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Addenda to photoluminescence and electron paramagnetic resonance studies of defect centers in porous silicon

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Abstract

This work includes addenda to the paper entitled photoluminescence and electron paramagnetic resonance studies of defect centers in porous silicon (PS) which was published in this journal. The readers can readily obtain the principal values of $g_\parallel$ and $g_\perp$ from the de-convolution of the effective principal g-values of the spin resonance data measured at various rotating angles of the magnetic field and the crystal axes. © 2002 Elsevier Science B.V. All rights reserved.

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In our previous works, we have demonstrated [1] the electron spin resonance (ESR) studies of point defects in porous silicon (PS). Many itinerant features of PS defects were revealed by various heat treatments. In this work, we attempt to express more thoroughly the derivation of the formula to achieve the effective principal g-values of the crystal. This technique can be followed by readers to manipulate their ESR data on account of the manifold rotations of the crystal axes with respect to the laboratory axes. This method also allows us to address the site of a particular defect, the structure symmetry, and the spin density change due to annealing effect.

Native defects generated during crystal growth such as vacancies, antisites, and interstitial control are the photonic properties for intrinsic semiconductors. Among the possible intrinsic defects, the isolated silicon dangling bonds demonstrate themselves to be the dominant interface defects, which crucially control the photoluminescence efficiency. The point defects in PS, can be a P_{b0}-like (i.e. Is ≡ Si), a P_{b1} (i.e. Si ≡ SiO$_2$), and a P_b-like centers. The ESR of P_{b0} yields a broad and small signal-to-noise ratio signal, while the P_{b1} is essentially capricious with thin oxides [2]. The most intricate P_b defects are associated with silicon dangling bonds and can be classified into three types. PS, which is modified from crystalline silicon, has a lower sym-

metry of C_{3V} than its original diamond T_d structure. The porous structure implies a large surface area to be oxidized when stored in air, which invokes dangling bonds at the interface between silicon and SiO$_2$. The commonly specified P_b centers [3] are the point defects concealed at the interface of Si(111)/SiO$_2$ [4,5]. There are four paramagnetic centers belonging to the P_b defects named as $S_1 = (1, 1, 1)$, $S_2 = (1, -1, -1)$, $S_3 = (-1, 1, -1)$, and $S_4 = (-1, -1, 1)$ corresponding to the dangling bonds at the interface of the specified Si surfaces and oxides.

For a defect center with a free spin $\vec{s}$, the spin Hamiltonian in a magnetic field $\vec{H}$ is [6–8]:

$$\mathfrak{R} = \beta \vec{s} \cdot \overline{\overline{g}} \cdot \vec{H}, \qquad (1)$$

where β is the electron Bohr magneton and $\vec{g}$ a dyadic tensor. Taking the cartesian coordinates (xyz), the magnetic field $\vec{H}$ has components of

$$\vec{H} = H(\ell_x \hat{x} + \ell_y \hat{y} + \ell_z \hat{z}), \qquad (2)$$

where ℓ_x, ℓ_y, and ℓ_z are the cosines along the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes, respectively. The spin Hamiltonian equation (1), then can be written as

$$\mathfrak{R} = \beta \cdot H(\ell_x, \ell_y, \ell_z) \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} \begin{pmatrix} s_x \\ s_y \\ s_z \end{pmatrix}, \qquad (3)$$

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where (s_x, s_y, s_z) are the components of the spin along the cartesian coordinates. We can define an effective g_{eff}, such as

$$g_{\text{eff}}^2 = (\ell_x, \ell_y, \ell_z)(\overline{\overline{g}} \cdot \overline{\overline{g}}^\sim)\begin{pmatrix} \ell_x \\ \ell_y \\ \ell_z \end{pmatrix}$$

$$= (\ell_x, \ell_y, \ell_z)\begin{pmatrix} (g^2)_{xx} & (g^2)_{xy} & (g^2)_{xz} \\ (g^2)_{yx} & (g^2)_{yy} & (g^2)_{yz} \\ (g^2)_{zx} & (g^2)_{zy} & (g^2)_{zz} \end{pmatrix}\begin{pmatrix} \ell_x \\ \ell_y \\ \ell_z \end{pmatrix}, \quad (4)$$

where $\overline{\overline{g}}^\sim$ is the transpose conjugate of $\overline{\overline{g}}$.

In this case, the Zeeman splitting energy ΔE for a spin $\frac{1}{2}$ transition can be readily written as $\Delta E = \beta g_{\text{eff}} H$ with

$$(\Delta E)^2 = \beta^2 g_{\text{eff}}^2 H^2 = \beta^2 (\vec{H} \cdot \overline{\overline{g}}) \cdot (\overline{\overline{g}} \cdot \vec{H})$$
$$= \beta^2 \vec{H} \cdot g^2 \cdot \vec{H}. \quad (5)$$

The elements $(g^2)_{ij}$ can be determined from the ESR spectra for successive rotating of the magnetic field with the crystal axes as addressed below. If the y-axis of the sample surface (the x–y plane with $\theta = 90°$) is rotated with respect to the magnetic field $\hat{H}$ with an intersection angle ϕ, then

$$g_{\text{eff}}^2 = (g^2)_{xx} \sin^2\phi + 2(g^2)_{xy} \sin\phi \cos\phi + (g^2)_{yy} \cos^2\phi. \quad (6)$$

We can readily determine $(g^2)_{yy}$ at $\phi = 0°$, $(g^2)_{xx}$ at $\phi = 90°$, and $(g^2)_{xy}$ at $\phi = 45°$, respectively. In the same way, with different rotating plane, we can evaluate the six tensor elements $(g^2)_{ij} = (g^2)_{ji}$, by which the g^2 is diagonalized to yield the principal values, such as

$$g^2 = \begin{pmatrix} g_x^2 & 0 & 0 \\ 0 & g_y^2 & 0 \\ 0 & 0 & g_z^2 \end{pmatrix}. \quad (7)$$

For crystals having axial symmetry, such as hexagonal, tetragonal, and trigonal, then

$$g = \begin{pmatrix} g_\perp & 0 & 0 \\ 0 & g_\perp & 0 \\ 0 & 0 & g_\parallel \end{pmatrix}, \quad (8)$$

where $g_\parallel$ and $g_\perp$ are the g-values obtained for the magnetic field H to be parallel or perpendicular to the symmetry axis. In this case, the experimental resonant position occurs at

$$H = \frac{h\nu}{g\beta}, \quad g = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}, \quad (9)$$

where θ is the angle between the dangling bond $\vec{S}_{i_i}$ and the magnetic field $\vec{H}$. In this experiment, we rotate the PS surfaces with respect to the c-axis by several angles δ which specifies the rotation angle between the rotating axis and the DC magnetic fields to detect the spectra.

Since the directly measured data are not the $g_\parallel$ and $g_\perp$, which are the effective $(gg)^{1/2}$ values, we require a transform matrix that rotating the crystal axes with the magnetic field. The transform matrix $\overline{\overline{R}}$ that rotates the spin $\vec{S}_i$ by an angle δ to yield

$$\theta = \cos^{-1}\vec{H} \cdot \overline{\overline{R}} \cdot \vec{S}_i \quad (10)$$

can be derived as follows. Firstly, we decompose the spin vector $\vec{S}_i$ into vectors $\vec{S}_{i\ell}$ and $\vec{S}_{it}$ which are the components to be, respectively, parallel and perpendicular to the c-axis:

$$\vec{S}_{i\ell} = (\vec{S}_i \cdot \hat{c})\hat{c}, \quad (11)$$

$$\vec{S}_{it} = \vec{S}_i - \vec{S}_{i\ell} = \vec{S}_i - (\vec{S}_i \cdot \hat{c})\hat{c}. \quad (12)$$

From $\vec{S}_{it}$, we then take a third vector $\vec{S}_{it}'$ to be perpendicular both to $\vec{S}_{it}$ and $\hat{c}$, such as

$$\vec{S}_{it}' = \hat{c} \times \vec{S}_{it} = \hat{c} \times (\vec{S}_i - (\vec{S}_i \cdot \hat{c})\hat{c}), \quad |\vec{S}_{it}'| = |\vec{S}_{it}|. \quad (13)$$

On rotating $\vec{S}_i$ with respect to the c-axis by an angle δ, the $\vec{S}_{il}$ retains its original value while $\vec{S}_{it}$ moves to a new direction

$$\vec{S}_{it}(\delta) = \frac{\vec{S}_{it}\cos(\delta) + \vec{S}_{it}'\sin(\delta)}{|\vec{S}_{it}\cos(\delta) + \vec{S}_{it}'\sin(\delta)|}|\vec{S}_{it}|. \quad (14)$$

The new spin direction $\vec{S}_i(\delta)$ becomes

$$\vec{S}_i(\delta) = \vec{S}_{i\ell} + \vec{S}_{it}(\delta) \equiv \overline{\overline{R}} \cdot \vec{S}_i. \quad (15)$$

The transform matrix $\overline{\overline{R}}$ is tedious and the matrix elements are

$$R_{xx} = cx^2 - \frac{(-1 + cx^2)\sqrt{1 + cx^4 + cx^2(-2 + cy^2 + cz^2)}\cos(\delta)}{\sqrt{(1 + cx^4 + cx^2(-2 + cy^2 + cz^2))\cos(\delta)^2 + (cy^2 + cz^2)\sin(\delta)^2}},$$

$$R_{xy} = cx\,cy - \frac{\sqrt{1 + cy^4 + cy^2(-2 + cx^2 + cz^2)}(cx\,cy\cos(\delta) + cz\sin(\delta))}{\sqrt{1 + cy^4 + cy^2(-2 + cx^2 + cz^2))\cos(\delta)^2 + (cx^2 + cz^2)\sin(\delta)^2}},$$

$$R_{xz} = cx\,cz + \frac{\sqrt{1 + (-2 + cx^2 + cy^2)cz^2 + cz^4}(-cx\,cz\cos(\delta) + cy\sin(\delta))}{\sqrt{(1 + (-2 + cx^2 + cy^2)cz^2 + cz^4)\cos(\delta)^2 + (cx^2 + cy^2)\sin(\delta)^2}},$$

$$R_{yx} = cx\,cy + \frac{\sqrt{1 + cx^4 + cx^2(-2 + cy^2 + cz^2)}(-cx\,cy\cos(\delta) + cz\sin(\delta))}{\sqrt{(1 + cx^4 + cx^2(-2 + cy^2 + cz^2))\cos(\delta)^2 + (cy^2 + cz^2)\sin(\delta)^2}},$$

$$R_{yy} = cy^2 - \frac{(-1+cy^2)\sqrt{1+cy^4+cy^2(-2+cx^2+cz^2)}\cos(\delta)}{\sqrt{(1+cy^4+cy^2(-2+cx^2+cz^2))\cos(\delta)^2+(cx^2+cz^2)\sin(\delta)^2}},$$

$$R_{yz} = cy\,cz - \frac{\sqrt{1+(-2+cx^2+cy^2)cz^2+cz^4}(cy\,cz\cos(\delta)+cx\sin(\delta))}{\sqrt{(1+(-2+cx^2+cy^2)cz^2+cz^4)\cos(\delta)^2+(cx^2+cy^2)\sin(\delta)^2}},$$

$$R_{zx} = cx\,cz - \frac{\sqrt{1+cx^4+cx^2(-2+cy^2+cz^2)}(cx\,cz\cos(\delta)+cy\sin(\delta))}{\sqrt{(1+cx^4+cx^2(-2+cy^2+cz^2))\cos(\delta)^2+(cy^2+cz^2)\sin(\delta)^2}},$$

$$R_{zy} = cy\,cz + \frac{\sqrt{1+cy^4+cy^2(-2+cx^2+cz^2)}(-cy\,cz\cos(\delta)+cx\sin(\delta))}{\sqrt{(1+cy^4+cy^2(-2+cx^2+cz^2))\cos(\delta)^2+(cx^2+cz^2)\sin(\delta)^2}},$$

$$R_{zz} = cz^2 - \frac{(-1+cz^2)\sqrt{1+(-2+cx^2+cy^2)cz^2+cz^4}\cos(\delta)}{\sqrt{(1+(-2+cx^2+cy^2)cz^2+cz^4)\cos(\delta)^2+(cx^2+cy^2)\sin(\delta)^2}}. \tag{16}$$

After a tedious manipulation of Eqs. (10)–(16), we obtain the effective g-values in terms of the rotating angle δ for the defect centers S_1, S_2, S_3, S_4. With the magnetic field $\vec{H}$ to be along $\langle 1,0,0 \rangle$, and rotating axis $\hat{c}$ to be along $\langle 0,-1,1 \rangle$, we can derive

$$g_{\text{eff}}\{S_1\} = \frac{1}{\sqrt{6}}[3(g_\parallel^2+g_\perp^2)+(-g_\parallel^2+g_\perp^2)\cos(2\delta)$$
$$-2\sqrt{2}(g_\parallel^2-g_\perp^2)\sin(2\delta)]^{1/2},$$

$$g_{\text{eff}}\{S_2\} = \frac{1}{\sqrt{6}}[3(g_\parallel^2+g_\perp^2)+(-g_\parallel^2+g_\perp^2)\cos(2\delta)$$
$$+2\sqrt{2}(g_\parallel^2-g_\perp^2)\sin(2\delta)]^{1/2},$$

$$g_{\text{eff}}\{S_3\} = \frac{1}{\sqrt{6}}[g_\parallel^2+5g_\perp^2+(g_\parallel^2-g_\perp^2)\cos(2\delta)]^{1/2}$$
$$= g_{\text{eff}}\{S_4\}. \tag{17}$$

The measured g-values at various rotation angles δ can be de-convoluted to yield the principal g-values by simple curve-fitting of Eq. (17).

The data were assessed at every $5°$ rotating angles from $0°$ to $180°$. The experimental data for rotating the crystal face $(0,-1,1)$ with respect to the magnetic field $\hat{H}$ at various angles are plotted in Fig. 1.

The experimental data are simulated to yield the true resonance positions for the four P_b point defects by least-mean-square curve-fitting. Rotating the crystal axis $\langle 0,-1,1 \rangle$ with respect to the magnetic field $\vec{H}$, the C_{3V} symmetry conveys that the defect centers at $S_3 = (-1, 1, -1)$ and $S_4 = (-1, -1, 1)$ do have the same angular dependence on the ESR spectra.

The least-mean-square fitting [9] is exploited to simulate the experimental data and extract the resonance field λ_i. Fig. 1 portrays the variation of g-values with rotation angles δ with respect to the four P_b defect centers. The four P_b defects in ideal should have the same principal g-value, but on account of the slight deviation of bond angles for dangling bonds on different faces, they imply three g-values as depicted in Table 1. The average g-values are given by $g_\parallel = 2.0016 \pm 0.0003$, $g_\perp = 2.0089 \pm 0.0003$ for P_b centers along the $\langle 1,1,1 \rangle$ axis. The angular dependence of g-values

of the P_b centers turns out that the virgin PS belongs to the C_{3V} symmetry.

In conclusion, we have studied the point defects of PS arising from the dangling bonds by ESR. The four P_b defects are identified to be $S_1, \ldots, S_4$ with C_{3V} symmetry. Thermal annealing at 200–$300\,°C$ increases the spin density vastly informing most of the weak bonds of PS has a strength $\sim 49\,$meV which will be broken into dangling bonds above this temperature. Annealing in H_2 gas can passivate [10] the dangling bonds but not for bond broken at high temperatures. The dangling bonds play an essential role of recombination centers and degrade the photoluminescence intensity.
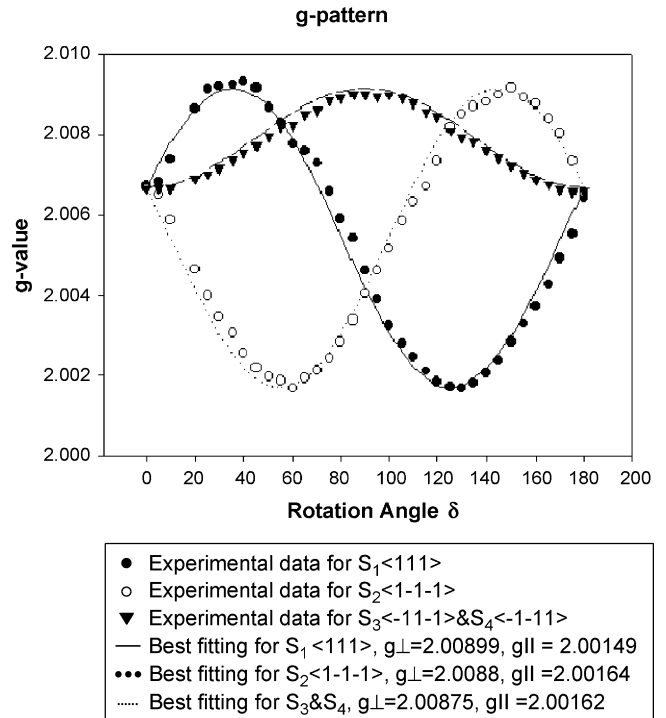

g-pattern

- ● Experimental data for S_1<111>
- ○ Experimental data for S_2<1-1-1>
- ▼ Experimental data for S_3<-11-1>&S_4<-1-11>
- — Best fitting for S_1<111>, $g\perp$=2.00899, $g$ll = 2.00149
- ••• Best fitting for S_2<1-1-1>, $g\perp$=2.0088, $g$ll =2.00164
- ······ Best fitting for S_3&S_4, $g\perp$=2.00875, $g$ll =2.00162

Fig. 1. The g-values at various rotating angles δ for the theoretical calculation by exploiting Eq. (11) (the smooth curves), and the experimental data fitting for the (●) S_1, (○) S_2, (▼) $S_3 = S_4$ of P_b centers.

Table 1
The principal *g*-values for different P_b defect centers

P_b defects	$g_\parallel$	$g_\perp$
S_1	2.0015 ± 0.0003	2.0089 ± 0.0003
S_2	2.0016 ± 0.0003	2.0088 ± 0.0003
$S_3 = S_4$	2.0016 ± 0.0003	2.0087 ± 0.0003

Acknowledgements

References

[1] H.T. Lue, B.Y. Huang, J.T. Lue, J. Mater. Chem. Phys. 65 (2000) 51.
[2] Y. Uchida, N. Koshida, H. Kayama, Y. Yamamoto, Appl. Phys. Lett. 63 (1993) 961.
[3] F.C. Rong, J.F. Harvey, E.H. Poindexter, G.J. Gerardi, Appl. Phys. Lett. 63 (1993) 920.
[4] V.Ya. Bratus, S.S. Ishchenko, S.M. Okulov, I.P. Vorona, H.J. von Bardeleben, Schoisswohl, Phys. Rev. B 50 (1994) 15449.
[5] A. Stesmans, Phys. Rev. B 45 (1992) 9051.
[6] E.H. Poindester, P.J. Caplan, B.E. Deal, R.R. Razonk, J. Sppl. Phys. 52 (1981) 879.
[7] J.T. Lue, Nuovo Cimento IL B 31 (1976) 372.
[8] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Paramagnetic Resonance, Wiley, New York, 1994 (Chapter 4).
[9] C.F. Gerald, Applied Numerical Analysis, Addison-Wesley, Reading, MA, 1983, p. 465.
[10] J.T. Lue, W.C. Huang, S.K. Ma, Phys. Rev. B 51 (1995) 14570.