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Classification

Physics Abstracts

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Spectroscopy of the neutral sulphur-related centres in silicon

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Résumé. — Quatre centres donneurs associés au soufre sont observés dans du silicium implanté au soufre et recuit par spectroscopie IR à haute résolution. La présence de ces centres dont l'un, d'une énergie d'ionisation de 82,2 meV, est observé pour la première fois, est due au type de recuit effectué. Les raies observées sont généralement fines et la position des niveaux impairs est en bon accord avec la théorie de la masse effective, tandis que les transitions vers les niveaux pairs sont caractéristiques de chaque centre. La largeur d'un grand nombre de raies est comparable à celle des raies du phosphore pour des concentrations similaires alors que d'autres présentent des processus d'élargissement spécifiques.

Abstract. — A high resolution infrared absorption study of silicon samples doped with sulphur by implantation and annealing reveals the presence of four sulphur-related centres, related to the way the samples were annealed out. The centre with an ionization energy of 82.2 meV has not been reported previously. The lines observed are generally sharp and the position of all the odd-parity levels closely match the effective mass theory values while the even-parity transitions are characteristic of each centre. For many lines, the width is comparable to that observed for phosphorus lines at similar concentrations while some specific broadening effects for other lines.

1. Introduction.

Sulphur, like the other group-VI elements is known to be a double donor in silicon, in accordance with its position in the periodic table [1]. It is also known to form at least two other donor complexes in silicon, bearing in this respect a close similarity with selenium [2, 3]. Contrary to phosphorus, which can be seen as the paradigm of the shallow donor centre, substitutional sulphur introduces in the silicon band gap two deep levels, at $E_C-318.4$ and $E_C-613.5$ meV corresponding to the ionization of the neutral and singly ionized charge states [4]. This makes sulphur a suitable dopant for extrinsic detection in the near IR atmospheric windows at moderate temperatures if the production of unwanted complexes can be controlled [5].

Previous spectroscopical results on sulphur in silicon include absorption and piezo-absorption measurements near 10 K [6] and photothermal excitation experiments between 20 and 80 K [2]. As shown by Swartz *et al.*, the spectra which can be observed in silicon doped with group-VI elements depend much on the starting material and on the thermal treatment imposed on the samples [3]. These authors observed

in Se-doped Si three double donor centres, Se, Se_y and Se_x with decreasing binding energies : the Se centre is isolated substitutional selenium, Se_y is tentatively assigned to a selenium pair and the nature of Se_x is not yet elucidated. We present here low temperature absorption results for the neutral charge state of sulphur-associated centres ; the high resolution Fourier transform technique used allows the observation of nearly all the transitions expected from effective mass theory [7] and the determination of the natural widths of the line. Moreover, a new sulphur-related centre with an ionization energy of 82.2 meV is observed in the samples studied.

2. Experimental details.

The S-doped samples used were obtained by implantation of 1×10^{16} S atoms/cm² through out 400 Å of silica on both sides of high purity Si samples (p-type 20,000 Ω.cm) with typically 10^{12} P atoms/cm³. After implantation, a thick layer of silica was grown and the diffusion carried out for 20 h at 1 200 °C. The conductivity of the resulting samples was n-type with $\rho \simeq 1.2$ Ω.cm. The interstitial oxygen concentration [8]

was raised by the doping procedure from 10^{15} to 10^{16} atoms/cm³. After polishing, the thickness of the samples was 0.9 mm. They were cooled in He gas in an Oxford Instrument CF 204 continuous flow cryostat adapted to be operated under vacuum in a Bomem DA3-01 Michelson interferometer. The spectra were usually obtained with an apodized spectral band pass (s.b.p.) of 0.25 cm^{-1} ($30 \mu\text{eV}$) and they were normalized to the absorption of an intrinsic Si sample. The present investigations have been limited to the spectral domain of the SiO₂ and KBr beam splitters.

3. Experimental results and discussions.

We have observed the spectra of the hydrogenic centres in the neutral charge state, with binding energies of 318.38, 187.66, 109.56 meV and 82.2 meV. In analogy with selenium, the centres with binding energies 187.7 and 109.6 meV are labelled S_y^0 and S_x^0 , respectively and the new centre is labelled S_z^0 . Figure 1 gives an overall view of these spectra. The strongest line in each spectrum is due to the $1 s(A_1) \rightarrow 2 p_{m=\pm 1}$ transition [9] ($2 p_{\pm}$ line). For both samples investigated, the relative intensities of the S^0 , S_y^0 , S_x^0 and S_z^0 spectra, taken as the ratio of the absorption coefficients of the $2 p_{\pm}$ line, were about the same (1, 6.5, 5 and 0.3, respectively). The relative concentrations of the corresponding centres are different, however, as the optical cross-section decreases with increasing ionization energy, but the above figures can be taken as a fair order of magnitude.

We have looked for the presence of the centre reported by Humphreys *et al.* with a binding energy of 155 meV, but failed to detect it in our samples. The lines observed in the S-doped samples are listed in table I. Owing to the low intensity of the S_z^0 spectrum, only the strongest lines are detected for this centre. In the S_x^0 spectrum, a weak line at 876.2 cm^{-1} is attributed to the $1 s(A_1) \rightarrow 6 h_{\pm}$ transition of this centre. This shows that under adequate resolution, the spectra are quite comparable to the ones observed for group-V substitutional donors and for Li- and Mg- related centres as long as the transitions towards odd-parity levels are only considered [10]. The S^0 spectrum shows the strong $1 s(T_2)$ line at 2288.36 cm^{-1} ; it is even stronger than the $2 p_0$ line and $I_{1s(T_2)}/I_{2p_0} \simeq 1.4$. This ratio, i.e. the p-like character of the $1 s(T_2)$ level decreases with the ionization energy of the impurity. It is ~ 1.2 for Se⁰ and ~ 0.35 for Te⁰ [6, 11, 12]. The strength of $1 s(T_2)$ of P, which is isocoric to S⁰ is very small, as the ionization energy of P is only 45.6 meV and very high phosphorus concentrations are required to observe this transition [13]. The $2 s(T_2)$ line of S⁰ is very weak and the S/N ratio of the spectrum had to be increased by calculating the Fourier transform of the high resolution interferogram truncated to produce a s.b.p. of 2 cm^{-1} , in order to observe this line.

The observation of intervalley phonon-assisted transitions of the S_y^0 centre resonating with the S_y^0

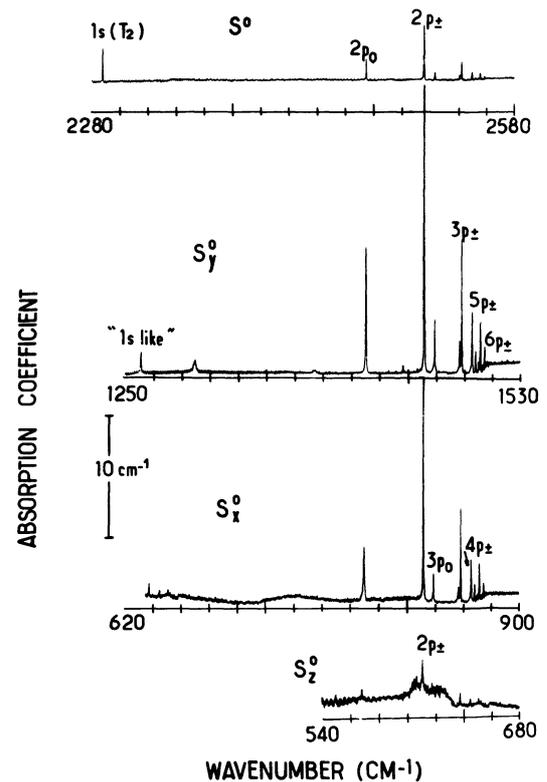


Fig. 1. — Spectra of the different S^0 -related centres in silicon at 6.5 K. The apodised spectral band pass is 0.25 cm^{-1} . The $2 p_{\pm}$ lines have been brought into coincidence. The humps in the S_x^0 and S_z^0 spectra are due to incomplete lattice absorption cancellation.

continuum is not unexpected and the results are similar to those of Humphreys *et al.* [2]. A « $1 s$ -like » level is detected with a binding energy of 34.7 meV, which is not observed in the no-phonon spectrum. For the S^0 centre, the $1 s(T_2) + 477.4 \text{ cm}^{-1}$ resonance (59.2 meV f-TO phonon) is observed, in good agreement with the position of the no-phonon $1 s(T_2)$ line. Other resonances are seen in the phonon-assisted S^0 spectrum, but the concentration of isolated sulphur in the samples investigated was not sufficient to ascribe the observed features to specific transitions with any certainty.

A comparison between the binding energy of the first even-parity levels of S^0 - and Se^0 -related centres is made in table II. If a C_{3v} symmetry is assumed for S_y and Se_y , the $1 s(T_2)$ and $1 s(E)$ states (T_d symmetry) are transformed into $1 s(\Gamma_1)_{T_2} + 1 s(\Gamma_3)_{T_2}$ and $1 s(\Gamma_3)_E$, respectively. The ground state transforms into $1 s(\Gamma_1)_{A_1}$ and the $1 s(\Gamma_1)_{A_1} \rightarrow ns(\Gamma_3)_E$ as well as the $1 s(\Gamma_1)_{A_1} \rightarrow ns(\Gamma_3)_{T_2}$ transitions are IR allowed. So, for the S_y^0 centre, the IR allowed quasi-effective mass states with binding energies of 31.3 and 8.9 meV (the one-electron model [7] yields 31.27 and 8.83 meV) could be the $1 s(\Gamma_3)_E$ and $2 s(\Gamma_3)_E$ states while the IR forbidden 34.5 meV state could be the $1 s(\Gamma_1)_{T_2}$ state, and the $1 s(\Gamma_3)_{T_2}$ and $2 s(\Gamma_3)_{T_2}$ IR allowed states could correspond to the 26.5 and 8.3 meV levels. We have

Table I. — Observed position (cm⁻¹ in vacuo) of the lines of the S⁰-related centres in silicon. For S⁰, the final state of the transitions labelled « ns-like » is the ns(T₂) level. Relative uncertainty less than or equal to 0.05 cm⁻¹ unless otherwise specified.

Line	S ⁰	S _y ⁰	S _x ⁰	S _z ⁰
« 1 s-like »	2 288.36	{ 1 261.30 1 299.5 ± 0.5	659 ± 1	568.3
2 p ₀	2 475.08		1 420.63	
« 2 s-like »	2 492.0 ± 0.5	{ 1 442.04 1 446.89	806.6 ± 0.5	611.3 ± 0.5
2 p _±	2 515.95		1 461.76	
3 p ₀	2 523.47	1 469.20	839.02	637.7 ± 0.5
4 p ₀	2 540.93	1 486.72	856.67	
3 p _±	2 542.42	1 488.24	858.29	645.1 ± 0.5
4 f ₀		1 494.62	865.4 ± 0.2	
4 p _± -5 p ₀	2 549.90	1 495.73	865.78	651.0 ± 0.5
4 f _±	2 552.25	1 498.10	868.15	
5 f ₀	2 554.37	1 500.19	869.98	651.0 ± 0.5
5 p _±	2 555.78	1 501.62	871.67	
5 f _±	2 557.3 ± 0.1	1 503.27	873.27	651.0 ± 0.5
6 p _±	2 558.82	1 504.65	874.70	

Table II. — Binding energy (meV) of the first even-parity states of S⁰- and Se⁰-related centres in silicon. The bracketed figures are obtained from Fano resonance spectra. See also reference [2] for the binding energies associated with S⁰.

State	S ⁰	Se ⁰	S _y ⁰	Se _y ⁰ (a)	S _x ⁰	Se _x ⁰ (a)	S _z ⁰
1 s(A ₁)	318.38	306.7 (a)	187.66	206.5	109.56	116.0	82.20
1 s(T ₂)	34.62	40.6 (a)					
1 s-like		34.5 (a)	{ [34.5] 31.3 26.5	31.3	27.8	28.3	
1 s(E)	[30.9] (b)	[30.8] (b)		26.0			
2 s(A ₁)	[18.6] (b)	[18.1] (b)					
2 s(T ₂)	9.4	9.3 (a)					
2 s-like			{ 8.9 8.3		9.6		

(a) Reference [3].
(b) Reference [12].

not found the equivalent of the level at 34.0 meV of Se_x⁰ for S_x⁰. The line corresponding to this level for Se-doped Si could actually be due to 2 p_± of the undetected Se_z⁰ centre, with an ionization energy of 88.4 meV, against 82.2 meV for S_z⁰. A weak line at 2 146.4 cm⁻¹, corresponding to a level with a binding energy of 40.6 meV, is observed in the Se⁰ spectrum [3]. The reason why a similar level was not found in the S⁰ spectrum can be due to the low concentration of isolated sulphur in the samples.

The observed width of the most intense and well separated lines of table I has been measured (see Table III). The natural widths are somewhat lower because of the 0.25 cm⁻¹ spectral band pass used. The natural width of the lines of the S⁰ spectrum (0.15 cm⁻¹ or 20 μeV) is similar to those of P in silicon for concentrations of the same order of magnitude [10, 14]. The 1 s(T₂) line is sharper (0.07 cm⁻¹ or 9 μeV) than the other lines of the S⁰ spectrum and no detectable spin-valley splitting is observed. The 1 s-like

Table III. — Observed widths (cm^{-1}) of some lines of the S^0 -related centres in silicon.

Line	S^0	S_y^0	S_x^0
1 s(T_2)	0.3	0.6 1.8	
2 p_0	0.4	0.5	0.75
2 p_{\pm}	—	0.45	0.45
4 p_0	—	0.45	
4 p_{\pm}	—	0.45	
3 p_{\pm}	0.4	0.4	0.4
5 p_{\pm}		0.4	0.35

line of S_y^0 at $1\,299.5\text{ cm}^{-1}$ is broadened with respect to the other lines of this centre. This could be due to some resonant effect through the coupling with Fano resonances of the S_x^0 centre. The asymmetrical broadening of the np_0 lines of S_x^0 , best seen for $2\,p_0$, can be an indication that the multivalley degeneracy associated with the np_0 levels in Si ($A_1 + E + T_2$) is split into two IR active sublevels by the symmetry of the defect. This is different from what is observed for the oxygen-related thermal donors produced in oxygen-rich silicon after annealing at $450\text{ }^\circ\text{C}$. For the oxygen-related centres, the $2\,p_0$ line is always sharper than the $2\,p_{\pm}$ line [12], indicating that these centres have a structure different from that of the S- and Se related centres.

The double donor character of S and S_y has been established, the optical ionization energy of S^+ is 614 meV and that of S_y^+ is 368 meV . Till now, the only evidence for the double donor character of S_x is indirect : Swartz *et al.* have shown that Se_x behaves like a double donor, so, from table II, we can suppose that S_x is also a double donor. In this case, an ionization energy, not very far from that of S_y^0 , is expected for S_x^+ . It could be the reason why this level escaped detection by D.L.T.S. while the two charge states of S and S_y were detected [16]. A comparison with the work of Brotherthon *et al.* shows that their sulphur I, II and III centres are what is called S_y , S and S_x here (S_z has not yet been identified by D.L.T.S.). The notation used in previous spectroscopical work for S-related centres (A, B, C, D) corresponds to S_x^0 , S_y^0 , S_y^+ and S^+ . S^0 and S_x have probably been overlooked

because of the low intensity of the spectra or because of a wrong position of the Fermi level. The slow cooling down after diffusion of the samples investigated here led to the formation of three detectable sulphur complexes besides substitutional sulphur and this is consistent with the high diffusion coefficient of sulphur in silicon [17] ($3 \times 10^{-8}\text{ cm}^2/\text{s}$ at $1\,200\text{ }^\circ\text{C}$). The fact that these centres were in the neutral charge state at low temperature stemmed from the fact that the residual acceptor concentration in the starting material was small, as checked by IR spectroscopy. The production of complexes during the cooling down step can be modified by quenching the samples from the diffusion temperature, but many results indicate that the sulphur pairs remain however the dominant centre [18]. The S^+ -related centres can be observed if the resistivity of the starting p-type material is carefully chosen, but it can easily be seen that no more than two S^+ -related centres can be observed simultaneously.

It has been assumed for some time that the S_y centre consists of sulphur pairs, but the exact location of these pairs (nearest neighbour substitutional or interstitials) has not yet been determined.

4. Conclusion.

In conclusion, we have characterized the S-related double donor centres produced by ion-implantation technique in silicon in the neutral charge state. It is shown that the doping technique used on high resistivity substrates provides samples where the dominant centre is presumably the S-pair. The centres display spectroscopically a highly hydrogenic behaviour for the p-like levels but the s-like components differ with the nature of the centres in a number of components and also in relative intensities. Piezo-spectroscopic studies and EPR studies should allow us to throw light upon the exact structure of complex centres.

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