$ and $\gamma_p(E)$, respectively. Following a procedure developed for the theory of laser breakdown in solids,[6,7] we can then obtain analytical expressions for the average energy $\langle E\rangle$ and for the multiplication rate β of hot electrons. It turns out that both expressions contain

$$\int_0^E dE'\, m^*\gamma_u(E')\gamma_p(E')$$

as the only nontrivial quantity. Therefore, our aim will be to determine the energy dependence of $m^*\gamma_u\gamma_p$ between kT and the gap energy.

Information about the transport properties of hot electrons can be obtained via photoelectron spectroscopy techniques. A number of substrate-overlayer studies have been made in order to determine the mean free path λ of photoelectrons in various materials. This search has resulted in the well-known pseudouniversal curve[8] with a minimum of $\lambda \sim 10$ Å near $E_{\rm kin} = 50$ eV. In particular for organic materials, however, data are very scarce in the $E_{\rm kin} < 10$-eV range.

In this Letter we present a photoemission technique which, combined with an analysis of the corresponding transport problem (Boltzmann equation), provides a powerful basis to obtain quantitative and energy-dependent results about the scattering of hot electrons in polymeric dielectrics. Our method of internal photoemission for transport analysis (IPTA) is based on the injection of hot electrons at a metal/dielectric interface into the insulator's conduction band. The photoelectrons transmitted through the insulator are analyzed with respect to the changes in their energy distribution, induced by the scattering events inside the dielectric.

In the past, some low-energy results for the photoyield transmitted through thin solid hydrocarbon films have been obtained,[9] but the analysis of such experiments is inherently difficult and their interpretation therefore rather arbitrary. More reliable information is obtained by measuring electron energy distribution curves (EDC's), rather than only the total photoyield. Recently, Bader *et al.*[10] have performed electron transmission experiments in

solid Xe and used a two-flux model to extract elastic and inelastic mean free paths from their data. They did, however, not take into account inelastic losses due to LO phonons (Frölich scattering[11]), which represent the dominant scattering mechanism in polymeric dielectrics, as we shall see below.

Our experiments were performed in the UHV chamber of a KRATOS ES300 photoelectron spectrometer equipped with a special low-voltage analyzer. The linear alkane hexatriacontane, n-$C_{36}H_{74}$, was used as insulator material because of its model character for PE-compounds,[12] its slightly negative electron affinity (no energy barrier at the dielectric-vacuum interface), and its *in situ* evaporation and UHV compatibility. Pt and Ir substrates with $C_{36}H_{74}$ overlayers of thicknesses $d = 5$–640 Å were investigated, and sub-band-gap light was used to avoid photoionization inside the insulator. The photon energy was varied to inject carriers at various excess kinetic energies into the conduction band of the dielectric.

Typical experimental results are presented in Fig. 1. The electrons with the highest kinetic energies are those lifted above the metal's Fermi energy E_F by $\hbar\omega_{photon}$. E_{kin} is defined with respect to the conduction-band (CB) edge E_c of the dielectric. The shift of the photoelectric threshold with alkane

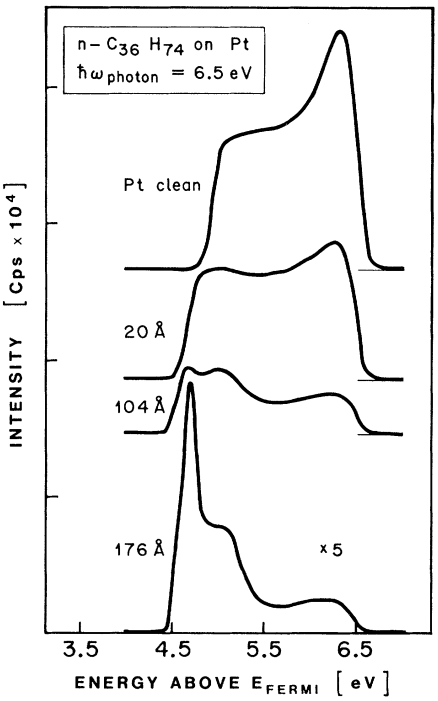

FIG. 1. Energy distribution curves of photoelectrons emitted from Pt after traversing n-$C_{36}H_{74}$ paraffin films of various thicknesses.

covering is small (~ 0.2 eV), which demonstrates good matching of the substrate and the overlayer work functions. E_F is located ~ 4.5 eV below E_c, quite precisely in the middle of the hexatriacontane's 8.8-eV energy gap.[13] Any charging of the dielectric due to traps would result in a further shift of the photoelectric threshold, but no such shift is observed for $d \gtrsim 20$ Å.

The decay of the EDC's with film thickness immediately confirms the high carrier mobilities inferred from the avalanche model for intrinsic breakdown at $F_{crit} \sim 5$ MV/cm: the characteristic length scale for the hot electrons is 50–100 Å. The intensity decrease is stronger for electrons with higher energies, and we observe a marked relative pileup in the slow electron intensity. This reflects the down scattering of the fast carriers by effective inelastic processes. The structure at ~ 5.0 eV above E_F ($E_{kin} \sim 0.5$ eV) can be identified as a final-state effect due to a sharp maximum in the alkane CB density of states.[14] The large low-energy peak at $E_{kin} < \frac{1}{3}$ eV for films thicker than ~ 100 Å corresponds to the carriers cascaded down to near the CB edge. Note that the resolution of the experiment is ~ 0.2 eV and does not allow for a detection of fine structure near the bottom of the CB. The low-energy peak directly leads to the identification of the main energy-loss mechanism in our PE model compound: The LO phonon associated with the C-H stretching mode must be a most effective inelastic scatterer since the observed scattering length rises dramatically below its characteristic energy of $\hbar\omega_{phonon} \cong 0.36$ eV. A comparison of the EDC's shown in Fig. 1 with similar curves obtained at different photon energies reveals very different shapes, particularly at the high-energy end of the spectra. This illustrates that the scattering rates involved vary strongly with energy, even above $E_{kin} \sim 2\hbar\omega_{phonon}$.

To obtain a quantitative analysis of the experimental results, we have to solve the Boltzmann transport equation, with appropriate boundary and initial conditions, for the plane-layer configuration used in our IPTA experiment. For a complete description of the EDC's one has to take into account the discrete inelastic cascade of the hot electrons down the energy axis in steps of $\Delta E = 0.36$ eV, the energy of the dominant inelastic scattering process. Such cascade calculations are in progress.[15] They are, however, rather involved, and a corresponding analysis of the EDC's in terms of (energy-dependent) transport parameters is not completely unambiguous. We have therefore decided to first restrict ourselves to the topmost ΔE

interval of the EDC's only. From this energy region, electrons are scattered down by inelastic processes, but none are supplemented from higher kinetic energies. Our original Boltzmann equation is therefore reduced to a comparatively simple one-speed transport equation which can be solved by various methods.[15] The energy dependence of the transport properties is then scanned by varying $E_{\mathrm{kin}}^{\max}$, the position of the topmost interval on the energy scale, via a variation of $\hbar\omega_{\mathrm{photon}}$.

Applying a two-flux approximation to the one-speed transport equation, the phototransmitted intensity through a layer of thickness d exhibits the following asymptotic dependences:

$$\frac{I(d)}{I(0)} \sim \begin{cases} 1-(l_e^{-1}+2l_i^{-1})d, & d \to 0, \quad (2a) \\ \exp(-\lambda_{\mathrm{eff}}^{-1}d), & d \to \infty \quad (2b) \end{cases}$$

where

$$\lambda_{\mathrm{eff}}^{-1} = 2[l_i^{-1}(l_i^{-1}+l_e^{-1})]^{1/2}, \quad (3)$$

and where we have assumed that particle injection and scattering mechanisms are isotropic. The elastic and inelastic scattering lengths are denoted l_e and l_i, respectively. It is seen that an exponential *Ansatz* for the damping of fast electrons in overlayers is justified for large d only, and that the corresponding effective scattering length λ_{eff} is not just given by the inelastic mean free path, as is often assumed.

Experimentally determined topmost-interval intensities are plotted logarithmically versus film thickness d in Fig. 2. For large d, the slope yielding $\lambda_{\mathrm{eff}}^{-1}$ is well defined. According to Eqs. (2), the small-d slope should be larger than $\lambda_{\mathrm{eff}}^{-1}$. However, an increase is only observed after a downward curvature in the 40–100-Å range. At present the origin of this discrepancy, which presents a separation of $l_e^{-1}(E)$ and $l_i^{-1}(E)$, is not clear; this point is under further investigation. Treating the first ~ 100 Å as a black box, and thus avoiding in particular problems with the image potential, the exponential decay at large d still allows for an incremental analysis of $\lambda_{\mathrm{eff}}(E)$. It is then, however, no longer possible to separate l_e^{-1} and l_i^{-1}.

Fortunately, we are not seriously hindered by this problem to answer our original question related to the energy dependence of $m^*\gamma_u(E)\gamma_p(E)$, as it can easily be shown that

$$m^*\gamma_u(E)\gamma_p(E) = [\lambda_{\mathrm{eff}}^{-1}(E)]^2\Delta E/2. \quad (4)$$

The experimentally determined function $\lambda_{\mathrm{eff}}^{-1}(E_{\mathrm{kin}})$ is shown in Fig. 3. Regarding its interpretation, we recall that for $E_{\mathrm{kin}} > \hbar\omega_{\mathrm{phonon}}$, $\gamma_u(E_{\mathrm{kin}})$ is dominated by LO-phonon emission. One therefore expects γ_u to exhibit a maximum in the vicinity of $E_{\mathrm{kin}} \cong 0.36$ eV and then to decrease according to $\gamma_u \sim E_{\mathrm{kin}}^{-3/2}$ (Fröhlich scattering, see also Ref. 7). This process largely controls the behavior of $\lambda_{\mathrm{eff}}^{-1}$ near $\hbar\omega_{\mathrm{phonon}}$. Acoustic-phonon processes apparently become important at $E_{\mathrm{kin}} \gtrsim 1.5$ eV. If we assume pure Frölich scattering, the resulting mobility value is $\mu \approx 20(m_e/m^*)^{1/2}$ cm^2/V·s at $E_{\mathrm{kin}} = 1.2$

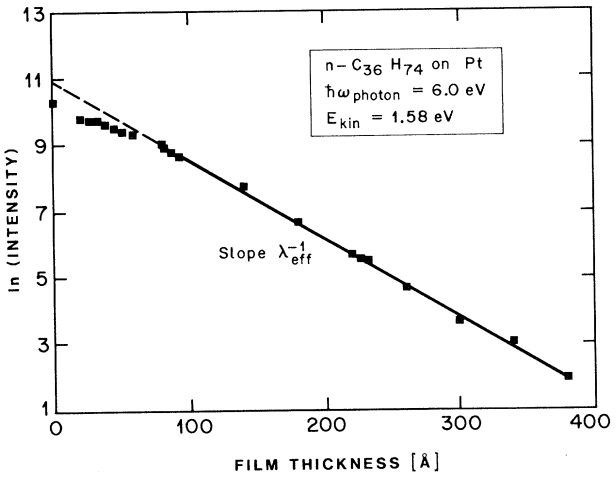

FIG. 2. Damping of photoelectrons originating from the vicinity of the Pt Fermi edge (topmost-interval analysis) by the scattering processes in n-$C_{36}H_{74}$ overlayers.

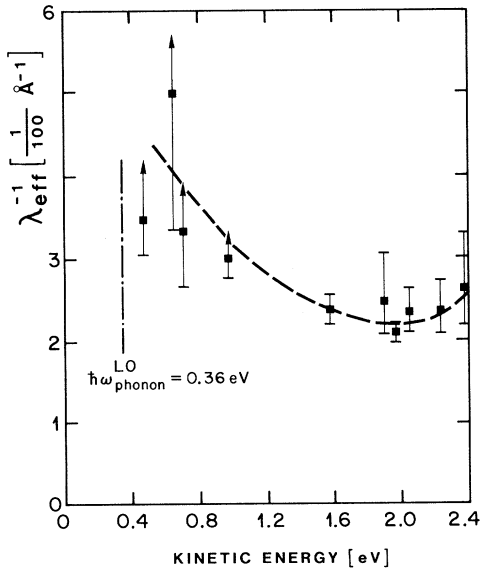

FIG. 3. Inverse effective scattering length of hot electrons in the organic insulator n-$C_{36}H_{74}$ as a function of their kinetic energy.

eV. In addition, our data are consistent with a mobility about an order of magnitude higher at $E_{\text{kin}} < \hbar\omega_{\text{phonon}}$.

In conclusion, we have shown that our internal photoemission method, combined with an appropriate Boltzmann equation analysis, can be successfully used to investigate the transport properties of hot electrons in polymeric dielectrics.

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