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Passivation of Electronic Centres in Silicon by Hydrogen

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Hydrogen has shown a strong ability to terminate the shallow or deep-level activity of electronic centres in semiconductors. The specific case of partial or full passivation of sulphur double donors in silicon has recently received a great deal of attention. Experimental results from deep-level transient spectroscopy, infrared optical absorption and magnetic resonance together with theoretical results based on cluster calculations are discussed. Models for the singly passivated sulphur double donor in silicon are presented.

INTRODUCTION

Just over ten years ago the first reports on the passivation by hydrogen of shallow acceptors and shallow donors in silicon appeared [1,2]. Since then it has been shown that hydrogen is able to passivate a wide variety of centres including the shallow donor and acceptor centres, deep centres such as transition metals, point defects as well as extended defects in various crystalline, polycrystalline or amorphous semiconductors. In microscopic detail, various bonding or anti-bonding sites were found to account for the passivation process.

The concept of passivation of an impurity implies that its atomic structure and consequently electronic properties are significantly altered, resulting in the removal of its bandgap electronic levels. Passivation is thus distinct from compensation of donors or acceptors by counterdoping. In this latter case both kinds of impurities remain present as separate entities, only their net effect on the conductivity is reduced. Passivation of a centre, however, results in its conversion to a centre in the neutral charge state, not being able to donate electrons or holes to the bands. By this property the passivated centres are difficult to be observed experimentally and to be studied. Also, in the usual case, the electron spins are paired-off in the passivation product, resulting in electron spin $S = 0$ for the centre, eliminating the possibility of spin-dependent methods to be applied for study. In this case, few experimental methods for study remain; one that is still applicable is the local vibrational mode spectroscopy which relies on mass differences between impurity, hydrogen or deuterium, and host crystal atoms. Also the theoretical methods remain in their own right.

Given this difficulty, the double donors in silicon present a favourable case. In a simple approach, one may adopt the view that association with a hydrogen atom saturates one of the electron bonding states of the double donor and destroys the typical structure required for a double donor. In this scheme a double donor can be converted to a single donor. The resulting structure from such partial passivation would still give electrical activity and can hence be observed by the many suitable methods. Also, with an odd number of electrons, the effective electron spin will be $S = 1/2$, allowing the application of magnetic resonance in all its varieties. This case can therefore be well investigated by experimental means. Following this sketch of the situation, this paper will discuss briefly experimental and theoretical studies of the passivation, partial or full, of sulphur as a well-known chalcogen double donor in silicon [3-5].

EXPERIMENTAL RESULTS
Deep-level transient spectroscopy

A sensitive method to determine ionisation energies of carriers bound to impurities, and the concentration of these centres, is provided by deep-level transient spectroscopy (DLTS). By this method, applied to sulphur-doped silicon, the levels of the single substitutional double donor were determined as 318.2 meV for the first ionisation stage S^o/S^+ and 613.2 meV for the second, S^+/S^{2+}. In these sulphur-doped samples a sulphur-sulphur pair, S_2, is easily formed. These pairs also act as double donors with ionisation energies of 187.5 and 370 meV for $S_2{}^o/S_2{}^+$ and $S_2{}^+/S_2{}^{2+}$, respectively. Figure 1 shows the corresponding DLTS signals [6]; the specific ionisations are labelled in the figure at the temperature where they take place and the DLTS signal appears. Integrated intensities of the peaks are an accurate measure of the concentrations. In this way the equal intensities of the peaks at about 75 K and 145 K, consistently throughout the experiments, indicates that two ionisation levels of one defect are involved rather than one level for each of two different defects. Likewise for the peaks at 190 K and 280 K corresponding to the sulphur double donor states.

Upon exposure of the sulphur-doped samples, kept at a temperature of 150 °C, to monatomic hydrogen for a duration of one hour, the sulphur-related DLTS signals are reduced by more than two orders of magnitude [7]. No new levels appear. This is ascribed in a straightforward manner to the formation of sulphur-hydrogen complexes, which are the fully passivated form of sulphur. These experiments do not provide easy evidence on the structure of the formed complexes. It is therefore not established whether the reported full passivation of the sulphur and the sulphur pair requires one or two hydrogen atoms. The temperature ramping in the experiments is from 40 K upwards. Properly reflecting its name, the DLTS does not probe the ionisation region of shallow centres, roughly a zone of 100 meV below the conduction band minimum. A defect with shallow level will escape detection.

Annealing of the passivated sample at 500 °C in a hydrogen-free atmosphere leads to full recovery of the original sulphur centres [8]. Figure 2 shows how the recovery has proceeded after 5, 10 and 30 seconds annealing time. Equal activation energies for hydrogen binding of 2.1 ± 0.15 eV were derived from the kinetics of this process. During such anneal the recovery of the two ionisation levels of S, and those of S_2 as well, proceeds at equal pace. Also during the recovery no new levels become observable.

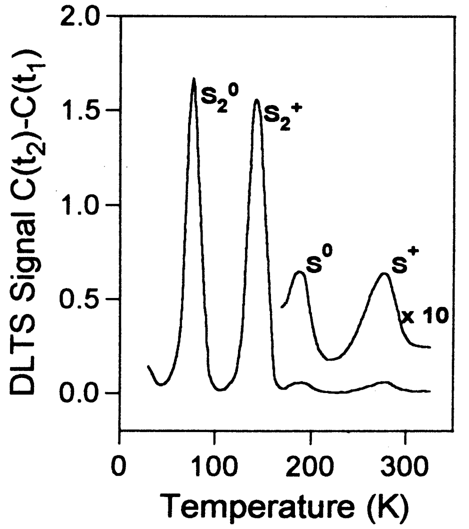


Figure 1. Deep-level transient spectroscopy signals of single sulphur and sulphur-sulphur pairs in silicon. After Pensl *et al.* [6].

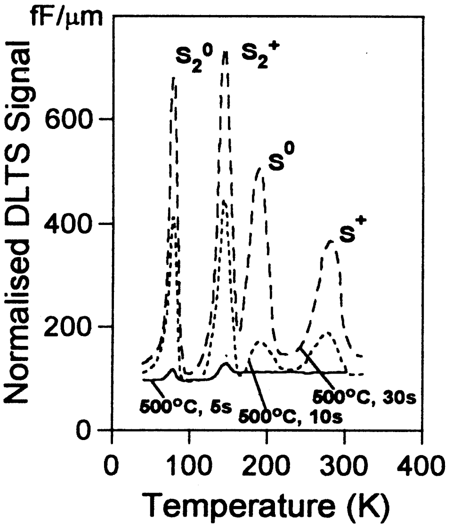


Figure 2. Recovery of the sulphur-related DLTS signals by thermal anneal at 500 °C for times of 5, 10 and 30 seconds. After Pensl *et al.* [8].

Infrared optical absorption

Applying high-resolution infrared optical absorption the spectra were observed of several sulphur-related donor centres in silicon. These included the substitutional single impurity S, the impurity pair S_2, as well as several more complex centres, which were labelled $S_c(X_n)$, n = 1,...,5 [9]. Specifically investigating the effect of hydrogenation of sulphur-doped silicon five donor levels appeared [10]. For one of these, originally labelled $S_f(X_2)$, the participation of hydrogen in the centre was demonstrated by a redshift of the line by 2.2 cm^{-1} when replacing hydrogen by deuterium. The absorption spectrum related to the 1s to 2 p_0 and 1s to $2p_\pm$ transitions of this centre is shown in figure 3(a). The ground state ionisation energy is determined as 91.7 meV by adding the ionisation energy of 6.40 meV for an electron in the $2p_\pm$ state, as given by the effective-mass theory [11], to the observed 1s to $2p_\pm$ excitation energy. For two new centres with very nearly equal energies the absorption spectra are depicted in figure 3(b). Ionisation energies were determined, as described above, as 135.1 and 135.4 meV. The absorption spectra as presented in figure 3 were obtained using a Fourier-transform infrared spectrometer with a resolution of 0.5 cm^{-1} [12] on identical samples as were also used for the magnetic resonance experiments (to be described in the next section). Also for the (S,H)[135.1 meV] and (S,H)[135.4 meV] centres a small hydrogen/deuterium isotope effect provides supporting evidence for the involvement of hydrogen. Figure 4 illustrates that the line separation for the 1s to $2p_0$ transitions increases from 3 to 3.5 cm^{-1} when hydrogen is replaced by deuterium. The relative concentrations of these two donors depended on the quenching rate following the sulphur diffusion. Slow quenching, as obtained by turning off the furnace, favours the formation of the shallower donor; rapid quench by dropping the ampoule into liquid nitrogen resulted in more prominent presence of the deeper centre. Different structural configurations of an otherwise the same complex are thus probably involved. A different atomic structure is also indicated by the opposite shift upon hydrogen/deuterium substitution, as shown in figure 4.

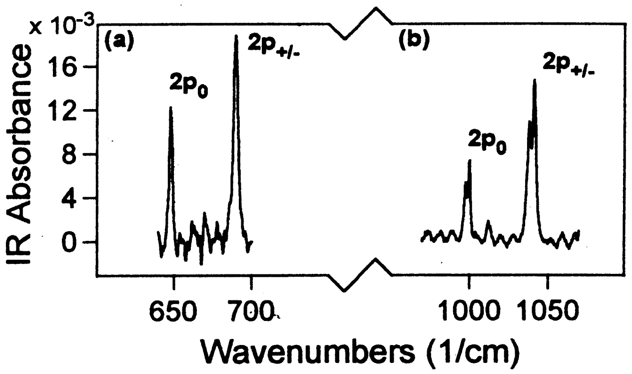


Figure 3. Infrared absorption spectra observed in hydrogenated sulphur-doped silicon showing the transitions from the donor ground state to the effective-mass states $2p_0$ and $2p_\pm$ for (a) the centre labelled (S,H)[91.7 meV] and (b) the (S,H)[135.1 meV] and (S,H)[135.4 meV] donors.

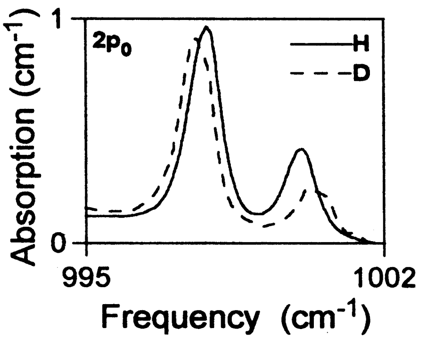


Figure 4. Isotope effect for the hydrogen/deuterium substitution on the 1s to $2p_0$ transition of the (S,H)[135.1 meV] and (S,H)[135.4 meV] donors. After Peale *et al.* [10].

Magnetic resonance

On the basis of the studies by Peale *et al.* by infrared absorption the presence of shallow single donors is expected after hydrogenation of sulphur-doped silicon. Such donor centres should be paramagnetic in their neutral charge state and thus observable in magnetic resonance. Observation of electron paramagnetic resonance (EPR) spectra has indeed been reported by Zevenbergen *et al.* [13]. Spectra for both hydrogenated and deuterated samples taken at frequencies near 23 GHz (K band) and with the magnetic field B parallel to a <100> crystal direction are shown in figure 5. The spectra reveal non-resolved structure, which varies with rotation of the magnetic field. The difference between the spectra observed in hydrogen and deuterium-treated samples suggests hydrogen involvement.

In order to more deeply investigate the electron spin resonance, the method of electron nuclear double resonance (ENDOR) was applied. In these experiments the expectation of hydrogen presence was fully confirmed. In figure 6 the nuclear magnetic resonance (NMR) transitions are shown which are responsible for the ENDOR effect. Their average value coincides with the proton resonance frequency 34.8068 MHz for the magnetic field 817.523 mT of the particular measurement. Resonances are symmetrically displaced above and below this central frequency by the hyperfine interaction between the bound donor electron and the hydrogen nucleus in the defect core. Upon rotating the magnetic field, keeping its direction in a crystallographic {011} plane, the angular dependence patterns as shown in figure 7 are obtained. Actually two independent patterns were found. For both of them the typical angular dependence indicated that they correspond to centres having a structure with the trigonal symmetry.

Having detected ENDOR signals it now becomes possible to apply the field-scanned ENDOR technique to disentangle some of the structure hidden in the EPR spectra (figure 5). As the resolution in the ENDOR experiment is more than adequate to separate the resonances a particular NMR transition can

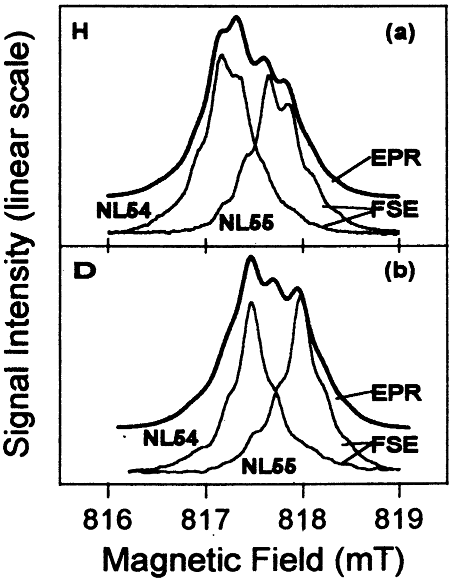


Figure 5. Electron paramagnetic resonance and field-scanned ENDOR spectra of Si-NL54 and Si-NL55 for silicon doped with natural sulphur and (a) hydrogen or (b) deuterium. Magnetic field $B \parallel <100>$, temperature of measurement 9 K, microwave frequency 22.8809 GHz (a) or 22.8851 GHz (b).

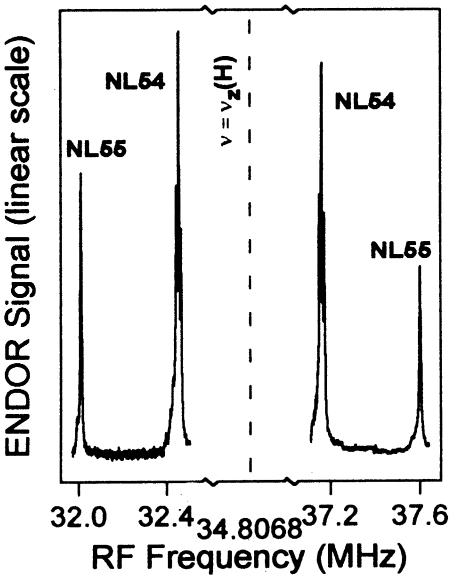


Figure 6. ENDOR scan showing the hydrogen-induced transitions around the hydrogen nuclear Zeeman frequency $\nu_n = g_n\mu_N B$ for the Si-NL54 and Si-NL55 centres. Magnetic field $B \parallel <100>$, magnetic field B = 817.523 mT, temperature of measurement 9 K.

be used to tag a double-resonance transition. When scanning the magnetic field through the EPR region, ENDOR is only recorded when also the EPR resonance condition is satisfied. In this way it is possible to select uniquely only the EPR signal belonging to a particular ENDOR. Using this field-scanned ENDOR (FSE) method, two independent components in the total EPR could be extracted. These are labelled the Si-NL54 and Si-NL55 spectra, for further reference. This underlying structure is also drawn in figure 5. Following this separation, the full angular dependence of the Si-NL54 and Si-NL55 spectra could be measured. The result, revealing also the trigonal symmetry for the fine structure, is shown in figure 8. One may then conclude that one hydrogen hyperfine pattern belongs to each of the two centres. As there is only one site in a shell of the trigonal symmetry the centres contain just one hydrogen atom. Equivalent results were obtained studying the deuterium hyperfine interactions by ENDOR or using the deuterium NMR transitions in the FSE method to separate Si-NL54 and Si-NL55 contributions in the EPR, as illustrated in figure 5(b). Following the analysis by a spin Hamiltonian the principal g values, $g_{\parallel}$ and $g_{\perp}$, are found as given in table I. It is noteworthy that g values are close to the free-electron value $g = 2.0023$, with small negative deviations, which is characteristic for shallow donor centres [14].

Having established the hydrogen involvement it remains to prove the presence of sulphur in the centres. In order to examine the role of sulphur, samples were prepared under similar conditions as before, with, however, the natural sulphur replaced by sulphur enriched to either 25.54 or 99.54% in the nuclear magnetic isotope ^{33}S. In these samples the same spectra Si-NL54 and Si-NL55 were observed but with an additional structure due to the hyperfine interaction with the ^{33}S nuclear spin, $I = 3/2$. An EPR spectrum for such a sample with the 25.54% enriched sulphur is shown in figure 9. Again applying the FSE technique based on hydrogen NMR, the individual spectra Si-NL54 and Si-NL55 were separated, as also illustrated by figure 9. The fourfold splitting where the intensity of the ^{33}S hyperfine structure lines amounts to about

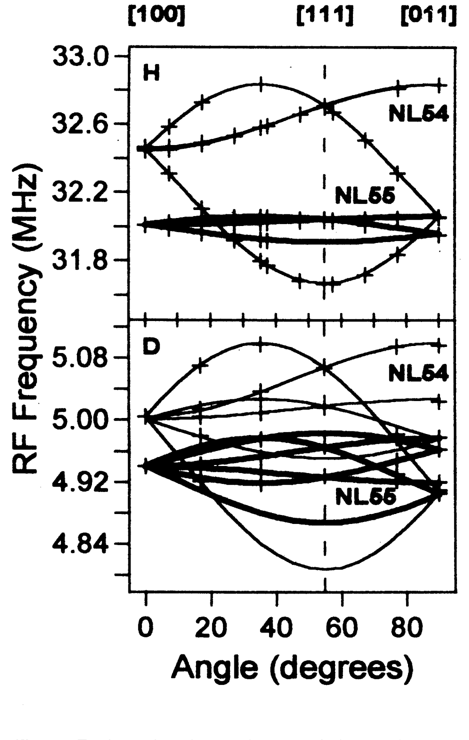


Figure 7. Angular dependence of the hydrogen and deuterium ENDOR detected on the Si-NL54 and Si-NL55 spectra. Magnetic field rotated in a {011} crystallographic plane.

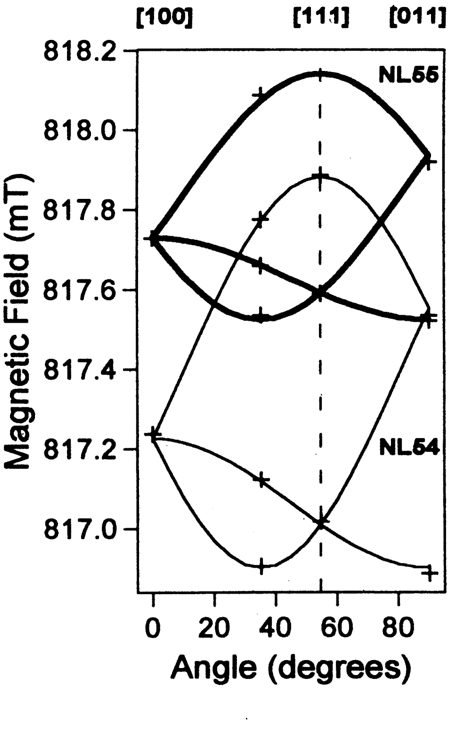


Figure 8. Angular dependence of the resonance fields of the Si-NL54 and Si-NL55 EPR spectra obtained by the field-scanned ENDOR method.

8% of the central line, which arises from the 74.46% isotopes with zero nuclear spin, demonstrates the presence of one sulphur atom. The hyperfine structure, i.e., the number and intensities of spectral lines, is inconsistent with the presence of two sulphur atoms in the studied centres. It can thus be excluded that by the detection of the Si-NL54 and Si-NL55 spectra the passivation of sulphur pairs, often present in sulphur-doped silicon, is observed.

As usual, the measured resonance fields of EPR and frequencies of ENDOR are analysed in the spin-Hamiltonian formalism. For the present case a Hamiltonian $\mathcal{H}$ representing the relevant interactions will read as

$$\mathcal{H} = \mu_B B.\mathbf{g}_e.S - (g_n)_H \mu_N B.I_H + S.\mathbf{A}_H.I_H - (g_n)_D \mu_N B.I_D + S.\mathbf{A}_D.I_D + I_D.\mathbf{Q}_D.I_D$$
$$- (g_n)_S \mu_N B.I_S + S.\mathbf{A}_S.I_S + I_S.\mathbf{Q}_S.I_S, \qquad (1)$$

with the electron spin $S = 1/2$ reflecting the single unpaired donor electron. The nuclear spin operators I have $I_H = 1/2$ for the proton, $I_D = 1$ for the deuteron and $I_S = 3/2$ for ^{33}S. Electron and nuclear Zeeman effects are represented by the $\mathbf{g}_e$ tensor and g_n scalars, respectively; **A** tensors account for the hyperfine interactions and **Q** tensors for the quadrupole effects. Parameters resulting from the analysis are collected in table I. Inspection shows that the two centres must be quite similar. The main distinction is in the eightfold difference in the anisotropy of hydrogen and deuterium hyperfine interactions.

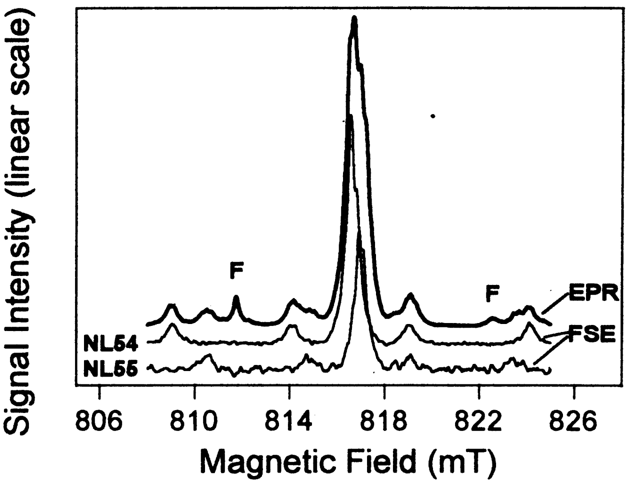


Figure 9. EPR and FSE spectra recorded for a sample doped with isotopically enriched sulphur, 25.54% of ^{33}S. To the central lines (I_S = 0: m_I = 0) of the Si-NL54 and Si-NL55 spectra belongs a fourfold hyperfine pattern (I_S = 3/2: m_I = -3/2, -1/2, +1/2, +3/2) indicating the presence of one sulphur atom.

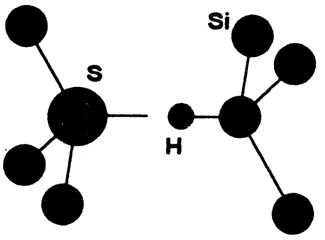
Table I. Spin-Hamiltonian parameters for the Si-NL54 and Si-NL55 centres obtained by analysis of ENDOR and FSE data with the spin Hamiltonian, equation (1). All tensors have the trigonal, i.e., <111> axial, structure. Units are MHz, except for g which is dimensionless.

Centre	$(g_e)_\parallel$	$(g_e)_\perp$	$(A_H)_\parallel$	$(A_H)_\perp$	$(A_D)_\parallel$	$(A_D)_\perp$	$(Q_D)_\parallel$	$(Q_D)_\perp$	$(A_S)_\parallel$	$(A_S)_\perp$	$(Q_S)_\parallel$	$(Q_S)_\perp$
Si-NL54	1.99886	2.00126	6.281	3.936	0.959	0.591	0.048	-0.024	143.1	137.7	6.6	-3.3
Si-NL55	1.99823	1.99974	5.801	5.500	0.867	0.823	0.038	-0.019	124.0	117.9	5.0	-2.5

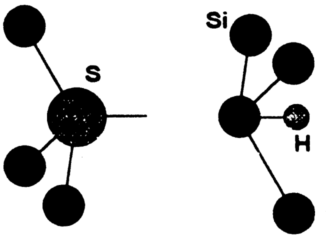
THEORETICAL RESULTS

In an early paper the hydrogen passivation of substitutional sulphur in silicon was described by Yapsir *et al.* [15]. The stable atomic configurations by adding one or two hydrogen atoms to a 32 atom cluster containing also one sulphur atom on a near-substitutional site were calculated applying LCAO (linear combination of atomic orbitals) wave functions and the MINDO (modified intermediate neglect of differential overlap) approximations. From these calculations it was found that the sulphur donor activity could be fully passivated by one or two hydrogen atoms. Hydrogen will occupy a site between sulphur and a nearest silicon atom. Hydrogen bonds primarily on the silicon neighbour, but interacts only weakly with the sulphur. The bonding induces distortion of the lattice around the S-H complex resulting in a monoclinic symmetry (pointgroup C_{1h}) for the one-hydrogen case and orthorhombic (C_{2v}) when two hydrogen atoms are accommodated. These results do not compare well with experimental findings as summarised in the preceding sections. Partial passivation as suggested by the optical and magnetic resonance experiments is not predicted; the S-H complex symmetries are not the trigonal ones as found in the magnetic resonance.

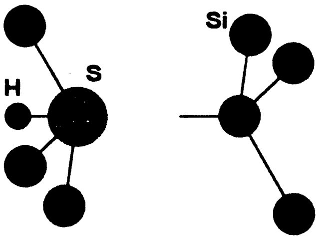
Very recently calculations were performed using a local spin density pseudopotential method [16]. These were applied to a cluster consisting of 44 silicon sites, of which one is occupied by sulphur and which is terminated by 42 hydrogen atoms. One hydrogen is introduced into the cluster. Following the conclusion from the magnetic resonance the starting configurations for the calculations were given the trigonal symmetry. This implies that hydrogen is given a position on a <111> axis passing through the sulphur atom on the substitutional site. For hydrogen then three different regions can be distinguished as illustrated by figure 10. In case (a) the hydrogen is between the sulphur atom and one of its nearest silicon neighbours, in a so-called bond-centre position. Cases (b) and (c) represent anti-bonding positions where hydrogen is either anti-bonded to silicon or to sulphur. In this scheme the forces between atoms in the cluster were calculated and full atomic relaxation was allowed without any symmetry constraints. All configurations were found to retain the trigonal, C_{3v}, symmetry. Two configurations have an approximately equal minimum energy, with a difference estimated at about 0.15 eV, close to the accuracy of the calculation. These are the bond-centre (figure 10(a)) and the silicon anti-bonding structures (figure 10(b)). The third structure, anti-bonding to sulphur (figure 10(c)), has an about 1.6 eV higher energy. By the presence of hydrogen one of the double donor levels of sulphur is pushed down into the valence band; one deep donor level remains. Some bond distances as obtained in the relaxed cluster configuration are given in figure 10.



(a) Bond centred
S-H = 2.24 Å
Si-H = 1.48 Å



(b) Anti-bonded to Si
S-H = 4.98 Å
Si-H = 1.52 Å



(c) Anti-bonded to S

Figure 10. Atomic models for the sulphur-hydrogen pairs. (a) Hydrogen on a bond-centred site, (b) hydrogen anti-bonded to a silicon first neighbour of the sulphur atom, (c) hydrogen anti-bonded to sulphur. Bond distances as indicated are from the theoretical calculation by Torres *et al.* [16].

DISCUSSION

It seems that through these studies the subject of passivation of the sulphur double donor by hydrogen has been clarified to large extent. All experimental and theoretical studies indicate a strong interaction of hydrogen with sulphur leading to the disappearance of the double donor structure and its electrical properties. The passivated complexes appear to be stable up to around 500 °C as reported from the DLTS studies. A rather similar result is obtained based on annealing studies monitoring the stability of the Si-NL54 and Si-NL55 EPR centres [17].

Comparing the results in more detail reveals, however, still discrepancies that remain to be solved. On the issue of partial passivation the available evidence largely supports this option. Magnetic resonance identifies two centres undoubtedly as being one sulphur-one hydrogen complexes which have all the characteristics of a shallow centre, such as the g value and the delocalisation of the wave function following from the weak hyperfine interactions. Shallow states with a hydrogenic level structure with ground states at 92 meV and two near 135 meV were directly observed in the optical absorption and were shown to arise from centres including hydrogen. The former one could have escaped the observation in DLTS as being too shallow. For the more deep states at 135 meV the two deviating observations are more puzzling.

All evidence is consistent with binding of one hydrogen in the observed processes. In EPR this result is positively reported. For infrared absorption the isotope effect is too small for unambiguous conclusions. In DLTS the reported first-order kinetics supports the reaction with one hydrogen only. Whether two hydrogen atoms can be bound leading to the full passivation of sulphur is beyond the potential of the experiments described. As remarked already, the observation of a fully passivated impurity is impossible in most experiments.

There appears also to be still ambiguity about the number of different passivation products that can exist as stable complexes. Magnetic resonance identifies two S-H complexes, which are similar in many aspects of their structure, but are still sufficiently different to give different ground state ionisation energies. Optical absorption reports three donor levels, of which the deeper two are very close in energy. As in the case of the thermal donors, the optical absorption spectroscopy may have the better resolution. It is thus conceivable that the latter two centres are observed as one in the magnetic resonance. The precise correlation is obviously not yet clear.

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