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Zeeman photoluminescence spectroscopy of isoelectronic beryllium pairs in silicon

T. Ishikawa [a,*], T. Sekiguchi [b], K. Yoshizawa [a], K. Naito [a], M.L.W. Thewalt [b], K.M. Itoh [a]

[a] School of Fundamental Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

[b] Department of Physics, Simon Fraser University, Burnaby, BC, Canada V5A 1S6

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ABSTRACT

Isoelectronic beryllium (Be) pair centers in silicon have been studied by photoluminescence spectroscopy under a magnetic field. The photoluminescence of the bound-exciton recombination at this center shows that the number of Zeeman split peaks is the smallest for the magnetic field applied along a ⟨100⟩ direction. This result provides direct evidence that the Be pairs orient themselves in ⟨111⟩ directions. The *g* values of the hole and electron in this bound exciton determined by fitting of the Zeeman diagrams support the shallow acceptor character of this isoelectronic center.

1. Introduction

Readout of individual quantum states is one of challenges towards the realization of quantum information processing that employs nuclear spins in silicon (Si) as qubits. A representative example of such qubits is ^{31}P nuclear spins of phosphorus donors. Optical initialization [1] and readout [2] of an ensemble of ^{31}P nuclear spins have been demonstrated recently utilizing isotopically enriched ^{28}Si crystals [3,4]. However, due to the predominance of a non-radiative Auger process [5], the quantum efficiency of photon emission from the phosphorus bound exciton is very low $\approx 10^{-4}$, i.e., the success probability of only one out of ten thousand trials makes this readout scheme unrealistic for a single ^{31}P qubit. While electrical readout via electrons emitted by the Auger process is shown to be much more useful for the case of phosphorus [2], an optical readout is desired especially when transmission of quantum information from one place to another and/or formation of entanglement between spatially separated qubits is required. Therefore, it is meaningful to turn our attention to isoelectric centers in Si that are expected to have nearly 100% radiative efficiency due to the absence of the Auger process. Such high emission efficiency was shown for the excitons bound to isoelecronic centers in indirect GaP semiconductors [6]. Optical readout of nuclear spins contained in an isoelectric center will enable quantum information processing based on nuclear spins and photons in Si [7].

One of the isoelectronic centers that may allow optical detection of their nuclear-spin states is a beryllium (Be) pair center in Si [8–18]. Beryllium is a monoisotopic element (^{9}Be) with the nuclear spin $I = 3/2$. In order to derive nuclear spin states from the luminescence arising from the beryllium pair, one has to identify the microstructure of the center which is reflected by the electronic structure of the bound exciton. Interestingly, the same group led by Lightowlers reached two different conclusions on the symmetry axis of the Be pairs in Si by photoluminescence (PL) spectroscopy: ⟨100⟩ from Zeeman study of the no-phonon (NP) lines [8,11] and ⟨111⟩ from a local-mode-phonon-assisted line [14]. In addition, this group suggested that the Be pairs appeared to favor ⟨111⟩ in a piezospectroscopic study of near-infrared absorption measurement [13]. However, Ref. [13] did not present the actual data leading to the ⟨111⟩ character. Furthermore, an *ab initio* calculation of the total energy of the Be pairs in Si supported the ⟨111⟩ interpretation [15].

The present work revisits the Zeeman PL spectroscopy of Be pairs to determine unambiguously that the two beryllium atoms configure themselves along ⟨111⟩ directions. Furthermore, we obtain *g*-values that support the shallow acceptor character of this center [13,16].

2. Experiments

Beryllium was introduced by thermal diffusion into Si following the method employed by Crouch et al. [10]. Si substrates were cut

* Corresponding author. Tel.: +81 45 566 1594; fax: +81 45 566 1587.
E-mail addresses: toyo_ishikawa@a3.keio.jp (T. Ishikawa), kitoh@appi.keio.ac.jp (K.M. Itoh).

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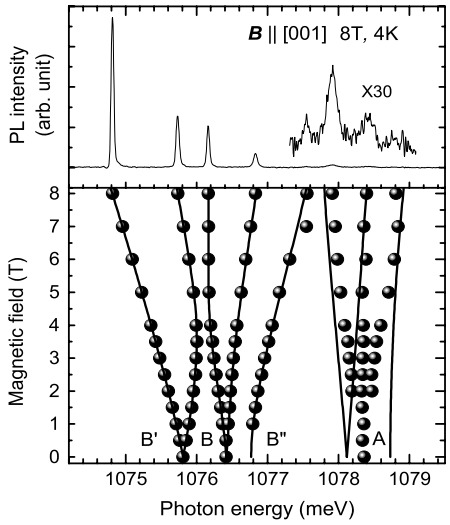

Fig. 1. The Zeeman spectroscopy of a Si:Be bound exciton at $T = 4$ K and $\boldsymbol{B} \parallel [001]$. The upper panel shows the PL spectrum at $B = 8$ T. The lower panel shows the NP peak energies as a function of the magnetic field up to 8 T. Solid lines are fitting curves based on the method described in the text.

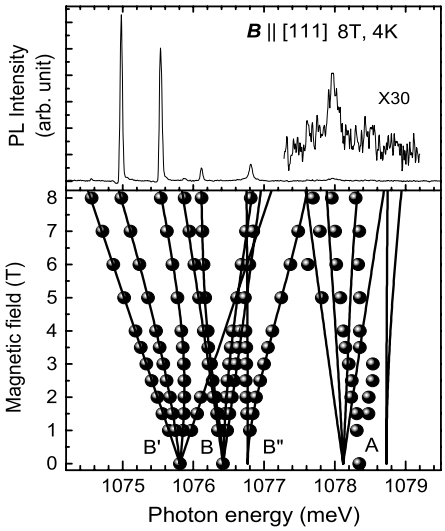

Fig. 2. The Zeeman spectroscopy of a Si:Be bound exciton at $T = 4$ K and $\boldsymbol{B} \parallel [111]$. The upper panel shows the PL spectrum at $B = 8$ T. The lower panel shows the NP peak energies as a function of the magnetic field B up to 8 T. Solid lines are fitting curves based on the method described in the text.

from n-type Fz–Si wafers (the resistivity higher than 2 kΩ cm) having three different surfaces: (001), (111), and (110). After deposition of Be films on these Si surfaces, the samples were sealed in Ar filled ampoules and annealed at 1000 °C for 1 h. The samples were cooled down to room temperature by simply taking the ampoule out of the furnace at the end of the annealing. Finally, the sample surfaces were lapped with SiC powders and etched with a mixture of hydrofluoric and nitric acids. The concentration 10^{14} cm^{-3} of the isoelectronic Be pairs in these samples were estimated by near-infrared absorption spectroscopy [9].

For PL measurements, the Be-doped samples were mounted in a strain-free manner and immersed in liquid helium. PL spectra with excitation by a 1047 nm Nd:YLF laser were recorded with a BOMEM DA8 Fourier transform interferometer. A superconducting magnet was used to apply magnetic field parallel both to the optical axis and to the sample surface normal directions [001], [111] and [110].

3. Results and discussion

Figs. 1–3 are the PL spectra of the bound exciton recombination associated with the isoelectronic Be-pair centers at a temperature $T = 4$ K under magnetic field $\boldsymbol{B}$ up to 8 T in [001], [111], and [110] directions, respectively. The upper panels show the PL spectra in the NP region at the magnetic field of 8 T, and the lower panels give the Zeeman diagrams plotting the NP peak energies as a function of B.

The NP spectrum in the absence of the magnetic field is composed of three lines labeled B′ (1075.81 meV), B (1076.41 meV), and A (1078.36 meV) [8,9], as seen at the bottom of the lower panels in Figs. 1–3. By applying the magnetic field, all these lines split, and another series of lines labeled B″ emerges between the lines B and A. The number of line splittings depends on the series of lines (B′, B, B″, or A), and the number of B′, B and B″ lines doubles for the field directions [110] and [111] compared to that for [001]. This doubling is explained by assuming that each Be pair is oriented in one of ⟨111⟩ directions. Fig. 4 shows all possible Be-pair orientations satisfying this assumption. When a magnetic field $\boldsymbol{B}$ is applied, the four orientations are distinguishable and separated into two nonequivalent groups for $\boldsymbol{B} \parallel [111]$ and $\boldsymbol{B} \parallel [110]$, while they remain equivalent for $\boldsymbol{B} \parallel [001]$. This is consistent with our Zeeman diagrams, which indicate that the bound exciton energy levels for $\boldsymbol{B} \parallel [111]$ and $\boldsymbol{B} \parallel [110]$ are twice as many as those for

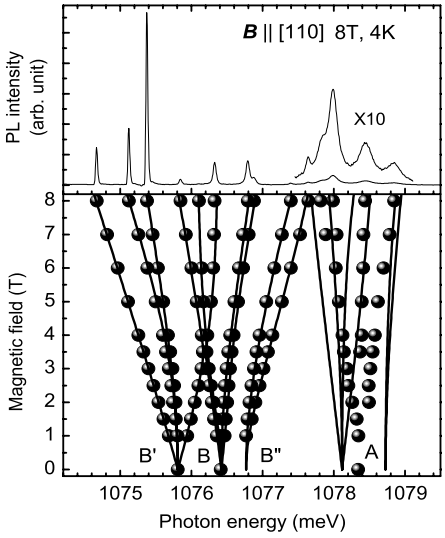

Fig. 3. The Zeeman spectroscopy of a Si:Be bound exciton at $T = 4$ K and $\boldsymbol{B} \parallel [110]$. The upper panel shows the PL spectrum at $B = 8$ T. The lower panel shows the NP peak energies as a function of the magnetic field up to 8 T. Solid lines are fitting curves based on the method described in the text.

$\boldsymbol{B} \parallel [001]$. If the Be pairs were oriented to the ⟨100⟩ directions, the simplest Zeeman diagram would be obtained for $\boldsymbol{B} \parallel [111]$ instead of $\boldsymbol{B} \parallel [001]$. If the Be pair were oriented in any other directions, no field direction would give a Zeeman diagram as simple as we obtained for $\boldsymbol{B} \parallel [001]$ in Fig. 1. Thus, our PL results unambiguously show that the Be pair center has the ⟨111⟩ axis of symmetry in agreement with Refs. [13–15].

To quantitatively analyze the magnetic field dependence of the PL spectra, we use the Hamiltonian for a bound exciton with a uniaxial stress at the isoelectronic center with an external magnetic field [19–21]. This Hamiltonian is described with the electron and hole angular momenta $\boldsymbol{s}_e$ and $\boldsymbol{j}_h$ ($s_e = 1/2, j_h = 3/2$) and divided into two parts: $H = H_0 + H_{LZ}$. Here, H_0 is the Hamiltonian in the absence of the magnetic field;

$$H_0 = -a\boldsymbol{j}_h \cdot \boldsymbol{s}_e - D\left(j_{hz'}^2 - \frac{j_h(j_h+1)}{3}\right). \quad (1)$$

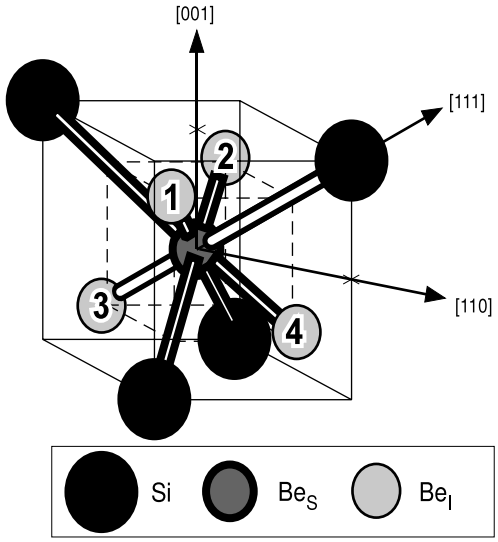

Fig. 4. All possible ⟨111⟩ configurations of the isoelectronic Be pair in a Si crystal. One of the Be atoms occupies the substitutional site (Be_S) and the other occupies one of the interstitial sites, which are indicated by the lightgray circles with the index 1–4. These interstitial Be atoms (Be_I) are oriented in the ⟨111⟩ directions. All these configurations are energetically equivalent due to the crystallographic equivalence of the ⟨111⟩ directions. While a [001] magnetic field keeps the four configurations equivalent, [110] and [111] magnetic fields separate the configurations into two nonequivalent groups. For $\boldsymbol{B}\|[111]$ the $Be_I(3)$ site becomes nonequivalent to the other Be_I sites. For $\boldsymbol{B}\|[110]$ the $Be_I(1)$ site is equivalent to the $Be_I(2)$ but nonequivalent to the others ($Be_I(3)$, $Be_I(4)$).

The first term represents the isotropic electron–hole exchange interaction, and the second term is the crystal field due to the uniaxial stress around the isoelectronic center with z' being the principal axis of the crystal field ⟨111⟩. H_{LZ} is the perturbation Hamiltonian due to the magnetic field $\boldsymbol{B}$. Here, only the linear Zeeman term is considered;

$$H_{LZ} = \mu_B \left[g_e \boldsymbol{s}_e \cdot \boldsymbol{B} + K \boldsymbol{j}_h \cdot \boldsymbol{B} + L \left(j^3_{hx} B_x + j^3_{hy} B_y + j^3_{hz} B_z \right) \right], \qquad (2)$$

where μ_B is the Bohr magneton (5.788×10^{-5} eV/T), g_e is the g value of the electron, K and L are the isotropic and anisotropic parts, respectively, of the g factor of the hole. Note that x, y, and z are the crystallographic cubic axes [20,22], e.g., z = [001]. Fitting of the B′, B, and B″ lines of the PL spectra in Figs. 1–3 with the total Hamiltonian H yields the following fitting parameters: a = 0.98 meV, D = 0.48 meV, g_e = 1.98, K = 1.10, and L = 0.03. The resulting fitting curves with these values are shown as solid lines in Figs. 1–3. The B, B′, and B″ lines agree very well with the fitting curves. However, the fitting of the A line is less satisfactory, particularly at low field $B \leq 5$ T. At $B = 0$ T, the width of the A line is ∼0.40 meV, which is comparable to the energy difference of 0.60 meV between B and B′ lines. The A line is broader than the B, B′ and B″ lines due to the short lifetime characteristic of an allowed transition [9]. On the other hand, B line is a partially allowed transition, and both B′ and B″ transitions are forbidden in this model [8,11]. Better fittings in the low magnetic field ($B < 5$ T) regime may be achieved in the future by including the effect of the mixing of the ground states with the excited states derived from the split-off Γ_7 hole state [11,13] and/or coupling to phonons [8] in the model.

Table 1 lists the hole g values (K, L) for the Be-pair bound exciton obtained in this study as well as those for shallow acceptors [23] and corresponding hole binding energies [16,24] reported previously. The values of g depend clearly on the binding energy. The binding energy of a hole in the Be bound exciton [16] is close to the values reported for those of shallow acceptors, especially to that of boron [24]. Moreover, values of K and L of a hole in the Be bound exciton determined in this study are almost same as those of boron. Therefore, the present work establishes the shallow acceptor character of the Be bound exciton in Si. While Lightowlers' group reported that the Be pair was an isoelectronic donor and the hole's g-values were $K = 1.26$ and $L = -0.12$ [11], the same group later revised this interpretation (see Ref. [8] of Ref. [15]) and concluded that it is actually acceptor-like [13]. The acceptor-like isoelectric center binds an electron more tightly than a hole. Therefore, we expect the difference of the g_e value between the Be pair and a shallow donor. It is known among the group V shallow donors in Si that the g_e decreases from 1.99858 to 1.99827 with increasing binding energy [25]. The present study finds g_e = 1.98(3). However, because of our experimental uncertainty of 0.03 on g_e, we cannot argue whether this value reflects the localization of the electron or not.

Table 1
The g values (K, L) and the binding energy E_h of the hole bound to shallow acceptors [23,24] and the Be pair [16] in silicon.

Be_2	K	L	E_h (meV)
	1.10[a]	0.03[a]	43
B	1.070	0.033	44.4
Al	0.997	−0.014	68.5
Ga	0.993	−0.017	74.0
In	0.885	−0.056	156.2

[a] Indicates the results in the present study.

4. Conclusion

Zeeman PL spectroscopy of the present study establishes that the isoelectronic Be pairs in Si are oriented in ⟨111⟩ directions. The g values of the hole in the exciton bound to the Be pair are determined and agree very well with those of holes bound to a shallow acceptor, especially boron, indicating the acceptor-like character of this bound exciton.

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