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Luminescence excitation and bleaching involving dangling bonds in silicon nitride

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Résumé. — Les bandes de luminescence du nitrure de silicium amorphe sont étudiées par la méthode d'émission anti-Stokes décroissante dans le temps, utilisant la stimulation par irradiation infra-rouge et les techniques ordinaires d'excitation UV. Les profondeurs de trois défauts sont situées à 1.47 ± 0.03 eV au-dessous de la bande de conduction, 2.1 ± 0.2 et 1.6 ± 0.2 eV au-dessus de la bande de valence. Nous proposons que ces défauts soient associés respectivement aux états de charge négative et positive de la liaison pendante du silicium, le dernier étant un trou auto piégé. Les résultats obtenus par luminescence sont expliqués de façon satisfaisante si on suppose une énergie de corrélation U positive. D'autre part, les lois de décroissance dans le temps de la luminescence suggèrent l'existence d'une large gamme d'énergie de séparation entre paires de défauts.

Abstract. — The origin of visible luminescence bands in amorphous silicon nitride is investigated by using time-decaying anti-Stokes luminescence methods with infra-red stimulation, in conjunction with standard UV excitation techniques. The optical depths of three centres are measured as being 1.47 ± 0.03 eV from the conduction band and, 2.1 ± 0.2 and 1.6 ± 0.2 eV from the valence band. It is argued that these defects are respectively the negatively and positively charged silicon dangling bond centres, and the self trapped hole. The luminescence results are best explained by allowing the dangling bond to have a positive correlation energy, U . Consideration of the time decay characteristics of the luminescence suggests that there is a wide range of intra-defect pair separations.

1. Introduction.

Silicon nitride is an important insulating material, finding uses in numerous technological applications, not least in controlling the non-volatile memory properties of metal-nitride-oxide semiconductor devices. For these devices, the properties of the defects within the material are crucial, and Ngai and Hsia [1] have argued that it is the silicon dangling bonds, DBs, that are of particular importance. These, being amphoteric in nature, are likely to be found in three charge states within the band gap, as the diamagnetic $(DB^{2-})^-$ and $(DB^+)^+$

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«donor» and «acceptor» type centres, and the paramagnetic but electronically neutral $(\text{DB})^\circ$; Krick *et al.* [2] produced experimental evidence to support this idea. (We use throughout this article the notation $(\text{DB}^x)^y$, x being the number of non bonding electrons located at the centre and y being the overall charge of the defect). Because of the ease of observing $(\text{DB})^\circ$ via electron paramagnetic resonance (EPR) techniques, it is this charge state of the defect that has been most extensively studied. Its position within the band gap has not, however, been experimentally determined, although Crowder *et al.* [3] have shown that it is photo bleachable for light in the energy range 1.8 to 4.7 eV and photo-excitabile for energies greater than 3.5 eV. Robertson and Powell [4] have calculated its position to be near midgap, at 3.1 eV from the conduction band. However, the properties of $(\text{DB})^-$ and $(\text{DB})^+$ have proved more elusive to study and the energy positions of the defect levels are unknown. It has therefore not been possible to resolve the debate [1, 4] as to whether the defect has a positive or negative correlation energy, U . For a positive U system, the donor-like state lies at a higher energy position in the band gap than the corresponding acceptor; for a negative U , this situation is reversed.

By using luminescence methods, it should in principle be possible to gain information on the dangling bond defect in all its charge states, as well as resolve the question as to the sign of U , and several such studies have previously been reported [5, 6]. From these investigations, the material is shown to exhibit emission bands at 3.2, 2.5 and 1.7 eV, the general consensus being that dangling bonds may be involved in the emission process, although what the exact transitions are is unclear. However, Pundur *et al.* [7] postulate an alternative model whereby the luminescence arises exclusively from the Si-Si bonds and self-trapped electrons and holes.

The primary aim of the present investigation was to resolve some of the outstanding questions outlined above. Luminescence methods are perhaps the most promising in this respect, but the previous investigations have left a confusing picture. We have therefore opted to use an unconventional method of measurement that would allow a more definite identification of the luminescence processes. It is based on the argument that, if the defects are important in non-volatile memory devices, they must be deep enough within the band gap to be thermally stable at room temperature. It should therefore be possible to employ a variation of the technique used by Huntley *et al.* [8] for monitoring charge accumulation at deep defects in quartz. In our experiments, all three dangling bond centres are expected to be populated after irradiation with above band gap light. If these are the dominant luminescence centres, then time decaying **high** energy emission can be stimulated in the material using **low** energy excitation (i.e. anti-Stokes shifted), by stimulating an electron to the conduction band from $(\text{DB})^-$ and allowing it to recombine at $(\text{DB})^+$ (or the reverse process, *via* the valence band), but *only* if the defects have positive correlation energy U . The energies of the defects concerned can also be easily measured. If, on the other hand, the system has negative correlation, the same excitation procedure would yield time decaying luminescence that is Stokes shifted in energy.

Experimentally, we observe *anti*-Stokes luminescence, and possible models for the emission excitation and quenching processes are discussed in relation to the results of light induced EPR measurements, carried out on the same samples.

2. Experimental details.

Amorphous samples of plasma enhanced, chemical vapour deposited (PECVD) silicon nitride were grown at 400 °C in a gas mixture of ammonia and silane, ratio 20 : 1. The material, removed from its substrate, was placed either in quartz tubes for EPR investigations or on metal alloy discs for the luminescence measurements. The EPR was carried out using a Bruker type 300 spectrometer operating at 9.5 GHz equipped with an optical access

TE₁₀₃ cavity, allowing *in situ* sample irradiation. The experimental arrangement for the optical investigations consisted of :

i) A 150 W deuterium lamp or 450 W UV xenon lamp, dispersed using a 1/8 m grating monochromator in the energy range 3-6 eV. This unit was used for EPR sample irradiation, standard (steady state, stokes-shifted) luminescence measurements, as well as for populating the deep centres prior to study *via* the anti-Stokes luminescence experiment ;

ii) an array of GaAs light emitting diodes (peak wavelength 930 nm (1.33 eV), FWHM 0.05 eV, with a high energy wing up to 1.5 eV and powers up to 120 mW) used for stimulating the anti-Stokes luminescence ;

iii) a photomultiplier for luminescence detection (sensitive from the UV to IR, Hamamatsu type R955), coupled to either a 1/8 m grating monochromator for wavelength resolved work, or filters for the time resolved work (Schott type BG38 or BG18 which transmit in the region 300-700 nm, but block the IR diode wavelengths at 933 nm) ;

iv) white light sources (150 W tungsten, or 450 W xenon) coupled to a 1/8 m monochromator for use in monochromatic bleaching of the defect centres within the energy range 1-5 eV.

All measurements were carried out at room temperature, and spectra have been corrected for instrumental response.

3. Results and discussion.

The EPR spectra from the samples used consisted solely of the silicon (DB)[°] dangling bond resonance, with a *g*-value of 2.003, as seen by others [2]. Illumination of the sample with above band gap light (e.g. 5.6 eV) yielded a ten-fold increase in the signal strength, which could subsequently be bleached using sub-band gap irradiation (e.g. 3.5 eV). These measurements, which we describe in more detail below, indicate that dangling bonds are present in the material and may play a significant role in any luminescence process. It also shows that the material is near stoichiometry (as expected, with the gas flow ratios used), since the *g*-value is known to increase with increasing silicon content [9]. These points, together with the measurement of the band gap at 5.1 eV, all suggest that the influence of Si-Si bonds in the material is minimal, simplifying interpretation of the luminescence results. We note that after irradiation, no additional resonances could be observed which might be attributed to electrons and holes trapped in band tail states.

The general features of the luminescence properties are now outlined. Following irradiation of the samples with deep-UV light (during which they typically received around 10 J of energy between 5 and 6 eV), visible luminescence can subsequently be stimulated by exposure to the infra-red radiation from the GaAs photo-diodes (1.3 eV, 930 nm). This emission, under *continuous* IR excitation, decays completely within a matter of a few seconds (see Fig. 1a), and can only be re-stimulated by subsequent exposure to the UV light.

To investigate the wavelength resolved *sensitization* of the luminescence (see Fig. 2a), we measured its intensity obtained after the samples were illuminated with monochromatic UV irradiation at successively greater energies. After correcting for changes in the incident photon flux, the results reveal that it is primarily photons with energy at or above the band gap that are responsible for the effect : the onset of sensitization is at 5.0 ± 0.2 eV and this compares, for example, with the value of 5.1 eV confirmed by Hiranaka and Yamaguchi [10] as being the band gap in PECVD silicon nitride. The same sensitization experiment on the dangling bond ESR resonance, shown as the dashed line in figure 2a, reveals an enhancement of the signal for energies greater than 4 eV, but this is again much more efficient for energies greater than the band gap.

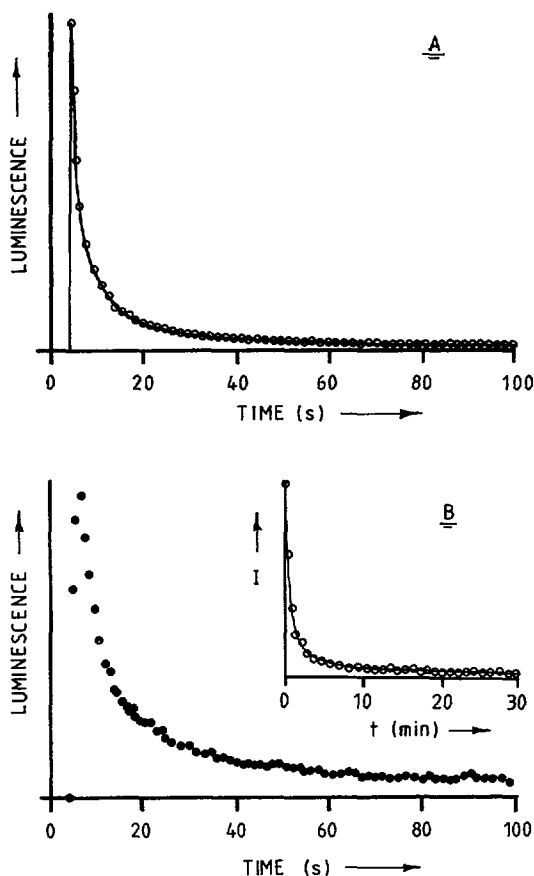


Fig. 1. — Decay curves for the stimulated UV/visible emission from silicon nitride under continuous infra-red excitation (930 nm, 20 mW); the IR is applied at $t = 4$ s. The samples need to be sensitized with deep UV irradiation prior to measurement; curve a) is for a 30 s delay between the end of sensitization and the application of the IR stimulation, whereas b) is for a 1 h delay (here the intensity scale is increased by a factor 4, compared with Fig. 1a). The inset to figure 1b shows the decay of phosphorescence in the material (without external stimulation) and is compared with the decay curve $I(t) = I(0)/(1 + 0.044 t)$. Taking this phosphorescence into consideration (it represents about 7 % of the emission if the IR stimulation is applied 30 s after UV stimulation is ceased), the decay of figure 1a is then shown to follow the relationship $I(t) = I(0)/(1 + 0.24 t)^2$, drawn as the solid line.

To investigate the wavelength resolved *bleaching* of the luminescence, we measured the intensity remaining after first sensitizing with 10 J of UV irradiation and *then* bleaching for 10 min with monochromatic IR irradiation, using the experimental arrangement described in section 2.iv. Figure 2b shows an onset of bleaching at 1.47 ± 0.03 eV: this remains very efficient for all energies between 1.6 eV and 3 eV. The corresponding bleaching experiment for the EPR dangling bond resonances shows a very different behaviour (the dotted line in Fig. 2b), with a low energy threshold at 3 eV and a maximum efficiency at 3.55 eV; for greater energies, competition with the excitation process decreases the bleaching efficiency.

Finally, we have wavelength resolved the emission of the IR stimulated luminescence, measured over the accessible region 300-700 nm. As shown in figure 2c, three reasonably well

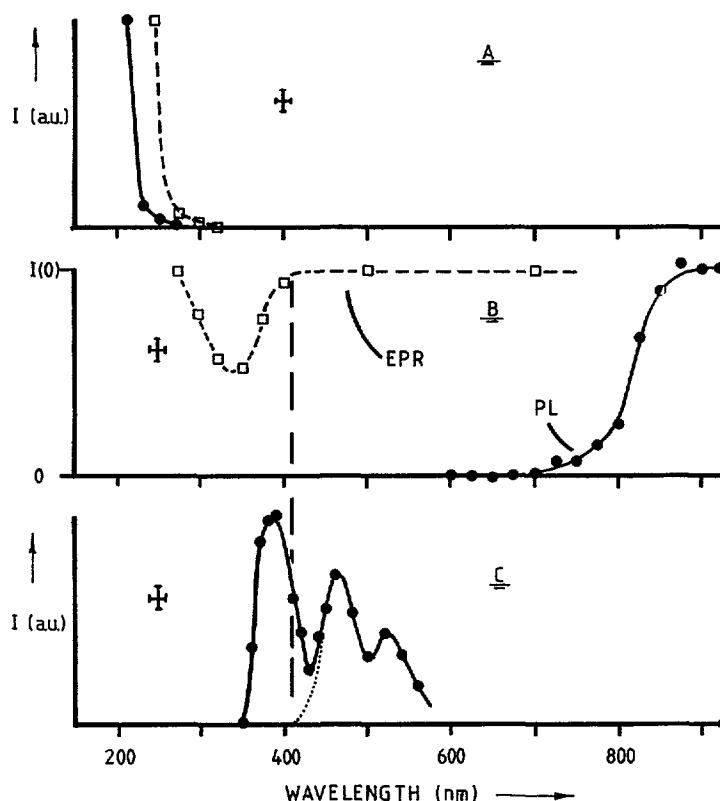


Fig. 2. — The wavelength resolved characteristics of the IR stimulated luminescence and light induced EPR signal : a) the UV sensitization, demonstrating that this takes place for photons of energy at or above the band gap for the luminescence (solid curve), but at sub band-gap energies for the EPR (broken curve); b) the bleaching, which, for the luminescence (solid curve) takes place after sensitization but before measurement. The low energy threshold of the luminescence bleaching curve yields the energy of the deep donor within the band gap. The low energy threshold for EPR bleaching (broken curve) is at the same energy as the zero phonon position of the 460 nm luminescence band ; c) the emission spectrum. Each point represents the maximum intensity of the IR stimulated light output, after the sample has received a standard exposure to UV irradiation. The high energy thresholds of the emission bands yield the energies of the recombination centres within the band gap.

resolved bands are observed peaking at 385, 460 and 515 nm (3.22 ± 0.05 , 2.70 ± 0.04 and 2.38 ± 0.05 eV respectively). The high energy emission thresholds for these bands are, respectively, 3.49 ± 0.05 eV, 2.95 ± 0.09 and 2.6 ± 0.1 eV.

The nature of the luminescence experiment means that a general model for the system is easy to develop : above band gap irradiation causes the excitation of electrons from the valence to conduction bands, and the resulting free electrons and holes then become trapped at deep lying centres in the material. Subsequent irradiation with low energy IR photons causes the release of charge from one of these centres, giving rise to luminescence as it recombines with charge located at the complementary centre. As we describe in more detail below, this emission comprises of a series of well defined peaks and so is much more likely to arise from band-to-bound transitions involving defects within the material of well defined energies, rather than from luminescence involving recombination between a continuum of

band tail states where only a broad, poorly defined emission spectrum is to be expected. The question naturally arises then as to whether IR stimulation causes the release of electrons or of holes (or both simultaneously). However, the excitation energy used is right on the low energy threshold of photobleaching of the luminescence (see Fig. 2b), and so will represent the excitation of *either* electrons, *or* holes, but not both. Because the mobility of free electrons in the material is expected to be much greater than that for holes, they are less likely to become retrapped at the centres from which they have just escaped. It is consequently probable that the luminescence arises from the recombination of free electrons with bound holes: the depth of the electron trap is thus 1.47 ± 0.03 eV from the conduction band, and the depth of the dominant hole centre is 1.6 ± 0.2 eV from the valence band. (This latter value is obtained by taking the band gap of the material as 5.1 eV, and the high energy emission threshold of the 385 nm peak to represent the depth of the centre from the conduction band, as in Ref. [11]). The identity of these centres is discussed shortly.

Within the general framework described above, there are more subtle features of the experiment that are of physical interest. The time decay of the luminescence is firstly considered. If the stimulation is applied immediately after UV sensitization is ceased (Fig. 1a), then the luminescence rises « instantaneously » (within the resolution of 0.5 s) to its maximum value, thereafter decaying in time non-exponentially. Under UV irradiation, equal numbers of electrons and holes will have been created (for charge conservation) and so it might be expected that the IR stimulated luminescence would decay in the same way as an isothermal process governed by bimolecular kinetics where heat (rather than photons) is stimulating electron eviction from the donor levels. In such a case, as shown in Curie for example [12], luminescence decays following the form $I(t) = A/(1 + Bt)^2$ and reference to figure 1a shows that this indeed appears to be the case. In the analogy, A is proportional to $n_0^2 J$ and B to $n_0 J$, where n_0 is the initial population of filled electron/hole traps, and J is the excitation intensity. As expected, the initial intensity was found to be proportional to the excitation power, but because of the very weak signals at low excitation powers (the range available was 10 to 100 mW), and the additional complication of phosphorescence of the sample (see below) it was not possible to accurately determine the variation of decay rate with J . However, as we describe below, the kinetics are much more complex than this simplistic situation since allowances for the charge mobility must also be included: further work, particularly at lower temperatures, is required to fully understand the system.

In a situation where a wide distribution of intra electron-hole defect separations have been created, it might be expected that the closest pairs recombine *via* tunnelling — i.e. *via* direct « donor-acceptor » pair recombination. This may or may not be radiative. However, after sensitization is ceased, weak phosphorescence is observed which decays to a negligible level within 30 min (see Fig. 1b). The non-exponential character of this decay suggests that it is unlikely to arise from the thermal release of charge from shallow traps to the conduction (valence) bands. However, Delbecq *et al.* [13] have shown that tunnelling recombination emission (where there is a random defect distribution) should be proportional to $1/t$. Since we commence measurement of the phosphorescence some time (t_1) after stimulation is ceased (typically 20 s), then emission *via* such a mechanism will decay in proportion to $1/(1 + t/t_1)$. Reference to the inset in figure 1b shows that the phosphorescence does follow this decay over the two orders of magnitude measurable.

The fact that the closest pairs can recombine *via* tunnelling affects the form of the decay of the IR stimulated luminescence. If, after the phosphorescence has decayed to a negligible level, the infra-red stimulation is now applied (see Fig. 1b, but note the change in intensity scale), the luminescence clearly starts from zero, building up to a maximum after 4 s; after 15 s, the decay is at much the same rate and intensity as if there had been no time delay

between sensitization and stimulation. A portion of the time-luminescence curve has in effect been removed, the amount of which directly corresponds to the amount of phosphorescent decay. This result indicates that there is competition in the luminescence process from two sources, since the pairs that recombine the quickest — i.e. the closest ones — have already recombined *without* external stimulation, probably by tunnelling, and clearly indicates that the IR released electrons are now having to move a much further distance (beyond the frontier radius of the tunnelling charge) to commence recombination at the hole centres. It also means that the rate of luminescence decay is strongly influenced by the low electron mobility (the material is amorphous). An important final point is that those centres that do not recombine *via* tunnelling are thermally stable at room temperature, at least over the time period of three days measured.

We try now to build a more specific model for the luminescence properties of the silicon nitride studied, which is consistent with the light induced effects on the dangling bond EPR spectra. All reports show that under deep UV irradiation, the population of the neutral silicon dangling bond (as measured by EPR) is greatly enhanced [3, 14-16], and this is confirmed by the present investigation. Perhaps the simplest model to explain this is given by Lenahan *et al.* [16] and involves dangling bonds with negative correlation energy, U . Here (in the ideal situation) the population of the centres are initially equally divided between the two diamagnetic charge states (as required by a negative U system), converting to the paramagnetic state *via* the capture of free electrons and holes generated by above band gap irradiation; photo bleaching would thus be expected for photons of mid-gap energies (consistent with Ref. [3]) where the defects' single electron is evicted to the conduction band; this is captured by a second paramagnetic dangling bond. In this way, the system returns to its starting equilibrium condition. Such a model is unfortunately inconsistent with other data; (i) very high temperatures would be needed to anneal the paramagnetic centres, yet heating only to 250 °C has been found to be sufficient [2]. (ii) It would be impossible to observe the IR stimulated luminescence reported here. (iii) Finally, all steady state photoluminescence involving the dangling bonds would be of low energy, and the model would certainly not predict the observed bands with a high energy threshold at 3.5 eV.

We consider now the possibility that the dangling bond has a positive correlation energy, U . As described above, the EPR tells us that the (DB)⁰ state is sparsely populated prior to UV irradiation and consequently that the vast majority of centres must either be in the (DB)⁻ state, or the (DB)⁺ state, or both. For the + U system the possibility that both these other states are populated can be excluded, since IR stimulated luminescence would then be observable *prior* to UV irradiation, and this is not the case. This result implies that there is not neutrality of charge associated with the dangling bonds at the start of the experiments. For the discussion here, we take the case that initially, nearly all the dangling bonds are in the (DB)⁺ state (this being supported by evidence presented below). Upon above band gap irradiation, electron capture by (DB)⁺ generates the rapid increase in EPR arising from (DB)⁰; some (DB)⁰ capture a second electron, converting to (DB)⁻. If the dangling bonds are the only cause of charge trapping in the material, the free holes liberated by the UV irradiation would recombine with the newly populated electron centres, thereby returning the sample to its initially charged situation (and therefore producing no change in the EPR signal intensity, and no IR stimulated luminescence). However, Jousse and Kanicki [15] have observed that there is a rapid build up of positive charge in silicon nitride upon UV irradiation and, as suggested by Pundur *et al.* [7], these holes could become « self trapped » at a predicted depth of 1.5 eV above the valence band. The low temperature annealing of the EPR can then be readily explained as arising from the thermally induced recombination between these self trapped holes and the (DB)⁰ centres, which then return to the original (DB)⁺ states. The low energy

photo-bleaching of the centres [3] would follow a similar path. The infra-red stimulated UV luminescence is also explained as being the recombination of conduction band electrons released from the scarcely populated $(DB)^-$ centres (hence the very low levels of emission) and the self trapped holes, the same mechanism in fact, as given by Pundur *et al.* [7]. Our experimentally measured value for the hole depth, 1.6 eV, thus compares well with the theoretical prediction of 1.5 eV. The second luminescence band seen in the material (peaking at 460 nm) which has a high energy threshold of 3 eV must also relate to a recombination process involving conduction band electrons, and is most likely to relate to electron recombination at $(DB)^+$ centres. In such a model, it would also be predicted that the IR stimulated (time decaying) emission spectrum would very closely resemble the UV stimulated (steady state) luminescence, whereby the dominant recombination processes are between conduction band electrons and either self-trapped holes, or the positively charged dangling bonds. Reference to figure 3 shows that this is indeed the case, the only difference being that the steady state luminescence is several orders of magnitude more intense, and not so well resolved.

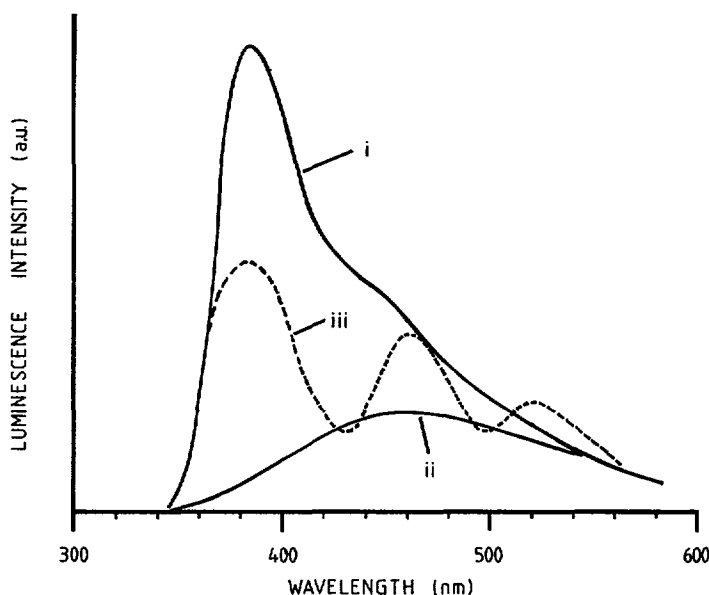


Fig. 3. — The steady state, Stokes shifted luminescence under i) 5 eV and ii) 4.6 eV excitation (same relative scale). Comparison can be drawn with the IR stimulated, time decaying emission in curve iii). Note that there are several orders of magnitude difference in the intensity of the steady state, and time decaying type spectra.

Whilst the IR stimulation (after UV irradiation) at 1.5 eV would in principle lead to an increase in the EPR signal, this is not observed in practice firstly because of the very small number of centres involved, but secondly, for energies greater than 1.6 eV, the increase is compensated for by the bleaching process involving the self-trapped holes; in our samples, there are near equal populations of both charges, as evidenced by the unobservable effects on the EPR bleach spectrum for energies lower than 2.5 eV. However, since Crowder *et al.* [3] observe bleaching of the EPR spectra for energies greater than 1.8 eV, it is likely (in the context of this model) that their self-trapped hole population is much larger than for $(DB)^-$.

The various processes thus postulated to explain the results are summarized schematically in figure 4, showing the involvement of both dangling bonds and self-trapped holes. However, since the configurational changes of the defect strongly influence the observed optical transition energies, a more specific model is shown in figure 5, showing the transitions involving *only* the dangling bond centre. The infra-red stimulated luminescence involves a pair of DB centres, whose final charge state is the paramagnetic (DB) $^{\circ}$. The energy of the sample involving just these two defects is taken as a reference zero-point energy; the lowest curve (1) of figure 5 represents the energy change with configurational distortion Q of one of the dangling bond defects; UV stimulation causes a transition of the centres' electron to the conduction band (curve 3), which also leads to the high energy bleaching of the EPR signal at a threshold energy of near 3 eV, as seen in figure 2b. The reverse transition gives rise to the 460 nm emission band, with the zero phonon energy position at 3 eV as seen in the steady state photoluminescence (fig. 3ii) under sub band gap excitation. This luminescence is also seen under IR stimulation involving transitions of electrons to the conduction band from the second defect, originally in the (DB) $^{-}$ state. Curve 2 thus represents the configurational energy change of this second centre; the IR transitions to the conduction band are represented as transitions from curve 2 to 3, and the ensuing 460 nm luminescence is as already described. Further configurational changes in the energy are expected as a valence band electron is stimulated directly into a (DB) $^{+}$ centre, which will be the threshold energy of EPR stimulation. (Note that this energy is much smaller than the threshold energy for sensitization of the IR stimulated luminescence, as demonstrated in Fig. 2a). This is represented as the difference between curves 2 and 4. Finally, any transitions involving excitation of electrons from the valence to conduction bands changes the energy of the sample as a whole, but induces no configurational changes in the defects; as an example, curve 5 lies 5.1 eV directly above curve 1.

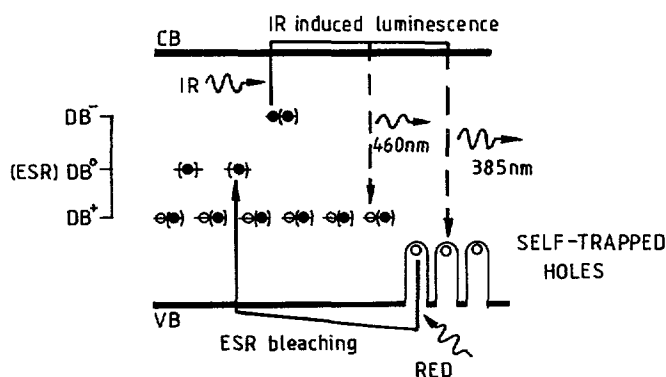


Fig. 4. — A simple model showing the involvement of dangling bonds and self trapped holes in the luminescence and EPR photo production and bleaching in silicon nitride.

4. Conclusions.

In order to arrive at a convincing description of the dominant charge trapping centres in silicon nitride, the results of four different types of measurement must be found to be mutually compatible. These are (i) the IR stimulated time decaying anti-Stokes emission, (ii) the UV stimulated steady state luminescence, (iii) the wavelength resolved photo production and bleaching of paramagnetic (DB) $^{\circ}$ centres and (iv) the thermal annealing of the metastable

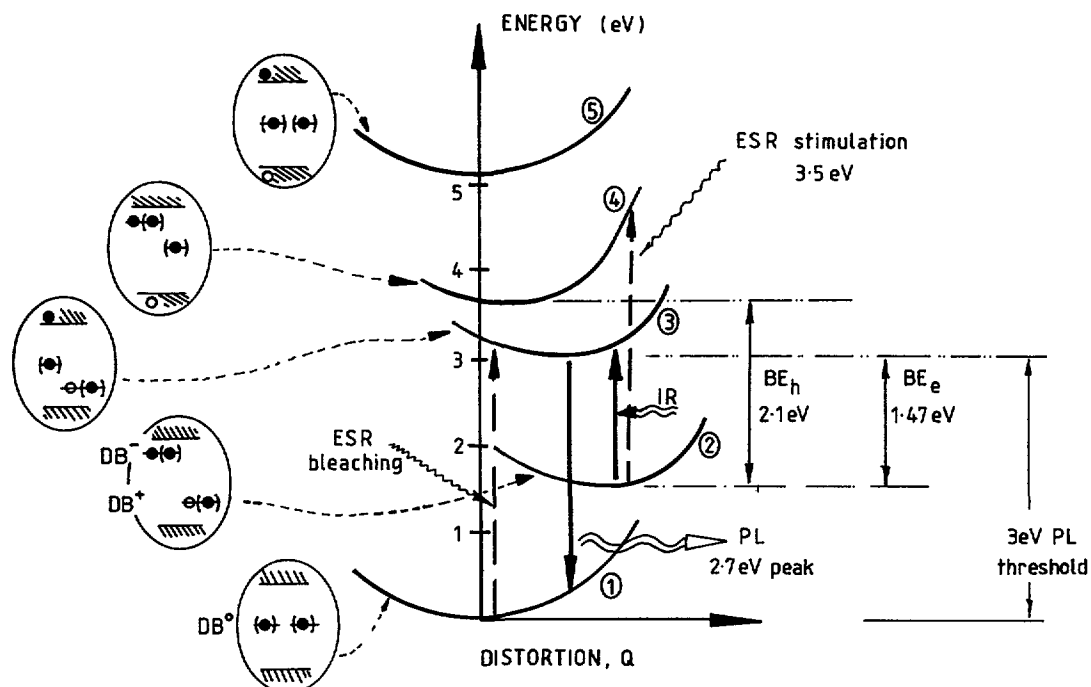


Fig. 5. — The configurational coordinate model for explaining the charge trapping properties of the silicon dangling bond in silicon nitride. The model yields a more precise picture of both the IR stimulated luminescence transitions (shown as solid lines), and the photo production and bleaching of the EPR signals.

(DB)[°] centres. We are unable to marry all these effects assuming that the dangling bond is the *only* cause of charge trapping, for either a positive or negative U system. However, all the results are satisfactorily accounted for if the dangling bond centre has a positive correlation energy U , and there is the possibility that valence band holes can become self trapped. Our measurements of luminescence and light induced EPR lead to the conclusion that the binding energy (BE) of an electron trapped at the negatively charged dangling bond centre is 1.47 eV, the BE of a hole trapped at the positively charged dangling bond centre is 2.1 eV, and for a self trapped hole, the BE is 1.6 eV. Finally, we suggest that the techniques outlined in this article would be extremely valuable in tracing the energy positions of the charged dangling bond centres in a variety of both amorphous and crystalline alloys, particularly silicon oxynitrides.

Acknowledgments.

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