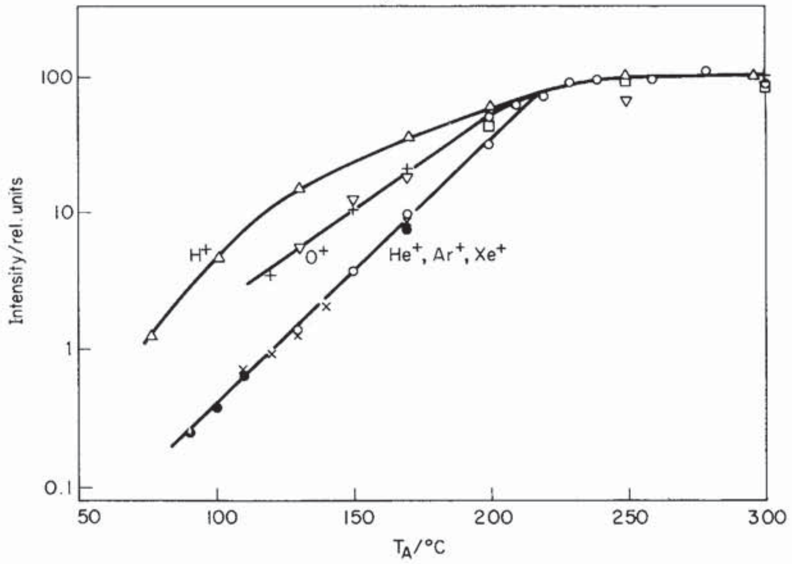
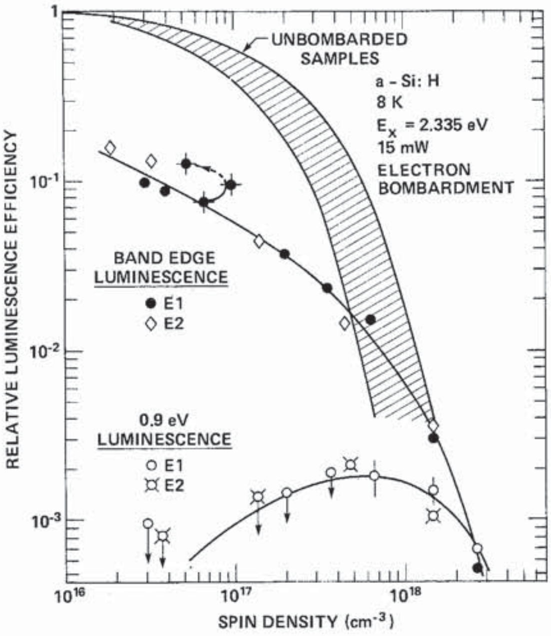
Fig. 52



Recovery of the luminescence intensity by annealing of ion bombarded samples showing the effect of different ions (Engemann *et al.* 1975).

(Engemann *et al.* 1975). As expected there is a reduction of the luminescence intensity after bombardment but annealing increases the intensity by almost three orders of magnitude. As shown in fig. 52, samples bombarded by H^+ or O^+ ions tend to recover at lower temperatures than with the other ions. The reasons for this are

Fig. 53



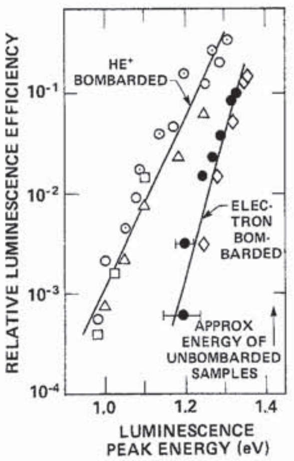
Recovery of the luminescence intensity and reduction of the spin density of electron bombarded samples. The data are compared to similar plots of as-deposited samples as in fig. 8 (Street *et al.* 1979).

discussed below. The recovery by annealing continues up to about 200°C above which there is no further improvement.

Bombardment by high energy electrons also causes damage that increases the dangling bond density and quenches the luminescence (Street *et al.* 1979 a, Voget-Grote *et al.* 1980). The recovery by annealing is shown in fig. 53 which plots the luminescence intensity versus E.S.R. spin density for the annealing sequence. A comparison to a similar plot for undoped, as-deposited a-Si : H shows that although the E.S.R. spin density is reduced to low values, the luminescence intensity is not restored to the maximum value observed in as-deposited material. Qualitatively similar results are found for He^+ ion bombarded material (Street *et al.* 1979 a). These results imply that after annealing non-radiative recombination centres remain which are not observed in E.S.R. and a similar conclusion is reached by Voget-Grote *et al.* (1980). It is not particularly surprising that such defects would occur after bombardment and annealing but apparently not after normal deposition because of the nature of the damage to the material. The structure of these spinless centres is not clear but they may be vacancies, divacancies or other centres.

Bombardment and annealing changes the luminescence peak energy as well as the intensity. Figure 54 shows how these two parameters are related through the annealing sequence for various electron and He^+ ion bombardment samples (Street *et al.* 1979 a). The two types of bombardment give characteristically different results, in that electron bombardment results in a smaller shift of the luminescence peak, even though the intensity changes are equivalent. The interpretation given to the data is that, in addition to defect formation, the disorder induced by bombardment tends to broaden the band edges so that carriers will thermalize to lower energies before recombination. The annealing reduces the disorder, sharpens up the band edges and the luminescence moves to a higher energy. The implication of fig. 54 is therefore that He^+ bombardment produces more disorder for a specific dangling bond density than the electrons. This is in fact to be expected because the momentum transfer that occurs during an ion collision is much larger than with an electron for the bombardment energies used. Ion collisions tend to create secondary

Fig. 54

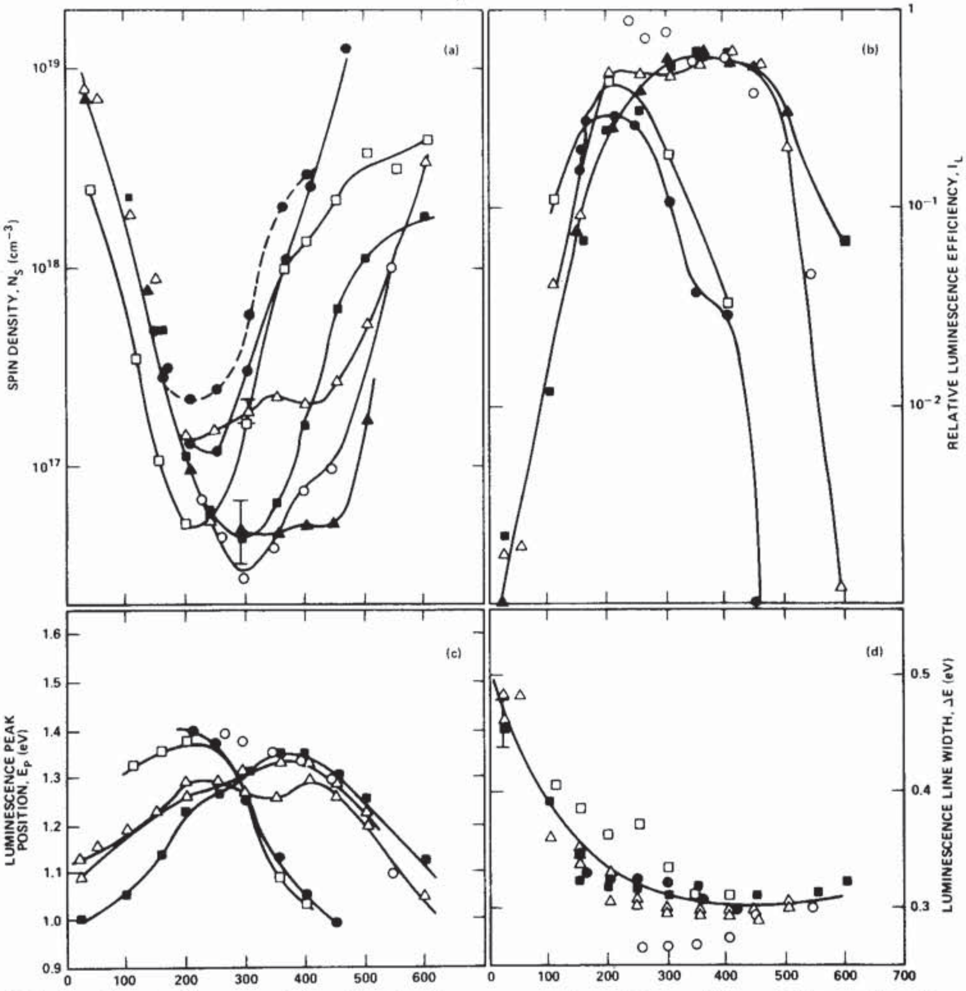


Plot of luminescence peak energy versus luminescence intensity in bombarded samples annealed to varing temperatures, showing the different behaviour of electron and He^+ bombardment (Street *et al.* 1979 a).

damage resulting in a cascade effect, and a high degree of local disorder. On the other hand an electron collision results in damage generally confined to a single atom. It would be interesting to investigate the temperature dependence of the luminescence intensity for the two types of bombardment to try to ascertain whether both band edges are equally affected by the damage, but this has not yet been reported.

Samples deposited at around room temperature have a high defect density and weak luminescence (Engemann and Fischer 1974, Biegelsen *et al.* 1979). Annealing of these samples up to about 250°C restores the luminescence just as it does for bombarded samples. Annealing to higher temperatures results in the evolution of hydrogen from the material and as this occurs, the spin density again increases whilst the luminescence is quenched (Pankove and Carlson 1977). Figure 55 shows typical E.S.R. and luminescence data for a series of samples with different deposition conditions (Biegelsen *et al.* 1979). Other properties such as photoconductivity also show evidence of the increased defect density (Voget-Grote *et al.* 1980).

Fig. 55



Spin density, luminescence intensity, luminescence peak position and line width as a function of annealing temperature in samples of widely varying deposition conditions (Biegelsen *et al.* 1979).

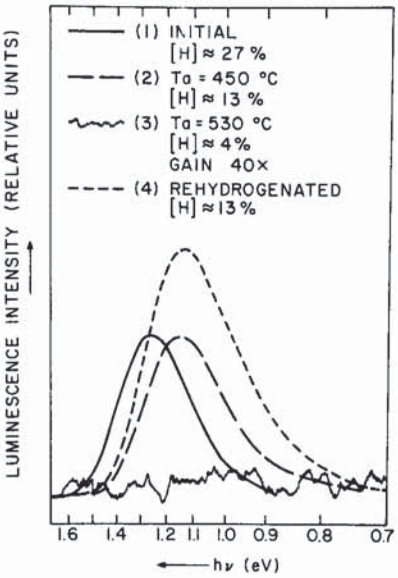
To a reasonable approximation, there is a common annealing behaviour for all samples in fig. 55 below 250°C. The annealing of bombarded samples is qualitatively similar as shown in fig. 52. Furthermore the luminescence and E.S.R. data obtained by varying the substrate temperature during deposition is also much the same (see fig. 49). It seems evident that the reduction in the dangling bond density in all three cases proceeds in essentially the same way. Two mechanisms have been discussed for the annealing (Street *et al.* 1979 a). One possibility is that dangling bonds can diffuse through the a-Si : H network and annihilate in pairs by reconstruction. An alternative is that instead hydrogen diffuses and saturates the dangling bonds by some undetermined process of reconstruction. There are various pieces of evidence for the latter process.

1. (1) Figure 52 shows that the annealing temperature is lowered after bombardment by H^+ or O^+ compared to several other ions. The conclusion is that the annealing is assisted by the hydrogen ions, and to a lesser extent by oxygen. These results can readily be explained if annealing occurs by hydrogen diffusion. A similar role for oxygen is also understandable from its low coordination.
2. (2) At high annealing temperatures, the dangling bond density again increases (fig. 58). The implication of this result is that dangling bonds are inherently stable to high temperature, so that a mechanism involving their diffusion and annihilation at much lower temperatures is unlikely.
3. (3) The motion of hydrogen at relatively low temperatures is seen by hydrogen evolution and by N.M.R. (Reimer *et al.* 1980). The actual temperature at which hydrogen is released depends on the hydrogen bonding type (Biegelsen *et al.* 1979).

At annealing temperatures above 250°C the luminescence and E.S.R. data depend strongly on the sample deposition conditions (fig. 55). However, it is found that the usual relation between spin density and luminescence intensity holds for each sample. The origin of the diverse behaviour is readily found to be due to the hydrogen evolution properties. The increase in spin density and quenching of the luminescence parallel the evolution for each of the samples in fig. 55. The evolution temperature is in turn determined by the type of hydrogen bonding in the material. The details of the processes are not yet fully resolved, but it is evident that polysilane structures, $(SiH_2)_n$, tend to evolve hydrogen at about 350°C, whereas SiH and SiH_2 units usually result in evolution at 400–600°C. It is easy to understand how the evolution of hydrogen results in dangling bonds. However, the density of dangling bonds formed is much less than the density of hydrogen evolved, and the probability of an evolved hydrogen atom leaving a dangling bond increases as more hydrogen is evolved (Biegelsen *et al.* 1979). Evidently there is reconstruction of the dangling bonds left behind by the hydrogen.

Just as hydrogen evolution reduces the luminescence intensity, it can be restored by rehydrogenation. This can only be achieved with atomic hydrogen and so the experiment has been performed in a hydrogen plasma (Pankove 1978, Pankove *et al.* 1979). Luminescence spectra in fig. 56 show that annealing eliminates the luminescence, but that the spectrum is restored essentially to the original intensity after rehydrogenation. The resulting film has a hydrogen content of about 20 at.% at the surface, and hydrogenation to a depth of more than 1000 Å is achieved.

Fig. 56



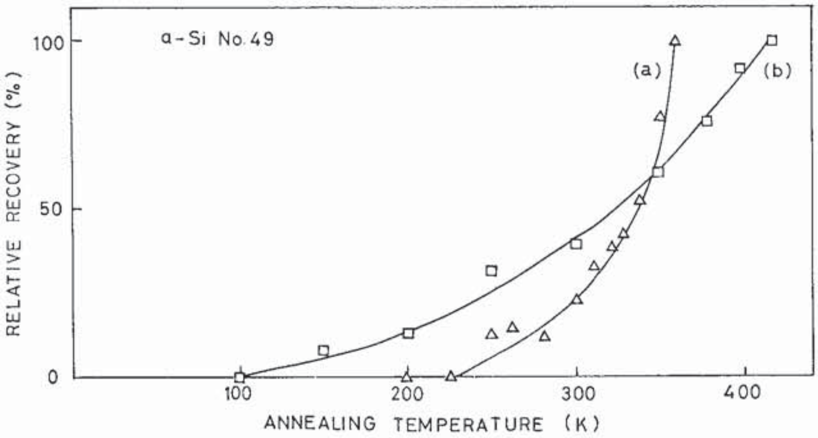
Luminescence spectra of rehydrogenated material compared to as-deposited a-Si : H. Note the absence of luminescence after the 530°C anneal, before rehydrogenation (Pankove 1978).

4.3. *Fatigue effects*

One of the most interesting luminescence properties of chalcogenide glasses is the fatiguing effect (Cernogora *et al.* 1973, Street *et al.* 1973). After a few seconds illumination, the luminescence intensity decreases, eventually down to only a few per cent of the initial intensity. The effect has been interpreted as a combination of the change in occupancy of centres, and the generation of new defects by illumination (Biegelsen and Street 1980). Initially a-Si : H was found to have no equivalent fatiguing effect. More recently, however, the effect has been observed although at much higher illumination levels (Morigaki *et al.* 1980). For example, an exposure of $2{\cdot}4 \times 10^5$ J/cm^2 of excitation at 2·41 eV was found to reduce the intensity by a factor of 2 (Shah and Di Giovanni 1981). The same change of intensity in As_2Se_3 occurs with an exposure 10^4 times smaller. An important difference between the two materials is that in chalcogenides, the fatiguing depends only on the total exposure, whereas in a-Si : H it depends also on the intensity, indicating a non-linear effect. Morigaki *et al.* (1980) and Shah and Di Giovanni (1981) report that no change in the luminescence spectrum occurs after fatiguing. However, Pankove and Berkeyheiser (1980) observe that the intensity at 0·8 eV is increased relative to the peak at 1·3–1·4 eV. The fatigue can be reversed by annealing as shown in fig. 57. The annealing begins at 100 K and is complete by about 400 K, although the details of the behaviour depend on the history of the sample.

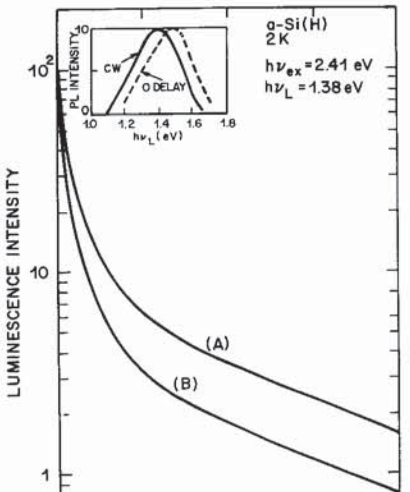
There is now reasonably strong evidence that the fatiguing is due to the generation of dangling bonds by strong illumination (Dersch *et al.* 1981, Shah and Di Giovanni 1981, Hirabayashi *et al.* 1980). Decay data in fig. 58 show that the fatigued sample has an enhanced initial fast decay, and this feature has been attributed to non-radiative tunnelling to defects, as in the discussion of § 2.3.2. Similar decay data

Fig. 57



Recovery of luminescence fatigue by annealing. Sample (*b*) was heat treated to 170°C before the fatiguing, whereas (*a*) was as-deposited (Morigaki *et al.* 1980).

Fig. 58



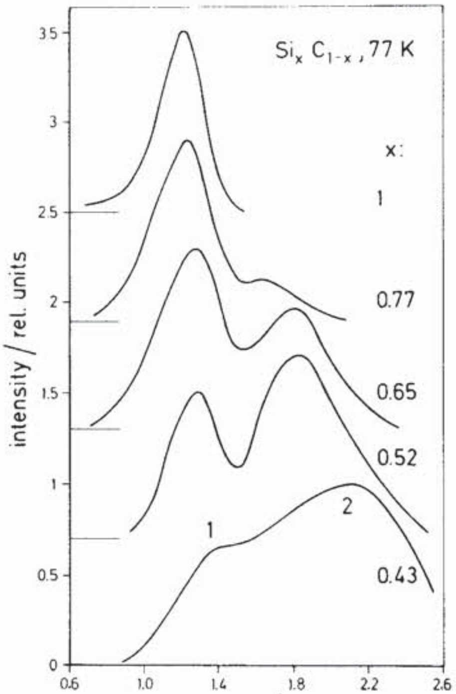
Luminescence decay (*a*) before and (*b*) after fatigue. The more pronounced initial decay is characteristic of a larger defect density (Shah and Di Giovanni 1981).

are reported by Hirabayashi *et al.* (1980). The relative enhancement of the spectrum at 0·8 eV also suggests the involvement of dangling bonds. Hirabayashi *et al.* report that after illumination an E.S.R. signal characteristic of a dangling bond is seen. This last experimental result is perhaps not as convincing as it seems, because a metastable E.S.R. signal is found in both doped and undoped a-Si : H due to trapped carriers (Biegelsen 1981). This signal occurs at low illumination levels and anneals away by 150 K, and is evidently distinct from the fatiguing of luminescence at high intensity. It is not clear whether this is the effect observed by Hirabayashi *et al.*

4.4. *Related materials*

Luminescence has been studied in various alloys of silicon, and has been looked for in other tetrahedral amorphous semiconductors. So far no III–V amorphous compound (hydrogenated or not) has been found to have a significant luminescence intensity. Those studied to date include GaAs, GaP, BP and BAs. In general these studies have not attempted to make accurately stoichiometric compounds. In contrast, the alloys of Si with germanium, carbon, nitrogen and oxygen do show luminescence. In these alloys two distinctly different types of behaviour are observed. Figure 59 shows luminescence spectra of Si–C alloys (Engemann *et al.* 1978). When the carbon content exceeds ~20% two features are observed in the spectrum. One peak remains close to 1·3 eV and is clearly characteristic of an amorphous silicon matrix. The second peak moves up in energy as the carbon content increases, and in fact follows the band gap of the material. The material is deduced to be inhomogeneous with substantial silicon clustering which results in the unshifted peak. The second peak is assumed to be the equivalent band edge transition of the alloyed regions of the material. Carius *et al.* (1981) have reported data on Si–O alloys, finding essentially the same behaviour. One luminescence peak remains unshifted, and another moves up in energy, although in this case not as fast as the band gap energy.

Fig. 59



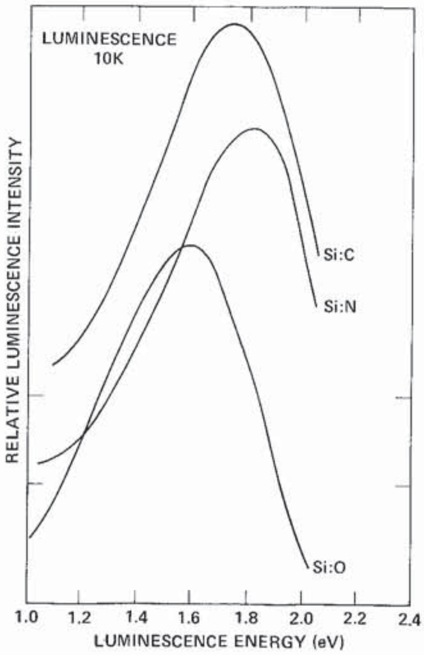
Luminescence spectra of Si_xC_{1-x} : H films showing two-peak structure (Engemann *et al.* 1978).

In contrast Knights *et al.* (1980) have found a single peak in Si–O alloys which shifts to high energy with increasing oxygen, and recently similar data has been found in Si–N, Si–C and Si–Ge alloys (Munekata *et al.* 1980, Mikkelsen and Street 1981, Hauschildt *et al.* 1981). Examples are shown in fig. 60. There is no sign of an unshifted peak in any of these alloys, from which it appears that these materials form homogeneous alloys. It is not clear what property of the deposition leads to inhomogeneity in one case but not in the other. Both types of sample are made by plasma decomposition.

The luminescence data of these three alloy systems are very similar and so we shall illustrate their characteristic properties with measurements from Si–O. Figure 61 shows the temperature dependence of the luminescence intensity in which the low temperature efficiency is seen to decrease as the oxygen content increases (Street and Knights 1980). This effect is observed in all the alloys and is attributed to an increase in defect density. In Si–N an increasing dangling bond density is observed in E.S.R. as a resonance that evolves from $g=2{\cdot}0055$. In Si–O the E.S.R. behaviour is more complex. As the oxygen content increases, the thermal quenching weakens, so that most of the alloys have more efficient room temperature luminescence than a-Si : H. The same result is true in Si–C and Si–N. According to the models for a-Si : H, the reason for the change is an increased electron binding energy indicative of a broader band tail. Possibly this increase is due to the compositional disorder, and may be a general property of alloy systems.

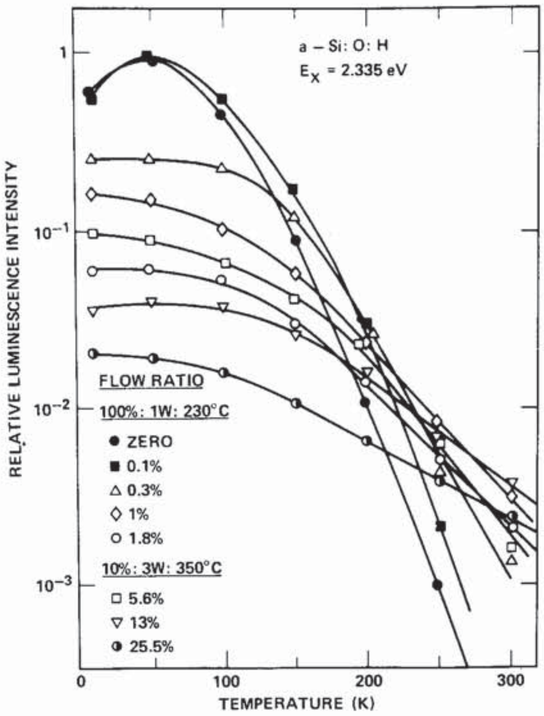
In glow discharge samples, the luminescence line-width increases with oxygen content as illustrated in fig. 60, and its temperature dependence changes (Street and

Fig. 60



Luminescence spectra of Si : O : H, Si : N : H and Si : C : H showing a single boad peak in each case.

Fig. 61



Temperature dependence of the luminescence intensity in various Si : O : H alloys (Street and Knights 1981).

Knights 1980). However, in sputtered material oxygen is found to reduce the line width (Paesler *et al.* 1978, Paesler and Paul 1980). There is no explanation given for the difference. It is argued that the increase in glow discharge samples is mostly due to a larger electron–phonon interaction, and this would explain why the luminescence peak energy does not follow the band gap energy, the difference being due to the increasing Stokes shift (Knights *et al.* 1980).

It is apparent that the luminescence mechanism is unchanged with alloying as can be inferred from the continuous shift of the luminescence peak. The decay data are also very similar to that of a-Si : H showing that the radiative tunnelling mechanism almost certainly applies (Street and Knights 1980). The time-resolved luminescence data of Si–O alloys has already been shown in fig. 28. The larger shift of the peak than in a-Si : H is interpreted as indicating an increased band tail width, as was deduced from the temperature dependence. No equivalent data on Si–C or Si–N has been reported.

It is of interest to speculate as to why luminescence is observed in various Si alloys, but not in III–V compounds. This is relatively easy to understand in Si–C since the elements are isoelectronic. We suggest that Si–O and Si–N have luminescence because the alloys are chemically ordered so that the probability of O–O or N–N bonds is very small. On the other hand, the III–V compounds are unlikely to be strongly ordered, and no doubt contain many like-atom bonds, which could act as non-radiative states. It would be useful to explore other alloy systems as a check on this possibility.

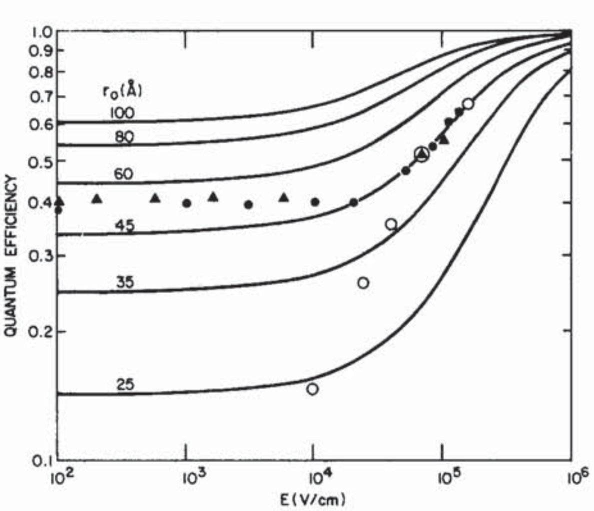
§5. Related recombination processes

5.1. *Room temperature geminate recombination*

The recombination model described in §2.3 involved geminate recombination. Competing with this mechanism at high temperatures is thermally activated diffusion of the electron–hole pair, such that at room temperature the efficiency of the radiative process is only about 10^{-4}. This model therefore implies that room temperature geminate recombination is negligible. However, recent experiments have reported a geminate process at 300 K by observing the electric field dependence of the photoconductivity quantum efficiency (Mort *et al.* 1980). There is considerable disagreement as to whether, and in what samples, this geminate mechanism occurs.

The evidence for the process is shown in fig. 62. The experiment is to measure the absolute collection efficiency of holes after a short pulse of light, at various electric fields. To avoid the problem of separating the hole lifetime effects from the generation efficiency at low fields, the experiment is performed by illuminating at the chosen field, and increasing the field 50 ns after the pulse to guarantee that all holes are collected. For the data of fig. 62, the low field efficiency is about 0·4, increasing at fields above 3×10^4 V/cm. These measurements are made with illumination at 4950 Å on samples deposited from 5% SiH_4/95% He. These samples are known to have a low defect density ($< 10^{16}$ cm^{-3}) and a high luminescence efficiency at low temperature (Knights *et al.* 1981). The results of fig. 62 are interpreted by the Onsager (1938) model. As shown in the figure, a thermalization length of 45 Å provides a good fit to the data, and is also in good agreement with the average electron–hole separation deduced from the luminescence data at low temperature (see §2.3). In fact a room temperature geminate behaviour of this form was predicted by Noolandi *et al.*

Fig. 62



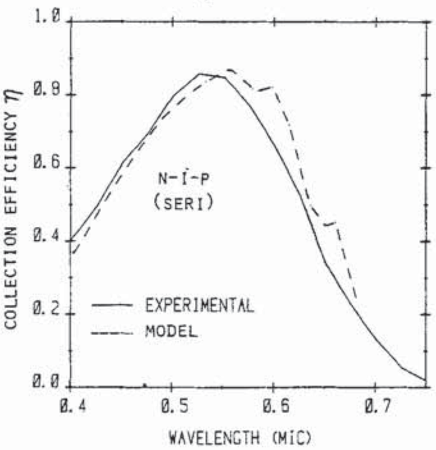
Electric field dependence of the hole quantum efficiency. Solid lines are fits to the Onsager model (Mort *et al.* 1980).

(1980 a) from a calculation that used the luminescence data to obtain the distribution of electron–hole pair separations after thermalization. However, the calculation assumed that a geminate recombination process occurred, which was not the radiative tunnelling mechanism.

Mort *et al.* (1980) have found that geminate recombination occurs in all samples measured, but that there is some variation in the low field efficiency and in the deduced value of the thermalization length. Other groups have performed various experiments that test the geminate recombination hypothesis, with very mixed results. Crandall (1980 a), for example, found that the carrier collection efficiency is a function of the width of the depletion layer in a Schottky solar cell, and interpreted the result as indicating an electric-field dependent quantum efficiency, and therefore geminate recombination. Recently various direct measurements of the collection efficiency in solar cells have been reported, with peak values of 85–90% at about 5000 Å. A typical example is shown in fig. 63. The decrease above 5000 Å is due to the decreasing absorption, since for a 0·5 μm thick cell, the transmission at 6000 Å is about 50%. There is also a decrease at short wavelengths which is often attributed to back diffusion of electrons. In these devices the depletion width is typically 3000 Å and so the internal field does not exceed about 3×10^4 V/cm, corresponding to the low field limit in fig. 62. Evidently the average collection efficiencies of 70% and peak values of 85–90% are in substantial disagreement with the data in fig. 62. Chen and Mort (1981) have also calculated the maximum short circuit current in a solar cell device. Assuming no reflectivity losses at the front or back surface, and no other losses, they find 17·3 mA/cm^2 at AM1, in agreement with Crandall's result. The authors suggest that geminate recombination is responsible for the observed values of about 12 mA/cm^2, but that losses due to other mechanisms must be minimal. Given that other losses must exist (for example, absorption in the n$^+$ and p$^+$ layers), then these results suggest that the geminate recombination in the best solar cell materials must be rather small.

From photoconductivity measurements, Madan *et al.* (1980) have reported that the carrier generation efficiency in a-Si : H : F samples is independent of electric field

Fig. 63



Spectral dependence of the carrier collection efficiencies on a-Si : H solar cells (Wronski *et al.* 1981).

up to at least 6×10^4 V/cm, and independent of excitation wavelength, which they interpret as indicating no geminate recombination. It seems, therefore, that the issue is not resolved. This controversy is important for the luminescence, because the room temperature geminate process is tacitly excluded by the recombination models discussed here. It is just possible that the geminate recombination is associated with certain sites in the material, which perhaps have low density in good solar cell material. This model could reconcile some of the experimental data described above, and would be relatively easy to accommodate in the present luminescence models. However, this solution seems rather unlikely.

It is worth making some general comments about mechanisms that give geminate recombination at high temperatures. In the present context we must assume that a non-radiative process is involved because the room temperature luminescence is negligible. Geminate recombination occurs when the recombination rate exceeds the ionization rate which is governed by the binding energy. In the semi-classical treatment of the Onsager model, the electron–hole binding energy is determined by the Coulomb interaction which can be made indefinitely large as the electron–hole separation decreases. The model therefore assumes that some separation exists below which geminate recombination inevitably occurs. In reality, the electron and hole will always have some maximum binding energy, which depends on the material involved. Geminate recombination can only occur if the recombination rate exceeds the ionization rate which is of order $10^{12} \exp(-E_B/kT)$ where E_B is the binding energy of the more weakly bound carrier. If the room temperature geminate process is intrinsic, in the sense of being unrelated to defect states in the gap, then the non-radiative process is presumably a multi-phonon transition, there being few alternative possibilities to consider. One can then consider two limiting cases. In one case, the electron binds to the hole with a weak electron–phonon interaction so that the binding energy will tend to be small, and the multi-phonon rate will be very slow (Mott *et al.* 1975). This situation favours ionization. On the other hand, a strong coupling will give a large binding energy and a fast multi-phonon process, favouring geminate recombination. Thus, if the geminate process is confirmed, it leads to the expectation that both electrons and holes are strongly coupled. Such an exciton should have a significantly larger binding energy than a band tail electron–hole pair. As such it would be expected to play an important role in the low temperature luminescence, because there is no reason why the band tail electron could not tunnel directly into the non-radiative exciton state. So far there is no indication of such a process.

5.2. *Photoconductivity*

Photoconductivity data contain information about both the transport and the recombination processes and have been used in both contexts. Because of the problems in understanding transport in amorphous semiconductors, it is often difficult to extract the recombination information. Photoconductivity tends to give general, rather than specific, information about the recombination through measurements of the photo-excited carrier density and its time and intensity dependence. The recombination kinetics are usually the most straightforward property to measure, but as shown below, even this can be a problem in an amorphous semiconductor.

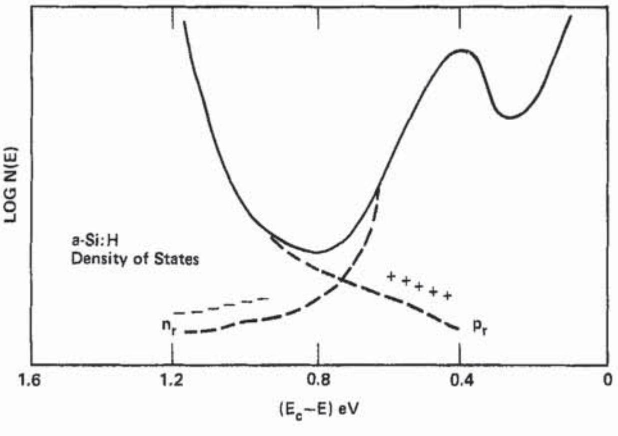
The photoconductivity σ_{ph} is given by,

$$\sigma_{ph} = Ne\mu = G\tau e\mu, \tag{36}$$

where N is the excess carrier density, μ is the effective mobility, G is the generation rate and τ is the recombination time. In at least some measurements the mobility is time dependent and this modifies the interpretation of the photoconductivity behaviour. There are many cases in which the intensity dependence of the photoconductivity follows a $G^{0\cdot7}$ dependence (Zanucchi *et al.* 1978, Spear *et al.* 1974, Moddel *et al.* 1980), which possibly should be interpreted in this way, as discussed below. In other cases the intensity dependence is close to $G^{0\cdot5}$ or G^1 and these are easier to interpret. Anderson and Spear (1977) report the exponent of the intensity dependence changing between these two extremes as a function of n-type doping. Their primary result is that as the doping, temperature and light intensity are varied, the exponent changes when the quasi-Fermi energy passes through an energy of about 0·35 eV below the conduction band. The larger exponent occurs when the quasi-Fermi energy is closer to mid-gap than 0·35 eV.

In a-Si : H the photocurrent is believed to be carried by electrons. An exponent of unity implies monomolecular recombination in which the rate-limiting step is the capture of electrons by deep traps whose density is invariant as the light intensity changes. On the other hand the exponent of 0·5 characterizes a bimolecular process in which the electron recombines with an equal density of holes. Anderson and Spear (1977) interpret their results using the schematic diagram as shown in fig. 64. They make use of the density of states as determined by field effect measurements and suppose that the broad minimum in the centre of the gap is derived from overlapping conduction band and valence band states. In undoped material, a band of negatively charged and positively charged states are expected in the region of overlap. Anderson and Spear suggest that these centres dominate the recombination because they have the greatest capture cross-section. In undoped material the recombination by electron trapping at the positive centres is expected to be monomolecular. However, in n-type samples when the light intensity is such that the quasi-Fermi energy has moved up to the E_x band, then the recombination must change. The E_x band is now negatively charged, neutrality being maintained by trapped holes or ionized donors. In this case bimolecular recombination is expected, in agreement with the observations.

Fig. 64



Schematic density of states diagram used to explain the photoconductivity of a-Si : H (Anderson and Spear 1977).

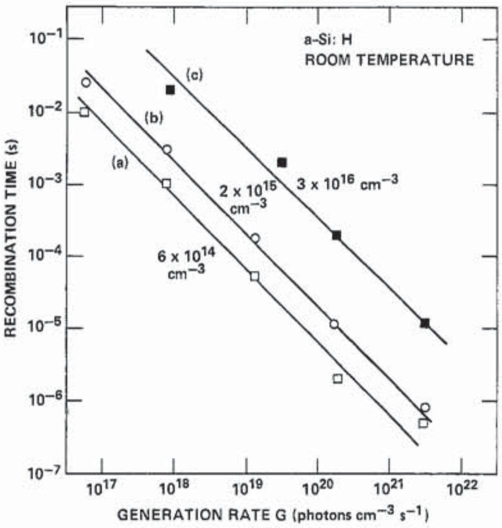
This recombination model differs from that derived from the luminescence data in that the effective recombination centres are assumed to be only a small fraction of the total density of localized states. If we tentatively associate the E_x peak with the dangling bonds, then the recombination model in § 2.3 would assume that capture of electrons into E_x was the dominant process. In fact if this were the rate limiting recombination, then it is easy to see that the kinetics would change from monomolecular to bimolecular as the quasi-Fermi energy moved through E_x. Since this is also in agreement with the data, it is not clear why this mechanism was not considered by Anderson and Spear. The choice between the two models presumably rests on the relative density of states and capture cross-sections of the charged and neutral defects.

The above discussion tacitly assumes that the effectively mobility is not time dependent. Only in this case are the recombination kinetics readily derived from the intensity dependence. Dispersive mobility has been found to occur in some a-Si : H samples, both doped and undoped (Fuhs *et al.* 1978, Tiedje *et al.* 1980, 1981). The mobility can be obtained from the transient photoconductivity response and is found to follow a $t^{-(1-\alpha)}$ time dependence (Hvam and Brodsky 1981, Street 1981 b). Once the mobility has been obtained, the transient photoconductivity experiments can also give the recombination time τ. Data are shown in fig. 65 in which τ is approximately inversely dependent on the illumination intensity,

$$\tau \sim G^{-1}. \tag{37}$$

This is an interesting result because the excess carrier density N, given by $G\tau$, is then almost independent of the illumination intensity. This compares with the usual monomolecular case for which $N \sim G^1$ and the bimolecular case when $N \sim G^{0\cdot5}$. It can be shown that the time dependent mobility modifies the expressions such that when $\alpha = 0\cdot4$, a simple bimolecular process results in $N \sim G^{0\cdot3}$ and $\sigma_{\mathrm{ph}} \sim G^{0\cdot7}$. This intensity

Fig. 65



Dependence of the recombination lifetime on the generation rate G as measured by transient photoconductivity on samples of different spin density as shown (Street 1981 b).

dependence of σ_{ph} is, in fact, observed in many reports, but the dependence of N from the data of fig. 65 is even weaker than the prediction. The reason for this is unclear and must presumably depend on the details of the recombination mechanism. However, it is evident that the process is basically bimolecular, which contrasts with the monomolecular kinetics found by Anderson and Spear (1977). Both results are on undoped samples and for similar illumination intensities, so the reason for the difference is not clear, although Griffith *et al.* (1980) have shown that trace impurities can modify the photoconductivity. Both types of samples have a low defect density and similar low temperature luminescence properties.

5.3. *Optically induced E.S.R. and absorption*

Measurements of induced E.S.R. and absorption gives further information about the density of optically excited carriers which can be related to the recombination through the lifetime τ, since $N = G\tau$. Both techniques have some advantages and some problems when used to study recombination. E.S.R. only measures centres with spin and so may not detect all the photo-excited carriers. On the other hand it has the ability to distinguish between different centres, provided the resonance can be clearly identified. The induced absorption experiment only gives N if the optical cross-section is known, which is frequently not the case. Some information about the energy level of the induced carriers is obtained, but the contribution of the final state of the transition is not easy to deconvolve, and one must rely on other experiments to identify whether electrons or holes are involved.

E.S.R. data has already been discussed because the measurements are often closely associated with luminescence. Three resonances have been identified in as-deposited undoped material (for a review, see Biegelsen 1981). There is the dangling bond resonance at $g = 2{\cdot}0055$ which is observed in equilibrium E.S.R. in samples of sufficiently large defect density. Light-induced E.S.R. of undoped samples has a broad (~ 20 G) resonance at $g = 2{\cdot}013$, attributed to band tail holes, and a narrow (5 G) resonance at $g = 2{\cdot}004$ attributed to electrons. These last two resonances have been associated with the recombining carriers (Street and Biegelsen 1980 a, b). Evidence for this identification is the similar temperature-dependence of the induced E.S.R. and the 1·4 eV luminescence, as well as the evidence of spin-dependent luminescence discussed in § 2.4.4.

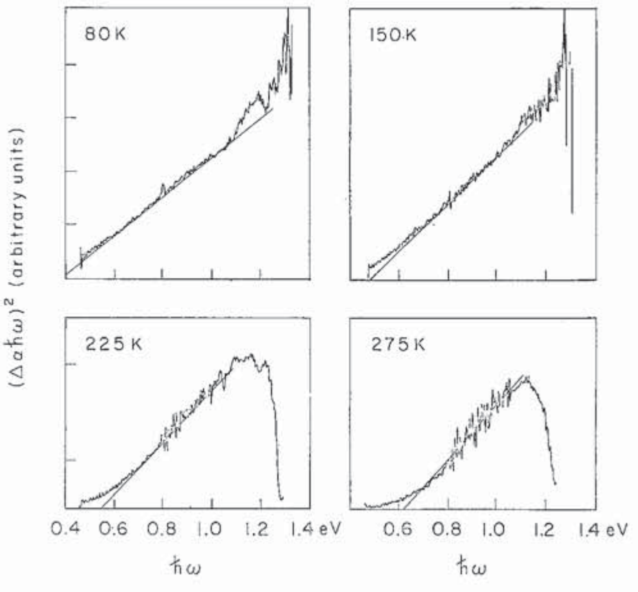
The induced spin density has been reported to be about 10^{17} cm^{-3} in undoped low defect density samples (Street and Biegelsen 1980 a, b). This measurement was made under relatively strong illumination for which the electron–hole pair density predicted from luminescence would exceed 10^{18} cm^{-3} (Tsang and Street 1979). Both measurements of the density are difficult to make accurately. However, there is a clear indication that a discrepancy exists, whose origin is unclear. One possibility is that the electrons and holes in the band tail states tend to pair so that the E.S.R. measurements undercounts the total density.

More information about the recombination could be obtained from the time decay of the induced E.S.R. If the same carriers are involved as in the luminescence, then the rate of change of the L.E.S.R. should equal the time dependence of the luminescence intensity. The L.E.S.R. decay has not been reported in undoped a-Si : H. In doped samples the L.E.S.R. decay has a time constant of 10–20 ms (Biegelsen and Knights 1977). This is comparable with the average radiative decay time, but in similar samples the luminescence is dominated by the fast non-radiative component of the decay. More measurements are required to find out if the decays are in fact related.

Induced absorption in a-Si : H is observed at energies below the band gap (O'Connor and Tauc 1979, Olivier *et al.* 1980). O'Connor and Tauc find an absorption threshold that increases from 0·38 eV at 80 K to 0·63 eV at 275 K. The spectra are shown in fig. 66, and the maximum induced absorption that is observed is 30–50 cm^{-1}. Olivier *et al.* (1980) have reported similar data. Both groups conclude that the absorption is from the excitation of holes. O'Connor and Tauc make this conclusion on the grounds that electrons would have a smaller threshold because deep localized electron traps of sufficient density have not been observed. The absorption is interpreted as a transition between a trapped hole and the valence band. A model of parabolic bands predicts the linear absorption data shown in fig. 66. On the other hand, Oliver *et al.* (1980) find that the induced absorption has a similar spectrum to the photoconductivity, and so deduce that an interband transition is involved, although this seems unlikely given the small value of the threshold. They find some contrasting properties of the induced absorption and photoconductivity which leads them to deduce that the absorption is due to holes. Both groups tacitly assume that the electrons must have a lower absorption coefficient and so are not observed.

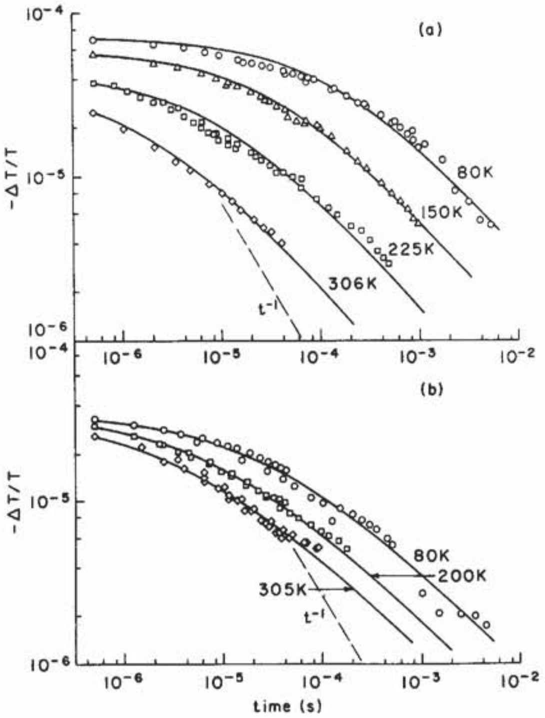
The decay of the photo-induced absorbtion is shown in fig. 67 (Vardeny *et al.* 1980, 1981). At low temperature the absorption decreases rapidly above 10^{-3} s, which is similar to the average luminescence decay, and so is consistent with the expectation that the recombination processes are the same. It is difficult to compare accurately the decay in different experiments because it is strongly dependent on the experimental conditions. At high temperature the decay time decreases, again in

Fig. 66



Induced absorption spectra of a-Si : H at different temperatures (O'Connor and Tauc 1979).

Fig. 67



The decay of photo-induced absorption is undoped and doped a-Si : H at different temperatures (Vardeny *et al.* 1980).

qualitative agreement with the luminescence. The decay is interpreted as bimolecular and involving a dispersive diffusion (Vardeny *et al.* 1980, 1981). This is a reasonable model at high temperatures, particularly since there is general agreement that hole transport is dispersive. At low temperatures the luminescence models would suggest that the mechanism is tunnelling rather than diffusion. It is hard to separate these two models just from the form of the decay.

Mort *et al.* (1981) have measured the time dependence of hole recombinations using a delayed-collection field technique. They find a room temperature lifetime of about 10^{-3} s, increasing at lower temperatures with an activation energy of about 0·4 eV. They attribute the decay to surface recombination—a monomolecular process—and show that the recombination velocity is proportional to the drift mobility. They also analyse the data of Vardeny *et al.* (1980) in fig. 67 in the same way and find a lower activation energy similar to that for electron transport. Mort *et al.* therefore suggest that the induced absorption is by electrons and the recombination monomolecular—a conclusion diametrically opposite to that of Vardeny *et al.* (1980, 1981). The contradictory interpretations made for the induced absorption, and to a lesser extent the photoconductivity make it difficult to draw any firm conclusion from these experiments about the recombination. Clearly much more data is needed.

§6. SUMMARY

This paper has attempted to describe in some detail the recombination mechanisms in a-Si:H as observed through luminescence measurements. In this author's opinion, many of the features of the recombination are reasonably firmly established: the electron–phonon interactions; the involvement of band tail states: dangling bond defects acting as non-radiative centres; the low temperature tunnelling processes; the importance of diffusion above 50 K; and the Auger and surface effects. Less clear is the origin of the above-gap luminescence, the properties of the recombination at the defect and oxygen bands and the nature of the room temperature recombination. Many of the details of the recombination mechanisms also need clarification. However, with a basic knowledge of the recombination, luminescence can be a useful technique for characterizing different sample properties of a-Si: H, and several examples of this have been given.

One aspect of the recombination that has not been satisfactorily explored is the relation between luminescence and other experiments. Specifically, the photoconductivity and induced absorption data that have been reported have been discussed without much attempt at a unified model. Since the same recombination mechanisms must be involved in the different experiments, a fully convincing description of the recombination cannot be given until a detailed connection is made between the different experiments.

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