Role of interactions in the energy-loss hopping and recombination of two-dimensional electrons and holes

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(Received 5 August 1996)

We study experimentally the slow relaxation of the mean energy and radiative rate of a system of interacting, two-dimensional electrons and holes in the presence of static disorder. The system evolves through two phases: an early, excitonic phase and a long-time, distant-pair phase. The results differ from the usual energy-loss hopping because of the dominant role of interactions in the present system. [S0163-1829(97)00407-4]

I. INTRODUCTION

Many disordered systems approach equilibrium through a series of ever-slower steps spanning many time scales.[1–4] Such slow relaxation is apparent in the structural relaxation of glasses and the energy relaxation of photoexcited electrons and holes in amorphous semiconductors, as well as in many other physical, biological, and chemical systems. In general, it is a challenge to understand the microscopic origin of the slow relaxation. In the case of electronic relaxation in disordered semiconductors, a description of the dynamics must include the effects of hopping conduction, Coulomb interactions, and dimensionality in a system far from equilibrium. No general theoretical framework exists.

In recent years, the recombination of photoexcited carriers in hydrogenated amorphous silicon (α-Si:H) has been an especially frequent vehicle for the study of slow relaxation because of the importance of that material in solar cell applications, and because of its mature growth technology.[5] One result of these works has been an interest in the role of interactions in the recombination process. For example, a noninteracting picture of geminate recombination was found to predict nonexponential decay kinetics including a long tail in the lifetime distribution.[6,7] Experiments confirmed the nonexponential decay, but with a much narrower lifetime distribution.[8–11] Simulations can shed some light on these questions. However, simulations of interacting, disordered systems are very difficult, and what efforts have been made have tended to focus on equilibrium, unipolar systems such as the Coulomb glass.[12] Thus, although interactions are thought to be unimportant in α-Si:H because of the $\approx$1 eV scale disorder, the situation is not clear.

It is tempting to realize studies of slow relaxation of electrons and holes using GaAs-based quantum wells. Such structures offer reduced dimensionality, millielectronvolt-scale disorder due to well width fluctuations, comparable Coulomb interactions, and are essentially free from nonradiative recombination. However, the subnanosecond recombination of electrons and holes in that system presents an obstacle. Here, we exploit a double-well structure to achieve the low electron-hole wave-function overlap and long lifetimes necessary to permit observations.[13] Specifically, we combine a two-well structure with a vertical electric field to create a system in which electrons and holes are confined to separate quantum wells. Excitons consist of spatially indirect pairs centered at the same in-plane point, and are bound by an energy of 2–3 meV.[14,15] Free pairs consist of spatially indirect electrons and holes centered at different in-plane points.

The spatial separation has a number of effects. First, it results in greatly enhanced recombination lifetimes due to the reduced overlap of electrons and holes. This lifetime enhancement is essential if we are to observe recombination and energy relaxation kinetics in the hopping regime, since the hopping motion is orders of magnitude slower than the usual radiative lifetimes in direct gap semiconductors. Separate confinement also affects the interactions. First, it reduces the Coulomb attraction between nearby electrons and holes. As we show below, the Coulomb attraction of spatially indirect electrons and holes, as measured by the binding energy of the spatially indirect exciton,[14] is nearly equal to the disorder energy. For the spatially direct (single well) case, the binding energy is substantially greater than the disorder, a limit that favors simple, exponential kinetics. Equally important, the spatial separation imparts a dipole moment to electron-hole pairs and makes them susceptible to electrostatic interactions, even at low densities.

This paper will set down the basic scenario of the recombination and energy dynamics of separately confined electrons and holes in a $GaAs/Al_{0.3}Ga_{0.7}As$ double quantum well. We show experimentally that the dynamics are determined by interactions, even at low densities.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The sample consists of 10- and 15-nm GaAs quantum wells separated by a 3-nm $Al_{0.3}Ga_{0.7}As$ barrier layer, and embedded in the 1 μm-thick intrinsic layer of a $Al_{0.3}Ga_{0.7}As$

pin diode, and was grown by molecular-beam epitaxy. For bias voltages more negative than ≈0.3 V (i.e., $V \leqslant 0.3$ V), the system is type II, i.e., the lowest interband excitation is spatially indirect in character. In this case, the radiative lifetime of spatially indirect excitons is an exponentially growing function of the bias field, and varies between nanoseconds and microseconds in practice. The exciton binding energy was estimated to be near 2 meV (Ref. 15) in a similar structure.

It is especially important to understand the origin of disorder in this system, and the possibility to vary that disorder through the applied electric field. As in other binary-well/ternary-barrier systems, the main source of disorder is the slight roughness of the heterointerfaces. Experiments and modeling presented in Ref. 16 support the following picture for the disorder in this system. (1) The disorder energy is several millielectronvolts in magnitude, and can be increased by increasing the applied field. (2) Field tuning of the disorder results from variation in wave-function amplitude at the interfaces. Experimental support for this idea was taken from the effect of the electric field upon the temperature dependence of the radiative lifetime. Specifically, it was found that the temperature dependence of the lifetime weakens dramatically as the electric field is increased. This result was interpreted as a field-induced increase in the mobility edge. In this work, we will adopt the idea that the static disorder is increased by the applied field.

It is also important to understand the process of excitation and capture to the quantum structure since these determine the initial conditions to the hopping problem. In the present experiments, the excitation light is absorbed mainly in the cladding and contact layers. Light absorbed in the contact layers gives rise to a fast luminescence that does not concern us here. Light absorbed in the 1 μm intrinsic layer creates pairs that then drift under the influence of the bias field. Electrons and holes drift in opposite directions so that electrons and holes captured into the wells originate from distinct pairs. For bias voltages more negative than ≈0.3 V, tunneling relaxation of electrons and holes to separate wells is favored and should occur within a few hundred picoseconds.[17] Thus, for the time scales of interest in the present measurements, the initial conditions are electrons and holes confined to separate quantum layers, and distributed at random within those layers, except insofar as interactions induce correlations. We expect nongeminate behavior at all densities.

The sample was held in an optical cryostat with base temperature 1.4 K. Time-resolved photoluminescence spectra were obtained using the time-correlated photon-counting technique. The excitation pulses were 1 nsec in duration with 100 kHz repetition rate and 1.96 eV photon energy. Measurements were made at pulse fluences of 4, 40, and 400 nJ/cm^2 corresponding to pair densities 3×10^9–3×10^{11} cm^{-2}. The absolute densities are estimated and may include an error of 2×. However, relative measurements were made using calibrated neutral density filters so that the excitation intensity change in these measurements is accurately known.

Figure 1 compares the time-integrated and time-delayed photoluminescence spectra for $T=1.4$ K, V$=-1.0$ V (electric field ≈26 kV/cm), and 400 nJ/cm^2 fluence. In this and other data, energies are measured with respect to the bulk GaAs band gap, 1.519 eV, and are taken to increase into the

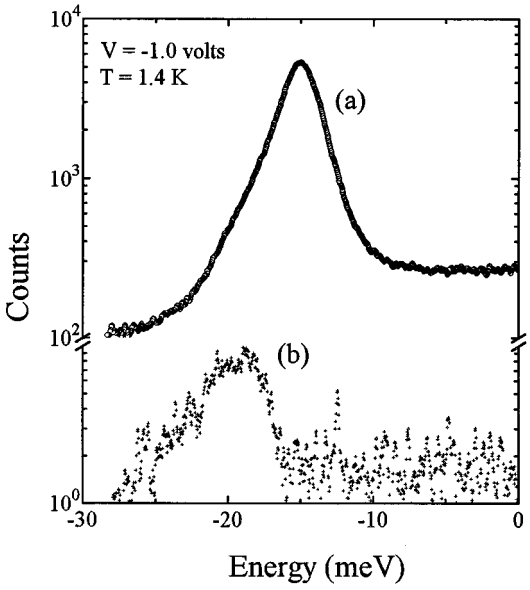

FIG. 1. Time-integrated (*a*) and time-resolved (*b*) photoluminescence spectra for excitation fluence 400 nJ/cm^2. Curve (b) is acquired 8.8 μsec after excitation. The energy is referenced to 1.519 eV.

allowed band, and decrease into the tails. The time-integrated spectrum [curve (a)] shows a very broad feature at high energies and a tail to low energies. Time-resolved spectra make the basic scenario clear: The high-energy feature is due to hot-carrier emission faster than the time resolution of the present measurement. It has no effect on the time-resolved spectra presented below. The red tail is due to the combination of emission and energy relaxation. Curve (b), acquired after an 8.8 μsec delay, illustrates this point, and underscores the role of the energy dynamics in determining the spectral shape.

Figure 2 shows the time evolution of the spectrally inte-

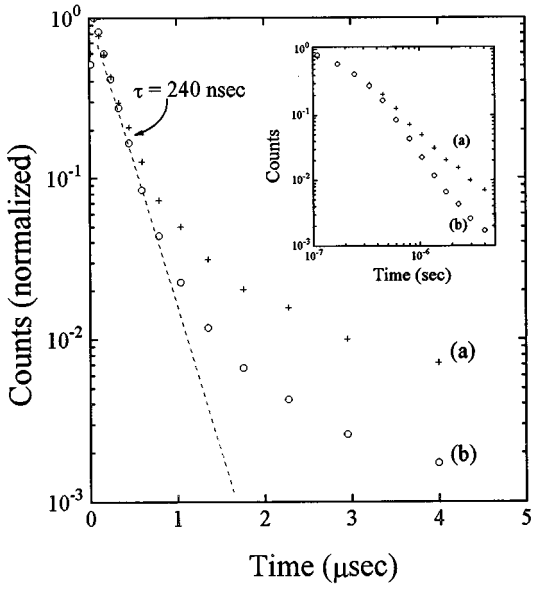

FIG. 2. Recombination kinetics for (*a*) 40 nJ/cm^2 and (*b*) 400 nJ/cm^2.

grated count rate for two fluences on semilogarithmic and log-log scales. For each fluence, the early decay is exponential with lifetime $\tau=240$ nsec, followed by a slower, near-power-law decay. For the 400-nJ/cm^2 excitation [curves (b)], the exponential decay persists to nearly 1 μsec while for 40 nJ/cm^2 [curves (a)] the crossover to the power law occurs by 300 nsec.

We next show that the early, exponential phase results from the recombination of spatially indirect excitons. As explained above, electrons and holes are initially distributed at random in their well layers. Due to fluctuations, some pairs are so close that the interaction energy dominates the disorder. Such pairs form spatially indirect excitons that decay exponentially. As the excitation intensity is increased, the fraction of the population that forms excitons grows; however, the lifetime is unaffected. The lifetime is, however, affected by changes in the electric field. We expect[16] and find an exponential increase in lifetime with electric field due to the reduced electron-hole overlap. This picture explains the exponential features of Fig. 2.

With excitons depleted, the decay consists entirely of distant pairs. Two features characterize this nongeminate regime. First, the recombination should proceed according to some slow, scaleless law because of the self-similar dynamics of the recombination.[18] This feature is evidently realized in Fig. 2 in the power-law decays at long times. Second, we expect the dynamics to slow for reduced fluences. This dependence of the rate of recombination upon initial pair density is the hallmark of distant pair recombination, and is also found in Fig. 2.

A number of theories of distant-pair recombination[18–20] predict power-law decays. For later discussion, we fit the observed decays (Fig. 2, long times) to the law,

$$\Gamma(t)=\Gamma_0(t_1/t)^q. \tag{1}$$

Here, Γ is the radiative rate, and Γ_0 and t_1 are constants. For weak excitation (40 nJ/cm^2) we find a good fit to $q=1.5$. For higher fluence (400 nJ/cm^2) the data are well fit by $q=2.0$.

Figure 3 shows the relaxation of the mean energy for three excitation fluences. The data show a strong trend toward higher energies per pair and faster energy relaxation at increased density. The data show the presence of a kink or crossover in the energy relaxation from the slow early phase to a faster later phase. This crossover corresponds in time to the exponential-to-power-law crossover shown in Fig. 2. There is some evidence that the decay slows progressively at the longest times, though the data are inadequate to establish this with certainty.

The effect of temperature upon the fluence dependence of the energy relaxation is illustrated in Fig. 4. The top panel (a) shows the energy relaxation for 400 and 40 nJ/cm^2 for lattice temperature $T=1.4$ K. The lower panel (b) shows decays at $T=3.0$ K under otherwise identical conditions. Several trends are apparent. With lower temperatures, the initial energy reaches higher values, and the difference between the 400 and 40 nJ/cm^2-data is enhanced. Also, for $T=1.4$ K, the energy relaxation continues to reflect the initial conditions to the longest times measured. For $T=3.0$ K the difference between the curves gradually diminishes.

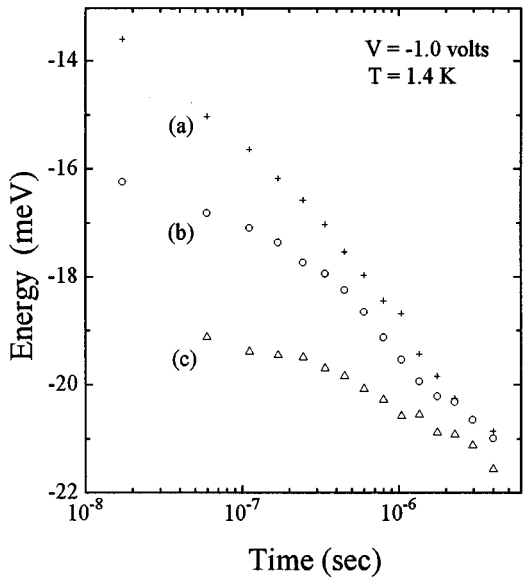

FIG. 3. Evolution of the mean energy for three fluences: (*a*) 400 nJ/cm^2, (*b*) 40 nJ/cm^9, and (*c*) 4 nJ/cm^2.

It is convenient for the discussion to fit the long-time data of Fig. 3 to straight lines, and to introduce the energy loss rate,

$$\epsilon=\frac{\partial E}{\partial \log_e t}. \tag{2}$$

Two observations regarding this rate are noteworthy. First, the rate grows logarithmically with fluence, as can be deduced from Fig. 3. Second, the rate is essentially insensitive to electric field. This result is shown in Fig. 5.

III. DISCUSSION

We first discuss the excitonic phase. The exponential decay of the low-density gas of excitons results from the Poissonian nature of the recombination, and is well known. We introduce a radius R such that electron-hole pairs with separation less than (greater than) R have Coulomb attraction greater than (less than) the characteristic disorder energy. Then the probability to form an exciton under random excitation conditions is proportional to the probability to find both an electron and a hole within a circle of radius R. This probability grows as the square of the initial density, so that the fraction of excitons within the gas grows roughly linearly with the density. This picture accounts for the persistence of the excitonic phase to longer times with increasing excitation fluence, seen in Fig. 2.

Recombination in the distant-pair regime is known to be a reaction-limited process. Electrons and holes hop through the complicated energy relief formed by the static and configuration-dependent disorder, and recombine at random. The system evolves in an essentially self-similar way, and we expect a scaleless recombination law. This argument accounts for the near-power-law decays shown in Fig. 2.

In a picture based upon the energy-loss hopping of noninteracting particles at zero temperature,[7] an electron hops to successively lower-energy states and, eventually, recombines

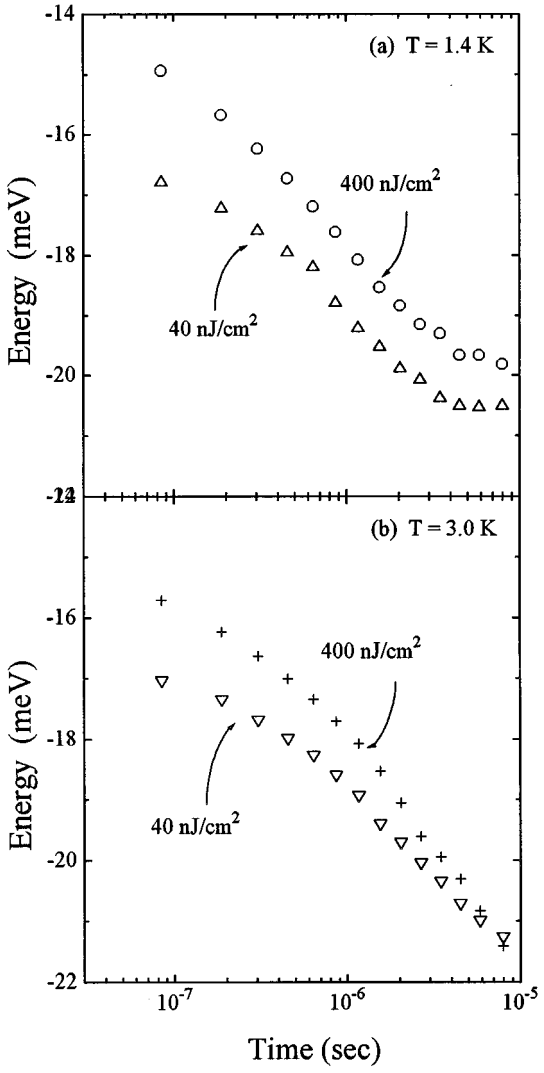

FIG. 4. Effect of temperature upon the intensity dependence of the energy relaxation. (a) $T=1.4$ K (b) $T=3.0$ K.

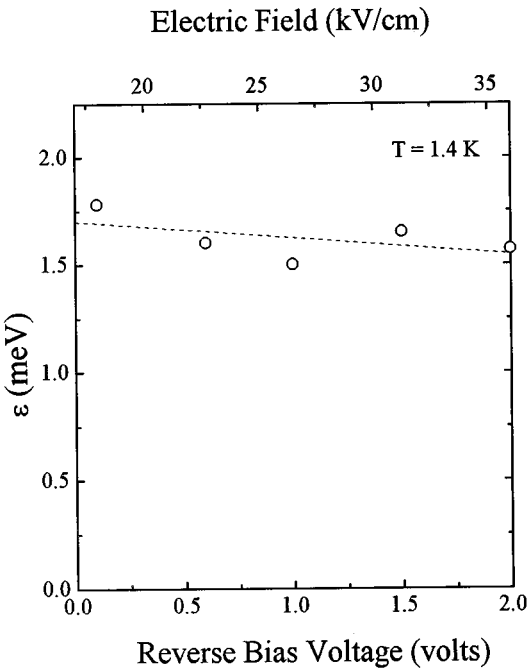

FIG. 5. Dependence of the energy loss rate ϵ upon reverse bias voltage.

with a hole. While the time required for recombination evidently depends strongly on the interparticle spacing (i.e., the density), the energy-loss rate is independent of density in this picture. Thus, the variation of the recombination kinetics with fluence (Fig. 2) is characteristic of both interacting and noninteracting pictures. But, the energy kinetics (Figs. 3 and 4) are unambiguous indications of the importance of interactions.

A second indication of the dominant role of interactions in determining the energy dynamics is the independence of the energy loss rate ϵ on electric field (Fig. 5). As discussed above, variations in the electric field cause a tuning of the disorder. Figure 5 indicates that the static, interfacial disorder does not play the key role in the energy relaxation.

We consider instead an interacting picture based on fluctuations in the local charge density. As discussed above, electron-hole pairs are initially distributed at random. Particles achieve a lower energy by hopping within the complicated energy relief formed by the random site energies, and, principally, the configuration-dependent interaction energy. In addition, by recombining, they achieve a lower density system with less correlation. Assuming first that the fluctuating potential is determined simply by a random initial distribution, we estimate the magnitude of the fluctuations as

$$\Delta\phi \approx \frac{[\sigma r^2]^{1/2}}{r} = \sigma^{1/2}. \tag{3}$$

Here σ is the average (areal) charge density, and r is a cluster radius. In two dimensions, we have the unusual result that the scale of the fluctuations is independent of cluster size. Two effects act to reduce the scale of real fluctuations. The first is screening during the initial excitation and capture phase. The second is diffusion. In general, we predict a positive correlation energy that grows more slowly than Eq. (2). The role of screening is confirmed by the $T=3$ K data of Fig. 4 which show a slower growth in pair energy with density at higher temperatures. We thus account for the basic features of Figs. 3 and 4.

During the excitonic phase (early times) we have essentially the same picture. Because of the separation of electron and hole in the double-well structure, excitons, too, are susceptible to charge fluctuations. We may naturally expect a reduced sensitivity since the exciton is, overall, neutral. This is manifested in Fig. 3 by the slower energy relaxation of excitons compared with pairs. We thus account for all essential features of Figs. 3–5.

We next discuss the effect of interactions on the recombination kinetics. Interactions make charge fluctuations energetically unfavorable, and tend to drive the system toward a homogeneous condition. Tunneling recombination by fixed carriers is known to result in a t^{-1} decay of the density,[18] whence $q=2$. Nongeminate recombination by mobile carriers has been treated[9] and is known to be of the simple bimolecular form $n\sim t^{-2}$ whence $q=3$. The observed decays [q(40 nJ/cm^2)$=1.5$, q(400 nJ/cm^2)$=2.0$] are slower than these results, possibly because of imperfect compensation in

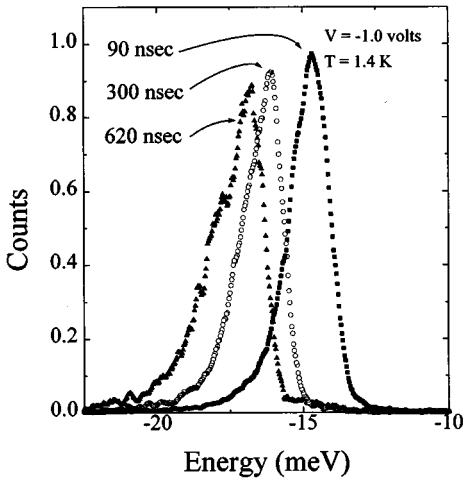

FIG. 6. Time-resolved spectra at 90, 300, and 620 nsec.

the present experiments. Monte Carlo calculations[20] also showed slower decays. However, the trend is toward more nearly bimolecular decay at higher densities. This trend accords with our physical picture based on charge fluctuations.

We next consider alternative explanations for the present data. It is natural to consider the possibility that state filling is responsible for the observed blueshifts. This idea is ruled out by the time-resolved spectra shown in Fig. 6. While in a picture based on band filling we expect the energy distribution to relax mainly by eliminating the high-energy side, here we find a simple shift in energy with time. This result is consistent with the Coulomb picture in which the energy per particle shifts to lower values as the correlation energy is gradually reduced over time. We may also rule out the multiple-trapping scenario in which particles equilibrate below the mobility edge by thermal excitation to Bloch states followed by band transport and recapture. In this scenario, the energy loss rate is kT, one order of magnitude smaller than the observed loss rates.

IV. CONCLUSIONS

In most bulk and thin-film hopping systems studied, the disorder dominates and interparticle interactions constitute a perturbation. This is believed to be the case, for example, in α-Si-H.[5] In the present work, we have studied a hopping system in which interactions give the leading contribution to the particle energy. We have compared the observations with predictions of the usual model of energy relaxation in disordered systems—energy-loss hopping—and have found interesting differences. For example, at densities above $\approx 3\times 10^{9}$ cm^{-2}, the main channel for energy relaxation may not be simply hopping motion, but also recombination, as photons carry off both the site and correlation energies. Fluctuations in the initial distribution of electrons and holes determine the spectrum and dynamics of the recombination.

ACKNOWLEDGMENTS

S.D.B. and P.T. highly appreciate the financial support of the Deutshe Forschungsgemeinschaft via SFB 383.

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