Non-Gaussian Transport Measurements and the Einstein Relation in Amorphous Silicon

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We propose an experimental procedure for testing the Einstein relation for carrier drift and diffusion in semiconductors exhibiting non-Gaussian or dispersive transport. We present corresponding hole time-of-flight and steady-state photocarrier grating measurements in hydrogenated amorphous silicon (a-Si:H). For a range of mobilities $10^{-5}-10^{-2}$ cm^2/V s we find that our estimates of hole diffusion are approximately twice as large as predicted by the Einstein relation and the mobility measurements. We consider the deviation to represent an upper bound to any true failure of the Einstein relation for hole transport in a-Si:H. [S0031-9007(96)00059-2]

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The Einstein relation $D = (kT/q)\mu$ connecting a carrier's drift mobility μ and its diffusion constant D is very widely used in the analysis of band transport in crystalline semiconductors and semiconductor devices. In these materials electrical transport is Gaussian: carriers initially generated in a well-defined sheet spread into a Gaussian profile with width $\delta x = (2Dt)^{1/2}$ for longer times. Thermal and structural disorder plays a quantitative role in determining the diffusion constant and mobility.

In noncrystalline materials disorder can lead to a more profound change: the spreading of a sheet of carriers is non-Gaussian (or dispersive) [1,2]. Although very commonly assumed to hold, the validity of the Einstein relation for non-Gaussian transport is not well established either theoretically or experimentally. Violations of the Einstein relation have been predicted for many models, including (i) hopping transport models with energetic disorder in the sites [3,4], (ii) band transport involving exponential band-tail traps [5], and (iii) random force models in which the random force is not the gradient of a potential [6].

To date, such predictions are nearly untested by experiment. There are at least two difficulties in comparing diffusion and drift processes in materials exhibiting dispersive transport. First, the mobility is not simply a constant: mobility measurements depend significantly upon the distance L traversed by the photocarriers [1,2]. This effect is illustrated in Fig. 1, in which the upper panel presents photocarrier time-of-flight (TOF) measurements of the hole drift mobility μ_D in a-Si:H as a function of reciprocal temperature and drift length L. The second difficulty is that, for dispersive transport, the spreading of the photocarrier distribution during the drift mobility measurement cannot generally be used to make inferences about photocarrier diffusion [7].

For a-Si:H and other materials in which both electrons and holes are mobile, this second difficulty can to some degree be surmounted by measuring an ambipolar diffusion constant using steady-state photocarrier gratings (SSPG)

photogenerated by laser interference fringes [8]. In the lower panel of Fig. 1 we show the results of such measurements in a-Si:H. Because holes are much less mobile than electrons in a-Si:H [9–11], they determine ambipolar diffusion, and the diffusion and hole mobility measurements should be comparable. However, it is unclear how the diffusion measurements, which depend upon the light intensity of the measurement, should be compared with the mobility measurements, which depend upon the particular drift length L.
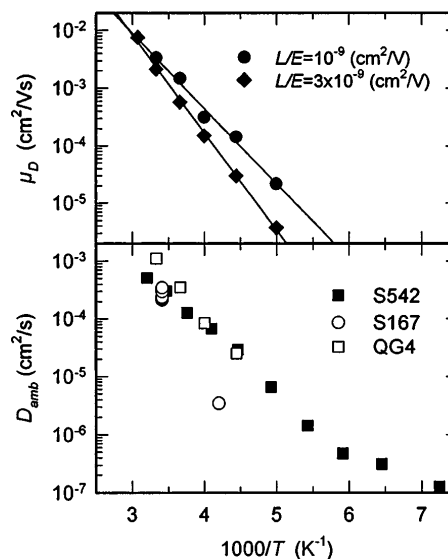

FIG. 1. Ambipolar diffusion constant measurements and hole drift-mobility measurements in hydrogenated a-Si:H as a function of reciprocal temperature $1/T$. (a) The hole drift mobility $\mu_D = L/Et_T$ was measured using transient photocurrent measurements of the transit time t_T for the specified ratios of drift length to electric field L/E. (b) The ambipolar diffusion constant $D_{amb} = L_{amb}^2/\tau_R$ was evaluated from steady-state photocarrier grating measurements of the ambipolar diffusion length L_{amb} and transient photoconductivity measurements of the recombination response time τ_R.

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In this Letter we propose a procedure for using photo-carrier drift and ambipolar diffusion length measurements to test the Einstein relation in strongly disordered materials [12]. We present a set of measurements in a-Si:H to which we have applied this procedure, and we obtain an experimental correlation of hole drift mobilities and diffusion constants based upon it. The diffusion coefficients we estimate are systematically about twice as large as would be inferred from the mobility measurements and the Einstein relation for the range of mobilities from $10^{-5}-10^{-2}$ cm^2/V s. We believe that this deviation places an upper limit on any true failure of the Einstein relation for hole transport in a-Si:H. The consistency of the analysis with the Einstein relation also offers a useful insight into hole recombination in a-Si:H, and of course discriminates in a-Si:H against transport theories for which signficant deviations from an Einstein relation are predicted.

The Einstein relation is fundamentally a relation relating the time evolution of the photocarrier drift $x(t)$ in an electric field E and the time evolution of photocarrier diffusion in the absence of an electric field. For a sheet of carriers at $x = 0$ generated at $t = 0$, we have

$$(kT/q)\frac{x(t)}{E} = [\delta x(t)]^2/2, \qquad (1)$$

where we have assumed that the drift $x(t)$ is proportional to the electric field E. For normal (Gaussian) transport $\delta x(t)$ is the root-mean-square spread of the packet around its mean. In this case Eq. (1) is unnecessarily complex. $x(t)/E$ and $[\delta x(t)]^2$ are simply expressed in terms of the mobility and the diffusion constant, respectively: $x(t)/E = \mu t$ and $[\delta x(t)]^2 = 2Dt$, leading to the conventional form for the Einstein relation $D = (kT/q)\mu$.

For non-Gaussian transport the mobility and diffusion constants are not simply constants, and we therefore return to Eq. (1) as the Einstein relation. Evaluation of the left side of Eq. (1) presents no experimental difficulty: the drift $x(t)$ of the mean position of a carrier packet is directly measured in photocarrier time-of-flight measurements. In Fig. 2 we show schematically the behavior of the hole drift $x(t)$ in a-Si:H near room temperature (curve labeled "drift"); we have normalized $x(t)$ by kT/qE to facilitate the comparison with Eq. (1).

The measurement of hole diffusion presents more difficulty. In the present Letter we emphasize diffusion estimates originating from the SSPG method [8]. We envision this experiment as illustrated by the curve labeled "diffusion + recombination" in Fig. 2, which shows schematically the time dependence of the square of the packet spreading $(\delta x)^2$. Presuming validity of the Einstein relation, this spreading $(\delta x)^2/2$ should agree with the drift $(kT/qE)x(t)$ for early times, when recombination can be ignored. The hole diffusion length L_D is then essentially the spreading which occurs up until recombination with electrons near the response time τ_R, as indicated in Fig. 2.

Figure 2 was calculated based on exponential decay of the hole population as $\exp(-t/\tau_R)$. For this model the
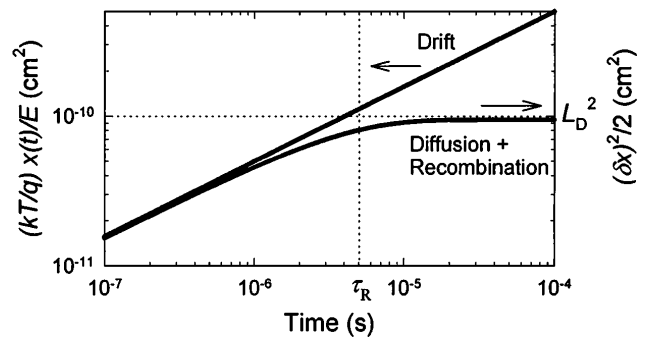

FIG. 2. Schematic comparison of hole drift in the dark from the time-of-flight technique and hole diffusion under optical bias from the photocarrier grating technique. Hole drift $x(t)$ is based on an analytical approximation suitable for a-Si:H near room temperature [$x(t)/E = (2\mu_0/\nu)(\nu t)^\alpha$, with parameters $\mu_0 = 1.0$ cm^2/V s, $\nu = 10^{12}$ s^{-1}, and $\alpha = 0.5$]. The curve labeled diffusion and recombination is based on numerical integration departing from $d(\delta x)^2/dt = 2(kT/qE)[dx(t)/dt]\exp(-t/\tau_R)$ with $\tau_R = 5 \times 10^{-6}$ s; the form for $x(t)/E$ just given was used.

figure suggests the following relationship of the drift and diffusion length measurements:

$$(kT/q)\frac{x(\tau_R)}{E} \sim L_D^2. \qquad (2)$$

Equation (2) is the basis of our procedure for comparison of the two measurements: presuming the validity of the Einstein relationship, we predict that the diffusion length L_D for holes inferred from the SSPG measurement should be calculable from the hole displacement (obtained from TOF) evaluated at the measured recombination time τ_R. Equivalently, we can use the *time-averaged* drift mobility [13] $\bar\mu = x(\tau_R)/E\tau_R$ and the time-averaged diffusion coefficient $\bar D = L_D^2/\tau_R$ to explore the Einstein relation in more conventional form $\bar D = (kT/q)\bar\mu$.

The specimens for the experimental work presented here were hydrogenated amorphous silicon (a-Si:H) films prepared by plasma deposition from silane at the Technical University of Munich and at Syracuse University. SSPG and recombination response time measurements were done on films deposited on glass with evaporated, coplanar metal electrodes. TOF measurements were done on films deposited on glass substrates with an evaporated metal "bottom" electrode; a small metal top electrode was evaporated following deposition.

SSPG and recombination response time measurements were done with a helium neon laser (633 nm). Procedures for estimating an ambipolar diffusion length L_{amb} from the SSPG data are described elsewhere [8,14]. To evaluate the recombination response time τ_R we measured the small-signal photocurrent decay in response to a small decrease in illumination; we defined τ_R as the time for the photocurrent response to fall to $1/e$ of its initial value. TOF measurements were done using 510 nm illumination with a pulsed laser. The detailed procedures have also been described in previous publications [11].
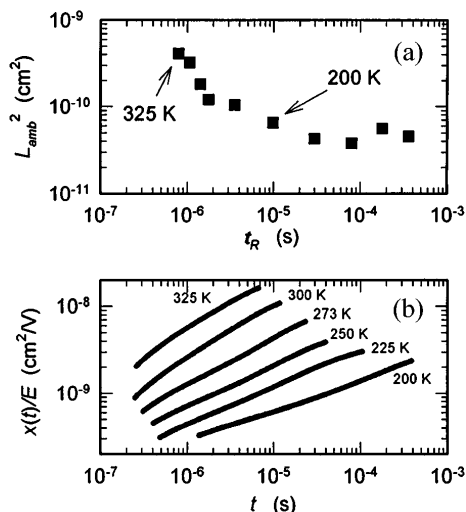
FIG. 3. (a) Correlation of experimental estimates of the ambipolar diffusion length L_{amb} (based on steady-state photocarrier grating measurements) with estimates of the recombination response time τ_R (based on transient photoconductivity). The points correspond to varying sample temperatures. (b) Experimental estimates of normalized hole displacement $x(t)/E$ in a specimen of a-Si:H for several temperatures based on time-of-flight measurements. The same a-Si:H thin film (S542) was used for all the measurements in this figure.

In Fig. 3 we illustrate the measurements we use to obtain the average mobilities and diffusion coefficients required to test $\bar{D} = (kT/q)\bar{\mu}$. In the upper panel we show the correlation of the ambipolar diffusion length L_{amb} with the response time τ_R measured in sample S542. The measurements were taken for varying sample temperatures (as indicated) and for a constant illlumination intensity; they did depend somewhat on the illumination intensity, although we have not shown this here [5,16]. In the lower panel of Fig. 3 we show the time dependence of hole displacements $x(t)/E$ measured using hole transient photocurrent and TOF techniques for the same sample S542. Results are again shown for several temperatures. We were careful to verify that our measurements of L_{amb}, τ_R, and $x(t)/E$ were taken in a low-field regime where they were independent of electric field E. For SSPG this required $E < 2 \times 10^3$ V/cm; for TOF high-field effects are quite temperature dependent, but were negligible at our typical measuring field of 10^4 V/cm.

As noted previously, our procedure involves comparing a hole diffusion constant $\bar{D} = L_D^2/\tau_R$ with a hole mobility $\bar{\mu} = x(\tau_R)/E\tau_R$ evaluated at the same time τ_R associated with L_D. However, the SSPG method does not directly yield L_D for holes, but rather an ambipolar diffusion length L_{amb}. L_{amb} includes the effects of the far more mobile electron photocarriers and the concomitant "diffusion electric fields." The simplest treatment of this effect yields $L_D^2 = L_{amb}^2/2$ [15]; we note that this treatment already assumes validity of an Einstein relation, since carrier drift in response to the diffusion fields is an essential aspect of ambipolar diffusion.
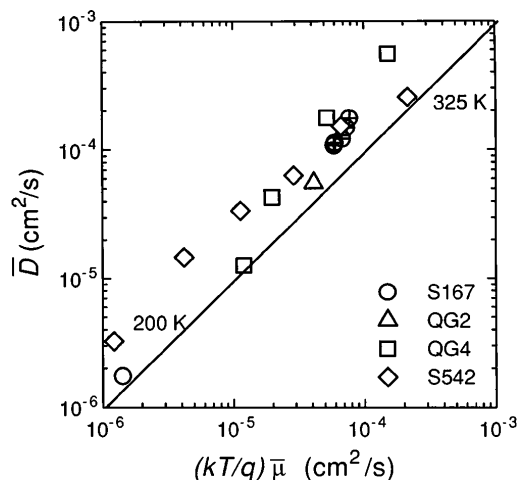

FIG. 4. Correlation of hole diffusion coefficient estimates $\bar{D} = L_{amb}^2/2\tau_R$ with normalized hole drift mobility estimates $(kT/q)\bar{\mu} = (kT/q)[x(\tau_R)/E\tau_R]$. The solid line is the Einstein relation $\bar{D} = (kT/q)\bar{\mu}$. The symbols represent measurements for four different specimens at various temperatures; diffusion length measurements were taken at a constant illumination intensity. The symbols with a center + indicate measurements at varying illumination intensity and room temperature.

In Fig. 4 we present the correlation of the time-averaged hole mobilities $\bar{\mu} = x(\tau_R)/E\tau_R$ and diffusion coefficients $\bar{D} = L_{amb}^2/2\tau_R$ for several specimens and a range of temperature and illumination conditions. For one of the specimens (S167) we did not perform hole time-of-flight measurements, and instead relied on "typical" literature values; the hole drift mobility is surprisingly consistent in specimens from different laboratories [11]. The agreement with the Einstein relation $\bar{D} = (kT/q)\bar{\mu}$ is quite satisfactory, although it is also apparent that the average diffusion constants exceed the average mobilities by more than would be expected based solely on the scatter in the measurements.

We briefly discuss an alternate procedure proposed by Liu *et al.* [16] which is closely related to that described here. The dispersive drift $x(t)$ of a hole across the specimen illustrated in Fig. 2 is attributable to multiple trapping of the hole by states in an exponential valence band tail [10,11]. In a-Si:H multiple-trapping behavior in the TOF measurement is ultimately interrupted by "deep trapping" of the hole, presumably by a dangling bond. If deep trapping can also be identified as the hole recombination channel for the SSPG measurement, then an Einstein relation $L_{amb}^2/2 = (kT/q)\mu\tau_t$ should hold connecting the deep-trapping mobility-lifetime product for holes $\mu\tau_t$ and the ambipolar diffusion length L_{amb}. Liu *et al.* [16] showed that $(kT/q)\mu\tau_t$ is of the same order as L_{amb}^2.

The present approach is more generally valid: the need to assume any specific recombination mechanism is largely eliminated by using a measured recombination response time to establish the time scale for comparing drift and diffusion. Indeed the present analysis shows that

hole recombination in the SSPG experiment occurs prior to hole deep trapping.

The twofold systematic deviation of our inferences of the diffusion coefficient and the mobility for a-Si:H from the Einstein relation may not indicate any true failure of a generalized Einstein relation. The analysis of ambipolar diffusion which we use [5,8] is based on Gaussian diffusion, and in particular upon the assumption that diffusion currents are calculable from the gradient of the photocarrier density. This analysis can certainly be challenged for non-Gaussian processes, and we speculate that an improved analysis might well reduce the apparent deviation from an Einstein relation.

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[13] Note that the time-averaged drift mobility denoted $\bar{\mu}$ is distinct from the conventional, distance-averaged drift mobility μ_D presented in Fig. 1. $\bar{\mu}$ is evaluated for a specified time; μ_D is evaluated for a specified distance, often the specimen thickness. $\bar{\mu}$ and μ_D are easily interconvertible; see Q. Wang, H. Antoniadis, E. A. Schiff, and S. Guha, Phys. Rev. B **47**, 9435 (1993).

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