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Luminescence from an Iron Related Deep Centre in Silicon*

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Abstract

We report the luminescence properties, under high resolution conditions, and the fine structure of a zero phonon line (ZPL) at 735 meV in silicon and the associated phonon side band. We relate this band to a complex defect containing iron.

1. Introduction

Transition metal (TM) impurities have very high diffusion coefficients in silicon and act very often as efficient recombination centres. It has been difficult so far to clearly identify the electronic levels in the gap with a particular impurity since the existing data is often controversial. More detailed measurements are then desirable and in the recent years transition metal associated defects in silicon have been the subject of growing interest [1–4].

We report detailed measurements on a centre at 735 meV first identified by Weber [1] and co-workers and commonly attributed to a complex containing iron.

In Section 2 we present the general photoluminescence data and detailed temperature behaviour of this centre and in Section 3 we investigate the asymmetry of the ZPL and relate this asymmetrical shape to an isotope shift.

We use a standard luminescence set-up consisting of a dispersive monocromator fitted with a 600 grooves/mm grating and a germanium North–Cost detector cooled at liquid nitrogen temperature. The samples were either immersed in liquid helium or mounted in a closed cycle variable temperature cryostat. Luminescence was excited at a 135° viewing geometry by a Spectra Physics argon laser or by a tungsten lamp followed by a monochromator. A strong luminescence band was always observed.

The sample preparation is discussed in the next section.

2. Photoluminescence spectrum

The samples were cut from an intrinsic silicon ingot float zone grown and high resistivity (4500 Ω-cm). The samples were etched and subject to 1.5 h diffusions in a furnace at 1000°C in the presence of iron oxide. The samples were always placed in clean quartz tubes in argon atmosphere and kept away from any metal contact while being diffused.

After diffusion the samples were rapidly quenched to room temperature by droping them in cold silicone oil. This procedure ensured cooling rates of the order of 1000°C/s. After diffusion the samples were chemically etched in a solution of hydrofluoric acid and nitric acid to remove any excess of metal from the surface.

In all circumstances a strong luminescence band can be observed (Fig. 1). In the luminescence spectrum (Fig. 1) we observe a sharp zero phonon line split into three components (*a*, *b*, *c*) and a set of three sharp phonons replicating themselves at lower energies. These phonons have widths very large compared to the zero phonon lines (Table I) and show very low energies (7.3 meV and 9.2 meV). Table I lists the line energies and other relevant parameters.

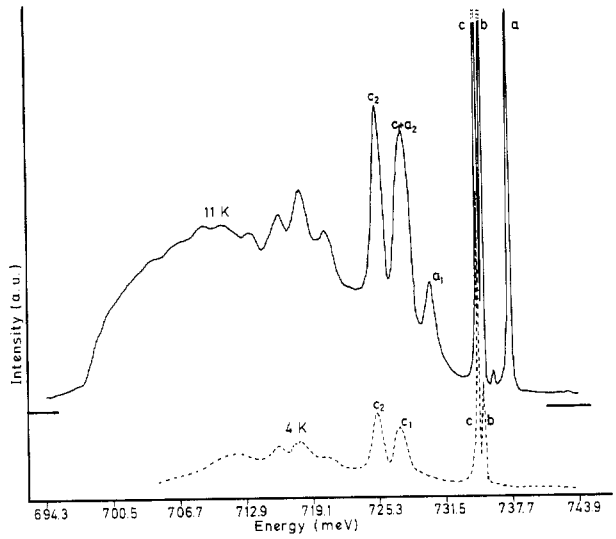

Fig. 1. Photoluminescence spectrum of 735 meV centre (intensity in arbitrary units) at two different temperatures.

At high temperatures hot bands can be observed on the high energy sides. The three zerophonon lines labelled *a*, *b* and *c* (Fig. 1) thermalise among themselves as can be seen from Fig. 2. The relative intensities of these lines follow an Arrhenius relationship with activation energies equal to their spectroscopic splittings (2.5 meV and 0.5 meV). The splitting is then assumed to occur in the excited state and the energy level scheme is shown in the inset of Fig. 2. If we extrapolate to infinite temperature the data in Fig. 2 we get for the transition probabilities ratios 8 : 1 : 1 for $a : b : c$ which reveals that transition *a* is strongly allowed.

This behaviour observed here and the structure of this

Table I.

Notation	Energy (meV)	Line width (meV)	Remarks	$\hbar\omega$ meV
a	737.5	0.285	ZPL	
b	735.0	0.220	ZPL	
c	734.5	0.230	ZPL	
a_1	730.2	1.150	a_1: Phonon 1 of ZPL *a*	7.3
$c_1 + a_2$	727.8	1.610	c_1: Phonon 1 of ZPL *c*	7.3
			a_2: Phonon 2 of ZPL *a*	9.2
c_2	725.3	1.230	c_2: Phonon 2 of ZPL *c*	9.2

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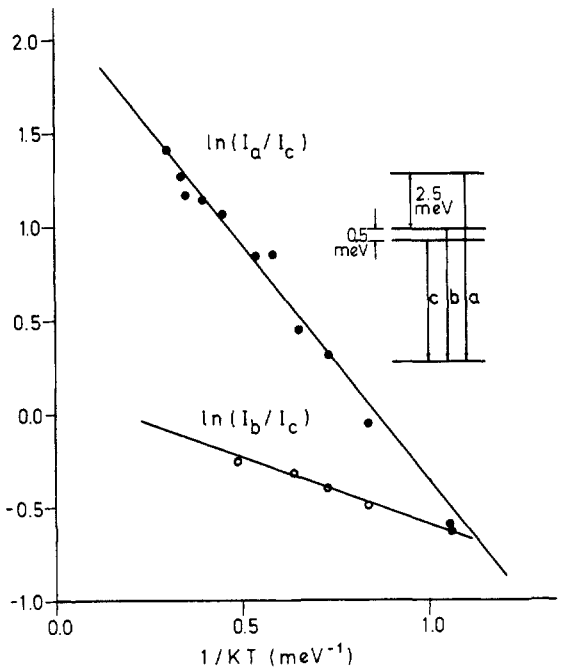

Fig. 2. Relative intensities vs. temperature of ZPL *a*, *b* and *c*. In the inset we show the proposed energy level scheme for the transitions.

centre is closely related to other transition metal centres namely the 1.067 eV tentatively assigned to a Fe-B complex [3] and the 1.014 eV centre commonly associated with a pair of copper atoms [5, 6].

The absolute intensities of the zerophonon line is depicted in Fig. 3. As can be seen the total luminescence is rapidly quenched from 20 K to 30 K. The same temperature behaviour was observed for the total band. The data can be fitted by the function

$$I(T) = I(0)/[1 + CT^{3/2} \exp(-E/K_B T)]$$

with a value for E of 13.5 meV which is close to 14.3 meV, the ionisation energy of an exciton in silicon [7].

With increasing temperature the 735 meV zerophonon

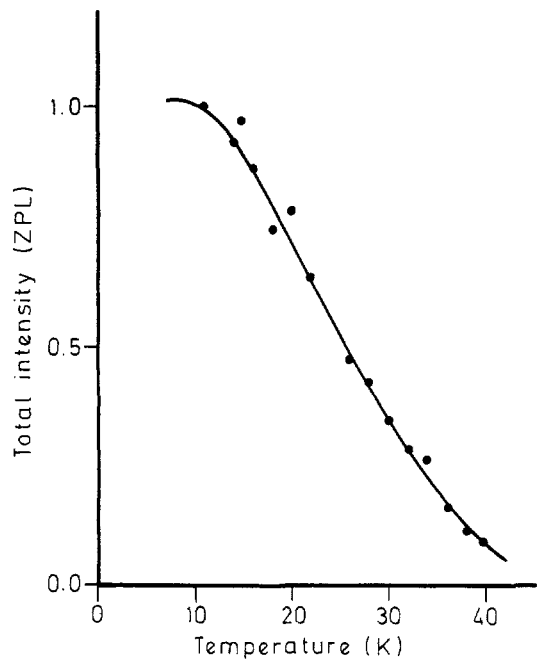

Fig. 3. Quenching of the luminescence intensity at $T > 20$ K.

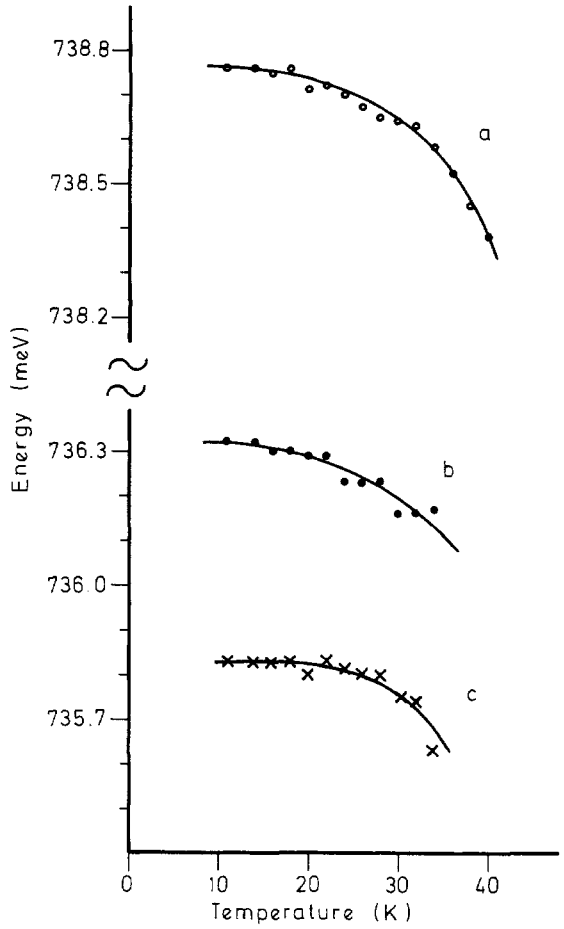

Fig. 4. Energy shift vs. temperature of the 3 components of 735 meV system.

lines shift to lower energies and broaden (Figs. 4 and 5). The shift is explained partly by the thermal properties of the silicon lattice and partly due to the quadratic terms in the electron-phonon coupling [8].

3. Silicon isotope shift

The spectral line shape is analysed in Fig. 6, the ZPL is clearly asymmetrical. The broken line, *c'*, shows the symmetrical part of the right hand side of line *c*. The symmetrised line can be fitted by a spectral line shape [9]

$$I(E) = 1\Big/\left[1 + 4(2^{1/n} - 1)\left[\frac{E - E_0}{\Gamma}\right]^2\right]^n$$

where $I(E)$ is the line intensity at energy E, $n = 1.5$, and Γ is the full width (0.3 meV).

The ZPL (full line) shows two shoulders (*a* and *b* in Fig. 6). Assuming the same line width and line shape two other lines (broken lines) can be drawn with relative intensities $a:b$ as 1 : 1.5. The convolution of the three lines *a*, *b* and *c* (dotted line) is very close to the experimental line shape.

The measured intensity ratio of lines $a:b:c$ is 1 : 1.6 : 30, very close to the natural abundance of the silicon isotopes ($^{28}Si:^{29}Si:^{30}Si = 0.922:0.047:0.031 = 29.7:1.5:1.0$).

It seems reasonable to assign this asymmetrical shape to the silicon isotope shift effect although more experiments are being carried out to confirm this point.

4. Conclusions

We have presented detailed data of the 1.7 μm band that we

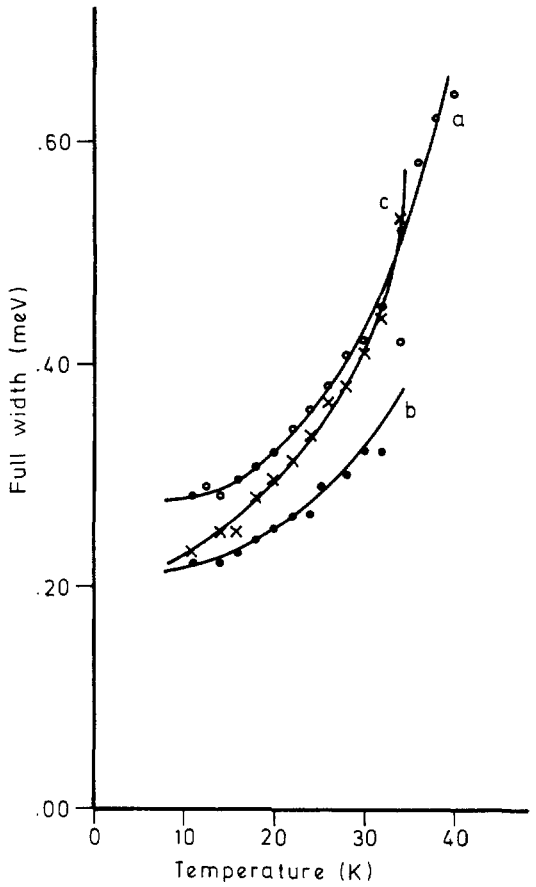

Fig. 5. Full width of 735 lines vs. temperature.

associate with an iron complex although we proceed with further work to prove this idea. The electronic structure of this centre closely resembles the structure of other transition metal related traps previously reported. The vibronic sideband shows quasi localized modes of low energy (7.3 meV and 9.2 meV) as is common in most transition metal related defects where the intersticial TM atom is vibrating.

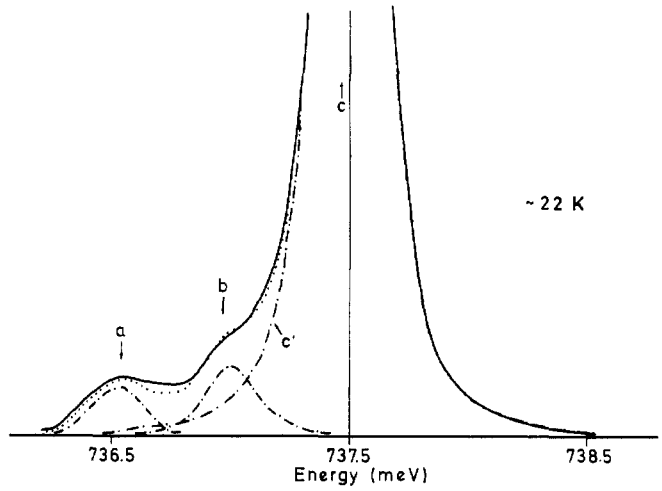

Fig. 6. The fine structure of the ZPL lines.

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References

1. Weber, J. and Wagner, P., J. Phys. Soc. Japan **49**, Suppl. A, 263 (1980).
2. Sauer, R. and Weber, J., Physica **116B**, 195 (1982).
3. Mohring, H. D., Weber, J. and Sauer, R., Phys. Rev. **B30**, 894 (1984).
4. Conzelmann, H., App. Phys. **A42**, 1 (1987).
5. Weber, J., Bauch, H. and Sauer, R., Phys. Rev. **B25**, 7688 (1982).
6. Watkins, S. P., Ziemelis, U. O. and Thewalt, M. L. W., Solid State Comm. **43**, 687 (1982).
7. Shaklee, K. L. and Nahory, R. E., Phys. Rev. Lett. **24**, 942 (1970).
8. Maradudin, A. A., Solid State Phys. **18**, 273 (1966).
9. Davies, G. and Carmo, M. C., J. Phys. C: Solid State Phys. **14**, L687 (1981).