SERI/PR 9079-1-T1

TECHNICAL PROGRESS REPORT
"STRUCTURAL AND ELECTRONIC STUDIES OF DEFECTS
IN AMORPHOUS SILICON"

RECEIVED BY TIC JUL 22 1980

report no. 1

contract no. XJ-0-9079-1

Report Period: March - May, 1980

Contractor: Xerox Corporation

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Overview

The various research projects performed during this quarter are summarized as follows.

1)NMR

We have collaborated with J. Reimer of Cal. Tech. in measurements of proton NMR to study the influence of annealing on the hydrogen environments of a-Si:H films. It was found that hydrogen diffuses internally before major evolution occurs, and that there is motion of hydrogen from a heavily clustered phase to a dilute phase coincident with hydrogen evolution (see Appendix 1 for details).

(2)Luminescence

Measurements of the excitation intensity dependence of the luminescence has shown that at low temperatures Auger recombination is an important non-radiative mechanism and is responsible for the increase in luminescence efficiency often observed between 10K and 50K. At higher temperatures the experiments demonstrate that the predominant non-radiative mechanism is the ionization of electron-hole pairs followed by capture at dangling bands (see Appendix 2 for details).

(3)Structural Modifications

a-Si:H samples have been deposited from SiH_4 diluted in the various inert gasses He, Ne, Ar and Kr. The structural and electronic properties of the resulting films vary in a systematic way. In particular there is an increase in the extent of columnar growth which is undetectable in films deposited from pure SiH_4 , and most pronounced in the Kr-deposited samples. The electronic properties as observed by ESR and luminescence measurements also deteriorate with the heavier rare gasses. Kr-deposited material is

also very prone to post-deposition oxidation because of the porous nature of the columnar structure.

(4)Drift Mobility

Time-of-flight drift mobility apparatus has been established. The apparatus is now operational and preliminary measurements are being made.

(5)Doping and Compensation

The effects of doping and compensation on the luminescence, ESR and conductivity are being investigated. We find that doping introduces defect states that are observed in ESR and which quench the band-to-band luminescence. To a limited extent compensation reduces the defect density and restores the luminescence efficiency. However, compensation apparently introduces states above the valence band edge which tends to lower the energy of the dominant luminescence transition.

PROTON NMR STUDIES OF ANNEALED PLASMA-DEPOSITED
AMORPHOUS Si:H FILMS

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Abstract

Proton magnetic resonance data are presented for plasma-deposited amorphous Si:H as a function of annealing temperature up to 650°C. The data indicate that hydrogen diffuses internally before major evolution occurs, that transfer of hydrogen occurs from a heavily clustered phase to a dilute phase coincident with evolution and that evolution occurs initially from the heavily clustered phase. Comparison with infrared data indicates that the heavily clustered phase can be either SiH_x (x = 2,3) or SiH.

*deceased

It has recently been established⁽¹⁾ that proton magnetic resonance data reveal unique information on the degree of clustering or intermingling of local hydrogen environments in amorphous silicon-hydrogen films. Specifically, there is two-phase compositional behavior of the hydrogen with the two phases differing in their local density of hydrogen, the more dilute containing hydrogen only in monohydride SiH configurations. It has also been shown that annealing of a-Si:H films in the temperature range 100°C - 650°C results in changes in paramagnetic defect densities and evolution of hydrogen accompanied by changes in the Si-H vibrational spectra.^(2,3) It is the purpose of this letter to report proton magnetic resonance data from similarly annealed samples that indicate: (1) that hydrogen diffusion occurs in the dilute phase coincident with the paramagnetic center density reduction, (2) that hydrogen transfer from the heavily clustered to the dilute phase occurs at the onset of evolution, and (3) that evolution at low (<400°C) temperatures occurs exclusively from the heavily clustered phase independent of the species identified from vibrational spectroscopy as being reduced in density by annealing.

The samples were prepared in an rf-diode deposition system⁽⁴⁾ and the proton NMR data taken with a solid state pulse Fourier transform spectrometer operating at 56.4 MHz (1.3 Tesla).⁽⁵⁾ The NMR spectra were obtained by Fourier transformation of the free induction decay following a 90° pulse. Signal averaging was required in all samples with the number of acquisitions varying from 128 to 1024 averages depending on the hydrogen content of the sample. Care was taken

to allow full spin-lattice relaxation between acquisitions so that accurate spin counts

could be obtained.

We have studied proton resonance in annealed samples deposited under a wide range of conditions. Since we find that the behavior is qualitatively similar in all samples studied, we describe here data from one sample that best illustrates all the features observed. This sample was deposited under the following conditions: 5% silane in argon, 18 watts net rf power into matching network, $\sim 25^{\circ}\text{C}$ substrate temperature and a negative DC self-bias of ~ 220 volts. The sample was deposited into ~ 2 -inch diameter aluminum foil with a thickness of $\sim 50\ \mu$ which resulted in ~ 0.1 g of material after removal of the substrate with a dilute acid etch. The sample was then placed in a quartz NMR tube and isochronally annealed at various temperatures under flowing nitrogen for 20 minutes. The NMR data were taken after allowing the sample to cool to room temperature subsequent to each 50°C increase in annealing temperature. All spectra were found to be temperature independent down to 80°K as well as field independent. The two-component NMR spectra were least squares fitted assuming the broad component to be Gaussian and the narrow component Lorentzian.⁽⁶⁾ The resulting excellent fits, as exemplified in Fig. 1, gave values for linewidth and relative areas of the two components. The errors are estimated from the reproducibility of the fits resulting from different starting parameters. Figure 2 shows the atom % hydrogen in the film as a function of annealing temperature and Fig. 3 shows how the full width at half maximum (FWHM) changes for the two components. Note that up to 600°C anneal the two-phase compositional behavior is still observable.

It is useful to consider the data in Figs. 2 and 3 in order of increasing annealing temperature. The first apparent change in these data appears at 150°C when there is a slight loss of hydrogen from the highly clustered (broad component) phase. Infrared and hydrogen evolution data has shown⁽³⁾ that in this temperature region, broad component room temperature deposited samples with SiH_3 sites evolve hydrogen. The NMR data in this region is consistent with this explanation although the hydrogen loss is too small to readily detect.

be detected in the IR in this particular sample. The second change is in the linewidth of the narrow component. While the hydrogen content associated with this line is roughly constant or even increasing up to 400°C, Fig. 3 shows a large reduction in the FWHM of the narrow component between 200°C and 400°C. The dipolar contribution to the FWHM is given by:⁽⁷⁾

$$\text{FWHM} = 3.36 \sqrt{M_2} = 3.36 (3/5 \gamma^4 \hbar^2 I(I+1) \sum r_{ij}^{-6})^{1/2},$$

where I is the nuclear spin, $1/2$ for protons, γ is the nuclear gyromagnetic ratio, and $\sum r_{ij}^{-6}$ is the lattice sum of internuclear distances. It is thus seen that the FWHM is proportional to the density of protons. The dipolar contribution to the FWHM of the narrow component is readily obtained from the observed FWHM since the only other contribution to the FWHM is from the proton chemical shift which is known from previous multiple pulse studies.⁽¹⁾ Figure 4 shows that the density change given by the dipolar contribution to the FWHM for the narrow component is an activated process with an activation energy of 0.31 eV. This density change is not due to hydrogen evolution since the atom % hydrogen does not decrease in this temperature range. We conclude then that the 0.31 eV activation energy corresponds to hydrogen diffusion to a less clustered state, which, from Eq. (1), is found to correspond to a homogeneous dilute distribution of monohydride species. It is interesting to note that this diffusion coincides with the reduction of the electron spin density,⁽³⁾ suggesting that hydrogen diffusion to defects is indeed the mechanism by which the spin density is reduced.

Above 300°C inspection of Figs. 2 and 3 show continuous hydrogen evolution from the highly clustered environment. From 300°C to 400°C the loss of hydrogen from this environment results both in evolution from the film and an increase in the total amount of hydrogen in the dilute environment. This increase could occur

neither by an increase in the volume occupied by this phase due to spatially inhomogeneous evolution from the highly-clustered environment or by diffusion of protons between the two environments. Although there is insufficient evidence to distinguish between these alternatives at present, the former would require not only a reduction in proton concentration but also the creation of a barrier or barriers to spin communication with the remaining highly-clustered protons and the opening of pathways for spin diffusion to the dilute phase. We therefore suggest that straightforward proton transfer is a more likely mechanism, particularly since diffusion is already occurring within the dilute phase. Inspection of Fig. 3 shows the effect of the hydrogen evolution on the FWHM of the broad component: above 400°C the loss of hydrogen causes the dipolar linewidth to reduce drastically. The corresponding changes after annealing in the SiH vibrational spectra for a similar sample indicate that the evolution below 400°C occurs exclusively from the environment which has a Si-H stretch frequency of 2000 cm^{-1} . This frequency is universally associated with SiH monohydride groups.^(7,8) In other samples we observe that this same temperature regime corresponds to evolution from environments with SiH mode frequencies of 2100, 890, and 845, a combination associated with $(\text{SiH}_2)_n$ groups.⁽⁸⁾ These results confirm the earlier indication⁽¹⁾ that the heavily clustered environment identified by NMR can arise from clustering of monohydride groups as well as dihydride, trihydride, etc. Finally, above 450°C hydrogen evolves from both environments until, at temperatures greater than 650°C, the two-phase behavior disappears and ~1 atom % of hydrogen remains in a dilute homogeneous phase.

In conclusion, we have shown the annealing behavior of the two phases of hydrogen in plasma-deposited amorphous Si:H to be different. The low hydrogen-density phase disperses to a homogeneous dilute bath of protons at annealing temperatures up to 400°C with an activation energy of 0.31 eV. After a slight loss

due to evolution from SiH_3 sites, the highly clustered phase evolves hydrogen above annealing temperatures of 300°C . Above 450°C both phases evolve hydrogen, until at 650°C , the clustered phase can no longer be identified and a single dilute phase containing ~ 1 atom % hydrogen is left. Of particular significance, is that the dispersion of hydrogen to a homogeneous dilute bath coincides with the paramagnetic center reduction observed previously⁽³⁾ and that monohydride clustering, presumably on internal surfaces, is clearly present in some films.

The authors wish to acknowledge the expert assistance of R. A. Lujan in sample preparation, and helpful discussions with S. I. Chan. This work was supported by the National Science Foundation under Grant No. DMR-77-21394, and by the Solar Energy Research Institute under Contract No. XJ-0-9079-1.

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FIGURE CAPTIONS

Figure 1. Experimental spectra with Gaussian and Lorentzian fits showing the quality of the fits. On the left is the spectra of the sample shown in Fig. 1 as deposited; on the right is the same sample annealed to 400°C.

Figure 2. Atom % hydrogen for high and low density hydrogen phases in a sample deposited at room temperature from 5% SiH₄/Ar onto a cathode substrate. T_{anneal} refers to the temperature the sample was annealed to.

Figure 3. The full width a half maximum (FWHM) for both high and low density phases of hydrogen in the sample shown in Fig. 1. Note the two different scales for the two components.

Figure 4. Activation process of the reduction in dipolar linewidth of the low density phase.

RECOMBINATION IN a-Si:H; AUGER EFFECTS AND NON-GEMINATE RECOMBINATION*

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ABSTRACT

Excitation intensity effects in the luminescence of plasma deposited a-Si:H are described. At low temperatures ($< 50\text{K}$) the luminescence quantum efficiency decreases at high excitation levels, and the results are interpreted as indicating Auger recombination of neighboring geminate electron-hole pairs. At high temperatures ($> 50\text{K}$) the quantum efficiency increases with excitation intensity, particularly in samples of low spin density. This result is attributed to the onset of bimolecular, non-geminate, radiative recombination. Analysis of the rate equations shows that the primary non-radiative process in a-Si:H involves capture of free carriers at singly occupied dangling bond defects. Estimates of the recombination rates are obtained.

INTRODUCTION

The low temperature luminescence of undoped a-Si:H is dominated by a broad transition with its peak at 1.3-1.4 eV which is attributed to recombination of electrons and holes at the band edges.¹⁻⁶ Studies of the time decay of luminescence have been very informative in determining the details of the recombination kinetics.⁷ A model has been developed in which the recombination is by radiative tunnelling of carriers in localized band tail states. Recombination is geminate at low excitation intensities, becoming non-geminate when the electron-hole pair density exceeds about $2 \times 10^{18} \text{ cm}^{-3}$. This change of mechanism is attributed to the overlap of adjacent pairs. At elevated temperatures, the average decay time decreases and an asymptotic $t^{-3/2}$ decay of the luminescence intensity is observed.⁸ This result is attributed to the thermally activated diffusion apart of the electron-hole pair. Accompanying this separation is a temperature dependent quenching of the luminescence intensity. The activation energy for this process ranges between 0.07 and 0.23 eV in different measurements,^{1,4,6,7} but the universal interpretation is that the activated process is the ionization of the electron-hole pair. This interpretation of the luminescence implies that ionized carriers recombine non-radiatively. In this paper we report on the temperature-dependence and excitation intensity-dependence of the luminescence, and show that the non-radiative recombination occurs predominately by capture at dangling bond defects. However if the dangling bond density is sufficiently low the free carriers can recombine radiatively by a non-geminate process.

The presence of dangling bonds is also known to reduce the low temperature quantum efficiency.⁹ The explanation given is that electrons tunnel from the

band tail into a nearby defect. We show that the temperature dependence of the luminescence is altered by the dangling bonds, and that the changes are in agreement with the tunnelling model.

The temperature dependence of luminescence between 0 and 50K has been a puzzling feature in the past. Some studies find the unusual property of an increase in quantum efficiency with temperature,^{3,6,7} while other data find this effect to be absent.^{1,4} Paesler and Paul⁶ report that the increase is largest in samples of high luminescence efficiency. The effect is accompanied by a decrease in the mean radiative decay time, attributed, in this temperature range, to the diffusion of the electron hole pair towards each other.⁷ However the change of luminescence intensity requires a competing non-radiative mechanism, the origin of which was unknown. The experiments described here show that this non-radiative process disappears at low excitation intensities, and therefore we attribute the effect to the Auger recombination of neighboring geminate pairs.

2. EXPERIMENTAL RESULTS

The method of preparing a-Si:H, and the techniques used for measuring luminescence have been described elsewhere.^{7,9} Suitable choice of deposition conditions results in samples with a spin density varying from $3 \times 10^{15} \text{ cm}^{-3}$ to above 10^{18} cm^{-3} . At low temperature and low excitation intensity, a substantial fraction of the total luminescence decay occurs at time constants larger than 1 msec. Therefore to avoid any possibility of signal roll-off due to modulation of the excitation light at too high frequency, all the data reported here use unmodulated excitation, and an S-1 photomultiplier in the photon counting mode for detection. Roll-off effects may have contributed to the magnitude of the low temperature change in intensity reported

previously.⁷ The photomultiplier also provided the large signal-to-noise required in measurements of the intensity dependence. The discussion of the data is divided into the low temperature (0-50K) and high temperature (>50K) regions. As is more apparent from the discussion, this distinction corresponds to whether or not thermally activated ionization of the electron hole pair occurs.

2.1 Low Temperature (<50K)

Figure 1 shows examples of the temperature dependence of the luminescence intensity for various excitation intensities. This sample has the lowest measured dangling bond density of any of our samples (spin density $\sim 3 \times 10^{15} \text{ cm}^{-3}$) and a high luminescence efficiency. The measurements are made near the peak of the luminescence spectrum. There is a small shift of the peak energy with temperature.⁷ However the shift is independent of the excitation intensity, so that the data in Fig. 1 are directly comparable. It is found that the increase of luminescence intensity I_L is largest at the highest excitation power, but is virtually absent at low power. The absorption depth at 1.915 eV is about an order of magnitude larger than at 2.41 eV, and the change in I_L is smaller. In the limit of low excitation intensity, we observe an increase in I_L with temperature of about 2%. This change can be accounted for, within experimental uncertainty, by the temperature dependent shift in energy of the luminescence spectrum, which changes the intensity at the wavelength of the measurement. Thus we conclude that the increase in I_L is completely absent at the lowest excitation intensity.

Figure 2 shows the relative temperature dependence of the ratio of I_L measured at high power (1 mW) and low power (0.01 mW) for the sample of Fig. 1, and for another sample with a spin density of $3 \times 10^{17} \text{ cm}^{-3}$ which has a

low temperature luminescence efficiency reduced by about an order of magnitude. The lower efficiency sample has a smaller change in I_L by about a factor of five. These results agree with the more extensive observations of Paesler and Paul,^{6,10} and also seem to account for the differing observations of others. For example Austin et al.⁴ report no low temperature change of I_L despite using samples of low defect density. However their excitation source is a Xenon lamp and monochromator, and therefore it seems likely that the excitation intensity is sufficiently low that the change in I_L is negligible.

2.2 High Temperatures (>50K)

We next describe results at temperatures above 50K when ionization of electron-hole pairs is important. Figure 3 shows the temperature dependence of the luminescence intensity between 70K and 250K for two different excitation powers (1 mW and 0.01 mW), and samples of differing spin density. The data are normalized to the maximum quantum efficiency of the brightest sample. The data are again measured near the peak of the low temperature spectrum, and are not corrected for the temperature shift of the peak. The shift is substantial at high temperature⁷ and introduces quite large errors in the absolute intensity. However to a good approximation the shift of the peak is independent of excitation intensity and sample, so that the various sets of data can again be directly compared. For the purpose of this paper we are only interested in relative changes, not in the absolute magnitudes. Two effects can be seen in Fig. 3. As the spin density of the sample increases, the low temperature efficiency decreases, as was known from previous data.⁹ However the thermal quenching is also reduced, so that at about 200K, the intensities of the different samples converge. Evidently the presence of dangling bonds changes the temperature dependence. The second effect is

that the form of the temperature dependence is intensity dependent. This effect is particularly strong in the low spin density sample. Above $\sim 150\text{K}$ the quantum efficiency is nearly an order of magnitude larger when the higher excitation intensity is used. As the spin density increases the effect of excitation intensity decreases. Note that this effect is different from the low temperature behavior, in that it is larger and of the opposite sign. At about 50K the efficiency is virtually independent of intensity, over the range investigated..

The intensity dependence of the quantum efficiency, and its dependence on spin density are seen in more detail in Fig. 4. This shows examples of the change of luminescence efficiency at 170K with incident excitation intensity G , for different samples. The relative quantum efficiency $Y_L = I_L/G$ is plotted versus the excitation intensity G . In general Y_L is constant at the lowest values of G , above which it increases, and eventually goes through a maximum. At the highest excitation intensities there is some sample heating, which reduces I_L because of the strong temperature dependence at 170K . This effect is minimized by measuring the luminescence in the first 100 msec of illumination. By comparing the calculated total temperature rise expected from the thermal properties of the sample substrate, with the observed decrease of luminescence intensity with time after illumination, we estimate that at the highest intensity, Y_L is underestimated by no more than $\sim 20\%$. Thus the flattening off of Y_L at high G in Fig. 4 is apparently a real effect, although the decrease above 10^2 mW/cm^2 may be an artifact due to the temperature rise.

Figure 4 confirms that the relative increase of Y_L is largest in samples with the smallest spin density N_s , and that the effect decreases steadily as N_s

increases. We can define the enhancement of the quantum efficiency as $Y_{\max}/Y_0 - 1$ where $Y_{\max}$ and Y_0 are the efficiencies at the peak and at the low intensity limit. We find that this parameter varies by about three orders of magnitude for undoped samples with spin densities ranging from 3×10^{15} up to $7 \times 10^{17} \text{ cm}^{-3}$.

3. DISCUSSION

There are three specific features of the data which are discussed separately. These are the low temperature (0-50K) increase in I_L which depends on excitation intensity; the effect of spin density on the temperature dependence at low excitation intensity; and the intensity-dependence and spin density-dependence of Y_L in the high temperature region.

3.1 Low Temperature Properties

Figure 1 shows that at sufficiently low excitation intensity, I_L is constant up to 30-40K, above which I_L decreases. At high intensity I_L increases by up to 30%, reaching a peak at about 50K. The measurements at different excitation wavelengths (giving different absorption depths) indicate that the excitation density rather than incident power is the important variable. Note however that the excitation density decreases exponentially into the sample, so that all the effects observed correspond to the appropriate average. A qualitative interpretation of the data is obtained by assuming that there is an intensity dependent non-radiative process with rate $P_{NR}(G)$. Thus the luminescence efficiency is given by

$$Y_L = P_R / (P_R + P_{NR}(G) + P_{NR}(T)) \quad (1)$$

where P_R is the radiative rate, and $P_{NR}(T)$ is the temperature dependent non-radiative rate attributed to ionization of the electron-hole pair. The real

experimental situation corresponds to an appropriate site average of Eq. 1 for the distribution in the various rates. From the measurements at low G , it is evident that $P_{NR}(T)$ is negligible below 50K, and so will be ignored in this discussion. It is known that P_R increases with temperature for reasons discussed elsewhere.^{7,8} Thus Y_L will generally be temperature dependent even if $P_{NR}(T)$ is negligible. Of course if $P_{NR}(G)$ is also negligible, Y_L is constant (equal to unity) and this corresponds to the low intensity limit. When $P_{NR}(G)$ is comparable with P_R , the temperature-dependent increase in P_R causes Y_L to increase with temperature, as observed. In Fig. 2 the data are fitted to Eq. 1 using measured average values of P_R ¹¹ and a value of $P_{NR}(G)/P_R(o)$ which is independent of temperature, where $P_R(o)$ is the low temperature value of P_R . Evidently Eq. 1 gives a reasonable description of the data. The deviation at high temperature for the low spin density sample is caused by the high temperature mechanism discussed in §3.3. The dependence on spin density can be understood in the following way. According to previous models^{9,12} the dangling bonds act as a rapid sink for electron-hole pairs excited within about 100Å of the defect. Their effect is therefore to reduce the population of electron hole pairs. Thus the radiative component of the decay is equivalent to that occurring in a sample of low spin density and lower excitation intensity. From this discussion we conclude that the low temperature behavior is determined by a non-radiative process whose rate increases with the density of optically excited electron-hole pairs.

We believe that this process is Auger recombination. We rule out reabsorption which is the only other possible mechanism that we are aware of. For the absorption depth of $\sim 1000\text{\AA}$, an unreasonably large induced absorption coefficient of $\sim 10^5 \text{ cm}^{-1}$ at the luminescence energy would be required. The Auger process has already been suggested by Rehm and

Fischer¹³ to account for a bimolecular non-radiative recombination process which they observe in time-resolved measurements at high intensities. Since Auger recombination requires an additional carrier, the process is expected to be significant only when the geminate photo-generated electron-hole pairs overlap. Previous measurements⁷ show that this occurs above an incident intensity of $\sim 3 \text{ mW/cm}^2$, for excitation at 2.4 eV, which corresponds to a laser power of $\sim 0.1 \text{ mW}$. (The unfocussed laser spot has a diameter of $\sim 2 \text{ mm}$). The onset of the effect in Fig. 1 at about this intensity therefore supports the Auger model.

Figure 5 shows a schematic diagram of the Auger process. There are several different possible processes involving the two neighboring pairs, of which only two are shown. Various Auger processes are known to occur in semiconductors, with transition rates that are large enough to dominate over radiative recombination. One example involving three localized carriers is the neutral donor or acceptor bound exciton. The Auger process for this complex was first identified in GaP.¹⁴ The Auger transition rate of $10^7 - 10^8 \text{ sec}^{-1}$ is about a factor 10^3 larger than the radiative rate. In the present situation the Auger rate will be much reduced by an overlap factor because the three particles are localized at different sites. Nevertheless, since rates of only $\sim 10^3 \text{ sec}^{-1}$ are required to explain the data, the mechanism is clearly plausible. Although there have been many calculations of the Auger rate for different physical situations,¹⁴ none applies well to the present case. As an illustration, the Auger rate of the exciton bound to a neutral acceptor varies as approximately the 5th power of the acceptor binding energy.¹⁶ This relation comes from the momentum conservation requirement so that the rate depends on the portion of the Brillouin zone which contributes to the effective mass acceptor wavefunction. In an amorphous semiconductor the

momentum conservation requirement is generally assumed to be relaxed. This presumably weakens the dependence on binding energy and may result in a relative enhancement of the Auger rates. A detailed calculation for an amorphous semiconductor would be very valuable.

Further analysis of the recombination does not seem justified at this stage because of the lack of knowledge of the Auger rate. The problem is also complicated by the random distribution both of photoexcited pairs, and of the electron-hole separation within a pair, and by the possibility of non-geminate radiative transitions. We believe that the bimolecular recombination studied previously by Tsang and Street⁷ is largely radiative as they assumed. If the Auger process were the only bimolecular mechanism, then the quantum efficiency should decrease more than the 30% observed in the data of Fig. 1. One simple argument can be made concerning this point. We assume that the electron Bohr radius is larger than that of the hole, and that wavefunction overlap is the determining factor in which type of transition dominates. Then one might expect that a four-particle configuration (two neighboring pairs) in which the electron-electron separation is less than the smallest electron-hole separation would favor Auger recombination, and if the reverse is true, radiative recombination would dominate. This argument predicts a maximum Auger contribution of ~50%, which is consistent with the observations.

3.2 The Temperature Dependence in the Low Intensity Limit

At sufficiently low excitation intensities, recombination is expected to be geminate. The lowest intensities used for the data of Fig. 4 corresponds to an estimated photoexcited pair density of $10^{14} - 10^{15} \text{ cm}^{-3}$ at ~50K, decreasing rapidly at higher temperature. The mean separation of pairs is therefore ~1000Å or greater and a geminate process is certainly indicated.

This section is concerned with the effect of dangling bonds with spin density N_s on the temperature dependence. As shown elsewhere,⁹ the low temperature quantum efficiency decreases when N_s is greater than $\sim 10^{17} \text{ cm}^{-3}$. A non-radiative process was proposed in which the electron tunnelled to the dangling bond. For a random distribution of defects, the low temperature quantum efficiency Y_L is given by¹²

$$Y_L = \exp(-4\pi R_c^3 N_s / 3) \quad (2)$$

with

$$R_c = (1/2) R_0 \ln(\omega_0 / P_R), \quad (3)$$

where R_0 is the electron Bohr radius, P_R is the average radiative rate, and ω_0 is the pre-exponential in the expression for the tunnelling rate, taken here to be 10^{12} sec^{-1} . These expressions can be adapted to apply at high temperature by allowing for an additional non-radiative process corresponding to the ionization of the pair. For the sake of simplicity it is assumed that P_R and the non-radiative tunnelling rate are independent of temperature, while the ionization rate P_I is temperature dependent. Eqs. 2 and 3 then become

$$Y_L = [P_R / (P_R + P_I)] \exp(-4\pi R_c^3 N_s / 3) \quad (4)$$

with

$$R_c = (1/2) R_0 \ln(\omega_0 / (P_R + P_I)) \quad (5)$$

In Fig. 6, Y_L is plotted versus N_s for various values of P_I corresponding to an increase of temperature. We assume average values of $P_R = 10^3 \text{ sec}^{-1}$ and $R_0 = 11 \text{ \AA}$ as indicated by experiment.^{7,9} In Fig. 6 it can be seen that as P_I increases the dependence of Y_L on N_s gets weaker. The reason is that the

reduced lifetime of the pair due to the ionization process leaves less time available for tunnelling to the defect. The temperature dependence of Y_L in different samples corresponds to vertical cuts in Fig. 6. Thus samples with a large N_s have a comparatively weak temperature dependence until a sufficiently high temperature is reached, above which Y_L is practically independent of N_s . This behavior is observed in Fig. 3 and therefore these results provide good confirmation of the tunnelling model. Note that our analysis ignores such effects as a variation in band tail width with different sample preparation conditions which would change P_i and alter the comparison of Y_L at high temperatures. Evidently such effects are of secondary importance in the samples measured.

3.3 The Intensity Dependence at High Temperature

Figure 4 shows that at 170K there is a region in which the quantum efficiency increases with excitation intensity G . The effect is most pronounced in samples of the lowest spin density, and is absent at 50K when Y_L is independent of G . Our explanation is that at 170K the majority of pairs are rapidly ionized. At low excitation intensity or at large defect densities, the free carriers are sufficiently dilute that they always recombine nonradiatively by capture at localized gap states. However when the excitation rate is large enough or the defect density low enough, the probability of bimolecular, non-geminate, radiative recombination of the free carriers becomes significant, and provides in effect a second chance for luminescence. The situation is modelled in the rate diagram of Fig. 7. In steady state N_p pairs, N_e free electrons and N_h free holes are assumed. The concept of a pair is not very precise, but is perhaps best defined as an electron and hole of separation less than about 50Å. It is necessary to include pairs specifically in order to

model the low intensity geminate recombination. Pairs are generated directly by illumination with rate G , and by electron-hole collisions at rate $\gamma N_E N_H$. Pairs are lost by ionization and radiative recombination. In steady state the rate equation for the pairs is

$$dN_P/dt = 0 = G + \gamma N_E N_H - N_P P_I - N_P P_R . \quad (6)$$

The luminescence efficiency is given by

$$\begin{aligned} Y_L(G) &= N_P P_R / G \\ &= Y_0 (1 + \gamma N_E N_H / G) \end{aligned} \quad (7)$$

where $Y_0 = P_R / (P_R + P_I)$ which is the low intensity geminate limit. Clearly we must now introduce a non-radiative process to obtain a quantum efficiency other than unity. Figure 4 indicates the importance of dangling bonds with unpaired spins in the non-radiative process. However we ignore direct tunnelling into the defect because of the discussion given in §3.2 and because of the relatively low spin density in the samples measured. In support of this assumption we find at 170K similar luminescence intensities at low G for all the samples investigated.

The most straight-forward model assumes that free electrons and holes are captured by dangling bonds giving non-radiative recombination. (Note that we believe that this process is weakly radiative at a different energy.¹⁷ This does not influence the present argument which is solely concerned with the band edge transition.) From Fig. 7 the rate equation for free electrons is

$$\beta N_E N_S = N_P P_I - \gamma N_E N_H = G - N_P P_R . \quad (8)$$

At 170K, $N_P P_R / G (= Y_L) \ll 1$, and therefore

$$N_E \simeq G/\beta N_S . \quad (9)$$

If it is further assumed that the density of trapped carriers is small compared to N_E and N_H , then $N_H \simeq N_E$ and so

$$Y_L(G) = Y_0[1 + \gamma G/\beta^2 N_S^2] . \quad (10)$$

This result gives a reasonably good description of the data. It predicts that at low G , Y_L is constant and given by the simple geminate model, while at high G , Y_L is enhanced by the bimolecular radiative process, by an amount inversely dependent on the spin density. These qualitative results are observed in the data of Fig. 4. The predicted dependence on G is only obeyed over at most two decades of G , and there are large departures at high G . This point is discussed further below. For each sample one can fit the intensity dependence of Y_L to the expression in Eq. 10 in the low intensity region. In Fig. 8, G_1 , which is the value of G when $\gamma G/\beta^2 N_S^2 = 1$ obtained from these fits, is plotted versus the spin density, for all the samples measured. The dependence on N_S^{-2} predicted by Eq. 10 can now be clearly seen, despite some scatter in the data. Thus provided the excitation intensity is not too high, Eq. 10 is a good description of the recombination. We therefore conclude that the primary mechanism of non-radiative recombination above 100K is by trapping of free carriers at singly occupied dangling bond defects. This model is generally supported by photoconductivity measurements which find that in undoped samples, recombination is by electron trapping at states in the gap, although different states have previously been assumed.¹⁸

The scatter in the data points in Fig. 8 seems to be typical of the attempts to correlate luminescence and ESR measurements.⁹ The origin of the scatter is

not clear as there are various possible reasons. For example

- a) An inhomogeneous spin distribution in some samples, possibly including a surface spin density.
- b) The presence of defects without spins. These could be defects of the vacancy type, or possibly doubly occupied (or empty) dangling bonds due to inadvertent doping.

A more significant discrepancy from Eq. 10 is the departure from the predicted dependence on G at high intensities. Again there are various possible explanations. For example the simple recombination model used to derive Eq. 10 may be inapplicable because:

- a) No account is taken of the exponentially decreasing excitation rate in the bulk due to absorption of the incident light. The observed data therefore represent some average over the thickness of the illuminated region. Diffusion of the free carriers may also be significant.
- b) At high excitation intensities the traps may saturate.
- c) The distinction between free carriers and pairs becomes blurred at high G because the mean separation of particles decreases.

Alternatively the turn-over of Y_L at high G might indicate the onset of another non-radiative mechanism. Since this dominates at high intensity, an obvious candidate is an Auger process. As before, a reliable calculation of the expected rate is not available, but the effect apparently occurs when the photoexcited carrier density is sufficient to give reasonable overlap between carriers. Thus the Auger process seems a plausible explanation.

From the fit to Eq. 10 for the data shown in Fig. 8 we obtain,

$$\gamma/\beta^2 = 1.1 \times 10^{13} \text{ cm}^3 \text{ sec} \quad (11)$$

with an uncertainty of about a factor 3. Mott et al.¹⁹ have estimated the recombination rates under various circumstances and their discussion is followed here. The pair formation process is an example in which ionization rather than recombination usually occurs, since we know that at 170K, Y_L is small. γ is the rate of pair formation, and is related to the ionization probability P_I by

$$\gamma = R^3 P_I \exp(V/kT) \quad (12)$$

where V is the coulomb interaction of the electron-hole pair, and R is the radius of the pair. Assuming R is $50\text{\AA}$,⁹ a dielectric constant of 10, and taking an average value of P_I of 10^6 sec^{-1} from luminescence decay data,⁸ we obtain $\gamma \simeq 10^{12} \text{ cm}^3 \text{ sec}^{-1}$. This value of γ is not very sensitive to the exact value of R because the coulomb term and the R^3 factor have opposite R -dependences. From Eq. 11, $\beta \simeq 3 \times 10^{13} \text{ cm}^3 \text{ sec}^{-1}$ is obtained. A comparable estimate of the trapping rate can in principle be obtained from photoconductivity data. However to the best of our knowledge this has not been evaluated. β can be predicted from a formula similar to Eq. 12, although in this case there should be no coulomb interaction because the singly occupied dangling bond is neutral. Since the coulomb term is relatively small, similar values of β and γ are expected. We therefore conclude that the trapping parameters obtained from the experiment are of reasonable magnitudes for the recombination model.

3.4 Summary

Our main conclusions are as follows:

1) The decrease of luminescence efficiency as the temperature is reduced below 50K is a consequence of Auger recombination of neighboring pairs. The Auger process is observed at excitation densities exceeding about 10^{20} absorbed photons $\text{cm}^{-3} \text{sec}^{-1}$.

2) The presence of singly occupied dangling bonds changes the temperature dependence of the luminescence through the mechanism in which an electron tunnels into the defect.

3) The radiative and non-radiative processes at high temperature have been determined in greater detail. At low excitation intensities, luminescence is by geminate recombination. The rate-determining non-radiative path is ionization of the pairs, which is followed by non-radiative recombination of the free carriers at dangling bonds. At high excitation intensities, bimolecular radiative recombination can occur, particularly in samples of low spin density. The efficiency of this process depends on the capture rate of free carriers by dangling bonds.

4) The recombination of free carriers is in reasonable quantitative agreement with a simple model of capture by singly occupied dangling bonds. As in previous measurements^{9,17} we find no evidence for defects other than dangling bonds in the as-deposited material. The recombination process tends to be complicated by many effects, and it probably requires a combined study of luminescence, photoconductivity and possibly drift mobility for a more detailed evaluation.

Finally, it should be pointed out that any attempt to interpret the temperature

dependence of the luminescence must take into account the effects reported

there. For example, the temperature dependence of the ionization rate can

only be obtained if measurements are performed at low excitation intensities, and on samples with a spin density below about 10^{17} cm^{-3} .

ACKNOWLEDGEMENTS

The author is grateful to J. C. Knights for providing samples.

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*Work supported by the Solar Energy Research Institute under Contract No. XJ-0-9079-1.

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FIGURE CAPTIONS

Figure 1 Temperature dependence of the luminescence intensity in the range 0-80K for various incident excitation powers and wavelengths as shown. The data are normalized such that the maximum intensity is 10 units of the vertical scale, and the different curves have offset zeros. The illumination spot diameter is 2mm.

Figure 2 Ratio of the luminescence efficiency measured at high excitation power I_{HP} (1 mW), to that at low power I_{LP} (0.01 mW), at different temperatures, for two samples of different ESR spin densities. The solid curves are fits to the data based on Eq. 1.

Figure 3 Temperature dependence of the luminescence intensity, measured at low (0.01 mW) and high (1 mW) excitation power for samples of different ESR spin density. The illumination spot diameter is 2mm.

Figure 4 Plot of the relative luminescence quantum efficiency versus incident excitation power for samples of differing spin density. Dashed curve illustrates the relation predicted by Eq. 10.

Figure 5 Schematic illustration of two possible non-radiative Auger recombination processes for two neighboring electron-hole pairs. Ovals are intended to denote geminate pairs.

Figure 6 Plot of the luminescence efficiency versus ESR spin density calculated from Eqs. 4 and 5. Values of $P_R = 10^3 \text{ sec}^{-1}$ and $R_0 = 11 \text{ \AA}$ are assumed. The curves correspond to different values

of P_1 as indicated.

Figure 7 Schematic recombination diagram showing N_P electron-hole pairs, N_E free electrons, N_H free holes and N_S dangling bond defects. The various generation, recombination and trapping rates are shown.

Figure 8 A plot of G_1 versus spin density N_S for various undoped samples. G_1 is the value of G for which $\gamma G / \beta^2 N_S^2 = 1$, and is obtained by fitting intensity dependence data such as in Fig. 4 to Eq. 10. The solid line is the predicted behavior for a value of the parameter γ / β^2 of $1.1 \times 10^{13} \text{ cm}^{-3} \text{ sec}$.

FIG 1

FIG 2

FIG 3

FIG 4

FIG 5

FIG 6

FIG 7

FIG 8