Comment on nonradiative-recombination kinetics in *a*-Si:H

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In a recent paper, Collins *et al.* [Phys. Rev. B 26, 6643 (1982)] have shown that a fast process, occurring in <10 ns, is important in the nonradiative recombination of photoexcited carriers in sputtered *a*-Si:H, and so the slow process of tunneling to defects, in a time scale comparable to that of the radiative recombination, is not dominant, as previously believed from studies on glow-discharge material. We consider their results in terms of the distant-pair model, and we conclude that the fast and slow processes are in fact successive steps in the nonradiative mechanism. Also, we find that a capture cross section for the defects comparable to that of the tail states is consistent with the data.

From measurements of the photoluminescence (PL) decay curves in samples of sputtered *a*-Si:H with different steady-state (cw) PL efficiencies, Collins *et al.*[1] deduce that the dominant low-temperature PL quenching mechanism is fast, occurring within 10 ns of excitation. They present data showing that the PL decay curves are very similar in all samples [in all cases the asymptotic decay is approximately power law $I(t) \sim t^{-1}$]. They discuss this result essentially within the model of recombination due to the Xerox group (see the review by Street[2]), in which recombination is geminate and nonradiative recombination (NRR) occurs if the electron escapes from the hole—at low temperature, by tunneling to a nearby defect. Collins *et al.*[1] modify this model to the extent of emphasizing the relative importance of direct capture of the electron by a defect during thermalization into the band tail (this is their proposed fast mechanism). They attribute the minor differences between the decay curves to the tunneling mechanism, occurring in a time scale comparable to that of the radiative recombination and therefore competitive with it.

Collins *et al.*[1] also show that their interpretation is consistent with data on the temperature quenching of the PL, and with the dependence of the PL efficiency on defect density. They propose, from the latter data, that the capture cross section of the defects is some 100 times that of the tail states, so that they would probably be charged before capture.

In several recent papers, we have developed a rather different model of the PL in *a*-Si:H (see Refs. 3, 4, and references therein). In particular, we have shown that the kinetics of recombination, under cw or repetitively pulsed excitation, are not geminate but distant pair. Consequently, it is not the escape of the electron from the hole which determines the rate of the nonradiative recombination. Most of the evidence for the geminate-pair model, from many different experiments, consists essentially of a transition from first-order kinetics (independent of excitation rate) at low intensities to nonlinear behavior at higher rates (corresponding to carrier densities above $\sim 10^{18}$ cm^{-3}.[2] We showed that, at least in the case of the PL decay curves, this transition is due to the presence of a metastable population of some 10^{17} cm^{-3} carriers[3]; we believe that further analysis will show this to be so in other experiments also.

The purpose of this Comment therefore is to consider the results and conclusions of Collins *et al.*[1] in terms of the distant-pair description. We arrive at conclusions broadly in agreement with Collins *et al.*, except that we find it likely that the fast and slow mechanisms are, in fact, both important, being successive steps in the nonradiative recombination path. Also, we find no necessity for a large capture cross section for the defects.

In the distant-pair model, because of the presence of the metastable population, the number density of electron-hole pairs varies only slightly with the cw excitation rate G: $N(G) \sim G^{0.2}$.[4] Instead, the average lifetime shifts to shorter times with increasing G.[3] In the pure tunneling model of NRR[5] this would result in a marked superlinearity of the PL intensity $I(G)$, which is not usually observed.[6] However, in the distant-pair description, the tunneling model is incomplete, for it ignores the fate of the hole after the electron has tunneled to the defect. Unless the hole (or the electron on the defect) has a Bohr radius comparable to that of the tail state electron, so that defect-hole recombination can take place, the defects will rapidly become saturated with electrons and the NRR will be quenched.

An important result from the theory of distant-pair kinetics is that the decay is power law over a wide range of decay time only if the numbers of centers of opposite sign are quite accurately equal.[3] If electrons can tunnel to both holes and defects, or holes to both electrons and defects, then, for the range of decay time reported by Collins *et al.*,[1] 10 ns to ~ 10 μs, and for the density of excitation used in their experiments ($\sim 10^{18}$ cm^{-3}), as few as 10^{18}cm^{-3} defects to which the electrons could tunnel would change the decay curves dramatically (Fig. 1). Since Collins *et al.*[1] found essentially unchanged decay curves up to 10^{19} cm^{-3} defects, we may conclude that the electrons cannot tunnel to *unoccupied* defects.

These considerations lead to the following model of the nonradiative mechanism. During thermalization, some of the holes are trapped directly in radiative tail states, and some in nonradiative defect states. The electrons then recombine by tunneling with the holes in either kind of state; the decay curves are independent of the density of defects because the density of holes to which the electrons can tunnel is always equal to the density of electrons. Thus, in this model, the fast and slow nonradiative paths of Collins *et al.*[1] are, in fact, successive steps in the nonradiative mechanism.

We do not consider here the possibility of direct capture of electrons into the defects for the following reasons. Firstly, if the electrons cannot tunnel to unoccupied defects, it is not unreasonable to suppose that this is because the defects do not have donorlike states. Secondly, the probability of direct capture by the same defect of an electron and a hole simultaneously would be much smaller than the probability of direct capture of one particle only. If electrons can be captured directly, and tunneling recombination between

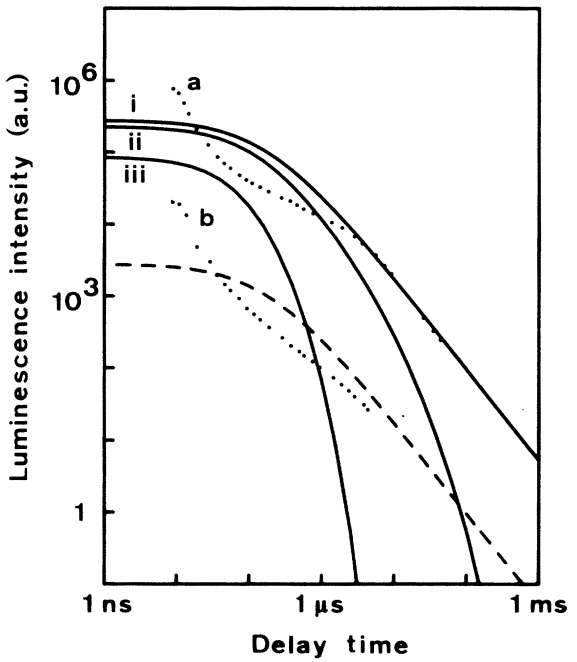

FIG. 1. Decay curves calculated as in Ref. 3 for a single excitation pulse of 10^{18} cm^{-3} electron-hole pairs. The transition probability to either holes or defects is taken to be $p(r)=\tau_0^{-1}\exp(-\alpha r)$ with $\tau_0=10$ ns and $\alpha=(6\ \text{Å})^{-1}$. Curves are given for defect densities (i) 0, (ii) 10^{18}, and (iii) 10^{19} cm^{-3}, and are calculated allowing electron tunneling to all defects. The data points are decay curves taken from Collins *et al.*[1] for two different defect concentrations: curve a 10^{16} and curve b 10^{19} cm^{-3}. The initial fast decay and the subsequent plateau to ~ 1 μs are not predicted in our model. The broken curve is the decay predicted by the model given in the text, for 10^{19} cm^{-3} defects with capture cross section twice that of the tail states, and predicts successfully the asymptotic decay curve.

defects and holes can subsequently take place, our argument given above is not affected, since it is, in principle, symmetrical in electrons and holes. However, the valence-band tail, and the defect states, are thought to be deeper than the conduction-band tail; it is therefore not unreasonable to consider holes and defect states as much more localized than band-tail electrons, and so to consider the tunneling of electrons only.

The model given here for the nonradiative recombination mechanism is undoubtedly an oversimplification, and further work is required to fully understand recombination in *a*-Si:H. In particular, Street[7] has recently shown that the dangling bond, thought to be the dominant NRR center,[2] acts as both a hole and an electron trap. Wake and Amer[8] deduce from a study of the kinetics of photoinduced absorption that the dangling bond is not an important recombination center. However, considering only the PL data, a unified picture of NRR, applicable to both sputtered and glow discharge *a*-Si:H, will probably be along the lines of the description of Collins *et al.*, as modified here for distant-pair recombination. In this connection, it is worth noting that decay curves in *gd a*-Si:H at various defect densities have been given by Tsang and Street[5]; they show the same behavior as the *sp a*-Si:H data of Collins *et al*: the form of the curve is almost independent of defect density. (This is not immediately apparent from the data, because of the choice of plot in Ref. 5, log$I$ against t, from 0–40 μs.) The principal difference in the data from Refs. 1 and 5 is in the dependence of PL efficiency on defect density; this is, however, not central to the argument of Collins *et al.* Indeed, this difference may be an effect of temperature (30 K in Ref. 5 and 77 K in Ref. 1) since data of Boulitrop[9] in sputtered samples at 15 K show the same behavior as that of Tsang and Street.[5] Consequently, we think that the model presented here is applicable generally to *a*-Si:H, based as it is primarily on the behavior of the PL decay curves.

Finally, we consider the question of the capture cross section of the defects. The argument of Collins *et al.*[1] is based on a comparison between the total density of tail states (taken as 10^{19} cm^{-3}) and the density of defects at which the NRR becomes significant (some 10^{17} cm^{-3}). It is, however, generally accepted that the carriers thermalize to their final radiative states through a large number of tail states (see Street[2]), and we have shown that the PL spectrum may be predicted successfully by the assumption that they thermalize to those tail states which do not have lower neighboring states sufficiently close that further thermalization would have a higher probability than radiative recombination. This results in thermalization to the lowest of some 50 neighboring tail states,[9] that is, to one of the lowest 2×10^{17} cm^{-3} tail states; and it is with these that the probability of capture into a defect state should be compared. From the graph given by Collins *et al.*,[1] this gives a capture cross section for the defects of only about one to two times that of the tail states.

In summary, we point out here that the asymptotic power-law dependence of the PL decay even at high defect densities requires that the densities of electrons and of centers to which the electrons can tunnel (holes and defects) must be quite accurately equal. Thus the data of Collins *et al.*[1] and of Tsang and Street[5] are consistent with a model of the nonradiative recombination mechanism in which the defect states capture holes directly, in a time $t < 10$ ns, and the subsequent nonradiative recombination occurs through tunneling of the electrons to the occupied defect states. We suggest, also, that taking into account the number of tail states through which a carrier thermalizes before it stops in a radiative state, the capture cross section of defect states may be taken as similar to that of the tail states.

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