

# Recombination Kinetics of Excitonic Molecules and Free Excitons in Intrinsic Silicon

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(Received 2 September 1969)

Time-resolved spectra and luminescence decay-time measurements prove that at 1.8°K the excitonic-molecule (EM) and free-exciton (FE) densities decay at different rates in pure silicon. The decay profile of the EM shows a postexcitation increase in luminescence followed by an approximately exponential decay with a decay time of 143 nsec. The FE decay consists of an initial transient followed by a longer nonexponential decay. These observations can be explained in detail by a pair of coupled differential equations governing the time decay of the EM and FE densities. The equations are based on the model used by Haynes to explain the EM recombination spectrum. Comparison of the theoretical and experimental decays shows that the EM decay time is 59 nsec, and the cross section at 1.8°K for the formation of an EM from two FE's is about  $2 \times 10^{-16}$  cm<sup>2</sup>. Based on these data, arguments are presented to show that the EM's decay primarily by a nonradiative Auger mechanism, which accounts for the low radiative efficiency. Thermal dissociation effects at higher temperatures can be semiquantitatively accounted for.

## I. INTRODUCTION

WITH the discovery of a new luminescence system in hyperpure silicon at low temperatures ( $\lesssim 10^\circ\text{K}$ ), Haynes<sup>1</sup> presented the first experimental evidence for the existence of the free excitonic molecule (EM). This entity, whose possible existence was predicted as early as 1958 by Lampert,<sup>2</sup> is formed by the binding together of two excitons into a free complex with small binding energy. The energies and shapes of the luminescence lines were explained by a model in which an electron and hole within the EM recombine with phonon emission, with the remaining electron and hole being ejected into the conduction and valence bands. The binding energy of the EM was deduced to be  $\leq 2$  meV, which is consistent with a value of 0.6 meV calculated later by Sharma.<sup>3</sup>

The work reported in this paper describes the measurement of the relevant luminescence decay curves at low temperatures, and interprets the kinetics of the recombination of EM's and free excitons (FE's) in terms of a pair of differential equations based on a slight modification of the above model required to take into account inherently nonradiative (Auger) recombination of EM's.

The equations contain cross-coupling terms which arise because FE's combine to form EM's and these become a source of FE's when they decay. This gives rise to an experimentally observed post-excitation increase in EM luminescence. By fitting computed FE and EM decay curves to the experimental curves, the true total EM luminescence decay time and the cross section for the formation of an EM from two FE's can be evaluated. The effects of thermal dissociation at higher temperatures can also be semiquantitatively accounted for.

## II. EXPERIMENTAL TECHNIQUES

The samples, freely suspended in the liquid helium or hydrogen refrigerants, were repetitively excited by

pulses of 300-keV electrons from a van de Graaff accelerator. The pulse length was 86 nsec with a fall time of 2.5 nsec; a maximum of  $10^{17}$  electron-hole pairs per cm<sup>3</sup> per pulse could be created in the sample. The detector was a specially selected, cooled RCA 7102 photomultiplier. The luminescence decay curves and time-resolved spectra were recorded on an X-Y recorder as described in a previous paper.<sup>4</sup> The spectral response of the spectrometer plus detector was obtained by using a calibrated light source (EGG model 590-20).

The observations reported here were taken on a 9500- $\Omega$  cm sample cut from a silicon ingot previously studied by Haynes.<sup>1</sup> Data consistent with these observations were also taken on some low-dislocation-density float zone, 10 000- $\Omega$  cm material purchased from the Wacker Chemical Corporation. The surface preparation of the silicon did not seem to affect the measured decay times. However, signals stronger by a factor of 2 or 3 were obtained when the luminescence emerged from a shiny silicon surface. Therefore, the samples were lightly etched with CP4 solution and rinsed in distilled water.

## III. RESULTS

Figure 1 shows time-resolved spectra taken at a sample temperature of 1.8°K. The time  $t=0$  coincides with the beginning of the excitation pulse. For the 86- and 186-nsec spectra, an instrumental time constant of 20 nsec was used. To improve the signal-to-noise ratio for the 586- and 886-nsec spectra, the instrumental time constant was increased to about 75 nsec. The various lines in the spectra are labeled according to the identification given by Haynes.<sup>1</sup> The rather poor spectral resolution used to obtain better signal-to-noise ratios caused the exciton line to be broadened.

The broad band peaking at  $\sim 1.06 \mu$  is believed to be bremsstrahlung radiation. This assumption is consistent with its observed decay time of  $\leq 4$  nsec. The measured position of this peak is governed by absorption of the radiation in the silicon and by use of the long wavelength

<sup>1</sup> J. R. Haynes, Phys. Rev. Letters **17**, 860 (1966).

<sup>2</sup> M. A. Lampert, Phys. Rev. Letters **1**, 450 (1958).

<sup>3</sup> R. R. Sharma, Phys. Rev. **170**, 770 (1968).

<sup>4</sup> J. D. Cuthbert and D. G. Thomas, J. Appl. Phys. **39**, 1573 (1968).

transmission filter which severely attenuates radiation shorter than about  $1.06 \mu$ .

The radiation at  $1.13 \mu$  (E) is due to free-exciton (FE) recombination with the emission of a TO phonon. At higher temperatures, other phonon replicas become visible. The lines at  $1.106 \mu$  ( $M_1$ ) and  $1.145 \mu$  ( $M_2$ ) correspond to the decay of EM's with the emission of TO and TA phonons, respectively, as described by Haynes.<sup>1</sup>

The time-resolved spectra clearly show that there is a large difference in the decay rates of the EM and FE luminescence, with the EM decaying more rapidly. The forms of the decays at various temperatures are shown in Fig. 2 for the EM and FE. Attention is drawn to the presence of a postexcitation increase in the EM luminescence, the peak of which occurs about 10 nsec after the exciting electron pulse has cut off.<sup>5</sup> The postexcitation peak is attributed to the delayed build up of the EM density by the combination of pairs of FE's into EM's. At  $1.7^\circ\text{K}$ , the EM decay time, measured in the time range  $140 \leq t \leq 500$ , is  $143 \pm 5$  nsec. Beyond this range, a slight increase in decay time is observed. At  $4.2^\circ\text{K}$ , an increase to  $155 \pm 5$  nsec occurs. Within an experimental error of  $\pm 20$  nsec, the decay times do not change when the injection level is decreased from  $10^{17}$  to  $2.5 \times 10^{16}$  electron-hole pairs per  $\text{cm}^3/\text{pulse}$ .

Within experimental error, the FE luminescence decays do not change with temperature between  $1.7$  and  $2.1^\circ\text{K}$ . They consist of a fast initial transient followed by a longer-lived nonexponential decay. Above  $2.1^\circ\text{K}$  the fast transient lengthens and merges with the longer low-level component, which itself lengthens. This increase in decay time is attributed to thermal dissociation of the EM's into FE's which decreases the net rate at which FE's disappear through the formation and recombination of EM's. The FE decay curves at  $2.5$  and  $3.0^\circ\text{K}$  are almost identical. Presumably this is caused by a small amount of sample heating by the electron beam as a result of the poorer heat transfer between the sample and the helium bath in this temperature range. There is no sign of any postexcitation increase in the FE luminescence at any temperature. Between  $14$  and  $20^\circ\text{K}$ , the FE decays are approximately exponential with a decay time of  $2.6 \mu\text{sec}$ .

At  $14$  and  $20^\circ\text{K}$ , the time-integrated spectra are almost entirely FE in content; however, the  $t = 86$  nsec time-resolved spectrum at  $14^\circ\text{K}$  clearly shows a component due to the EM with an intensity approximately equal to that of the FE spectrum. Above  $20^\circ\text{K}$ , the EM spectrum is unobservable.

The efficiency of the silicon luminescence was obtained by a substitution procedure,<sup>4</sup> using a sample of

<sup>5</sup> The post-excitation peak was found to be real and not instrumental since it was observed even when the response time of the detection system was reduced to 4 nsec. Furthermore, it was established that the usual response time of 20 nsec did not cause any significant errors in measuring the position of the post-excitation peak by examining the system response to pulsed electrical signals adjusted in shape to approximate the luminescence pulse shapes.

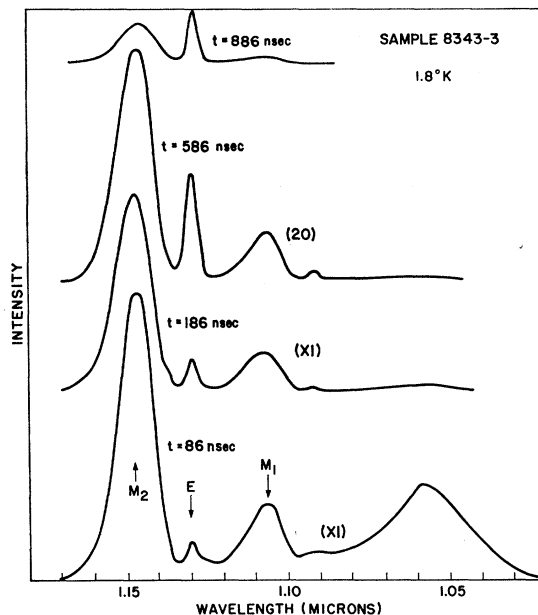


FIG. 1. Time-resolved spectra of the excitonic molecule-free exciton luminescence system in intrinsic silicon at  $1.8^\circ\text{K}$ . The zero of time is at the beginning of the 86-nsec-long excitation pulse.

bismuth-doped GaP as a luminescence standard. After corrections were made for the wavelength response of the detection system and the different band-gap values, it was found that the EM luminescence efficiency at  $1.8^\circ\text{K}$  was  $5 \times 10^{-4}$ , within a factor of 2. Approximately the same efficiency was measured at  $20^\circ\text{K}$  for the FE luminescence.

#### IV. DISCUSSION

In Haynes's model,<sup>1</sup> the decay of an EM occurs radiatively, with the total binding energy of the EM being shared between an outgoing photon and the remaining electron and hole, which are ejected into the valence and conduction bands.

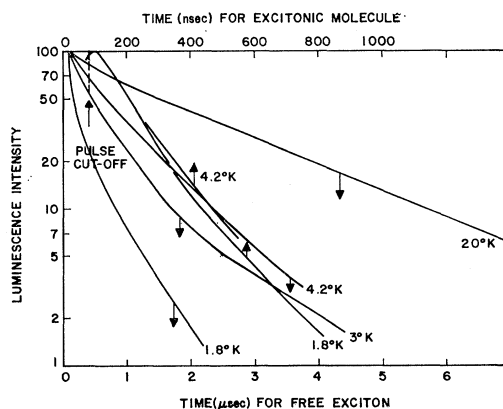


FIG. 2. Measured luminescence decay curves of the excitonic molecule and free exciton at several temperatures.

In the present analysis, the same model is used, but allowance is made for the possibility of totally non-radiative (Auger) recombinations. The FE concentration  $n$  and the EM concentration  $N$  are then governed by the following coupled differential equations<sup>6</sup>:

$$dn/dt = g - \alpha n^2 - n/\tau_{FE} + N/\tau_{EM}, \quad (1)$$

$$dN/dt = \frac{1}{2}\alpha n^2 - N/\tau_{EM}, \quad (2)$$

where  $\tau_{FE}$  and  $\tau_{EM}$  represent the combined radiative and nonradiative decay times of the FE's and EM's, respectively,  $\alpha$  is the capture coefficient governing the formation of EM's from FE's, and  $g$  is the generation rate of FE's by the electron beam and is finite for  $0 \leq t \leq 86$  nsec. It is assumed that the cross section for the direct creation of EM's is small. The term  $-\alpha n^2$  in Eq. (1) represents the loss of FE's due to the formation of EM's. Since two FE's are required to form an EM, the rate of formation in Eq. (2) is  $\frac{1}{2}\alpha n^2$ . The term  $-N/\tau_{EM}$  in Eq. (2) represents the loss by radiative and nonradiative transitions of EM's. Each of these transitions results in the liberation of a dissociated electron-hole pair. It is assumed that these particles quickly regroup into excitons with the net effect that a FE becomes available for each EM that decays. Hence the term  $+N/\tau_{EM}$  in Eq. (1).

Thermal dissociation of the EM's back into FE's at higher temperatures can be taken into account by modifying Eqs. (1) and (2), which become

$$dn/dt = g - \alpha n^2 - n/\tau_{FE} + (N/\tau_{EM}')(1 + \beta), \quad (3)$$

$$dN/dt = \frac{1}{2}\alpha n^2 - N/\tau_{EM}', \quad (4)$$

with

$$1/\tau_{EM}' = 1/\tau_{EM} + 1/\tau_{EM}^d$$

and

$$\beta = 1 - \frac{\tau_{EM}'}{\tau_{EM}} = \frac{\tau_{EM}}{\tau_{EM} + \tau_{EM}^d}, \quad (5)$$

where  $\tau_{EM}^d$  is the lifetime of the excitonic molecule against thermal dissociation.

<sup>6</sup> In these equations it is assumed that the time constant governing the formation of FE's from electron-hole pairs is small so that, in effect, excitons can be regarded as being produced directly by the electron beam. The following argument shows that this is a valid approximation at temperatures in the liquid-helium range. The equation governing the density,  $p$ , of electron-hole pairs during the exciting pulse is  $dp/dt = g - \langle\sigma_+v\rangle p^2$ , where  $\sigma_+$  is the cross section governing the capture of a free hole by a free electron. Since  $p=0$  at  $t=0$  this equation can be solved for  $p$ :

$$p = (g/\langle\sigma_+v\rangle)^{1/2} \tanh(g\langle\sigma_+v\rangle^{1/2}t).$$

Taking  $\langle\sigma_+v\rangle \approx 10^{-6}$  cm<sup>3</sup>/sec and  $g = 10^{17}/85 \times 10^{-9}$  electron-hole pairs/cm<sup>3</sup>/sec,  $\tanh(g\langle\sigma_+v\rangle^{1/2}t) \approx 1$  for  $t \gtrsim 2$  nsec. Therefore, about 2 nsec after the exciting pulse is switched on, the equilibrium value of  $p$  is  $p_{eq} \approx (g/\langle\sigma_+v\rangle)^{1/2}$  and the generation rate of excitons is  $\langle\sigma_+v\rangle p_{eq}^2 = g$ . When the generation of electron-hole pairs ceases, the  $1/e$  decay time of the electron-hole pair density is

$$\tau_{1/e} = (e-1)/(g\langle\sigma_+v\rangle)^{1/2}.$$

Substituting,  $\tau_{1/e} \approx 2$  nsec. This is consistent with lack of a post-excitation peak in the FE luminescence.

In the case of steady-state excitation,  $dn/dt = dN/dt = 0$ . The steady EM luminescence intensity is  $I_{EM} = (N/\tau_{EM})\eta_{EM}$ , where  $\eta_{EM}$  is radiative efficiency and is simply the ratio of the radiative to total recombination rates. A similar expression gives the FE luminescence intensity  $I_{FE}$ . Equations (1) and (2) then give

$$I_{EM} = \frac{1}{2}\alpha\eta_{EM}(\tau_{FE}/\eta_{FE})^2 I_{FE}^2 \quad (6)$$

and

$$g = \frac{I_{FE}}{\eta_{FE}} + \frac{1}{2}\alpha\left(\frac{\tau_{FE}}{\eta_{FE}}\right)^2 I_{FE}^2 = \frac{I_{EM}}{\eta_{EM}} + \frac{1}{\tau_{FE}}\left(\frac{2}{\alpha\eta_{EM}}\right)^{1/2} I_{EM}^{1/2}. \quad (7)$$

Equation (6) shows that  $I_{EM}$  should vary as  $(I_{FE})^x$  with  $x=2$ . Replotting Haynes's data confirms this relationship exactly at low-excitation levels. At the higher excitation levels,  $x < 2$  probably because of sample heating. Equation (7) shows that  $I_{FE}$  and  $I_{EM}^{1/2}$  do not increase linearly with generation rate.

For the present case of pulsed electron-beam excitation,  $g$  is zero except in the time interval  $0 \leq t \leq 85$  nsec. Between 1.7 and 2.1°K, the spectral and decay-time features change very little, indicating that thermal-dissociation effects are small in this range. Equations (1) and (2) are therefore applicable. The primary unknown parameters,  $\tau_{EM}$  and  $\alpha$ , were obtained by fitting computer-generated curves to the 1.8°K experimental data. A value of  $\tau_{FE} = 2.6$   $\mu$ sec was used except where noted later. This is the value of  $\tau_{FE}$  measured at 20°K where the EM population is negligibly small and therefore does not affect the FE decay time.

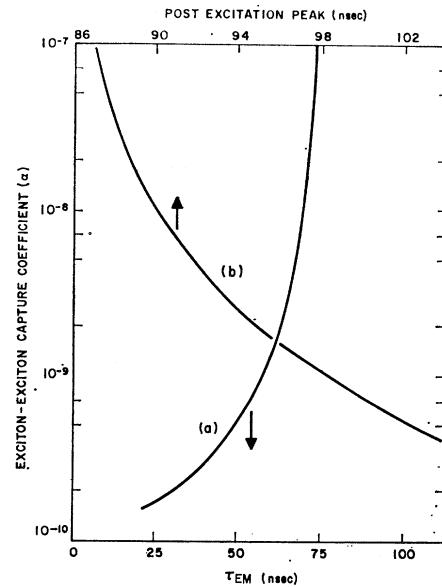


FIG. 3. Curve (a) relates the  $\alpha$  and  $\tau_{EM}$  values which together give a calculated excitonic molecule decay time of 143 nsec in the time range  $150 \lesssim t$  (nsec)  $\leq 400$ . From the corresponding calculated decay curves, the value of  $\alpha$  is plotted [curve (b)] against the calculated position in time of the post excitation peak. The calculations are based on Eqs. (1) and (2).

The value of  $\tau_{EM}$  and  $\alpha$  were obtained by the following procedure. For a wide range of  $\alpha$  values, decay profiles were synthesized which, by adjusting  $\tau_{EM}$ , agreed with the measured decay time of 143 nsec evaluated within the interval  $150 \lesssim t \leq 400$  nsec. Each value of  $\alpha$  was plotted against the value of  $\tau_{EM}$  so derived along with the position in time of the calculated postexcitation peak. The resulting plots are shown in Fig. 3. Corresponding to the position in time ( $t=96$  nsec) of the experimentally determined postexcitation peak,  $\alpha=1.5 \times 10^{-9}$  and  $\tau_{EM}=61.0$  nsec.

The shapes of the FE and the EM decays at times longer than 400 nsec are quite sensitive to the values chosen for  $\tau_{EM}$  and  $\alpha$ . Figures 4 and 5 show the over-all fit of the calculated and experimental curves for several pairs of  $\alpha$  and  $\tau_{EM}$  values near the above. Because of the rather long instrumental response time used to take the FE decays there is an estimated error of  $\pm 5\%$  in the strength of the fast initial transient. Therefore the calculated and experimental FE decay curves may be displaced vertically with respect to each other by  $\pm 5\%$ .

The experimental data are consistent with values of  $\alpha$  between 1 and  $3 \times 10^{-9}$  and  $\tau_{EM}=59 \pm 5$  nsec. As Fig. 3 shows, regardless of the value chosen for  $\alpha$ ,  $\tau_{EM} \leq 143/2 = 71$  nsec.<sup>7</sup>

Figures 6 and 7 show the effect on the computed EM and FE decay curves of varying  $\tau_{FE}$ . Clearly the decays become significantly sensitive to the value of  $\tau_{FE}$  only

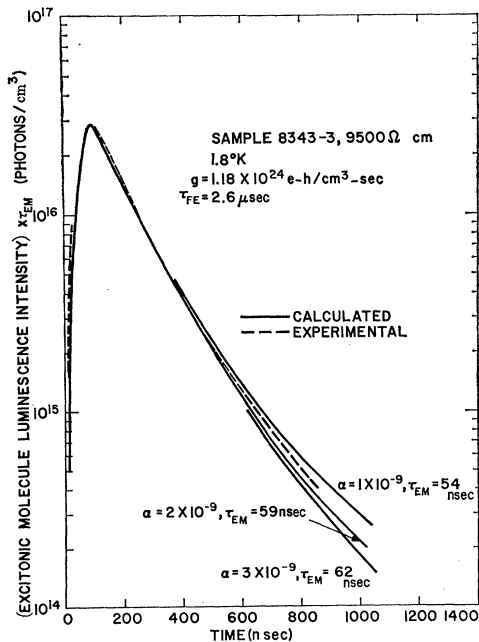


FIG. 4. Computed excitonic molecule luminescence decay curves compared to the experimental curve for 1.8°K. The  $\alpha$ ,  $\tau_{EM}$  combinations were chosen to give a good fit to the experimental curve in the range  $86 \lesssim t \leq 400$  nsec.

<sup>7</sup> This receives justification as follows. For large  $\alpha$  values,  $dn/dt \approx -\alpha n^2 + N/\tau_{EM}$ , so that  $d/(d(n+2N)) \approx 2(dN/dt) = -N/\tau_{EM}$  and the measured decay time is  $2\tau_{EM}$ .

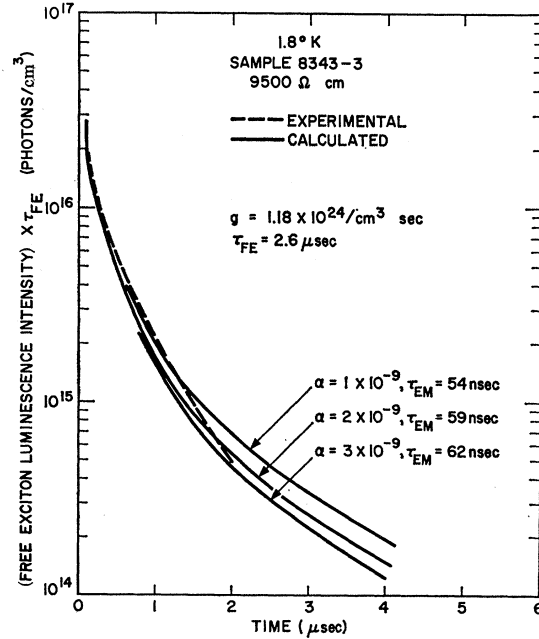


FIG. 5. Computed free-exciton luminescence decay curves compared with the experimental curve for 1.8°K. The  $\alpha$ ,  $\tau_{EM}$  combinations are the same as those used to calculate the excitonic molecule decays shown in Fig. 4.

beyond those times at which their respective intensities have declined by a factor of more than 10.

Figure 6 also shows that significant changes in the

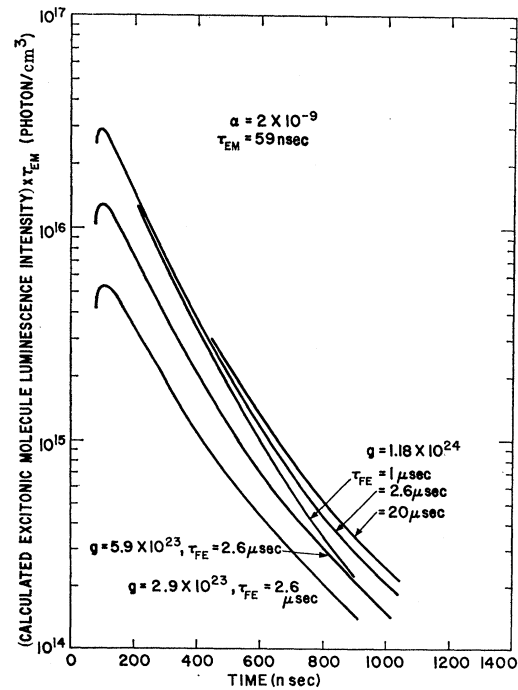


FIG. 6. Computed excitonic molecule luminescence decays which display the effects of altering  $g$ , the density of electron-hole pairs generated per pulse and  $\tau_{FE}$ , the free-exciton total decay time.

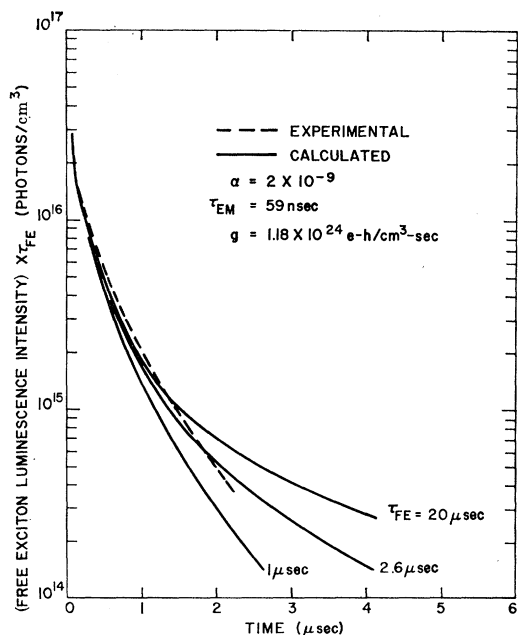


Fig. 7. Computed free-exciton luminescence decays which display the effect of changing the parameter  $\tau_{FE}$ , the free-exciton total decay time.

shape of the EM decay curve should not occur until the excitation intensity has been reduced by more than a factor of 4, in agreement with experiment.

The integrated pulse luminescence intensity of the EM at 1.8°K was found experimentally to vary as  $g^{1.3}$ . For  $\alpha = 2 \times 10^{-9}$  cm<sup>2</sup>/sec,  $\tau_{EM} = 59$  nsec, and  $\tau_{FE} = 2.6$   $\mu$ sec, the computed dependence is  $g^{1.2}$ .

The increase in the FE decay time as the temperature is raised is a consequence of the thermal dissociation of the EM and of the temperature dependence of  $\alpha$ . In the range immediately above 2.1°K, the major changes are probably the result of thermal dissociation of the EM. Assuming this, EM and FE decay curves for higher temperatures were computed from Eqs. (3), (4), and (5) for several values of the EM thermal dissociation lifetime,  $\tau_{EM}^d$ , and the results are plotted in Fig. 8. From this it is concluded that the shape of the calculated FE and EM decay curves are in reasonable agreement with the experimental curves up to about 3°K, at which temperature decreasing  $\tau_{EM}^d$  alone causes the EM decay to lengthen too much.

A very rough estimate of the binding energy  $\epsilon_b$  of the EM can be obtained from these calculations. Since  $\tau_{EM}^d \approx 59$  nsec at 2.1°K and  $\tau_{EM}^d \approx 14$  nsec at 3°K,  $\epsilon_b$  is found to be  $\approx 0.6$  meV. This is consistent with the previous experimental value of  $\epsilon_b \lesssim 2$  meV and the calculated value<sup>3</sup> of  $\epsilon_b = 0.63$  meV.

Discussion of the luminescence efficiencies of the FE and EM is prefaced by some estimates of the importance of surface recombination. Experimental values for the diffusion constants of EM's and FE's are not available for silicon. It is assumed that these diffusion constants

are not significantly larger than those estimated for electrons in silicon at low temperatures. A projected mobility<sup>8</sup> at 20 and 1.8°K of 20 000 cm<sup>2</sup>/V sec yields diffusion constants of 34 and 3.1 cm<sup>2</sup>/sec. The diffusion length at 1.8°K of an EM whose lifetime against recombination is 59 nsec, is  $4 \times 10^{-3}$  compared to a penetration depth of about  $25 \times 10^{-3}$  cm for the exciting electrons. Therefore, in the time, temperature, and excitation ranges where the excitonic molecule decay governs the population of FE's and EM's, it is probably safe to conclude that the effects of the surface are small for excitation by fast electrons.

The experimental lifetime against decay for the FE at 20°K is 2.6  $\mu$ sec at an injection level of  $10^{17}$  e-h pairs per cm<sup>3</sup> per pulse. The calculated diffusion length is  $9 \times 10^{-3}$  cm. If the FE lifetime is shortened because of surface recombination, this diffusion length is an underestimate.

However, experiments in which the EM luminescence (at  $\sim 7^\circ$ K) and FE luminescence (at  $\sim 20^\circ$ K) were stimulated with pulses of 15 keV electrons (with a penetration depth in silicon of a few microns), gave decay times very close to those reported earlier in this section when the bombarded face was appropriately etched. When the bombarded surface was deliberately roughened, the EM luminescence decay time was unaffected

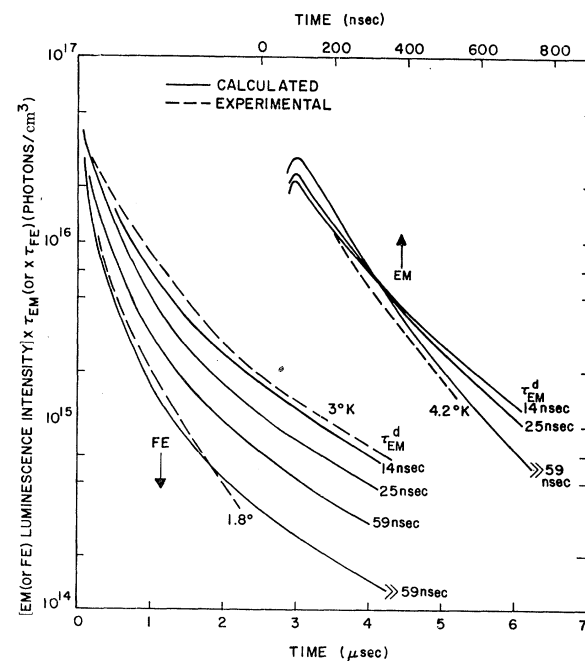


Fig. 8. Computed excitonic molecule and free-exciton luminescence decay curves compared with the experimental curves when thermal ionization of the excitonic molecule is allowed for at the higher temperatures. The calculations are based on Eqs. (5)–(7).  $\tau_{EM}^d$  is the lifetime against thermal dissociation. Thermal dissociation effects are negligible when  $\tau_{EM}^d \gg \tau_{EM}$ , but become important when  $\tau_{EM}^d \leq \tau_{EM}$ , and show up principally as a lengthening of the free-exciton luminescence decay.

<sup>8</sup> F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).

while the FE luminescence decay time (at 20°K) was reduced by approximately 50%. This evidence<sup>9</sup> supports the conclusion that the effects of surface recombination are not serious when highly penetrating 300-keV electrons are used to excite the luminescence. The rapid decay and low efficiency of the EM luminescence at 1.8°K therefore appear to be properties of the bulk material.

The purely radiative decay time of an exciton bound in an EM should not be too different from that of an FE because of the very weak bonding between the constituent excitons. In fact, the analyses of the energetics and kinetics of the transition giving rise to the EM spectrum are predicted on the present model of a loosely structured molecule composed of two excitons, each retaining most of its individual characteristics. At 1.8°K the radiative decay time of an FE is estimated at about 200  $\mu$ sec.<sup>10</sup> The very rapid decay of the EM (59 nsec) in comparison to this is attributed to a nonradiative, four-particle Auger process in which the recombination energy released in the decay of one of the EM's component excitons is given to the electron and hole of the remaining exciton. This is analogous to Auger recombination of bound excitons decaying at neutral donors in silicon.<sup>11</sup>

In the latter process, the energy is given primarily to the Auger electron, since the positive particle is the massive donor atom. Within experimental error the radiative efficiency was found to be just the ratio of the measured luminescence decay time to that calculated from absorption data using detailed balance theory.

In the present work, no absorption cross sections for the EM are available with which to calculate the optical decay time of EM. With the tenuous justification given above the best available estimate is  $\approx 200 \mu$ sec, so that the ratio of the measured luminescence decay time (59 nsec) to the optical decay time (200  $\mu$ sec) is  $3 \times 10^{-4}$ . This is close to the measured luminescence efficiency of  $5 \times 10^{-4}$ , and supports the Auger recombination model.

<sup>9</sup> A full report on this work will appear in a future publication.

<sup>10</sup> A value of 60  $\mu$ sec for the FE optical decay time at temperatures higher than 1.8°K was estimated by J. R. Haynes, M. Lax and W. F. Flood [in *Proceedings of the International Conference on Semiconductor Physics Prague, 1960* (Academic Press Inc., New York, 1961), p. 423], using emission and absorption data along with the principle of detailed balance. Recently a 1.8-meV valley-orbit splitting of the FE state has been discovered by P. J. Dean, Y. Yafet, and J. R. Haynes (to be published). Because of the prominence of transitions from the lowest exciton state, an increase in the FE lifetime by a factor of about 3 is expected at 1.8°K.

<sup>11</sup> D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, *Phys. Rev. Letters* **17**, V552(C) (1966).

## V. SUMMARY

Time-resolved spectra and luminescence-decay time measurements prove that at low temperatures the EM and FE populations decay at different rates in pure silicon. The decay profile of the EM shows a post-excitation increase in luminescence followed by an approximately exponential decay with decay time of 143 nsec. The FE decay consists of an initial transient followed by a longer nonexponential decay. These observations can be explained in detail by a pair of coupled differential equations governing the time decay of the EM and FE densities. The equations, which assume thermal equilibrium and no thermal dissociation at 1.8°K, are based on the model Haynes used to explain the principal low-temperature spectral features. By calculating the luminescence profiles of the EM and FE and fitting them to the experimental profiles, it is concluded that  $\tau_{EM} = 59 \pm 5$  nsec, and  $1 \times 10^{-9} \lesssim \alpha \lesssim 3 \times 10^{-9}$ .

Assuming equipartition of energy, the cross section  $\sigma$  for the formation of an EM from two FE's at 1.8°K lies in the range  $1 \times 10^{-15} \lesssim \sigma (\text{cm}^2) \lesssim 3 \times 10^{-15}$ . This is less than 1/100 of the geometrical cross section of a FE in its ground state and is interpreted to mean that only 1% of the FE-FE encounters result in the formation of an EM at 1.8°K. This low probability is caused by the small acoustic phonon population available to carry away the small binding energy ( $\leq 2$  meV) appearing upon the formation of an EM.

The low efficiency ( $5 \times 10^{-4}$ ) of the EM luminescence at 1.8°K is postulated as being due to a preponderance of totally nonradiative transitions over the radiative transitions. In the nonradiative transitions the total recombination energy is shared between the remaining electron-hole pair forming the excitonic molecule. Support for this view is gained from a comparison of the ratio of the EM lifetime (59 nsec) to the estimated EM radiative lifetime (200  $\mu$ sec), which is equal to the luminescence efficiency within experimental error.

At higher temperatures the decay of the FE lengthens and grows in intensity. The corresponding changes occurring in the EM decay are rather minor up to 4.2°K. By suitably modifying the equations to take into account thermal dissociation of the EM, the changes occurring up to about 3°K can be predicted. At higher temperatures, the effects of the temperature dependence of  $\alpha$  appear to be significant.

## ACKNOWLEDGMENTS

It is a pleasure to thank D. K. Wilson and R. R. Holmes for several profitable discussions, and P. J. Dean for prompting the author to attempt this research.