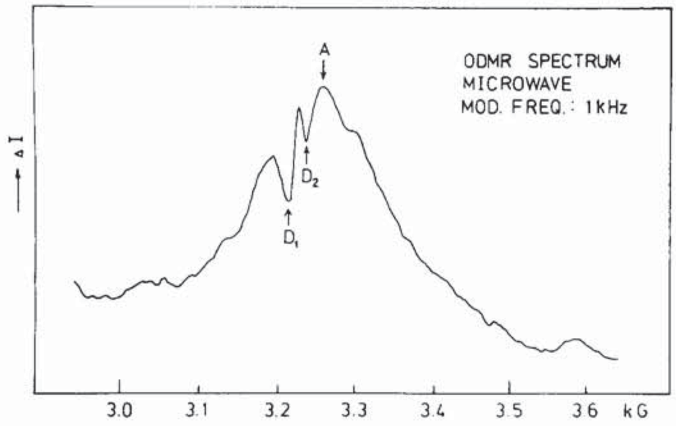
Fig. 32



Low temperature (2 K) spin dependent luminescence signal showing broad enhancing and narrow quenching lines (Morigaki *et al.* 1978).

cence energy. Morigaki *et al.* report two peaks in the luminescence spectrum at 1·3 and 1·43 eV. As discussed in § 2.1, compared to virtually all other data, this is an anomalous result whose origin is not clear.

Several papers have analysed different aspects of the theory of the spin dependent recombination (see, for example, Kaplan *et al.* 1978, Movaghar *et al.* 1980). All agree that the origin of the effect is the spin selection rules for the electron–hole recombination. For the simple example of spin $\frac{1}{2}$ particles, the recombination will be allowed in the singlet configuration, but forbidden for the triplet states. In resonance the electron–hole pair makes rapid transitions between the singlet and triplet states which changes the average recombination rate. An immediate result is that the S.D.P.L. effect can only be observed with a resonance near the free electron g-value, if the exchange coupling between the electron and hole is very small compared to the Zeeman splitting of each particle. The electron and hole must therefore be very weakly coupled, and this result is in agreement with the radiative tunnelling recombination model described in § 2.3, since this mechanism assumes a weakly coupled pair.

If the electron and hole spins are thermalized, then the maximum observable spin dependent effect is given by the product of the polarizations,

$$\Delta L/L = (\mu_B H/kT)^2, \tag{31}$$

where $g = 2$ is assumed. This is referred to as the normal spin dependent effect and $\Delta L/L$ has a characteristic T^{-2} dependence, and a value of $1{\cdot}5 \times 10^{-5}$ at 100 K. In a-Si : H, the quenching lines have $\Delta L/L$ nearly temperature dependent and with a magnitude nearly 100 times larger than this value. An anomalously large effect was also observed in the spin dependent photoconductivity (Solomon *et al.* 1977), and the explanation is that the spin relaxation times are sufficiently long so that the singlet and triplet populations are not in thermal equilibrium. In this case a simple model might assume that random pairing of electrons and holes occurs, so that initially $\frac{3}{4}$ of the pairs are triplets and $\frac{1}{4}$ are singlets (Kaplan *et al.* 1978). The triplets can only recombine radiatively if they are converted to singlets by resonance, so it is easy to see that the spin dependent effects can now be very large, potentially of the order of unity. This type of process is referred to as the anomalous spin dependent effect.

This basic model for the anomalous process can be applied to the recombination in various ways. For example, geminate electron–hole pairs are predominantly created as singlets since this transition has the greatest oscillator strength. A quenching resonance is therefore expected as the singlets are converted into triplets by the resonance. However, at decay times which exceed the spin relaxation times, the spins will have thermalized, and then an enhancing, normal, spin dependent effect should occur. Alternatively we can consider the non-radiative mechanism in which the electron tunnels to a singly occupied dangling bond. This is not a geminate process, and initially the two spins (electron and dangling bond) should be randomly oriented. Kaplan *et al.* (1978) have shown that in this situation the recombination rate is enhanced in an anomalous spin dependent process. However, since this is the competing non-radiative recombination, the luminescence will show a quenching effect.

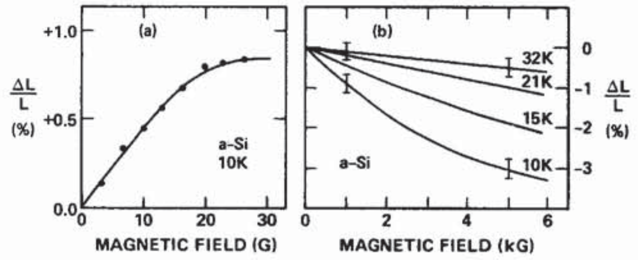
Table 2. A list of the recombination mechanisms discussed in §2.3 and the expected sign of the spin dependent process for both the normal and anomalous effect.

Process	Normal	Anomalous
Geminate radiative	+	−
Non-geminate radiative	+	+
Tunnelling to defects	−	−
Auger	−	?
Thermal quenching	No effect	

Table 2 lists the relevant recombination mechanisms that have been discussed in §2.3 and the sign of the expected spin dependent process based on the above arguments. Both anomalous effects for decay times less than the spin relaxation time T_1, and the normal effects at larger times, are shown. A more detailed discussion of the possibilities is given by Movaghar *et al.* (1980). It seems evident from table 2 that the normal enhancing effect must be due to the radiative process, but a more specific model cannot be deduced. At present it is not at all clear why the enhancing effect occurs predominantly at low energy, nor what is the origin of the very broad resonance. The most likely explanations of the anomalous quenching effect is either the geminate radiative process, or the non-radiative tunnelling. Since the resonance spectrum evidently involves the 20 G wide hole resonance, the former interpretation is perhaps favoured. A possible test of this model would be to measure the excitation-intensity dependence of the effect.

The luminescence is also influenced by a d.c. magnetic field through mechanisms which are apparently related to the spin dependent effects. A surprising result is that a magnetic field of only 20 G increases the luminescence intensity by about 1% (Street *et al.* 1978 a). Typical data in fig. 33 show a linear increase of intensity with saturation at about 25 G. At much higher fields the luminescence intensity decreases slowly as shown in fig. 33. The magnitude of the decrease has a temperature dependence of approximately T^{-2}, and so it has been associated with thermalized carriers, and with the normal spin dependent effect. The sign of the magnetic field dependence is as expected, since it is presumed that the resonance would in effect

Fig. 33



Magnetic field dependence of the change in luminescence intensity $\Delta L/L$ in a-Si : H: (*a*) low field increase at 10 K; (*b*) temperature dependent decrease above 30 G (Street *et al.* 1978 a).

restore the low field situation, and so give an enhancing signal. The magnitude of the change in the d.c. field is larger than the spin dependent change by about a factor of 10. The most likely explanation seems to be that the resonance is inhomogeneously broadened, and so only about 10% of the spins are in resonance at any part of the E.S.R. spectrum. Street *et al.* (1978 a) associate this low field process with the anomalous spin dependent effect, and suggest that the decrease of intensity below 20 G is because singlet and triplet states are again coupled, as during resonance. They propose that the origin of the coupling is a low frequency fluctuating magnetic field due to the excitation and recombination of all electron–hole pairs. The magnetic field at which the effect saturates is found to be in rough agreement with the prediction of this model assuming the distribution of frequencies of the fluctuating field has a cut-off corresponding to the fastest observed decay time of the luminescence.

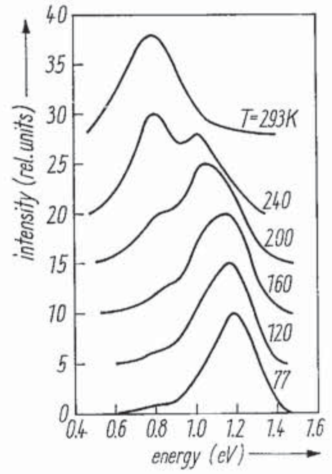
Clearly many more experiments are needed to resolve the spin dependent, and magnetic field effects. These are important experiments because they provide a stringent test of the various recombination models, and offer the possibility of obtaining detailed information about the electron and hole spin properties.

2.5. *Defect luminescence*

As discussed in § 2.1, a luminescence peak at 0·8–0·9 eV is frequently observed, particularly in samples in which the band-to-band transition has a low quantum efficiency. The transition is observed in undoped samples, or in samples with a doping level of $\sim 10^{-3}$, as described further in § 3. In both cases the luminescence band is characterized by a weaker thermal quenching than the peak at 1·3–1·4 eV. It is therefore most readily observed at high temperatures as shown by the spectra of fig. 34. The temperature dependences of the two luminescence bands are shown explicitly in fig. 35. Similar data are reported by Nashashibi *et al.* (1977 b). Room temperature luminescence, when detectable, is generally dominated by the defect band.

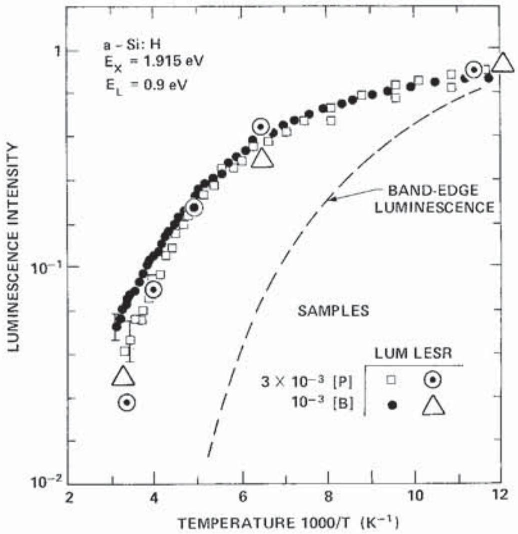
The 0·8–0·9 eV transition has a temperature independent line-width of about 0·35 eV (Street 1980 b), although a peak at 0·8 eV in sputtered samples is reported to have a width of only 0·18 eV (Anderson *et al.* 1979 a). Unlike the band edge transition, the temperature dependence of the peak position follows that of the band gap (Street 1980 b). The luminescence has been associated with an extrinsic absorption band as shown by the data of fig. 36 for n-type a-Si : H. Illumination at energies above the

Fig. 34



Examples of luminescence spectra of undoped a-Si : H showing the dominance of the 0·8–0·9 eV peak at high temperature (Engemann and Fischer 1977).

Fig. 35

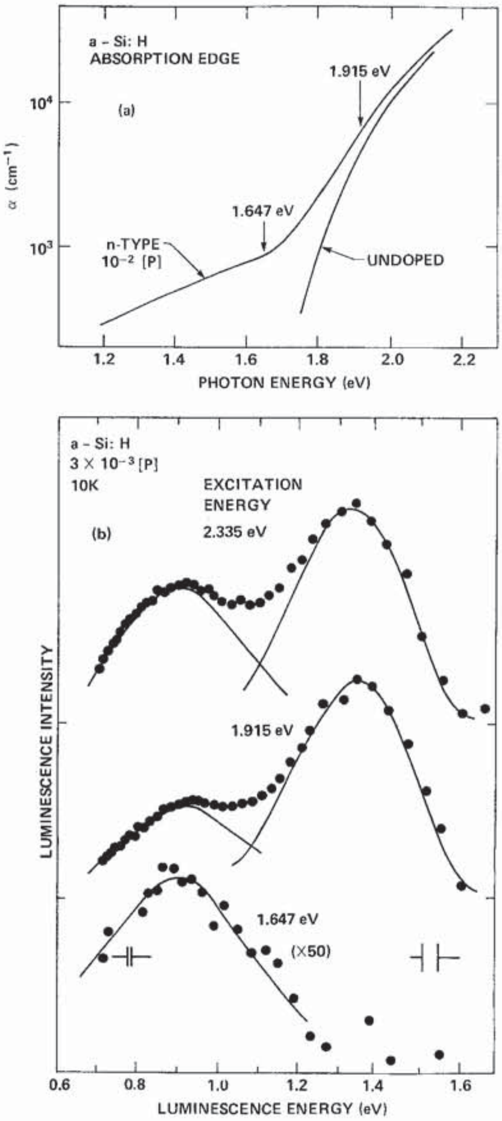


Temperature dependence of the defect luminescence compared to that of the band edge transition. The temperature dependence of L.E.S.R. is also shown (Street 1980 b).

absorption edge excites both defect and band edge transitions. However, absorption in the extrinsic absorption tail only excites the defect transition. This behaviour is as expected for a transition involving a deep localized state. The experimental evidence for an extrinsic absorption band due to defects has been discussed further in § 2.2.

The general assumption is that the 0·8–0·9 eV luminescence is due to defects. There is, in fact, specific evidence from light induced E.S.R. (L.E.S.R.) for

Fig. 36



(*a*) The absorption spectrum of a-Si : H showing the extrinsic tail in doped samples (Knights 1976). (*b*) Luminescence spectra of doped a-Si : H at different excitation energies showing that absorption in the extrinsic tail quenches the band edge transition but not the defect luminescence (Street 1980 b).

associating the luminescence with dangling bonds. In both p-type and n-type material, the dangling bond resonance at $g = 2{\cdot}0055$ is observed in L.E.S.R., but no dark E.S.R. is seen (Street and Biegelsen 1980 a, b). This result demonstrates that dangling bonds are present in these samples and the change of occupancy with illumination suggests that there is a recombination channel through these states. In addition, the temperature dependence of L.E.S.R. is identical to that of the luminescence efficiency as is shown in fig. 35. The similar temperature dependences can be understood as follows. If the luminescence is described as a competition between a radiative process with rate P_R and a nonradiative process with rate P_{NR}, then the decay time τ and efficiency y_L are given by

$$y_L = P_R/(P_R + P_{NR}), \tag{32}$$

$$\tau = (P_R + P_{NR})^{-1} = y_L/P_R. \tag{33}$$

If the L.E.S.R. is governed by the same recombination mechanisms, then the spin density N_s for a specific illumination intensity G is given by

$$N_s = G\tau = Gy_L/P_R. \tag{34}$$

Since we expect P_R to be at most only weakly temperature dependent, the similar temperature dependences of N_s and Y_L seen in fig. 35 argue strongly for the same recombination mechanism in both experiments. Thus it is inferred that dangling bonds are involved in the recombination.

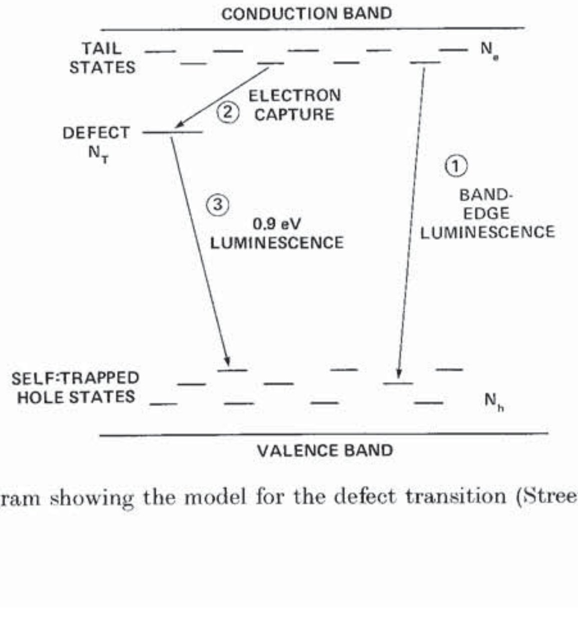
A model for the defect transition, proposed by Street *et al.* (1979 a), is shown in fig. 37. The recombination is believed to be between an electron captured at a dangling bond, and a valence band tail hole. Two reasons for adopting this model are as follows.

(1) It is known from the discussion in § 2.3 that electrons are captured into dangling bond states as the primary competing process to the 1·4 eV luminescence band.

(2) Since thermally assisted diffusion of electrons is believed to be responsible for the temperature dependence of the 1·4 eV band, the weaker thermal quenching of the defect luminescence implies that the electrons are localized in states deeper than the band tail.

As in the case of the band edge transition, the line width of the defect transition is attributed primarily to a strong electron–phonon interaction. This gives a consistent model since it is assumed that the same hole states are involved in both transitions.

Fig. 37



Schematic diagram showing the model for the defect transition (Street *et al.* 1979 a).

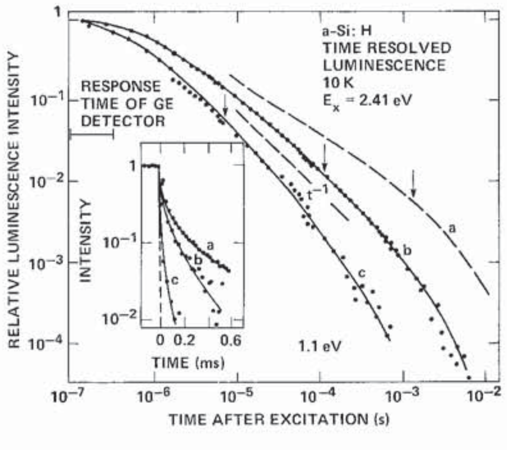
The additional width of the defect band may be due to some distortion of the doubly occupied dangling bond, or to the energy distribution of the localized states. Using these arguments Street (1980 b) obtains a rough estimate of 1·3 eV for the zero-phonon energy of the defect transition, and an approximate binding energy of 0·5 eV for the dangling bond electron trap.

Assuming that localized electrons and holes are involved in the defect luminescence, it is most probable that the transition occurs by radiative tunnelling. Figure 38 shows the luminescence decay of the 0·9 eV peak compared to the band edge transition. The luminescence shows a distribution of decay times characteristic of radiative tunnelling, but the distribution is shifted to shorter times by at least two orders of magnitude compared to the band edge transition. However, the luminescence efficiency of the defect band is very low, so the decay is presumably dominated by the non-radiative processes, the details of which are at present unknown.

The low efficiency of the 0·9 eV luminescence is one of its most striking properties. The efficiency does not exceed about 10^{-2} even when the band edge transition is strongly quenched. The implication is that either the transition through the dangling bond states is mostly non-radiative, or else there is another non-radiative process involving different states which dominates in samples of high defect density or at a high temperature. Of relevance to this issue is the evidence of the intensity dependence of the band edge transition discussed in § 2.3.4 which showed that the non-radiative recombination (from the point of view of the 1·4 eV band) is indeed dominated by dangling bonds and there is no indication that other states are involved.

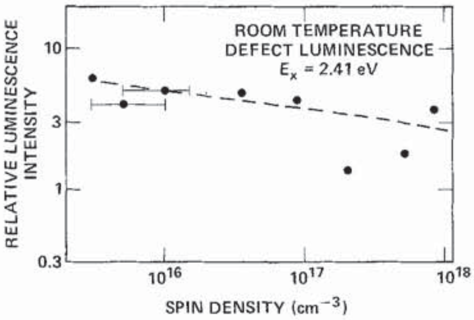
Additional information about the role of dangling bonds is shown in fig. 39. It is found that at 300 K the intensity of the defect transition is almost independent of the dangling bond density as measured by the E.S.R. spin density. At this temperature the electron–hole pairs are almost completely ionized, and so we consider a model in which the free electrons are captured either by N_D dangling bonds giving the 0·9 eV luminescence, or by N_x other non-radiative centres. At room temperature, the

Fig. 38



Luminescence decay of the 0·9 eV peak (*c*) compared to that of the band edge transition (*a*), and of a compensated sample (*b*). The insert shows the decay after a long excitation pulse (Street *et al.* 1981).

Fig. 39



Plot of the room temperature intensity of the defect peak versus spin density in various samples.

carriers are mobile and so it seems appropriate to describe the recombination in terms of capture cross-sections. The efficiency y_D of the defect band is then given by

$$y_D = y_D^0 N_D \sigma_D / (N_x \sigma_x + N_D \sigma_D), \tag{35}$$

where σ_D and σ_x are the capture cross-sections for the two types of centres, and y_D^0 is the radiative efficiency of the defect transition. It is now seen that only in the case $N_x \sigma_x \ll N_D \sigma_D$, is the defect luminescence intensity independent of N_D.

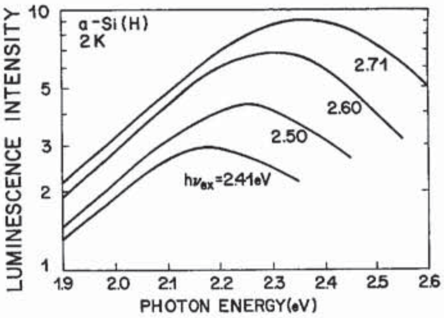
These results support the model that recombination through dangling bonds is the dominant process, and that no other localized states are involved. This implies that the dangling bond transition is largely non-radiative. One possible non-radiative mechanism is an Auger transition. The transition supposedly involves a doubly occupied dangling bond and a valence band hole, and is therefore analogous to a bound exciton, which often has a large Auger component to the recombination. However, since the location of the energy levels is not known exactly, it is not easy to determine whether there is sufficient recombination energy to promote the second electron from the dangling bond to the conduction band. An alternative mechanism to explain the non-radiative process is a multi-phonon transition. Clearly more work is needed to resolve the details of the recombination mechanism of the defect transition.

2.6. *Above band gap luminescence*

A broad photoluminescence band is observed at energies substantially above the band gap of amorphous silicon (Shah *et al.* 1980 a). The efficiency of this luminescence is very low, of the order of 10^{-4}, and the peak energy and intensity varies with the excitation energy as shown in fig. 40. Strikingly similar luminescence properties have also been observed in chalcogenide glasses (Shah and Bosch 1979). The luminescence spectrum is virtually independent of temperature from 2 to 300 K, and also independent of excitation intensity over a very wide range. This luminescence is unlike any observed in crystalline semiconductors and therefore seems to be a specific property of the amorphous network, being apparently insensitive to the type of amorphous semiconductor.

Two models have been discussed by Shah *et al.* (1980 a) to explain the luminescence. Initially it was believed that a small fraction of electron–hole pairs were

Fig. 40



Spectra of above band gap luminescence for different excitation energies (Shah *et al.* 1980 a).

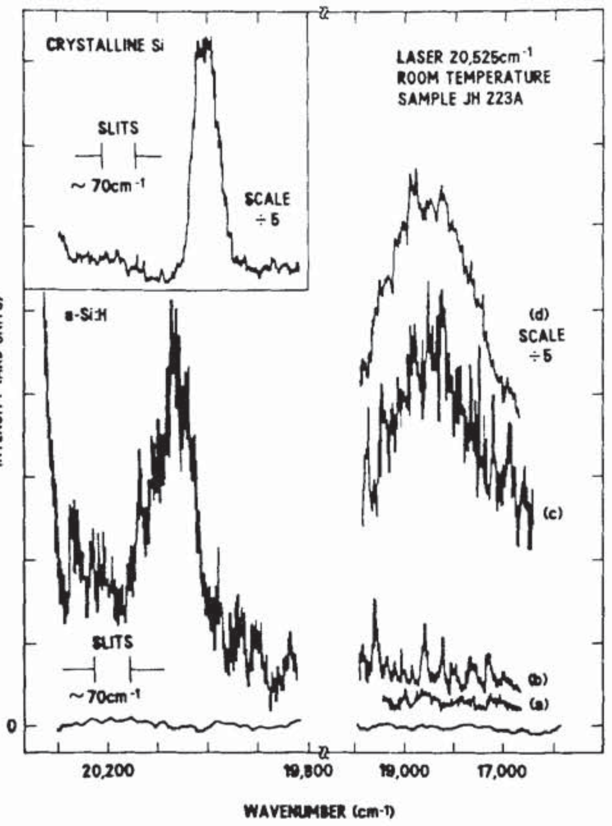
localized at some specific atomic clusters. Auto-ionization of the pair is assumed to be inhibited by the distortion of the atomic structure. In this way the pairs could be localized for long enough to emit luminescence at energies above the gap. The second model proposed is based on the common ideas of thermalization in amorphous semiconductors. After optical excitation it is expected that the electron and hole will diffuse apart whilst thermalizing down towards the mobility edges. During the short time that the electron and hole remain strongly overlapping the radiative recombination rate P should be of order $10^8\ \mathrm{s}^{-1}$. As the pair separates the rate will decrease because the wavefunction overlap is reduced. The thermalization time t_0 is expected to be of order 10^{-12} s, and the rate of phonon emission should decrease as the carriers lose energy because the density of states decreases as the mobility edge is approached. Radiative recombination occurring during thermalization is therefore expected to extend from the excitation energy down to the band gap energy, with a broad maximum in between. This is in qualitative agreement with the data, as is the expected efficiency of $Pt_0 \sim 10^{-4}$.

Recently Wilson (1981) has found that surface contamination of a-Si : H can give above band gap luminescence similar to that reported by Shah *et al.* (1980). An example of the spectrum and the effect of cleaning the surface are shown in fig. 41. Wilson (1981) points out that the spectrum has the properties expected for hydrocarbon contamination, and that similar effects have been observed on some SiO_2 surfaces. It is also known that in a-Si : H with columnar structure, hydrocarbon contamination can be adsorbed below the surface and cannot be easily removed (J. C. Knights 1981, private communication). Thus the effect could be observed even on a surface subjected to normal cleaning procedures. At the time of writing, it remains controversial whether contamination explains all the above-gap luminescence in a-Si : H. It is clear, however, that the similar data on chalcogenide glasses must be re-examined.

§3. DOPED AND COMPENSATED a-Si : H

a-Si : H can be doped n- or p-type by the addition of phosphorus, arsenic, boron or other dopants (see, for example, Spear and Le Comber 1975). The doping efficiency, defined as the fraction of impurity atoms which are active dopants, is estimated to be only 10–30% (Spear and Le Comber 1976, Knights *et al.* 1977). Thus it is expected that some dopants will be in fourfold coordination giving electronic states at or near

Fig. 41



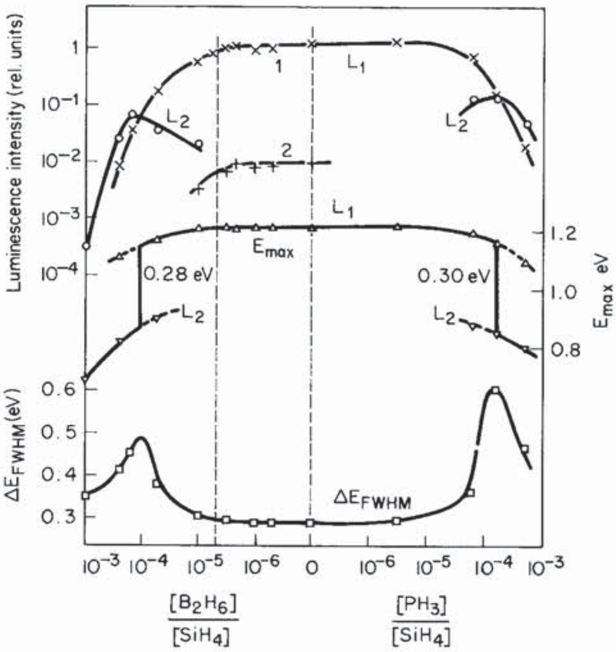
Strength of above band gap emission in a-Si : H relative to the Raman phonon spectrum as a function of cleaning procedures: (*a*) after vapour degreasing; (*b*) after methanol cleaning; (*c*) off-the-shelf; (*d*) beam hitting dusk speck (Wilson 1981).

the band tails, and other dopant atoms will be threefold coordinated, resulting in the possibility of other localized states of unknown energy. In addition, the introduction of dopants may change the defect density. Each of these states can potentially influence the luminescence properties, and so it is of interest to observe the effects. Furthermore a-Si : H films are routinely contaminated by oxygen, nitrogen, and carbon at concentrations which are usually in the range 0·01–1 at.%. It is therefore also important to investigate the effects of these impurities.

3.1. *Phosphorus and boron doping*

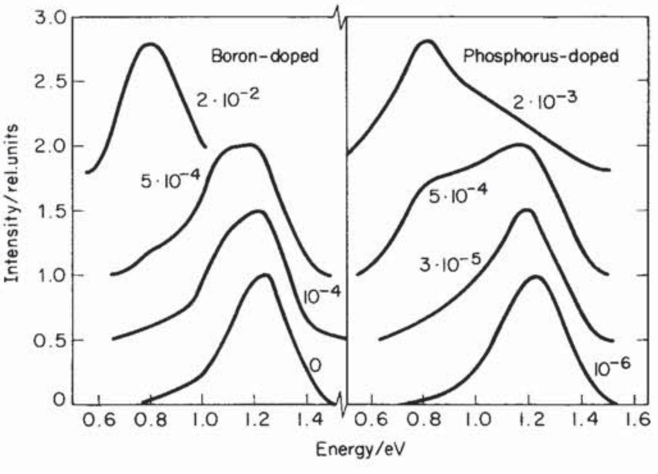
Doping with boron or phosphorus results in strong quenching of the luminescence as shown by fig. 42 (Fischer *et al.* 1980). Other groups have reported very similar data. The two dopants give almost identical luminescence properties, which seems a surprising result given the very different photoconductivity properties. At doping levels above 10^{-3}–10^{-4}, the luminescence spectrum contains both the band edge transition and a peak at 0·8–0·9 eV. This peak is identified as the defect band discussed in § 2.5. As the doping level increases, the defect band tends to dominate as

Fig. 42



Luminescence intensity, peak position and line width as a function of doping. L_1 and L_2 refer to the band edge and defect transitions (Fischer *et al.* 1980).

Fig. 43

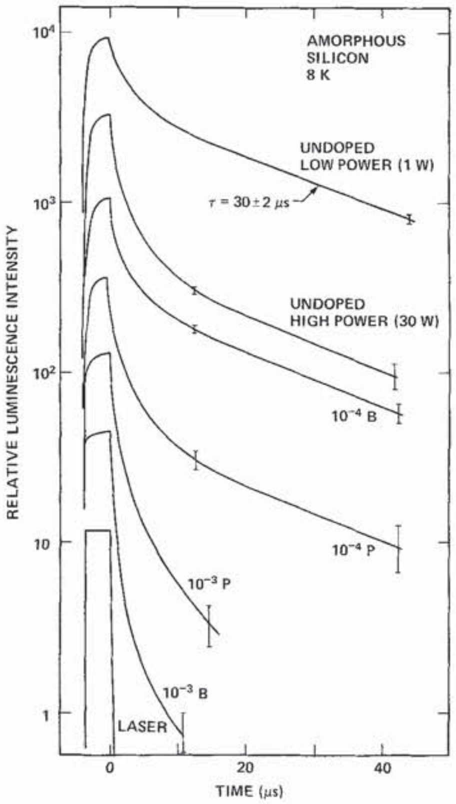


Examples of luminescence spectra in doped a-Si : H (Rehm *et al.* 1976).

seen by the discontinuous change in the peak energy in fig. 42. Typical luminescence spectra are shown in fig. 43 (Rehm *et al.* 1976). The defect band has essentially the same spectrum and temperature dependence for both types of dopant and in undoped material. For this reason it cannot be associated with an impurity. At sufficiently high doping levels the intensity of both luminescence bands is so low that they are undetectable.

Two models have been proposed to explain the quenching of the luminescence with doping. One models assumes that the effect is due to internal electric fields generated by the charged dopants (Rehm *et al.* 1976, Nashashibi *et al.* 1977 a, b, Rehm *et al.* 1980). It is expected that a large fraction of the dopant atoms will be ionized, since the excess carriers are needed to occupy localized states in the gap as the Fermi energy is moved. The random distribution of charged donors and oppositely charged gap states leads to a fluctuating internal electric field. As described in §2.4.3, it is known that an electric field of more than 10^5 V/cm will quench the luminescence. Calculations show that the internal field is of the correct order to explain the magnitude of the quenching, given a simplified model, and a comparison of prediction and experiment is given by Nashashibi *et al.* (1977 b). However, it is not easy to do an accurate calculation of this effect. The doping efficiency is not known accurately, nor is the dopant ionization fraction at high

Fig. 44



Luminescence decay in doped and undoped a-Si : H (Tsang and Street 1978).

doping levels. Furthermore the electron–hole pair separation, estimated to be ~50 Å in § 2.3, is similar to the average separation of dopant atoms when the doping level is 10^{-4}–10^{-3}. Under these circumstances the electric fields acting on the electron and hole could be very different, and the resulting behaviour is hard to predict. Some specific evidence against this model is provided by decay data. Austin *et al.* (1979 a) report that doping enhances the non-radiative component of the decay, but that the radiative component is unchanged, and from this they rule out any electric field effect on the radiative component of the decay. Tsang and Street (1978) agree with this data, and also find no change in the decay with an applied electric field. Although the reason for this is not clear, it does argue strongly that the quenching in doped material is not primarily an effect of the internal field.

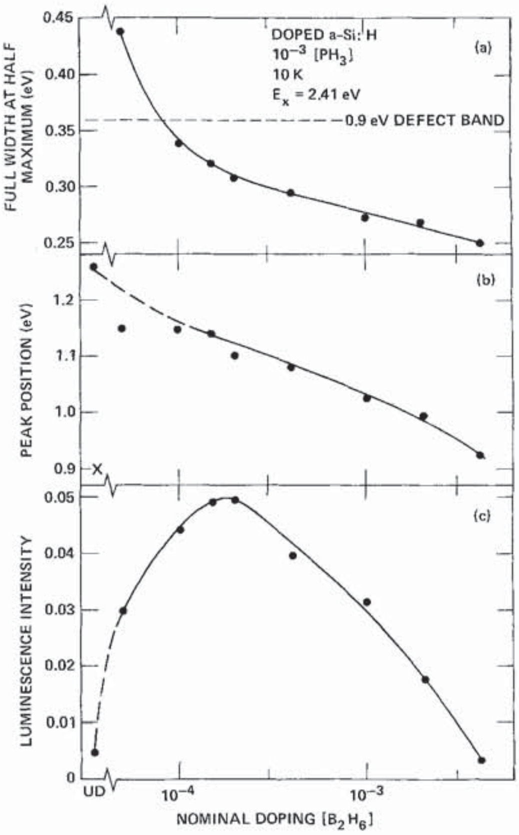
The other model to explain the quenching is that dopants introduce additional defect states and that these act as non-radiative centres as in undoped material. There is now substantial experimental evidence for these defects. For example, as mentioned above, the initial fast component of the decay becomes more pronounced, whilst the long time decay is unchanged (Tsang and Street 1978). Examples of the data are shown in fig. 44. These results are essentially identical to those found in undoped samples as the defect density is increased (Tsang and Street 1979), and the interpretation of this data in terms of tunnelling to defects is discussed in § 2.3.2. In addition, it is found that the excitation-intensity dependence, and the temperature dependence of the luminescence in doped samples parallels that found in undoped material of high defect density (Street *et al.* 1981). However, the clearest evidence for the additional defects is given by light induced E.S.R. in which a rapid increase in the spin density of defects of the dangling bond type is observed with doping of either boron or phosphorus (Knights *et al.* 1977). Recent optical absorption measurements using a photothermal deflection technique find an increase in the extrinsic absorption attributed to defect transitions in doped material (Jackson and Amer 1981). The reasons why doping would introduce defects is discussed in the next section along with data on compensated samples.

3.2. *Compensated a-Si : H*

Doping with both boron and phosphorus results in electrical compensation of a-Si : H (Allen *et al.* 1977, Street *et al.* 1981). Compensation occurs with approximately equal amounts of PH_3 and B_2H_6 added to SiH_4 during the plasma reaction, and is demonstrated with electrical conductivity and thermopower data. Compensation results in several interesting changes in the luminescence and E.S.R. properties. Luminescence data of a typical series which is doped with $10^{-3}[PH_3]$ and compensated with varying amounts of B_2H_6 are shown in fig. 45. Through this series, the band edge transition shifts steadily to lower energy as the boron content increases, and the defect peak, which is evident in the singly doped material, disappears in the compensated material. The identity of the peak in compensated material as derived from the band edge transition is shown by the trend in the peak energy, the line width, and also by the temperature dependence. This result is confirmed in the data of fig. 46 which shows the peak position in nominally compensated samples as a function of doping level. Up to levels of 10^{-4} there is little change in the peak energy, but at higher doping levels the peak shifts continuously down by about 0·5 eV.

The second interesting feature of the luminescence in the compensated samples is the change of intensity. As shown in fig. 45, compensation increases the luminescence

Fig. 45

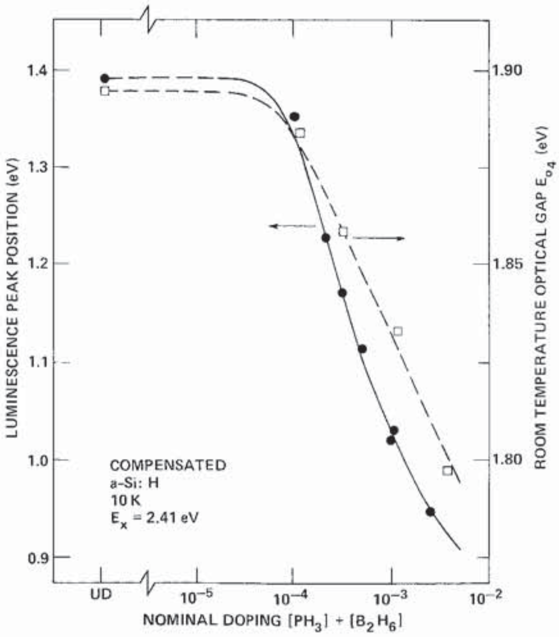


Luminescence intensity, peak position and line width in a-Si:H samples doped with 10^{-3}[PH_3] and compensated with differing amounts of boron (Street *et al.* 1981).

intensity substantially—up to an order of magnitude in the example shown. This increase occurs at all doping levels, although in no case is the intensity restored to the highest values observed in undoped samples. The increase in the luminescence intensity demonstrates that non-radiative recombination is reduced. According to the model of internal electric fields, compensation will, if anything, reduce the luminescence intensity because ionization of the dopants should be complete. In fact, in early measurements. Nashashibi *et al.* (1977 a) reported a small decrease of intensity with compensation, and used this as evidence for internal fields. It is not clear why this data should give an opposite effect as that reported by Street *et al.* (1981).

Within the model that doping introduces defects, the increased intensity with compensation implies a reduced defect density . Again, strong evidence for this result is given by light induced E.S.R. as shown in fig. 47. The dangling bond spin density decreases with compensation and eventually becomes undetectable at nominal compensation. Since in addition, no equilibrium E.S.R. is detected in these samples, the dangling bond density is deduced to be very small. However, a broad resonance, characteristic of holes but shifted to a higher g-value is observed in compensated samples and its origin is discussed further below.

Fig. 46



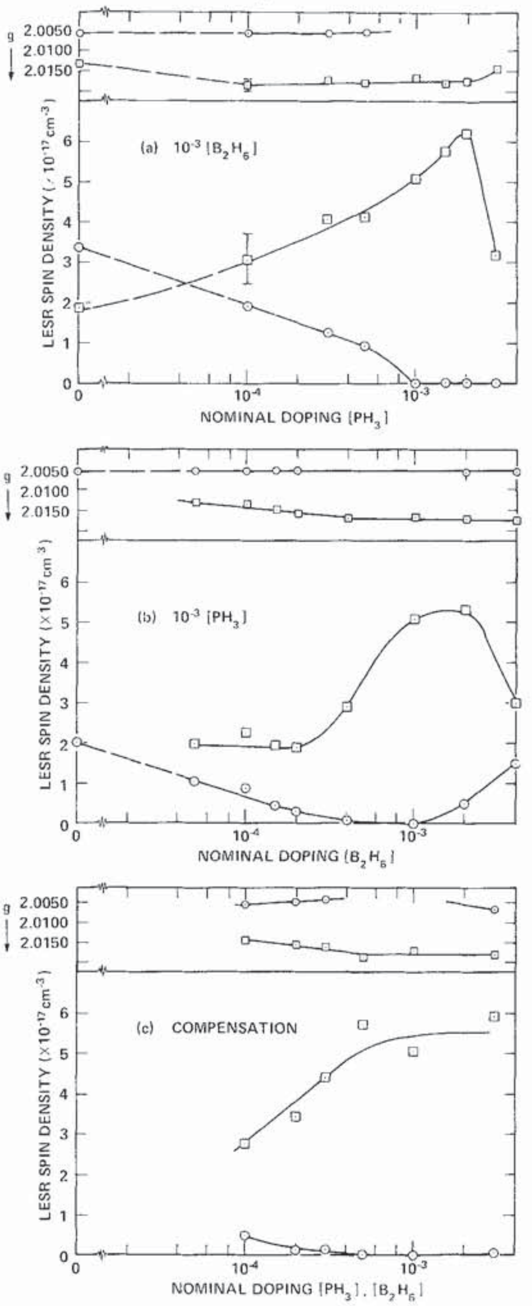
Luminescence peak position as a function of doping level in nominally compensated material. Also shown is the similar, but much smaller shift of the optical gap (Street *et al.* 1981).

From the luminescence and E.S.R. data Street *et al.* (1981) infer that there is a mechanism that causes an increase in the dangling bond density with doping and a reduction with compensation. They argue that the mechanism is unlikely to be related to changes in plasma chemistry during deposition due to the presence of dopant gases. Instead they suggest an autocompensation mechanism in which defects are introduced to compensate for the shift of the Fermi energy (Biegelsen *et al.* 1981). This mechanism is known to occur in III–V and II–VI crystals, and can easily apply to a-Si : H. It is also proposed that the additional dangling bonds may occur in the form of impurity complexes. Again there is a parallel with the behaviour of crystalline semiconductors.

The shift of the band edge luminescence to low energy is thought to be unrelated to the mechanism which determines the luminescence intensity through the defect density but instead indicates a shift in the band edge states. The temperature dependence and decay properties of the luminescence indicate that the electron states are not grossly affected by doping and compensation and a similar result is found from electron transport measurements (Allen *et al.* 1977). It is therefore inferred that compensation must introduce a broad band of states above the valence band which allows holes to thermalize further into the gap than the band tail (Street *et al.* 1981).

The broad line observed in light induced E.S.R. data as shown in fig. 47 is further evidence of new hole traps introduced by compensation. Street *et al.* (1981) have suggested that the origin of these states is boron–phosphorus complexes but this supposition remains to be confirmed. However, there is some other indirect evidence for such complexes. It appears that the co-doping process is not additive for the two

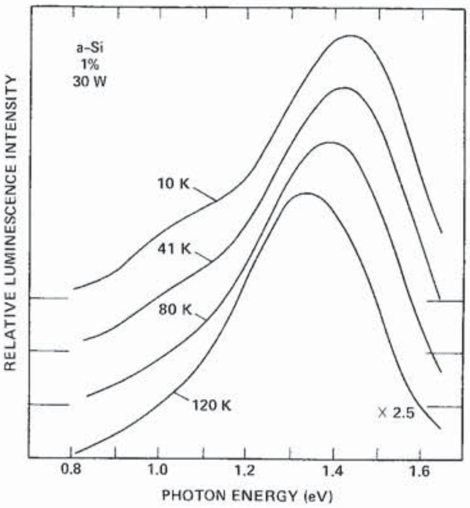
Fig. 47



L.E.S.R. spin density of electron (circles) and hole (squares) resonances in doped and compensated a-Si : H. The *g*-values are also shown (Street *et al.* 1981).

dopants. Instead there is some reaction during plasma deposition which tends to equalize the two dopant concentrations. The experimental evidence is the observation that if the proportions of PH_3 and B_2H_6 in the gas are very different, then there is a strong tendency for the minority constituent to become incorporated in the film much more efficiently (Street *et al.* 1981). The implication is that there is a tendency for boron and phosphorus to pair during deposition.

Fig. 48



Luminescence spectra of deliberately oxygen-contaminated samples showing low energy shoulder which disappears at high temperatures (Street *et al.* 1978 b).

3.3. *Other impurities*

Both oxygen and nitrogen in doping concentrations have been reported to influence strongly the photoconductivity of a-Si : H (Griffith *et al.* 1980). There is evidence of cooperative effects between these two impurities, which may be similar to those of B and P discussed above. In luminescence studies no effect of nitrogen has been detected when the concentration is less than 1% (R. A. Street, unpublished 1980 results). The alloying effects at higher concentrations are described in §4.4. There have been no reports of any effect of carbon at low concentrations. However, oxygen has been found to result in an additional luminescence band at 1·1–1·2 eV (Street *et al.* 1978 b, Street and Knights 1980). This band is observed when oxygen is added during deposition, or by post-deposition oxidation of samples with a columnar structure. Examples of typical luminescence spectra are shown in fig. 48. The oxygen band usually appears as a weak shoulder on the low energy side of the band edge transition; there are no examples reported in which the oxygen band dominates. A characteristic feature of the luminescence is that its intensity is quenched at a lower temperature than the band edge transition as is shown by the spectra of fig. 48. This result is interesting because the usual explanation of quenching by thermal ionization of electron–hole pairs, implies that the binding energy of the pair is less than that of the band edge transition. It seems unlikely that this transition could involve shallower states than the 1·4 eV peak, particularly as the luminescence lies at a lower energy. A possible explanation is that the luminescence arises from a transition between a band tail electron and a neutral centre. In this case the Coulomb attraction is absent and the binding energy could be reduced sufficiently to explain the low temperature of quenching.

There is little definite evidence about the recombination centre introduced by oxygen. Oxygen in twofold coordination seems unlikely to generate localized states in the gap. The evidence for this assertion is described in §4.4 in which the effects of alloying with oxygen, the majority of which is twofold coordinated, is primarily to increase the band gap. Possibly the oxygen luminescence originates from singly or threefold coordinated oxygen. In this case the recombination may have the same character as in chalcogenide glasses (Street 1976). These materials are believed to have charged over- and under-coordinated defects in their ground state. One model for luminescence is a transition between a conduction band electron and a hole trapped at a negatively charged defect (Street 1976). The trapped hole constitutes a neutral centre, and so the proposed interpretation of the thermal quenching discussed above follows from this model. These ideas are rather speculative and require much more experimental investigation. It would be interesting to investigate other chalcogen impurities in a-Si : H, such as selenium.

§4. RELATED MATERIALS ISSUES

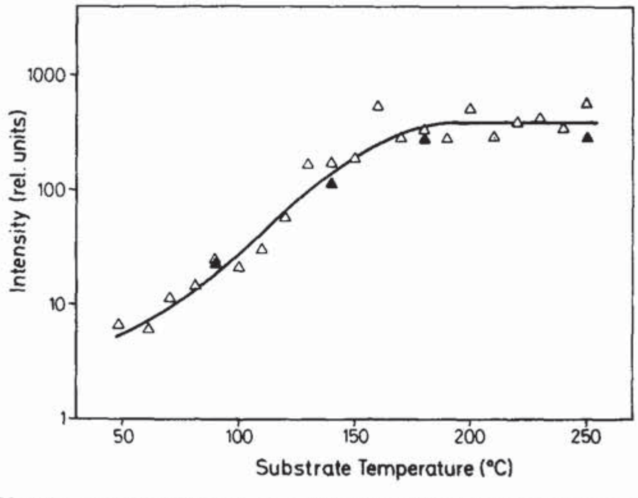
Provided the recombination mechanisms are reasonably well understood, luminescence can be used as a technique for investigating material properties. In this section some experiments on a-Si : H which use luminescence in this way are described. It is apparent from the discussion of §2.3.2 that there is a direct link between the luminescence intensity and the E.S.R. spin density and in many of these material studies, both experiments have been performed. However, the link appears to be sufficiently strong that, with the exception of ion or electron bombarded material (§4.2), the spin density can be inferred from the luminescence intensity and vice versa, with reasonable accuracy.

4.1. *Glow discharge and sputtered material*

As mentioned in §1.2, the properties of a-Si : H are very sensitive to the method of preparation. In particular the dangling bond density can vary from $\sim 10^{15}$ to over 10^{19} cm^{-3} with a corresponding change in the luminescence intensity. This property has proved to be extremely useful for the understanding of luminescence because it provides a controllable variable which can be directly linked to the recombination. In this section we discuss the specific deposition conditions which cause the variation in luminescence and spin density in both glow discharges and sputtered a-Si : H.

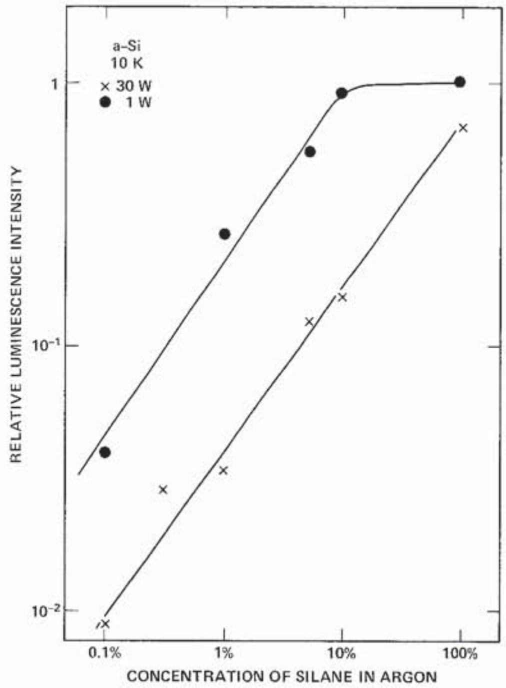
Figure 49 shows the luminescence intensity as a function of substrate temperature for an inductive glow discharge system (Engemann and Fischer 1974). Similar

Fig. 49



Dependence of luminescence intensity on substrate temperature for glow discharge a-Si : H (Engemann and Fischer 1974).

Fig. 50



Dependence of luminescence intensity on r.f. power and gas dilution for a fixed substrate temperature (Street *et al.* 1978b).

(but not identical) results are found in a capacitative system (Street *et al.* 1978b). There is no equivalent luminescence data for sputtered samples, but from other properties it is fairly evident that the same sort of behaviour occurs. E.S.R. measurements confirm that the increase in luminescence intensity is due to a corresponding decrease in the spin density. Thus, as has been found from other electrical properties, films deposited at 200–300°C have the best electronic properties in terms of the lowest rate of trapping and recombination at the defects. At higher substrate temperatures, the luminescence intensity again decreases because the sticking coefficient of hydrogen decreases and more dangling bonds are formed. This process is related to hydrogen evolution which is discussed in § 4.3. In glow discharge material the properties of the films are also sensitive to the r.f. power and dilution of SiH_4 in argon (Street *et al.* 1978b). Typical data in fig. 50 show that even at a substrate temperature of 230°C, the luminescence intensity can decrease two orders of magnitude as these parameters are varied. Some changes in the luminescence intensity also occur when the gas pressure and flow rate are varied, but these seem to be relatively minor effects.

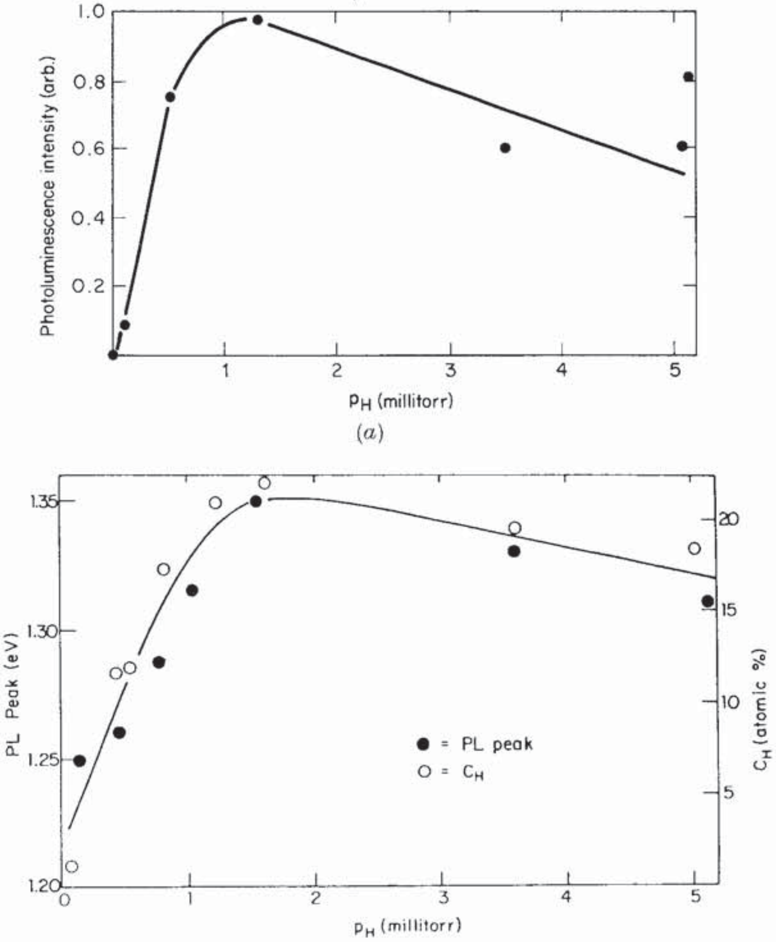
It is known that dilution with argon and other inert gasses leads to columnar growth structures in a-Si : H films (Knights and Lujan 1979). The material between the columns is relatively rich in hydrogen compared to the bulk of the columns (Knights 1979, Nemanich *et al.* 1980, Reimer *et al.* 1980, Street and Knights 1981). There is also clear evidence that the formation of dangling bond defects is correlated with the columnar structure (Knights and Lujan 1979). However, apart from the effect of the dangling bonds, there is no indication that the columnar structure has any other influence on the luminescence properties. For example, a model in which defects are randomly distributed adequately describes the luminescence. Because of its high hydrogen content, the region between the columns tends to oxidize. However, even under these circumstances there is little change in the luminescence (Street and Knights 1981). The reason for this surprising insensitivity to microstructure is probably that at low temperature the luminescence is a local process involving electron–hole pairs that do not diffuse, so that even in a column of only 100 Å diameter, the probability of a pair being close to the surface of the column is still quite small.

The luminescence spectrum also changes when the deposition conditions are changed. For example, at low substrate temperatures, the luminescence peak shifts to low energy and becomes broader (Street *et al.* 1978 b). Possible reasons for this effect are a broadening of the band tails, a decrease of the band gap, or an increase in the Stokes shift. In this case, the absorption edge actually moves to higher energy at low substrate temperatures, so an increase in the Stokes shift is indicated. A bias voltage during deposition also has the effect of shifting the luminescence peak to low energy, but in this case the band gap is found to decrease (Rosenblum *et al.* 1981). A similar tracking of the luminescence energy and band gap is found by Kurita *et al.* (1979). When a bias voltage is applied the dependence of the luminescence on the other deposition parameters such as r.f. power is modified (Street *et al.* 1978 b). Although the effects of deposition conditions on the luminescence and other properties of a-Si : H are well documented, the underlying reasons for the changes are not well understood because the chemical reactions that occur in the plasma are not yet understood in detail.

In sputtered material, the partial pressure of hydrogen and argon are important parameters (Paesler and Paul 1980, Anderson *et al.* 1979 b). The luminescence intensity and peak position are shown as a function of hydrogen pressure in fig. 51 and the line width has a similar dependence. The peak at 1–2 mtorr actually represents a peak in the hydrogen content of the films, as shown in fig. 51. In these materials the band gap approximately follows the hydrogen content, which also explains the shift of the luminescence. Austin *et al.* (1979 b) have made a direct comparison of the luminescence of sputtered and low defect density glow discharge material. They find that the maximum luminescence intensity of the sputtered films equals that of the glow discharge material. The spectrum of the sputtered material is slightly broader and shifted to higher energy by about 0·1 eV compared to glow discharge films.

The conclusion of these studies is that the major effect of the deposition conditions is to vary the intensity of luminescence which is determined by the change in defect density, and this can be controlled over a wide range in either sputtering or glow discharge. All the indications are that the properties of the films are accurately repeatable, provided the same deposition conditions are used. The energy of the luminescence peak and its width probably depend more on the details of the hydrogen bonding than simply on the defect density. Here one is concerned with the total hydrogen content and the relative abundance of the different components—SiH, SiH_2, $(SiH_2)_n$, SiH_3, etc.—as well as the presence or absence of columnar structure. In general it seems unlikely that the conditions generated by glow discharge with some specified deposition conditions, could ever be exactly reproduced by sputtering. However, one expects that the range of sample structures accessible by the two types of deposition systems overlap so strongly that one does

Fig. 51



(*a*)

(*b*)

Dependence of luminescence intensity, peak energy and hydrogen content of the sample on the hydrogen partial pressure in reactively sputtered material (Paesler and Paul 1980).

not anticipate any fundamental characteristic differences in the luminescence properties from samples of the two types of deposition systems.

4.2. *Bombardment damage, hydrogen evolution, annealing and rehydrogenation*

In §4.1 the changes in material property caused by different deposition conditions were described. In this section we discuss various means of changing the structure and properties of a-Si : H after deposition has occurred. One of the most direct methods is to use electron or ion bombardment. This is known to result in the rupture of bonds and the creation of a large defect density in crystals and evidently a similar process occurs in amorphous silicon. The increase in defect density can be observed directly by E.S.R. and is inferred from changes in conductivity and photoconductivity as well as luminescence. As in crystalline semiconductors the damage induced by bombardment can be reversed to some extent by annealing. Figure 52 shows data following bombardment by several different types of ions