"Properties of Crystalline Silicon", EMIS Datareviews Series No. 20
(INSPEC, IEE, London, UK, 1999) p. 659-662

11.3 Shallow thermal donors in c-Si

C.A.J. Ammerlaan

January 1998

A INTRODUCTION

This Datareview describes the shallow thermal donors formed in crystalline silicon containing oxygen upon heat treatments at 300–600°C. Energy levels due to these defects and to defects formed in the presence of nitrogen, hydrogen, aluminium and carbon, all together with oxygen, are tabulated.

B EXPERIMENTAL DATA

In a similar fashion to the thermal double donors (TDDs) [1], another family of heat-treatment centres, known as shallow thermal donors, STDs, is formed in oxygen-rich silicon upon heat treatment at temperatures between 300 and 600°C for short times, ≈10 min, or prolonged periods of several hours. These are single donors with ionisation energies in the range from 280 to 300 cm^{-1}. Usually, the concentration of STDs is low, around 10^{13} cm^{-3}, requiring a sensitive detection method such as photothermal ionisation spectroscopy (PTIS). With this technique seven different optical excitation spectra were observed related to seven very similar, but distinctly different, centres [2–4].

The energy levels of excited states are well described by the effective-mass theory. Central-cell corrections for the ground states are small. Energies of the transitions from the 1s ground state to the higher energetic states $2p_0$, $2p_\pm$, $3p_\pm$ and $4p_\pm$ are given in TABLE 1, under the heading STD(PTIS). It appears to be well established that the generation of STDs is related to some form of oxygen aggregation, similar to that occurring in the formation of the TDDs. The presence of nitrogen may affect STD growth in a more subtle, e.g. catalytic, manner [4]. It has been found that the formation of nitrogen-oxygen complexes in silicon by thermal treatment leads to a series of shallow donors with very similar ionisation energies to those of the STD(PTIS)s [5–8]. The reported excitation energies are in good agreement with the effective-mass theory for a monovalent donor; energies are given in TABLE 1, in column STD(NO). [5]. An identity of the STDs as observed in PTIS and the NO complexes has been suggested [8].

The presence of hydrogen or aluminium together with oxygen enhances the production of STDs, facilitating their detection and identification by high-resolution optical absorption spectroscopy. On the basis of such studies it was recently reported that three structurally different families of STDs exist [9]. One of these is preferentially formed in silicon containing hydrogen, either introduced by hydrogen plasma treatment or indiffusion at high temperatures. Excitation energies are given in TABLE 1, column STD(H). Upon substituting deuterium for hydrogen, a small shift of the line positions of the 1s to $2p_\pm$ transitions is observed, demonstrating the presence of hydrogen in the donor core [10].

.TABLE 1 Transition energies, in cm^{-1}, of the shallow thermal donors observed by photothermal ionisation spectroscopy and by optical absorption in the infrared. Ionisation energies E_i were calculated by adding to the observed 1s to $2p_\pm$ energies the binding energy 51.6 cm^{-1} (6.40 meV, [22]) of the $2p_\pm$ state according to the effective-mass theory. Central-cell corrections E_{cc} are with reference to the 1s energy of 31.27 meV in the effective-mass approximation [22]. Following [4] the seven species are labelled STD-A to STD-G.

	STD(PTIS) [4]	STD(NO) [5]	STD(X) [9]	STD(H) [9]	STD(Al) [9]
STD-G 1s-$2p_0$	207.3	207.4	207.3	208.7	206.4
1s-$2p_\pm$	249.6	249.9	249.8		248.6
1s-$3p_\pm$	275.9		276.2	278.5	275.1
1s-$4p_\pm$	283.5				
$E_i(cm^{-1})$	301.3	301.5	301.4		300.2
(meV)	37.35	37.38	36.37		37.22
E_{cc}(meV)	6.09	6.12	6.11		5.96
STD-F 1s-$2p_0$	203.8				
1s-$2p_\pm$	246.8		247.1	246.8	
1s-$3p_\pm$	273.9			273.0	
1s-$4p_\pm$	281.7				
$E_i(cm^{-1})$	298.5		298.7	298.4	
(meV)	37.01		37.03	37.00	
E_{cc}(meV)	5.75		5.77	5.74	
STD-E 1s-$2p_0$	198.9	200.2			
1s-$2p_\pm$	242.4	242.4			
1s-$3p_\pm$	268.7	268.8		267.1	267.3
1s-$4p_\pm$	275.9				
$E_i(cm^{-1})$	294.0	294.0			
(meV)	36.46	36.45			
E_{cc}(meV)	5.20	5.19			
STD-D 1s-$2p_0$	197.6	197.7	197.6	198.2	198.3
1s-$2p_\pm$	240.4	240.5	240.4	241.1	
1s-$3p_\pm$	266.5	266.7	266.6		
$E_i(cm^{-1})$	292.0	292.1	292.0	292.7	
(meV)	36.21	36.21	36.20	36.29	
E_{cc}(meV)	4.95	4.95	4.94	5.03	
STD-C 1s-$2p_0$	194.9	195.0	194.7	195.4	195.0
1s-$2p_\pm$	237.9	237.9	237.8	238.4	237.4
1s-$3p_\pm$	264.2				
$E_i(cm^{-1})$	289.5	289.5	289.4	290.0	289.0
(meV)	35.90	35.89	35.88	35.96	35.83
E_{cc}(meV)	4.64	4.63	4.62	4.69	4.57
STD-B 1s-$2p_0$	190.9	190.8	190.9	190.7	189.7
1s-$2p_\pm$	233.8	233.7	233.8	233.7	232.3
1s-$3p_\pm$	260.3		259.9		
$E_i(cm^{-1})$	285.4	285.3	285.4	285.3	283.9
(meV)	35.59	35.38	35.39	35.37	35.20
E_{cc}(meV)	4.13	4.11	4.13	4.11	3.94
STD-A 1s-$2p_0$	188.0		187.8	187.4	187.0
1s-$2p_\pm$	230.9		230.7	230.6	229.3
1s-$3p_\pm$	257.0				
$E_i(cm^{-1})$	282.5		282.3	282.2	280.9
(meV)	35.03		35.00	34.99	34.83
E_{cc}(meV)	3.77		3.74	3.73	3.57

Extensive studies have been made on the passivation by hydrogen of TDDs [11,12]. It was found that binding of one hydrogen atom suffices to fully passivate the donor activity. Complexes already dissociate well below 200°C, reactivating the TDDs. In view of these results it cannot be concluded that STD(H)s represent the unique form of partially hydrogen-passivated TDDs. Anneals at 550°C destroy the STD(H) centres, yielding a set labelled STD(X), spectroscopically identifiable with the STD(PTIS) centres. The STD(X)s are lost after an anneal at 650°C. Formation of STDs in aluminium-doped Czochralski silicon produces a third family of STDs with slightly shallower character; see TABLE 1, column STD(Al). The STD(Al)s appear to be the thermally most stable form.

A striking parallel between these optical observations and the features of the Si-NL10 magnetic resonance centre exists. The Si-NL10 spectrum arises from families of very similar centres with extended defect electron localization. The presence of oxygen in the centres was proven by electron-nuclear double resonance (ENDOR) [13,14]. ENDOR analysis also revealed that different Si-NL10 centres exist either containing aluminium [14,15] or hydrogen [16] in their core structure. On the basis of the production conditions a correlation in the detection of Si-NL10 signals and the presence of nitrogen in the form of NO complexes was inferred [17,18]. This suggests a link between the infrared and magnetic resonance centres, and possibly their identity. Magnetic resonance on the Si-NL10 spectrum thus far does not provide an explicit indication of nitrogen involvement by failing to detect nitrogen hyperfine interactions [19].

For a series of even shallower donors the 1s to $2p_{\pm}$ transitions were observed in silicon doped with oxygen, nitrogen and carbon, heat treated in the range 450 to 635°C; they were termed ultra-shallow thermal donors, USTDns [20,21]. Binding energies are reported to be 27.90, 28.24, 28.65, 31.40, 31.51, 32.40, 33.19, 33.30, 33.9, 34.59 and 34.85 meV, respectively, for USTDn, with n = 1,....,11. As can be noted, the first three species have a negative central-cell correction.

C CONCLUSION

Thermal treatments, at 300–600°C, of silicon containing oxygen (and also together with nitrogen, hydrogen, aluminium and carbon) produce various defect centres. The energy levels have been determined by photothermal ionisation spectroscopy and are tabulated in this Datareview. Confirmation of the presence of oxygen in these defects also comes from electron-nuclear double resonance measurements.

REFERENCES

[1] C.A.J. Ammerlaan [Datareview in this book: *11.4 Thermal double donors in c-Si*]

[2] H. Navarro, J. Griffin, J. Weber, L. Genzel [*Solid State Commun. (USA)* vol.58 (1986) p.151-5]

[3] J.A. Griffin et al [*J. Phys. C, Solid State Phys. (UK)* vol.19 (1986) p.L579-84]

[4] J.A. Griffin, J. Hartung, J. Weber, H. Navarro, L. Genzel [*Appl. Phys. A (Germany)* vol.48 (1989) p.41-7]

[5] M. Suezawa, K. Sumino, H. Harada, T. Abe [*Jpn. J. Appl. Phys. (Japan)* vol.25 (1986) p.L859-61]

[6] M. Suezawa, K. Sumino, H. Harada, T. Abe [*Jpn. J. Appl. Phys. (Japan)* vol.27 (1988) p.62-7]

[7] A.G. Steele, L.C. Lenchyshyn, M.L.W. Thewalt [*Appl. Phys. Lett. (USA)* vol.56 (1990) p.148-50]

[8] D. Yang, D. Que, K. Sumino [*J. Appl. Phys. (USA)* vol.77 (1995) p.943-44]

[9] R.E. Pritchard et al [*Semicond. Sci. Technol. (UK)* vol.12 (1997) p.1404-8]

[10] R.C. Newman et al [*Phys. Rev. B (USA)* vol.54 (1996) p.R6803-6]

[11] D.I. Bohne, J. Weber [*Phys. Rev. B (USA)* vol.47 (1993) p.4037- 40]
[12] J. Weber, D.I. Bohne [in *Early Stages of Oxygen Precipitation in Silicon* Ed. R. Jones (Kluwer, Dordrecht, 1996) p.123-40]
[13] T. Gregorkiewicz, D.A. van Wezep, H.H.P.Th. Bekman, C.A.J. Ammerlaan [*Phys. Rev. Lett. (USA)* vol.59 (1987) p.1702-5]
[14] T. Gregorkiewicz, H.H.P.Th. Bekman, C.A.J. Ammerlaan [*Phys. Rev. B (USA)* vol.38 (1988) p.3998-4015]
[15] T. Gregorkiewicz, H.H.P.Th. Bekman, C.A.J. Ammerlaan [*Phys. Rev. B (USA)* vol.46 (1992) p.4582-9]
[16] Yu.V. Martynov, T. Gregorkiewicz, C.A.J. Ammerlaan [*Phys. Rev. Lett. (USA)* vol.74 (1995) p.2030-33]
[17] A. Hara, I. Hirai, A. Ohsawa [*J. Appl. Phys. (USA)* vol.67 (1990) p.2462-5]
[18] A. Hara, M. Aoki, M. Koizuka, T. Fukuda [*J. Appl. Phys. (USA)* vol.75 (1994) p.2929-35]
[19] A. Hara, T. Fukuda, T. Miyabo, I. Hirai [*Jpn. J. Appl. Phys. (Japan)* vol.28 (1989) p.142-3]
[20] A. Hara, M. Aoki, T. Fukuda, A. Ohsawa [*Mater. Sci. Forum (Switzerland)* vol.117-118 (1993) p.219-24]
[21] A. Hara [*Jpn. J. Appl. Phys. (Japan)* vol.34 (1995) p.3418-25]
[22] R.A. Faulkner [*Phys. Rev. (USA)* vol.184 (1969) p.713-21]