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D^- centers in uniaxially stressed Si and in Si/SiO$_2$ quantum wells

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The spin-singlet ground states of a D$^-$ ion both in uniaxially stressed Si and in Si/SiO$_2$ quantum wells have been investigated for two types of donors, substitutional P and interstitial Li atoms, using a diffusion quantum Monte Carlo method. The valley-orbit interaction due to the singular donor ion potential is taken into account by diagonalizing the multiplet Hamiltonian matrix in the basis set of the ground-state wave functions assigned by the valley indexes. In the uniaxial compressive stress along the [100] direction, the binding energy of a negative P donor with A$_1$ symmetry decreases at first and then increases gradually with the stress-induced splitting in the valley energy. This nonmonotonic dependence is attributed to the disparity between the population probability in the stress-deepened valleys for the neutral donor and that for the negative donor. As for Li donors with E symmetry, the binding energy of a negative donor decreases linearly with the stress-induced splitting and then takes a constant value, caused by the transition of the ground state of the negative donor from the intervalley configuration to the intravalley configuration. These calculated behaviors agree with the experiment. In the quantum well in the [100] direction, the quantum confinement effect deepens the binding energy of a negative donor without the valley-orbit interaction. The same confinement effect is predicted for a Li negative donor ground state with E symmetry, and the binding energy increases monotonically with decrease in the well width. As for a P negative donor with A$_1$ symmetry, the enhanced binding energy is recovered at the well width of 5 nm although the valley-orbit interaction suppresses the enhancement of the binding energy in wider wells.

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I. INTRODUCTION

Very recently, dopants have been expected as the functional part of a device instead of just providing charges. They have been the subject of renewed interest for their potential use as the basic element in Si quantum electronics.[1] The electronic states of single dopants in gated silicon nanostructures has been studied through the transport spectroscopy and the neutral D^0 and negatively charged D$^-$ states are observed by resonant tunneling between source and drain.[1,2] Single-electron transfer in a silicon device implanted with exactly two phosphorous donors have also been detected.[3] Furthermore, there has been a great deal of activity to develop a silicon-based quantum computer architecture such as direct exchange interaction[4] between two electrons in a two-donor system, charge qubits[5,6] composed of two donors, optically induced spin-to-charge transduction in donor-spin readout,[7,8] and quantum control of donor electrons at the Si-SiO$_2$ interface,[9–11] following the proposal by Kane.[12] In the spin to charge transduction process proposed by Kane,[12] measuring the state of the qubit of the P nuclear spin is turned into a spin-dependent electron charge transfer event induced adiabatically by surface gate such as D^{0}D$^0 \rightarrow$ D$^+$D$^-$ for a two-donor system. The process was analyzed and was shown that the field strength required places severe constraints due to the small binding energy of a D$^-$ ion.[7]

In calculation of a two-donor system in the effective-mass approximation,[4,6] the multivalley structure of the Si conduction band causes the intervalley quantum interference. Further, the valley-orbit (VO) interaction was taken into account as perturbation in the effective-mass approximation, in addition to the uniaxial strain along [001].[13] In calculation of donor states at the Si-SiO$_2$ interface in the effective-mass approximation,[10,11] both the multivalley structure of the Si conduction band and the valley-orbit interaction due to the species-dependent microscopic variation in the donor potential in the central cell, i.e., the so-called central cell correction, were taken into account as quantity critical to silicon qubits. Calculation beyond the effective-mass approximation of the electronic wave function for a phosphorus donor in silicon was also tried by numerical diagonalization of the donor Hamiltonian in the basis of the pure crystal Bloch function.[14]

A neutral donor in the bulk semiconductors can bind weakly the second electron and this negative donor is called a D$^-$ ion. With respect to the D$^-$ state, a lot of theoretical studies have been performed by various methods, variational method,[15–17] diffusion quantum Monte Carlo (DQMC) method,[18] and full configuration-interaction approach[19] but they have been applicable only to the single-valley semiconductors with an isotropic effective mass. Silicon is multivalley semiconductor and the minima of the conduction band are located in the vicinity of six equivalent X points in the Brillouin zone. The effective mass parallel or perpendicular to the longitudinal axis in each valley is different and the multivalley semiconductors have anisotropic effective masses, contrary to the case of single-valley semiconductors such as GaAs. The consideration to the anisotropy of the effective mass is essential to interpret the isolated donor states in Si. Faulkner showed the anisotropic variational wave function for the donor state could give good results for the excited state in the absence of the magnetic field.[20] To predict the species-dependent lift of sixfold degeneracy of 1*s*-like ground state of a donor in silicon,[21] it is necessary to take into account the valley-orbit coupling produced by the singular impurity potential in the central cell.

As for an isolated D^- ion in Si, extensive experimental studies had been performed by Narita's group and it was pointed that preparation of samples having very low impurity concentration and as small compensation as possible were very important. The concentration dependence of the D^- state spectra indicates the transition from a shallow isolated D^- state to a deeper bound state of an electron trapped by more than one neutral donors.[22] The binding energies of the D^- states in Si are determined to be 1.73 meV, 2.05 meV, and 1.75 meV for P, As, and Li impurities, respectively, in the stress free case.[23] Norton obtained a similar value of 1.7 meV for both P and As impurities from the photoconductivity spectra[24] at a low temperature. The multivalley structure of the silicon conduction band can be controlled by the uniaxial stress. As for the stress dependence of the D^- state, the binding energy for an interstitial Li impurity decreases linearly from 1.75 meV but suddenly changes to a constant value of 1.55 meV as the [100] stress increases.[23] This change was suggested to be the transition of the D^- ground state induced by the uniaxial stress.[25] The observed values of 1.75 meV and 1.55 meV were assigned to the D^- binding energies, ϵ_{ij} of the intervalley, and ϵ_{ii} of the intravalley configurations, respectively. As for a substitutional P impurity, the D^- binding energy decreases first and then increases gradually with the stress-induced splitting between the valley energies.[23] This stress dependence was explained by disparity between the valley populations of electrons in the inner and outer orbitals of a negative donor.[25,26] Here, the valley-orbit interaction caused by the central cell correction to the donor ion potential is essential to induce this disparity. In our previous paper,[27] we studied negative donors in multivalley semiconductors using a DQMC method,[28] without the valley-orbit interaction. We succeeded in producing well the experimental results for Si and Ge in which the intravalley or the intervalley configuration is well controlled. For Si, we obtained $\epsilon_{ij}=1.82$ meV and $\epsilon_{ii}=1.57$ meV in good agreement with 1.75 meV and 1.55 meV for an interstitial Li impurity.[23] In a preceding paper,[29] we studied negative donors in Si/SiO_2 quantum wells in a presence of the magnetic field without the valley-orbit interaction and found that strong confinement effect was induced by both the well and the magnetic field.

Our aim of this paper is to clarify the effect of the valley-orbit interaction on the binding energy of a negative donor for P and Li impurities both in uniaxially stressed Si along the [100] direction and in Si/SiO_2 quantum wells. The binding energy of a negative donor is very small and hence the correlation effect between two trapped electrons is essentially important. To treat the correlation effect accurately, we used the DQMC method with the importance sampling.[28]

II. CALCULATION METHOD

In the effective-mass approximation without the valley-orbit interaction, each electron of a negative donor in Si belongs to a specific valley among six equivalent valleys. Therefore, electron configuration of a D^- ion is assigned by their valley indexes.[30] We call the configuration as (i,i) intravalley when the two trapped electrons belong to the equivalent valleys (i) and as (i,j) intervalley when the two electrons belong to inequivalent valleys (i) and (j). In the effective-mass approximation without the valley-orbit interaction, the Hamiltonian for a D^- ion with the (1,1)-intravalley configuration in the presence of the uniaxial stress along the [100] direction can be written as (see Fig. 1)

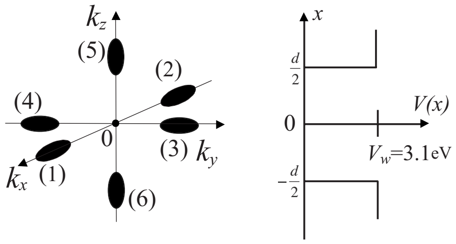

FIG. 1. The schematic figure of a Si/SiO_2 quantum well and the equal energy surfaces in k space in the vicinity of the conduction-band minima of the bulk Si.

$$H_{\mathrm{eff}}(\boldsymbol{r}_1,\boldsymbol{r}_2)=H_1(\boldsymbol{r}_1)+H_1(\boldsymbol{r}_2)+\frac{1}{r_{12}},$$

$$H_1(\boldsymbol{r}_n)=-\frac{1}{2}\left(\frac{\partial^2}{\partial y_n^2}+\frac{\partial^2}{\partial z_n^2}\right)-\frac{1}{2M_{\mathrm{r}}}\left(\frac{\partial^2}{\partial x_n^2}\right)-\frac{1}{r_n}+H_S. \qquad (1)$$

Here, r_{12} is the distance between two trapped electrons, $H_1(\boldsymbol{r}_n)$ is the single-electron Hamiltonian for a neutral donor, D^0, and H_S represents the stress term. M_{r} in Eq. (1) is the ratio of the longitudinal effective mass m_{l}^* to the transverse effective mass m_{t}^*, defined as $M_{\mathrm{r}}=m_{\mathrm{l}}^*/m_{\mathrm{t}}^*$. The stress energy operator H_S has the properties,[25,26]

$$H_S u_j(\boldsymbol{r}_n)=-2Su_j(\boldsymbol{r}_n)/3 \quad (j=1,2)$$

$$=Su_j(\boldsymbol{r}_n)/3 \quad (j=3-6), \qquad (2)$$

where $u_j(\boldsymbol{r}_n)$ is the Bloch function at the jth valley and S is the stress-induced splitting in the valley energies. Similarly, the single-electron Hamiltonian for an electron in the valley (3) can be written as

$$H_1(\boldsymbol{r}_n)=-\frac{1}{2}\left(\frac{\partial^2}{\partial x_n^2}+\frac{\partial^2}{\partial z_n^2}\right)-\frac{1}{2M_{\mathrm{r}}}\left(\frac{\partial^2}{\partial y_n^2}\right)-\frac{1}{r_n}+H_S. \qquad (3)$$

In Eqs. (1) and (3), the energy and the length are measured in the effective atomic units of $Ha^*=m_{\mathrm{t}}^*e^4/(4\epsilon^2\hbar^2)$ and $a_{\mathrm{B}}^*=\epsilon\hbar^2/(\pi m_{\mathrm{t}}^*e^2)$, respectively. For Si, $Ha^*=35.4$ meV, $a_{\mathrm{B}}^*=3.36$ nm, and $M_{\mathrm{r}}=4.81$.[31]

We assumed a Si/SiO_2 quantum well in the x direction as shown in Fig. 1 and a donor was located at the center of the well. As for the well potential $V(x)$, we adopted the well depth of 3.1 eV corresponding to the band offset between Si and SiO_2. With respect to the single-electron Hamiltonian for the quantum wells, both differences between the effective masses and between the dielectric constants of Si and SiO_2 were not considered. Hence, the effect of image charges are not included.

In the effective-mass approximation without the valley-orbit interaction, the single-electron wave function is written as the product of the envelope function $\psi_j(r_n)$ and the Bloch function $u_j(r_n)$ at each valley. The valley-orbit interaction mixes the wave functions assigned by the different valley index. We assumed the following form for the valley-orbit interaction in the limit of a vanishing range for the central cell correction:[26]

$$H_{\mathrm{VO}} = \sum_{k=1}^{6}\sum_{j=1}^{6} V_0 \delta(r_n)|u_k\rangle\langle u_j|. \tag{4}$$

Hence, the wave functions for a neutral donor and a D^- ion with the valley-orbit interaction can be expressed by the linear combination of the basis wave function assigned by the valley index as

$$\Psi_{D^0} = \sum_{j=1}^{6} a_j \psi_j(r_n) u_j(r_n),$$

$$\Psi_{D^-} = \sum_{j=1}^{6}\sum_{k=1}^{6} a_{jk}\psi_{jk}(r_1,r_2)u_j(r_1)u_k(r_2). \tag{5}$$

Here, ψ_{jk} is the envelope function for a D^- ion, i.e., the ground-state wave function for H_{eff}. The value of V_0 in Eq. (4) was determined from the observed split in the $1s$-like ground-state energies of a neutral donor in the bulk Si, the level with A_1 symmetry and the weighted center of levels with E and T_2 symmetries[20] since the assumed form of Eq. (4) cannot reproduce the observed small energy split between levels with E and T_2 symmetries. The values of V_0 were determined to be -1.53 and 0.23 meV a_B^{*3} for P and Li donors, respectively.

The Hamiltonians for a neutral donor and a D^- ion with the valley-orbit interaction can be written as

$$H_D(r_n) = H_1(r_n) + H_{\mathrm{VO}}(r_n),$$

$$H_{D^-}(r_1,r_2) = H_{\mathrm{eff}}(r_1,r_2) + H_{\mathrm{VO}}(r_1) + H_{\mathrm{VO}}(r_2). \tag{6}$$

We first calculate the ground-state energies for the basis wave functions assigned by the valley index in Eq. (5) and then treat the valley-orbit interaction as perturbation.[10]

We used a DQMC method with an importance sampling[28] to calculate the ground-state energies of a neutral donor and a D^- ion without the valley-orbit interaction, i.e., the diagonal matrixes for the Hamiltonians, H_1 and H_{eff}. In DQMC method, the accurate ground state can be obtained asymptotically in the limit of infinite imaginary time[28] and the correlation effect between two electrons in a D^- ion can be considered accurately in principle. Indeed, the magnetic field dependence of the calculated binding energies[18] of D^- ions in GaAs in DQMC method reproduced well experimental data.[32] In DQMC method, anisotropy of the effective mass can be taken into account easily by taking an anisotropic diffusion constant for each electron since it is inversely proportional to the effective mass. Hence, DQMC method can incorporate easily both the anisotropy of the effective mass and the multivalley structure into the computer program code, in addition to the electron correlation effect.

The VO interaction, H_{VO}, in Eq. (6) has the matrix element for both the diagonal and the off-diagonal parts. The magnitude of the diagonal part is proportional to the single-electron probability amplitude at the origin of the basis wave function,

$$\langle \psi_j u_j | H_{\mathrm{VO}} | \psi_j u_j \rangle = V_0 |\psi_j(0)|^2,$$

$$\langle \psi_{jk} u_j u_k | H_{\mathrm{VO}}(r_1) | \psi_{jk} u_j u_k \rangle = V_0 \langle \psi_{jk}(0,r_2) | \psi_{jk}(0,r_2)\rangle. \tag{7}$$

We determined the single-electron probability amplitude at the origin by using the Hellman-Feynman operator sampling method[33] for the operator of $\delta(r-r_0)$ in DQMC simulation with an importance sampling.[28] Here, we took the extrapolated value of the probability distribution to the origin, to reduce the fluctuation. As for the jk off-diagonal element of H_{VO} for a neutral donor, it is just the geometric average of the jj and kk diagonal matrix elements. With respect to a negative ion, on the other hand, the off-diagonal matrix element of $H_{\mathrm{VO}}(r_1)$ between $\psi_{jk}u_j u_k$ and $\psi_{lm}u_l u_m$ is proportional to δ_{km} due to the orthogonality among the Bloch functions. As for the magnitude, we assumed it to be the geometric average of the diagonal matrix elements for each basis function. We calculate the ground-state energies of a neutral donor and of a D^- ion with the valley-orbit interaction, by diagonalizing the 6×6 matrix for H_D and 36×36 matrix for H_{D^-}, respectively.

DQMC method with an importance sampling uses the trial function[28] and we adopted the following simple trial function for the D^0 state which traps an electron in the valley (1):

$$\psi_{D^0}^{\mathrm{tr}} = \exp\left(-\sqrt{\frac{y^2+z^2}{a_1^2} + \frac{x^2}{b_1^2}}\right). \tag{8}$$

In the quantum well, we assumed the following trial function in the importance sampling for the D^0 state trapping an electron in the valley (3):

$$\psi_{D^0}^{\mathrm{tr}} = \exp\left(-\sqrt{\frac{x^2}{a_2^2} + \frac{y^2}{b_2^2} + \frac{z^2}{c_2^2}}\right). \tag{9}$$

We assumed the spin-singlet ground state for a D^- state since the spin-singlet state has the largest binding energy.[19] Hence, two electrons in a D^- ion have not the same spin and the exchange interaction between them vanishes, irrespective of the intravalley or the intervalley configuration. It should be mentioned that the exchange interaction between electrons in different valleys is also very small if the envelope function varies slowly in the unit cell of the crystal due to the orthogonality between the Bloch functions.[34] We adopted the simple direct product form of the donor wave functions, as the trial function for the D^- state in the importance sampling. In fact, DQMC with this simple trial function can reproduce the accurate D^- binding energy of 0.055Ry* in the case of the isotropic effective mass.[27] It should be mentioned that the product of the exact ground-state wave function and the trial function can be obtained as the asymptotic distribution func-

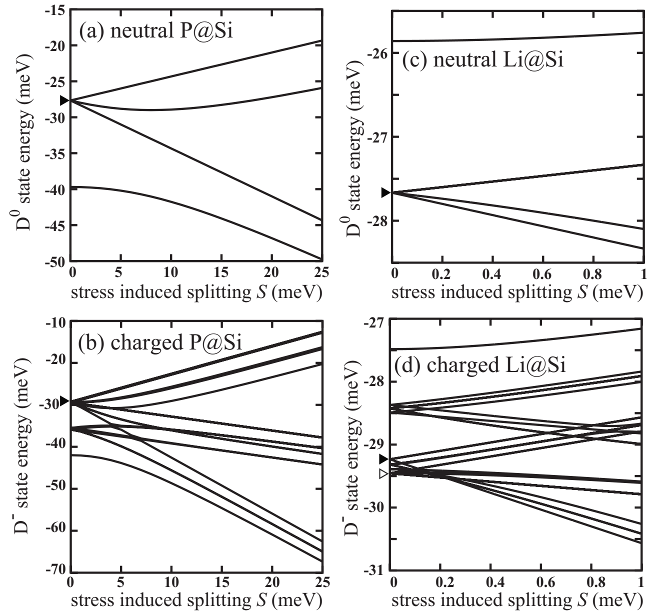

FIG. 2. (a) The ground-state energies $E_G(D^0)$ of a neutral P donor, (b) the ground-state energies $E_G(D^-)$ of a negative P donor, (c) the ground-state energies $E_G(D^0)$ of a neutral Li donor, and (d) the ground-state energies $E_G(D^-)$ of a negative Li donor with the VO interaction, as a function of stress-induced splitting S. The values calculated in the effective-mass approximation without the VO interaction are indicated by arrow heads (the solid arrow head for the intravalley configuration and the open arrow head for the intervalley configuration of a negative donor).

tion in DQMC method with an importance sampling.[28] In Eqs. (8) and (9), a_i, b_i, and c_i are the variational parameters related to the extension of the trial wave function in each direction, and they are determined by optimization with a variational Monte Carlo simulation.

The binding energy of a D$^-$ ion is calculated as

$$E_B^{D^-} = E_{D^0} + E_{\rm free} - E_{D^-}, \tag{10}$$

where E_{D^0}, $E_{\rm free}$, and E_{D^-} are the lowest ground-state energies of a neutral donor, D^0, the free electron, and a negative donor, D$^-$, respectively.

III. NUMERICAL RESULTS

A. Uniaxial stress

At first, we show in Figs. 2(a) and 2(b) both ground-state energies, E_{D^0} and E_{D^-}, of the neutral and the negatively charged states for substitutional P impurities in the compressive uniaxial stress along the [100] direction, as a function of the stress-induced splitting S in the valley energies. The sixfold valley degeneracy at $S=0$ of the ground state for a neutral donor without the VO interaction is split into two levels, one with the A$_1$ symmetry and another with the T$_2$ and E symmetries. The degeneracy between the latter two states is caused by assumed δ-function form for the valley-orbit interaction. As the [100] compressive stress is applied, the level with T$_2$ symmetry is split into two levels with A$_1$ and E symmetries, and the lowest level has the A$_1$ symmetry for P impurities with a negative V_0 value. Similarly, the valley degeneracy at $S=0$ of the ground state for a negative donor is split by the VO interaction into many levels with the A$_1$ and E symmetries in the uniaxial [100] compressive stress and the lowest energy ground state has the A$_1$ symmetry for P. In Figs. 2(c) and 2(d), we present both the ground-state energies of a neutral donor and a negative donor for interstitial Li impurities. The ground states for both a neutral Li donor and a negative Li donor have the E symmetry in the [100] uniaxial compressive stress, contrary to the case of P. This difference is attributed to the positive V_0 value for Li donors, contrary to P donors.

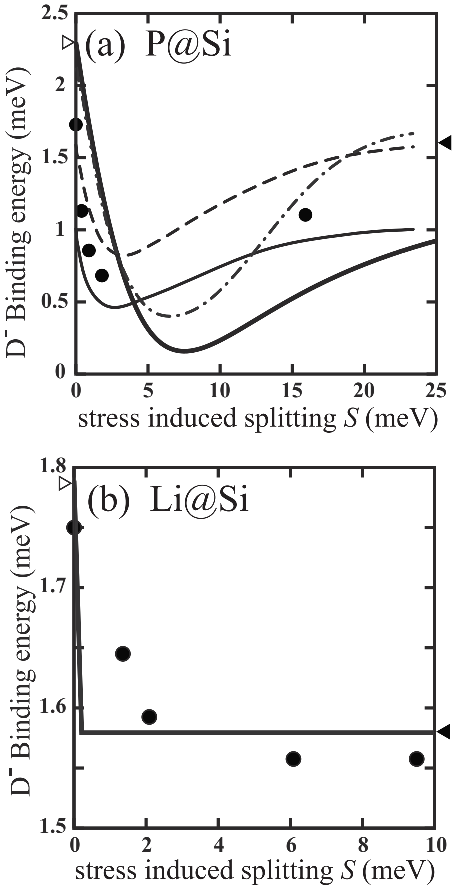

FIG. 3. The binding energies $E_B(D^-)$ (a thick solid line) of a negative donor for (a) P and (b) Li, as a function of stress-induced splitting S, with their experimental values (Ref. 23) (solid circles). Here, calculated result by Larsen (Ref. 25) is shown by a thin solid line and those by Oliveira (Ref. 26) are shown by a thin broken line (VO interaction for the inner orbit) and a dashed-dotted line (VO interaction for both the inner and the outer orbits), respectively. The arrow heads on the left and the right vertical axes indicate the calculated binding energy at zero stress and in the high stress limit, respectively.

Next, we show in Figs. 3(a) and 3(b) the binding energy $E_B(D^-)$ of a negative donor for P and Li impurities as a function of stress-induced splitting S. The binding energy of a negative P donor decreases first with the stress-induced splitting and then increases monotonically. In the high stress limit, it has a value of 1.60 meV. On the other hand, the

TABLE I. The value of the valley-orbit interaction, V_0, and the binding energy of a D^- ion for P and Li impurities in stress free and in the limit of high stress along the [100] direction.

	V_0 [meV a_B^{*3}]	Binding energy in stress free (meV)	Binding energy in high stress (meV)
P	−1.53	2.30	1.60
Li	0.23	1.79	1.58

binding energy of a negative Li donor decreases linearly with the stress-induced splitting and then has a constant value. These uniaxial stress dependences reproduces the observed behavior.[23] We summarize the calculated results for P and Li impurities in Table I and those in the effective-mass approximation without the valley-orbit interaction in Table II.

Let us consider the reason for these behaviors. We show in Fig. 4 the valley population probabilities in the ground states of both the neutral donor and the negative donor of P. The valley population probabilities for the jth valley for a neutral donor, $P_{\mathrm{D}}(j)$, and that for a D^- ion, $P_{\mathrm{D}^-}(j)$, are calculated from the coefficient in Eq. (5) as

$$P_{\mathrm{D}}(j) = |a_j|^2,$$

$$P_{\mathrm{D}^-}(j) = 2\sum_{k=1}^{6} |a_{jk}|^2 - |a_{jj}|^2. \qquad (11)$$

The population probability in the stress-deepened valleys (1) and (2) rises up more readily with the stress-induced splitting for the negatively charged state than for the neutral state. The former envelope function extends wider than the latter one caused by repulsive electron-electron interaction, and has a smaller single-electron probability amplitude, $P(0)$, at the origin (see Table II). Hence, the energy gain in the stress energy by transfer to the deepening valleys prevails over the energy loss in the valley-orbit interaction at a weaker compressive stress for the negatively charged state than for the neutral state. This is the origin of the first decrease in the binding energy of a P negative donor in the [100]-uniaxial stress. As the stress increases further, the valley population of the neutral donor changes also remarkably and the energy gain by the VO interaction for the neutral donor is decreased. Then, the binding energy of a P negative donor increases gradually and approaches a constant value of 1.60 meV. The valley population probability in the deepening valleys of a neutral donor approaches unity near $S=50$ meV in Fig. 4 and the high stress limit of the binding energy is realized for S above 50 meV. In the case of Li, on the other hand, the symmetry of the ground state is quite different from that of P. We present in Fig. 5 the ground-state energy $E_{\mathrm{G}}(\mathrm{D}^-)$ of a Li negative donor in a magnified scale of Fig. 2(d) in the low stress region. The lowest ground state changes from the (i,j) intervalley configurations with $i=1$ or 2 and $j=3$ or 4 or 5 or 6 to the (i,j) intravalley configurations with $i,j=1$ or 2, just as predicted by Larsen.[25] The transition of the ground state corresponds to the kink point in the D^- binding energy in Fig. 3.

TABLE II. The binding energy and the single-electron probability density $P(0)$ at the origin for a neutral donor, D^0, and a negative donor, D^-, of the intravalley and the intervalley configurations in the bulk Si, in the effective-mass approximation without the VO interaction.

	Binding energy (meV)	$P(0)$ (a_B^{*-3})
D^0	27.67 ± 0.01	1.31 ± 0.01
D^- (intravalley)	1.58 ± 0.07	0.66 ± 0.01
D^- (intervalley)	1.79 ± 0.07	0.70 ± 0.01

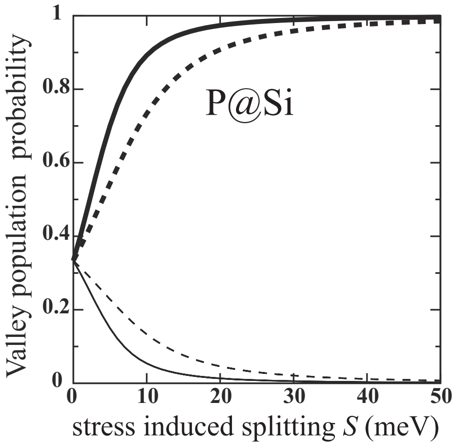

FIG. 4. The valley population probability of a neutral donor (broken line) and a negative donor (solid line) for Si:P, as a function of the stress-induced splitting S. Here, thick lines present the valley population probability for the stress-deepened valleys (1) and (2) and thin lines do those in other valleys, (3)–(6).

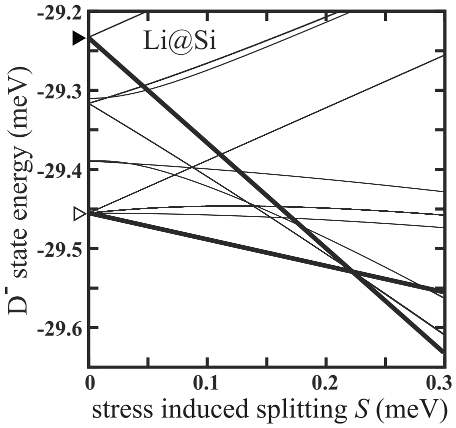

FIG. 5. The ground-state energies $E_{\mathrm{G}}(\mathrm{D}^-)$ of a Li negative donor in a magnified scale of Fig. 2(d) in the low stress region, as a function of stress-induced splitting S. The values calculated in the effective-mass approximation without the VO interaction are indicated by arrow heads (the solid arrow head for the intravalley configuration and the open arrow head for the intervalley configuration of a negative donor).

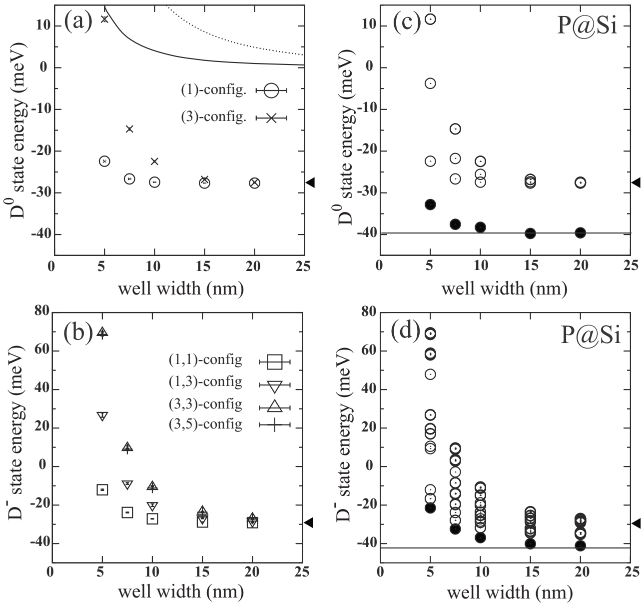

FIG. 6. (a) The ground-state energies $E_G(D^0)$ of a neutral donor without the VO interaction, in addition to the free-electron ground-state energies in the valley (1) (a solid line) and in the valley (3) (a broken line), (b) the ground-state energies $E_G(D^-)$ of a negative donor with their bulk values (arrow heads) without the VO interaction, (c) the ground-state energies of a neutral P donor, and (d) the ground-state energies of a negative P donor with the bulk value of the lowest-energy state (solid lines), in the Si/SiO_2 quantum well. In (c) and (d), the lowest energy level is represented by the solid circle.

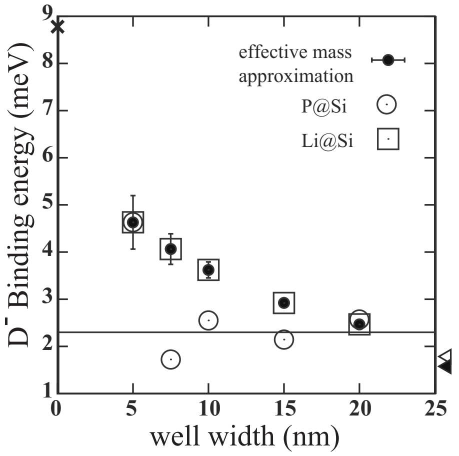

FIG. 7. The binding energies $E_B(D^-)$ of a negative donor of P and Li impurities in the Si/SiO_2 quantum well as a function of the well width, with the bulk value for P (solid line). The binding energy in the effective-mass approximation without the VO interaction is also plotted. The binding energies for the intervalley and intravalley configurations without the VO interaction in the bulk are also indicated by open and solid arrow heads, respectively. The × on the left axis indicates the calculated binding energy without the VO interaction for the two-dimensional electrons.

B. Quantum well

At first, we show the well width dependence of the ground-state energies of both a neutral donor and a negative donor in a Si/SiO_2 quantum well, without the VO interaction. We show in Figs. 6(a) and 6(b) the energy levels of the ground states of both a neutral donor and a negative donor in the quantum well, as a function of the well width. In Fig. 6(a), the lowest energies of the free-electron state are also plotted. For the free-electron state in the valley (3), the quantum confinement effect is already prominent at the well width of 25 nm. The ground-state energy of a neutral donor is affected by the quantum confinement effect for the well width less than about 15 nm and is increased compared to the bulk value. For a neutral donor in the well, the valley (1) electron takes a lower energy than the valley (3) electron similarly to the free electron but the quantum confinement effect is much more weakened. On the other hand, the quantum confinement effect for a negative donor is more prominent and appears already at the well width of 20 nm. In such a narrow well, the electron configuration of the ground state of a negative donor changes to the (1,1)-intravalley configuration from the intervalley configuration in the bulk. In Figs. 6(c) and 6(d), we plot the well width dependence of the ground-state energies of both a P neutral donor and a P negative donor. They are calculated by diagonalizing the 6×6 matrix for H_D or the 36×36 matrix for H_{D^-}. In the quantum well, the valley degeneracy is split similarly to the case of the compressive stress along the [100] direction and the state with A_1 symmetry has the lowest energy.

Second, we plot in Fig. 7 the binding energy of the lowest energy state of a negative donor of P and Li as a function of the well width, in addition to the binding energy without the VO interaction. The binding energy of a negative donor without the VO interaction increases monotonically with decreasing the well width, owing to much stronger confinement effect for the free electron than for a negative donor. In Fig. 7, the binding energy of a D^- ion for two-dimensional electrons is also plotted on the left axis. This gives the lower limit for the binding energy of a D^- ion without the VO interaction at a vanishingly small well width since the Coulomb interaction between two electrons in a D^- ion is most enhanced for the two-dimensional electron. In the case of Li donors, the ground state has E symmetry with a vanishing amplitude at the origin for both the neutral and the charged states and hence the binding energy of the negative donor is not affected by the VO interaction. In the case of P donors, on the other hand, its well width dependence is quite different from that without the VO interaction. The disparity between these two binding energies is caused by the VO interaction and increases first and then decreases steeply nearly to zero at 5 nm as the well width decreases, i.e., the binding energy of a P negative donor is suppressed above 7.5 nm although enhancement by the quantum confinement effect is recovered at 5 nm. The former suppression is caused by the larger ascent of the D^- ground-state energy of P compared to that without the VO interaction [see Figs. 6(b) and 6(d)] and the recovery is caused by the subsequent larger ascent of the D^0 ground-state energy of P compared to that without the VO interaction [see Figs. 6(a) and 6(c)]. These ascents are induced by reduction in the effect of the VO interaction with decreasing the well width.

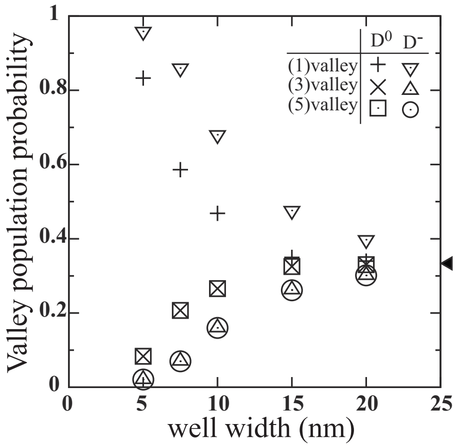

FIG. 8. The valley population probability for a P neutral donor and a P negative donor in a Si/SiO_2 quantum well, as a function of the well width. The arrow head indicates the bulk value of 1/3.

To reveal the physical reason for the steep increase in the binding energy at 5 nm for a P negative donor, we plot in Fig. 8 the valley population probabilities of the neutral and the charged states, as a function of the well width. For the neutral state, the valley population probability in the deepening (1) and (2) valleys increases steeply at the well width of 5 nm. It means that the energy gain by transfer to these valleys prevails over the energy loss in the VO interaction. To confirm the mechanism, we plot in Fig. 9(a) the single-electron probability amplitudes $P(0)$ at the origin for the neutral and the charged states. $P(0)$ increases monotonically with decreasing the well width by the quantum confinement effect. In Fig. 9(b), we plot $V_0P(0)$ which is the diagonal matrix elements of the valley-orbit interaction H_{VO} for a neutral P donor and a negative P donor. The magnitudes of the VO interaction in Fig. 9(b) increases as the well width decreases and enhances the effect of the VO interaction. However, the dispersion in the diagonal element of the Hamiltonian, the split width of the energy levels in Figs. 6(a) and 6(b), also increases as the well width decreases. The latter factor suppresses the valley mixing of inequivalent valleys. The suppression of the effect of the VO interaction emerges at the well width of 5 nm for a neutral P state, much smaller than 10 nm for a charged P state, as seen in Fig. 6.

IV. DISCUSSION AND CONCLUSION

Let us compare our results on the stress dependence of the binding energy of a negative donor in Fig. 3 with those by Larsen[25] and by Oliveira *et al.*[26] They used the variational scheme with a Chandrasekhar-type isotropic variational wave function with A_1 symmetry for a negative donor. As for the VO interaction, they assumed the similar form to us and the lowest lying T_2 and E states of a donor are degenerate at zero stress. Larsen neglected the VO interaction for the outer orbit of a D^- ion and assumed the same VO interaction for the inner orbit as a neutral donor. Hence, Larsen failed in interpreting the observed chemical shift for the zero-stress D^- binding energies. Oliveira treated two cases; the VO interaction for both the outer and inner orbits and the VO interaction only for the inner orbit. By considering the VO interaction for both the inner and the outer orbits, the binding energy of a negative donor deepens remarkably at zero stress and it decreases strongly as the stress increases.[26] The calculated binding energy of 2.23 meV at zero stress is similar to ours and is rather close to the observed value of 2.2 meV by Gershenzon *et al.*[35] They ascribed the nonmonotonic change in the D^- binding energy to the disparity between the valley distributions of the inner and the outer orbitals, i.e., the weakest binding at the intermediate stress, which is strong enough to drive the electron in the outer orbital into the stress-deepened valleys but too weak to do the same to the electron in the inner orbital. The disparity induces a substantial admixture of the high-energy configuration into the D^- ground-state wave function and decreases the binding energy.[25,26] In our calculation, on the contrary, disparity between the valley distributions of a neutral donor and a negative donor induces a substantial decrease in the binding energy due to difference between effects of the valley-orbit interaction. The behavior of the D^0 orbit under stress, however, is very similar to that of the inner orbit of a D^- ion.[26]

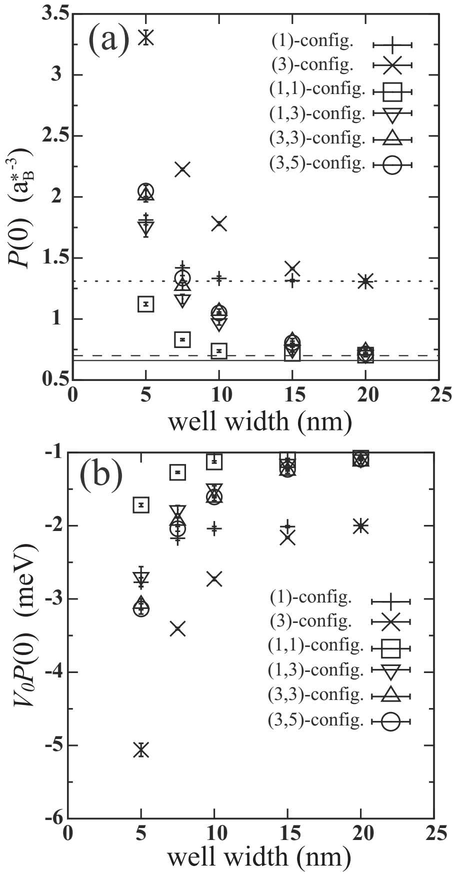

FIG. 9. (a) The single-electron probability amplitude $P(0)$ at the origin calculated in the effective-mass approximation without the VO interaction and (b) $V_0P(0)$, for a P neutral donor and a P negative donor in the Si/SiO_2 quantum well, as a function of the well width. In (a), the dotted, broken, and solid lines indicate the bulk values for a neutral donor, a negative donor with the intervalley configuration, and that with the intravalley configuration, respectively.

Hence, disparity between the valley distributions of the inner and the outer orbitals is almost equivalent to that of the D^0 state and the D^- state. Our calculated result in Fig. 3 is similar to the result with the VO interaction for both the inner and outer orbits by Oliveira in a low stress region but is rather similar to the result by Larsen in a high stress region. The deviation of our result from the experiment[23] can be attributed to both the simple form for the VO interaction and the perturbative treatment for the VO interaction. As for Li, on the other hand, our calculation is the first numerical result and it reproduces well the experiment.[23]

We studied the spin-singlet ground states of a D^- ion for two situations, one in uniaxially stressed Si along the [100] direction and another in Si/SiO_2 quantum wells in the [100] direction. Let us discuss the similarity and the difference between them. In the two cases, the sixfold valley degeneracy is lifted and the ground state of the free electron in the (1) and (2) valleys has a lower energy than those in other valleys. Hence, the effect of the VO interaction for the ground state is reduced for the high stress limit or for the narrow well limit because of the decrease in the valley degeneracy from 6 to 2. In the effective-mass approximation without the VO interaction, on the other hand, the quantum confinement effect deepens the binding energy of a negative donor with decreasing the well width while the uniaxial compressive stress reduces the binding energy similarly to the case of Li impurities. Furthermore, the single-electron probability amplitude $P(0)$ at the origin does not change with the stress but it increases with decrease in the well width by the quantum confinement effect. This factor complicates the behaviors of both the neutral and the charged states for a P donor in the quantum well, by means of the VO interaction.

In summary, we studied the spin-singlet ground states of a D^- ion in uniaxially stressed Si along the [100] direction and in Si/SiO_2 quantum wells in the [100] direction for two types of donors, a substitutional P and an interstitial Li impurities, using a diffusion quantum Monte Carlo method. The valley-orbit interaction is taken into account by diagonalizing the multiplet Hamiltonian matrix in the basis of wave functions assigned by the valley index. In the uniaxial compressive stress along the [100] direction, the binding energy of a P negative donor decreases first and then increases gradually with the stress-induced splitting. This nonmonotonic dependence is attributed to the difference between the population probabilities in the stress-deepened valleys of a neutral donor and a negative donor. As for Li impurities, the binding energy of a negative donor decreases linearly with the stress-induced splitting and then takes a constant value. This behavior is attributed to the transition of the ground state of a Li negative donor from the intervalley configuration to the intravalley configuration in the uniaxial stress. In the quantum well in the [100] direction, the quantum confinement effect deepens the binding energy of a negative donor if the valley-orbit interaction is negligible. The same enhanced binding energy is expected for a Li negative donor with E symmetry. However, the enhancement is expected only in narrow wells less than about 5 nm for a P negative donor with A_1 symmetry, owing to the valley-orbit interaction.

A negative P donor in such a narrow Si/SiO_2 quantum wells is able to have a much deeper binding energy compared to the bulk Si and it is promising for realizing a spin-dependent electron charge transfer event $D^0D^0 \rightarrow D^+D^-$ in donor-spin readout proposed by Kane.[12]

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