Uniaxial stress studies of the Be pair bound exciton absorption spectrum in silicon

M O Henry†, Keith A Moloney†, J Treacy†§, F J Mulligan† and E C Lightowlers‡

† School of Physical Sciences, National Institute for Higher Education, Glasnevin, Dublin 9, Ireland
‡ Wheatstone Physics Laboratory, Kings College, Strand, London WC2R 2LS, UK

Abstract. We report the results of preliminary uniaxial stress studies of the beryllium pair isoelectronic bound exciton absorption spectrum in silicon. Our results confirm that the exciton behaves as an isoelectronic acceptor.

1. Introduction

Recent spectroscopic studies of silicon in the near infrared have been devoted largely to isoelectronic bound exciton systems. Watkins *et al* (1984) list the majority of the systems reported to date. The variety of isoelectronic centres discovered has produced a rich vein of material for both experiments and theoretical study. In general, results obtained broadly confirm the basic theoretical framework developed by Hopfield *et al* (1966) for isoelectronic bound excitons in III–V and II–VI compound semiconductors. A comprehensive review of this subject is given by Dean and Herbert (1979). The basis of the Hopfield *et al* (1966) model is that the exciton binding centre sequentially captures the electron and hole. If the electron (hole) is trapped first and a hole (electron) subsequently bound in the coulombic field of the first particle then the exciton formed is classified as an isoelectronic acceptor (donor). In general, a bound exciton system can be classified as either acceptor-like or donor-like on the basis of the nature of the vibronic sidebands produced in the optical spectra (Hopfield *et al* 1966). Direct experimental evidence for the acceptor or donor nature of a bound exciton in the form of a series of effective-mass-like excited states is rare, being confined to one example in GaP (Cohen and Sturge 1977) and one example in Si (Wagner and Sauer 1982). This scarcity of data is partly due to the fact that many isoelectronic centres exist at low concentrations, so that absorption spectroscopy often fails to reveal their presence. It is noteworthy that in the two examples cited above luminescence excitation spectroscopy using tunable lasers was required to reveal the excited state structures.

In this study we return to one of the first isoelectronic bound exciton systems identified in Si, the beryllium pair centre (Henry *et al* 1981). The Be pairs form a split interstitial about a silicon site in the crystal, and on the basis of magnetic field splittings have been assigned $\langle 100 \rangle$ axial symmetry (Henry *et al* 1981). Uniaxial stress data in

§ Visiting from the Regional Technical College, Tralee, Co Kerry, Ireland.

luminescence at 4.2 K (to be published) appear to favour ⟨111⟩ axes for the Be pairs. This discrepancy will be fully discussed in a future publication; for the present study it is not critical, as we explain below. The Be pair centres can be produced at concentrations in the region of 10^{16} cm^{-3} and a series of excited states are clearly evident in absorption and in luminescence excitation (Thewalt *et al* 1982). Although the isoelectronic bound exciton was tentatively identified as donor-like, the absorption spectrum could not be fitted to a hydrogenic series of donor-like states. A recent study by Labrie *et al* (1984) reveals that transitions in the far infrared from the ground state of the bound exciton into its excited states indicate acceptor-like behaviour by this system. We present in this study the results of preliminary uniaxial stress measurements on the near-infrared exciton absorption lines which support the designation of the bound exciton at Be-pair centres in Si as acceptor-like.

2. Experimental

The samples used in this study were prepared in the manner described by Henry *et al* (1981). For the absorption measurements a 200 W tungsten halogen lamp was used as a radiation source. A Spex 1704 spectrometer and North Coast Ge detector were used to respectively analyse and detect the radiation transmitted by the samples. A micro-computer was used in conjunction with the spectrometer controller to control the operation of the spectrometer and to record and process the data. All measurements reported here took place at 85 K in a stream of cold nitrogen vapour using a cryostat of the Maeda (1965) type. The stress apparatus was based on the use of lead weights and a lever arm, and the system was calibrated using a load cell. The absorption features of interest fall in the energy range 1070–1120 meV which encompasses a group of strong water-vapour absorption lines. To eliminate these features from our spectra a background spectrum was recorded with the sample removed from the optical path and the sample spectra normalised with respect to this background.

3. Results

An absorption spectrum recorded at 85 K is shown in figure 1. The general features are essentially the same as those observed at 2 K (Thewalt *et al* 1982). The line widths at 85 K are a factor of about four greater than at 2 K, and the weakest lines detectable at 2 K do not show up in the 85 K spectrum. Nevertheless, the four main lines in the absorption spectrum, labelled 1 to 4 in order of increasing energy in figure 1, are sufficiently sharp and well resolved to enable high-stress effects to be examined. Line 1 in our notation corresponds to the electric-dipole-allowed A line transition in the conventional notation used for isoelectronic bound excitons (Dean and Herbert 1979, and references therein). The forbidden B line transitions are not observed in absorption, but show up clearly in luminescence at low temperatures (Henry *et al* 1981). Note that the width of line 1 (the A line) at 85 K, 2 meV, is comparable with the total spread of energies in the exciton A and B line manifold (Henry *et al* 1981). This broadening of the spectral lines precludes any study of the fine structure which may exist in the spectra due to the electron–hole exchange and/or axial strain splittings of the exciton states. We are obliged, therefore, to exclude consideration of the axial symmetry of the Be pairs in this study and to limit our analysis to large-stress effects. In the limit of large stresses, the
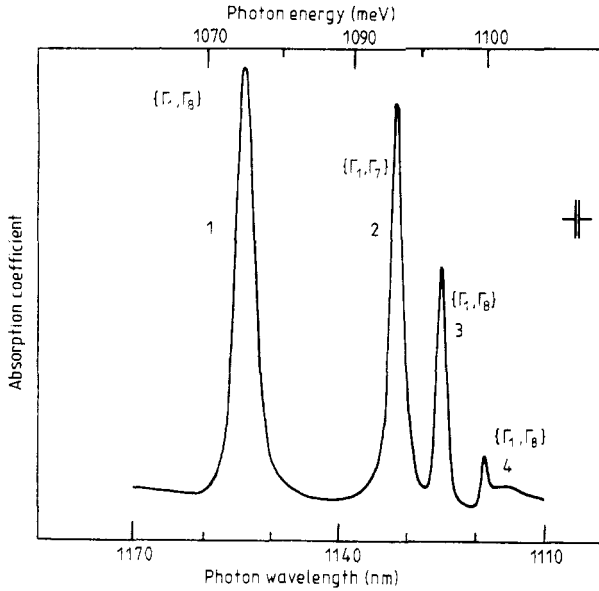
Figure 1. The absorption of Si : Be at 85 K. The peak of the strongest line in the spectrum corresponds to an absorption coefficient of 0.15 cm^{-1}. The four lines in the spectrum are labelled according to the electron–hole pairs which constitute the exciton, after the model of Labrie *et al* (1984).

magnitude of the axial strain splittings becomes negligible and, for the data analysis, the exciton binding centre can be assumed to possess the $\bar{T}_d$ point group of a silicon site.

Figure 2(*a*) shows a series of spectra recorded for uniaxial stresses along a ⟨111⟩ crystal axis. Line 1 splits into three components, whose relative intensities are stress dependent. Similar behaviour is observed for line 1 for stresses along the ⟨001⟩ and ⟨011⟩ crystal axes, as shown in figure 2(*b*) and 2(*c*) respectively. Line 2 does not split for any stress while lines 3 and 4 both show two components under all stress directions. There is evidence of considerable interaction among several subcomponents for all three stress directions. Figure 3 shows the energy positions of the stress-split components of all lines as a function of the applied stress for the three principal stress directions.

4. Discussion

Before analysing the details of the stress data we provide a summary of the results implicit in the study of Labrie *et al* (1984). These authors propose acceptor-like nature for the Be pair bound exciton in silicon. Thus the electron is tightly bound and assumed to occupy a Γ_1 state, as is observed for the ground state of substitutional donor electrons (Kohn and Luttinger 1955). The hole of the exciton is considered to be weakly bound in a series of effective-mass-like states by the coulombic field of the electron. We assume that for the ground state of the bound exciton (line 1 in our absorption spectrum) the hole occupies the usual Γ_8 ground state. In the manner originally adopted by Kirczenow (1977) for bound exciton systems, we identify line 1 with the creation of an electron–hole pair denoted by {Γ_1, Γ_8}. Similarly, the remaining lines in the absorption spectrum
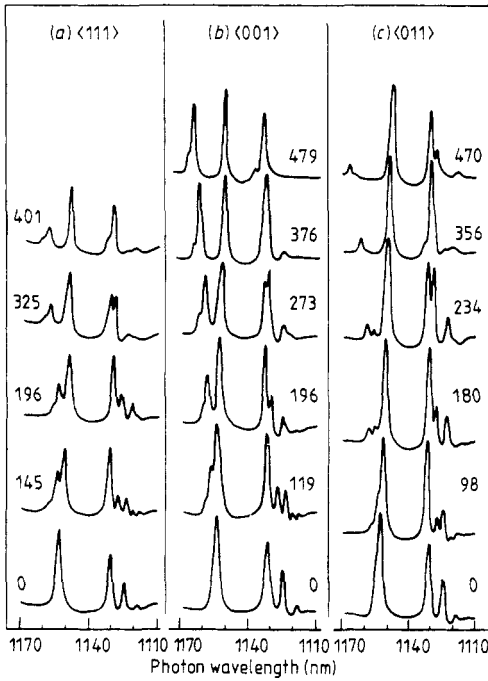
Figure 2. Absorption spectra of Si:Be at 85 K for uniaxial stresses (marked on curves in MPa) along (a) ⟨111⟩, (b) ⟨001⟩ and (c) ⟨011⟩ crystal axes.

in figure 1 are labelled $\{\Gamma_1, \Gamma_7\}$, Γ_1, $\Gamma_8\}$ and $\{\Gamma_1, \Gamma_8\}$ in order of increasing energy. This labelling scheme treats the electron and hole as quasi-independent particles. This is certainly an incomplete description for the lowest exciton manifold. However, as we pointed out above, the effects produced by the exchange interaction between the
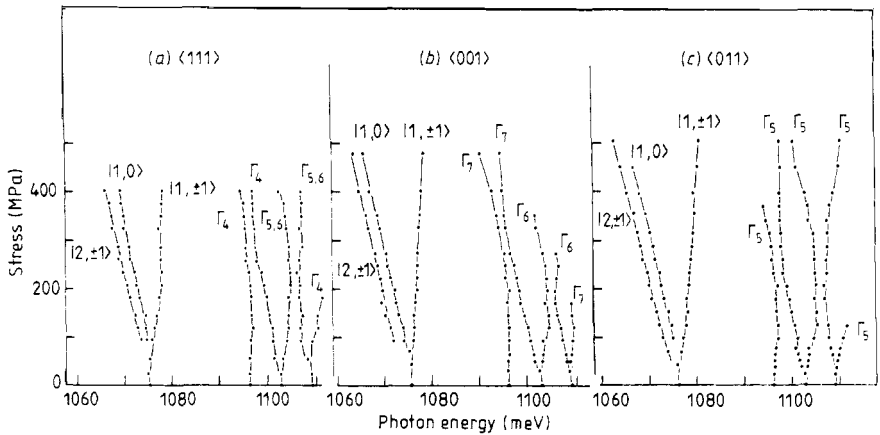

Figure 3. Stress splittings of the Si:Be absorption lines at 85 K for stresses along (a) ⟨111⟩, (b) ⟨001⟩ and (c) ⟨011⟩ crystal axes. Line 2 and the components of lines 3 and 4 are labelled with the irreducible representation of the hole involved in the exciton states observed. The components of line 1 are labelled in the $|J, M_j\rangle$ notation for the exciton.

electron and hole and the axial strain at the Be pair centre are barely detectable for the exciton ground state manifold in the present study. Furthermore, there is no evidence in the study of Labrie *et al* (1984) for exchange or strain splittings in the exciton excited state manifolds. For our present purposes, therefore, it is adequate to describe the exciton states in terms of quasi-independent electron–hole pairs. A unique feature of the foregoing discussion is the assignment of the first excited state manifold of the exciton to an electron–hole pair involving a Γ_7 hole. There is considerable theoretical support for the existence of a low-lying Γ_7 state for effective mass acceptors in silicon (Lipari and Baldereschi 1978). Raman scattering studies in boron-doped silicon by Wright and Mooradian (1967) and Cherlow *et al* (1973) and infrared absorption studies by Chandrasekhar *et al* (1973) provide experimental evidence for the existence of this state. In this study further evidence for a low-lying Γ_7 hole state is presented and the acceptor-like nature of the Be pair bound exciton is confirmed.

The most striking feature of the data presented in figures 2 and 3 is the behaviour of line 2 which does not show any evidence of stress-induced broadening or splitting. This specific result and the general trends in the stress splittings for lines 2, 3 and 4 can be explained on the basis of effective-mass-like acceptor states. Since the electron in each case occupies a non-degenerate Γ_1 state, stress-induced splittings are not allowed for the electron. Thus, whichever splittings are observed are due to the behaviour under stress of the hole states. The influence of uniaxial stresses on the effective-mass acceptors is well documented theoretically (Rodriguez *et al* 1972) and experimentally (Chandrasekhar *et al* 1973). We present in table 1 the results which apply to Γ_6, Γ_7 and Γ_8 holes (the only classifications allowed for acceptors in T_d). Γ_8 hole states are seen to produce two components for all stress directions, whereas the Γ_6 and Γ_7 holes (both Kramers doublets) cannot be split by any stress. Accordingly, we can positively rule out the involvement of a Γ_8 hole in the exciton state corresponding to line 2 in our absorption spectrum. There is not sufficient information in this study to determine whether line 2 involves a Γ_7 or Γ_6 hole. However, as Labrie *et al* (1984) have pointed out, the separation of lines 1 and 2 strongly favours a Γ_7 assignment to the hole. Based on this assumption, the information given in table 1 can be used to label line 2 for all stresses, as shown in figure 3. Table 1

Table 1. Effects of uniaxial stress on acceptor states in silicon.

$\bar{T}_d$	⟨111⟩ C_{3v}	⟨001⟩ D_{2d}	⟨011⟩ C_{2v}
Γ_6	Γ_4	Γ_6	Γ_5
Γ_7	Γ_4	Γ_7	Γ_5
Γ_8	$\Gamma_4, \Gamma_5 + \Gamma_6$	Γ_6, Γ_7	Γ_5, Γ_5

can also be used to explain the occurrence of interactions between various components of the absorption lines under stress. For example, under ⟨011⟩ stress the Γ_7 hole of line 2 transforms according to Γ_5, while both components of line 3 also transform as Γ_5. The expected interaction between pairs of Γ_5 levels as they approach is clearly evident in figures 2(*c*) and 3(*c*). We have used the information in table 1 to label all components of lines 2, 3 and 4 for ⟨011⟩ stresses in figure 3(*c*).

Line 2 interacts with the lower-energy component of line 3 for all stresses, and this enables the line 3 components to be assigned on the basis of the data in table 1. Thus, for ⟨111⟩ stress, the lower-energy component of line 3 is labelled Γ_4 and the upper component

$(\Gamma_5 + \Gamma_6)$. Similarly, for $\langle 001 \rangle$ stress the lower and upper components of line 3 are designated Γ_7 and Γ_6, respectively. In order to designate the components of line 4, evidence of interactions, if any, between components of lines 3 and 4 is required. There is a gradual drop in the intensity of the line 4 components as stress is increased, which is probably caused by the hole state involved becoming less tightly bound in the exciton. Nevertheless, the limited data available suggest that under both $\langle 111 \rangle$ and $\langle 001 \rangle$ stresses the components of lines 3 and 4 which approach interact weakly. We conclude, therefore, that the ordering of the components of line 4 is reversed compared with line 3, and figure 3 is labelled accordingly. A similar reversal of the ordering of some hole state sublevels occurs for acceptors in silicon (Chandrasekhar *et al* 1973).

We now consider in outline the case of line 1. The stress data reveal three components, with stress-dependent relative intensities. In the absence of polarisation data, the analysis of the relative intensities is postponed. The effects of uniaxial stress on isoelectronic bound excitons was originally analysed by Morgan and Morgan (1970) and Onton and Morgan (1970). Under a uniaxial compression the $J = 1$ and $J = 2$ states of the exciton form five levels denoted in a $|J, M_J\rangle$ notation by $|1, \pm 1\rangle$, $|1, 0\rangle$, $|2, \pm 2\rangle$, $|2, \pm 1\rangle$ and $|2, 0\rangle$ in order of decreasing energy. Transitions into the $|2, \pm 2\rangle$ and $|2, 0\rangle$ states are forbidden, so three transitions are expected in absorption. Of these, transitions into the $|2, \pm 1\rangle$ state are allowed only by virtue of mixing with the $|1, \pm 1\rangle$ state. Onton and Morgan (1970) show that the energy separation between the states $|1, \pm 1\rangle$ and $|1, 0\rangle$ equals the basic Γ_8 hole state splitting of the $J = 1$ exciton state under stress. The separation between the $|1, 0\rangle$ and $|2, \pm 1\rangle$ states at large stresses is approximately 75% of the exchange splitting between the $J = 1$ and $J = 2$ levels. Our data for Si:Be correlate closely to the theory outlined above. In figure 3 we have labelled the three components of line 1 with the appropriate $|J, M_J\rangle$ labels. Thus, the behaviour of line 1 is qualitatively explained. We must point out that stress measurements in luminescence at 4.2 K provide a wealth of detail not evident in the present study. This detail will be presented in a quantitative analysis of the exciton A and B line system which is at present underway.

Finally, we extract estimates of the deformation potentials b and d for the Γ_8 holes involved in lines 1, 3 and 4 of the Be pair bound exciton absorption spectrum. These coefficients are defined by the relations (Laude *et al* 1971)

$$\Delta_{\langle 001 \rangle} = 2b(s_{11} - s_{12})T \qquad \Delta_{\langle 111 \rangle} = (d/\sqrt{3})(s_{44})T$$

where $\Delta_{\langle 001 \rangle}$ and $\Delta_{\langle 111 \rangle}$ denote the energy separation of the Γ_8 hole sublevels under $\langle 001 \rangle$ and $\langle 111 \rangle$ stresses, respectively, for an applied stress T. s_{11}, s_{12} and s_{44} are the silicon elastic compliance constants. For lines 3 and 4, the separation of the stress-split components gives a direct measure of the hole state splitting. For line 1, the separation between the two highest-energy components describes the effective Γ_8 hole state splitting for the $J = 1$ exciton state under large stresses (Onton and Morgan 1970). Using published values of the elastic compliance constants at liquid nitrogen temperatures (Laude *et al* 1971), our data yield the values of b and d shown in table 2. In the table our results are compared with the corresponding free-exciton parameters obtained by Laude *et al* (1971). The values obtained for d are very close to the free-exciton values, while the values of b show a reduction of at most 50%. This result for Si:Be is in contrast with an order-of-magnitude reduction in the value of b (their D_u) obtained by Onton and Morgan (1970) for the GaP:Bi bound exciton. The latter is an example of an isoelectronic donor for which the deeply bound hole is clearly non-effective-mass-like. Although our data provide approximate estimates only, they clearly favour the isoelectronic acceptor model for the Be pair bound exciton in silicon.

Table 2. Deformation potentials b and d for Γ_8 holes in the Si : Be bound exciton.

	Line 1	Line 3	Line 4	Free exciton[a]
b (eV)	1.2	1.1	1.1	2.10 ± 0.10
d (eV)	3.8	4.8	4.9	4.85 ± 0.15

The values estimated for b and d are accurate to ~10%.
(a) Laude *et al.* (1971).

5. Conclusion

The results we have presented in this study provide a qualitative analysis of the behaviour under stress of the Si : Be bound exciton absorption spectrum. The bound exciton excited states are shown to be consistent with isoelectronic acceptor-like behaviour for the Be pair bound exciton. In particular, the data support the assignment of a Γ_7 hole state to the first excited state manifold of the bound exciton.

Acknowledgments

References

Chandrasekhar H R, Fisher P, Ramdas A K and Rodriguez S 1973 *Phys. Rev.* B **8** 3836–51
Cherlow J M, Aggarwal R L and Lax B 1973 *Phys. Rev.* B **7** 4547–60
Cohen E and Sturge M D 1977 *Phys. Rev.* B **15** 1039–51
Dean P J and Herbert D C 1979 *Excitons; Springer Topics in Current Physics* vol 14, ed. K Cho (Berlin: Springer) pp 55–182
Henry M O, Lightowlers E C, Killoran N, Dunstan D J and Cavenett B C 1981 *J. Phys. C: Solid State Phys.* **14** L255–61
Hopfield J J, Thomas D G and Lynch R T 1966 *Phys. Rev. Lett.* **17** 312–5
Kirczenow G 1977 *Solid State Commun.* **21** 713–7
Kohn W and Luttinger J M 1955 *Phys. Rev.* **98** 915–25
Labrie D, Timusk T and Thewalt M L W 1984 *Phys. Rev. Lett.* **52** 81–4
Laude L D, Pollak F H and Cardona M 1971 *Phys. Rev.* B **3** 2623–36
Lipari N O and Baldereschi A 1978 *Solid State Commun.* **25** 665–8
Maeda K 1965 *J. Phys. Chem. Solids* **26** 595–7
Morgan J van W and Morgan T N 1970 *Phys. Rev.* B **1** 739–49
Onton A and Morgan T N 1970 *Phys. Rev.* B **1** 2592–604
Rodriguez S, Fisher P and Barra F 1972 *Phys. Rev.* B **5** 2219–33
Thewalt M L W, Watkins S P, Ziemelis U O, Lightowlers E C and Henry M O 1982 *Solid State Commun.* **44** 573–8
Wagner J and Sauer R 1982 *Physica* **117/118B** 113–5
Watkins S P, Thewalt M L W and Steiner T 1984 *Phys. Rev.* B **29** 5727–38
Wright G B and Mooradian A 1967 *Phys. Rev. Lett.* **18** 608–10