Nonexponential Relaxation of Conductance near Semiconductor Interfaces

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Photoinduced excess charge at a GaAs interface barrier relaxes nonexponentially. A fit to experiment with a statistically motivated Kohlrausch formula is possible but unjustified. Serial relaxation by hierarchies of systems with increasing spatial separation of carriers furnishes a convincing explanation and exemplifies recent theoretical proposals to describe nonexponential relaxation processes.

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Relaxation of disequilibrated systems towards equilibrium often obeys a time law which is not exponential. The rate of change is instead initially rapid, but becomes continually slower as time progresses. The first observation is described by Kohlrausch,[1] whose name has now become associated with a "time-extended exponential" of the form $\exp(-t/\tau_K)^\gamma$, where of the two fit parameters, τ_K is some characteristic decay time during the earlier phase of observation, while the exponent γ usually remains without a convincing physical interpretation.

This longstanding problem of interpreting nonexponential relaxation has recently found renewed attention. Dielectric relaxation has been thoroughly discussed, and its universal non-Debye-type behavior has been stressed.[2,3] Glassy materials and spin-glasses have received particular interest. The dynamics of glassy relaxation has recently been investigated by Palmer, Stein, Abrahams, and Anderson (PSAA).[4] These authors emphasized the inappropriateness of the usual assumption involving weighted distributions for relaxation times describing parallel, independent processes. They suggested instead a novel method of serial relaxation of hierarchies of correlated systems.[4] A general model was presented by PSAA, from which a Kohlrausch formula could be derived; no detailed microscopic models were introduced.

In this Letter, I describe a simple solid-state system where nonexponential relaxation prevails and can easily be studied. A single-crystalline semiconductor with a charge-separating interfacial potential barrier is used. Charge can be created in excess of thermal equilibrium by illumination. This charge remains frozen in at sufficiently low temperatures and decays slowly. The amount of charge can very sensitively be measured because it contributes to a nonequilibrium excess conductance which is easily accessible to precision measurements. This system of a well-controlled semiconductor interface can be characterized by independent measurements; thus it is less prone to arbitrary parametrization than other, more complex systems. The results can be explained quantitatively. Thus, the principles proposed by PSAA and, in particular, the constraints and their actual satisfactions of the model can be compared to experiment and indeed be verified.

The model is represented by a thin ($\cong 3\ \mu$m), highly perfect layer of n-type (typically 10^{15} donors/cm^3) gallium arsenide on top of a single-crystalline substrate, also of GaAs, but of high resistance ($\cong 10^8\ \Omega$ cm) by doping with chromium.[5] When photons are administered at small dose levels ($\cong 10^{11}$ photons/cm^2 sec), one can perceive a gradual increase of conductance in the n-type layer.[6] This increase is proportional to the logarithm of the cumulative photon dose and has been quantitatively explained earlier.[6] A model of *spatial charge separation* was used. The interface potential between layer and substrate separates many of the photon-generated electron-hole pairs. The holes diffuse into the substrate, which is their region of minimal electrical potential. There they are localized through capture by traps, whose ionization energies greatly exceed the thermal energy of the carriers. The electrons remain in the layer, which represents their potential minimum. Here they stay mostly delocalized in the conduction band and become detectable by their contributions to an excess nonequilibrium conductance, which is often called *"persistent photoconductivity."*[7] Such excess conductances can exceed the equilibrium dark conductances by large factors; usually one measures enhancements of about 10% to 50%.[6,7]

The explanation of this accruing conductance showed[6] the significance of the spatial distribution of available trap sites. Initially, the closely spaced traps become filled; later the holes must reach consecutively more distant traps, which becomes decreasingly probable. Trap profiles can actually be ascertained by measuring the conductance increase of the partner electrons.[8] Here, I discuss the relaxation of this excess conductance *after termination* of the disequilibrating illumination. The inverse process occurs: Initially, the close partners recombine and can do so quickly because of a large wave-function overlap of the holes and the electrons; later, only the distant holes are left as recombination partners for the electrons, and thus their decay is retarded by the increasing distance between electrons and the rigidly localized holes in the substrate. A nonexponential relaxation therefore

arises.

Figure 1 shows a typical result, here for a GaAs sample at 140 K. A detailed report of further experiments as well as a complete treatment of a theory for this conductance relaxation for various experimental situations will be published elsewhere.[9] A review talk was recently presented.[10]

The curve of Fig. 1 gives experimental data from 5 to 600 s after illumination. These data might be subjected to a fit with a Kohlrausch expression

$$\sigma(t) = \sigma_0 \exp(-t/\tau_K)^\gamma, \quad (1)$$

where a seemingly excellent fit to better than 10^{-3} can be achieved with the following parameters: $\ln\sigma_0 = 3.39$, $\tau_K = 312$ s, and the exponent (for which a Kohlrausch fit demands $0 < \gamma < 1$) $\gamma = 0.035$. The typical shape is revealed by this semilogarithmic plot: a rapid early fall of σ, described by the time τ_K, followed by an increasingly sluggish approach to the original equilibrium. In most cases, even an approximate restoration of equilibrium is unobservable, hence the name *persistent* photoconductivity.

Standard interpretations of such effects in semiconductors use two or more relaxation times or a statistical spread for some other relevant parameter, such as capture cross sections, to describe the recapture of the excess electrons by a donor trap undergoing large lattice relaxation.[10,11] This customary resorting to a statistical approach is the method criticized by PSAA.[4] It assumes a concept of parallel relaxation in which each degree of freedom relaxes independently with some characteristic time τ_i. I concur with PSAA in interpreting the relaxation by a series of sequential, correlated activation steps (here identical in their physical mechanism but different in spatial separation).

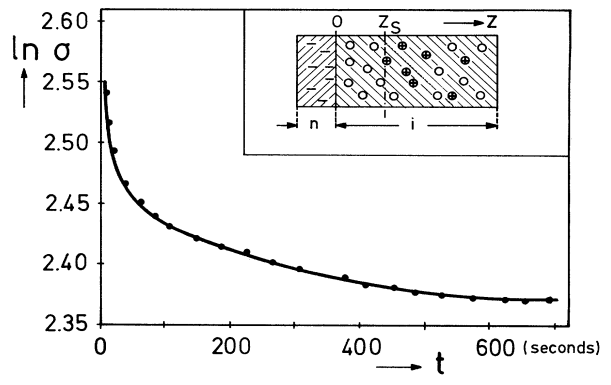

FIG. 1. Nonexponential decay of a photoinduced excess conductivity σ in an n-type GaAs layer on an insulating GaAs:Cr substrate at 140 K as a function of time t. The experimental points could be force fitted with a Kohlrausch curve of Eq. (1) but are better interpreted with Eq. (4), based on spatial charge separation as indicated in inset. From the left: first, the conducting n layer with free excess electrons (minus signs); then, the insulating ("i") substrate, a zone where holes have already recombined; next, a region of remaining trapped holes; finally, the unaffected substrate. A front at $z = z_s$ (dash-dotted line) is the demarcation for completed hole recombination; it moves with time t toward increasing z, according to Eq. (3).

The inset of Fig. 1 pictures the sample in its relaxing state. It shows how the hierarchy of spatial separations translate into temporally subsequent relaxation of decreasing rapidity. The left side shows the layer with its remaining excess conduction electrons. Immediately to their right exists a zone of emptied traps (open circles) out of which the holes have already recombined. Farther to the right, hole occupancy still remains (circles with plus signs). A front $z = z_s$ separates empty from as yet filled traps (dash-dotted vertical line). This front z_s moves with time t toward increasing z, i.e., into the substrate. Equilibrium would be restored once this front has traversed the farthest trapped hole.

This model can be treated in a simplified fashion.[9] A distance-dependent recombination time $\tau(z)$ is introduced:

$$\tau = \tau_0 \exp(2z/a), \quad (2)$$

where τ_0 is carrier lifetime of uniform bulk material, typically 10^{-9} s in GaAs. The parameter a is the Bohr radius of the electron, a measure for the extent of its wave function, typically 10^{-6} cm in GaAs. An expression for recombination rates, such as Eq. (2), is used to describe radiative decay at donor-acceptor pairs.[12,13] Equation (2) is fairly general; similar, but more differentiated expressions arise for more specific recombination, such as by tunneling[14] or, for example, by dipole interaction. The removal of the trapped holes can be approximated by the motion of the front z_s [9]:

$$z_s = \tfrac{1}{2} a \ln[1 + (t/\tau_0)] \quad (3)$$

which assumes that at time t all holes with a lifetime $t + \tau_0$ and only those have recombined. This assumption holds for many experimental cases.[9] The excess conductivity is proportional to the amount of charge beyond z_s, which can be obtained by integration if the initial trapped charge profile is known. Such profiles can be approximated by simple distributions, such as rectangles or triangles, for many experimental realizations.[9] As a good approximation, one gets thus a relaxation law for the excess conductivity:

$$\sigma(t) = \sigma(t=0) - \tfrac{1}{2} AaH \ln(t/\tau_0), \quad \text{for } t \gg \tau_0, \quad (4)$$

where H is the volume density of the traps. The constant $A = e\mu d^{-1}$ contains electron charge and mobility, e and μ, and the width of the conducting layer d.

The physical reason for long-lived nonequilibria of this kind is that the buildup of trapped charge is

governed by a mean free path L in $\exp(-z/L)$,[6] whereas its decay is ruled by a wave-function extent a in $\exp(-z/a)$. The decay is much slower due to typical range ratios of $L/a \cong 50$ in GaAs.[9]

The data of Fig. 1, as well as many other experiments,[9] are well described by Eq. (4), when known values for a, τ_0, $H = 10^{16}$ cm^{-3} are inserted rather than misusing these parameters as adjustable. The initial $\sigma(t=0)$ can be estimated from data, during illumination. The choice of Eq. (1) and even the semilogarithmic convention of plotting are therefore not as well justified for our experiments as is Eq. (4).

The seemingly long time of observation to 600 s covers in reality only a very short motion of the front. This admission probably holds generally for many experiments on nonexponential decay. Detailed studies of the range dependence of the recombination law would require data from $\tau_0 = 10^{-9}$ s to times of more than 10^5 s. Only then one could, for instance, study if the finite temperature causes hole replenishment into closer-lying traps or if other transport, such as hopping, accelerates the relaxation. *Meaningful relaxation measurements require extensive observational times.* PSAA distinguish three regimes of time scales and processes: (i) effectively frozen processes; (ii) fast ones, includable in an entropy term; and (iii) intermediate processes, being active and observable depend in their classification on the time scale of observation.[4] Our experiments give a lucid example of that classification.[15]

A Kohlrausch fit and the assumption of a statistically weighted treatment of independent, parallel relaxation are thus clearly unphysical for this example of nonexponential relaxation. The first requirement stated by PSAA, demanding a dynamical approach rather than mere statistics, is thus proven correct. Their second requirement is a postulate of constraints over large time scales. Processes of relaxation are constrained by the previous motion of other systems. The presence of constraints is very easily seen in the present experiment. Trapped charge closer to the interface screens the further-lying traps and must be removed first before more distant charge is affected.

The third requirement is that of a hierarchy ruling the subsequent activation of processes. The hierarchy in the experiment here described is simply a spatial one, since close distances mean rapid relaxation. The series approach rather than a statistically motivated parallel approach has become apparent in the model concept of the moving front of relaxing excess charges. Although the present example cannot be regarded as a strongly interacting system, it is evident that the different lifetimes are *not* a consequence of some statistical averaging but belong to identical physical processes in a spatially determined hierarchy.

In conclusion, an illustrative experimental proof is furnished for a novel theoretical approach to interpret nonexponential relaxation, which causes long-lived phenomena in the time domain (or, equivalent anomalies at low frequencies in the frequency domain) in many branches of physics.

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