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Origin of the ESR signal with $g = 2.0055$ in amorphous silicon

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Defect-state wave functions for threefold- and fivefold-coordinated Si atoms in amorphous silicon clusters have been calculated with use of a first-principles linear combination of the atomic orbitals method in order to clarify the origin of the ESR signal with $g = 2.0055$ in amorphous silicon. The wave function of the defect state originating from the threefold-coordinated Si atom is strongly localized on this atom. On the other hand, that for the fivefold-coordinated Si atom is extended on this atom and its nearest neighbors. By comparing these results with the observed hyperfine structure of the ESR signal, we conclude that the origin of this ESR signal is the threefold-coordinated Si atoms.

There exist two defect models as the origin of the ESR signal with $g = 2.0055$ in amorphous silicon (*a*-Si). We shall call this ESR center "the *D* center." One is the threefold-coordinated Si atom (dangling bond) and the other is the fivefold-coordinated one (floating bond).[1] Both of them are expected to have an energy level in the band gap.

The *D*-center doublet ESR signal observed in ^{29}Si-enriched *a*-Si:H has a splitting of about 75 G.[2] This hyperfine interaction has also been observed by electron-nuclear double resonance (ENDOR) measurement.[3] In addition, each in the doublet has a linewidth of about 60 G.[2] Stutzmann *et al.* analyzed the *D*-center ESR signal and supported the dangling-bond model.[4] On the contrary, Stathis *et al.* rather supported the floating-bond model.[5]

In order to clarify the origin of the *D* center, we calculate the hyperfine interactions between the unpaired electron in the defect state and ^{29}Si nuclei for various defect models and compare them with the results obtained from ESR and ENDOR measurements. Until now, several theoretical investigations have been carried out and they showed that the *D* center in *a*-Si is more likely to be the threefold-coordinated Si atom.[6–10] Previously we obtained, from the calculations using the nonorthogonal tight-binding method, the results that the dominant isotropic hyperfine interaction for the floating bond is larger than that for the dangling bond.

In these empirical and semiempirical calculations,[6–9] only 3*s* and 3*p* atomic orbitals for each Si atom are adopted as the basis functions, and 3*d* atomic orbitals are not included in the basis functions. It is important to include the 3*d* atomic orbitals in the basis functions for atoms with coordination numbers higher than four. So, the conclusion[7–9] that the possibility for the fivefold-coordinated Si atom being the *D* center is very small, is not so convincing. Accordingly, it is necessary to calculate the electronic structure for the defect model with the fivefold-coordinated Si atom using the first-principles method with the 3*d* atomic orbitals in the basis functions for Si atoms.

In this paper, we present the results of electronic-structure calculations for the realistic *a*-Si clusters with the threefold- and fivefold-coordinated Si atoms using a first-principles linear combination of the atomic-orbitals method according to Ren *et al.*[11] In this method, the site-decomposed atomic potential $V_a(r)$ was constructed from a superposition of atomic charge densities,[11] which includes the Slater-type local exchange potential $V_{\rm ex}$,[12]

$$V_{\rm ex} = -\tfrac{3}{2}\alpha \left[-\frac{3\rho(\mathbf{r})}{\pi} \right]^{1/3} \quad \text{with } \alpha = \tfrac{2}{3} , \tag{1}$$

where $\rho(\mathbf{r})$ means the bulk electron-charge density. This atomic potential $V_a(r)$ is not for a free atom but for an atom in the solid. Atomic orbitals as the basis functions $\varphi_\mu(\mathbf{r})$'s were constructed from eigenfunctions of the eigenvalue problem for a Si atom with the atomic potential $V_a(r)$, and are represented by the linear combination of twelve Gaussians.[11] Though $V_a(r)$ and $\varphi_\mu(\mathbf{r})$'s for the Si atoms listed in Ref. 11 are determined for Si atoms in $\mathrm{Si_3N_4}$, the energy bands of crystalline Si calculated by them are in good overall agreement with those of Chelikowsky *et al.*,[13] except for the Γ_2' state and its neighbor in the energy-band diagram. Accordingly, we used $V_a(r)$ and $\varphi_\mu(\mathbf{r})$'s listed in Ref. 11 for the atomic potential and the basis functions including the 3*d* atomic orbitals for Si atoms.

For the model cluster with a threefold-coordinated Si atom in the vicinity of the center of the cluster, we used the 110-atom *a*-Si cluster in Ref. 6, which was constructed to minimize the Keating potential[14] for the hand-made cluster without changing the topology of this cluster. This cluster has the bond-length fluctuation of 1.5% and the bond-angle fluctuation of 5.2%. The bond angles around the threefold-coordinated Si atom in this cluster are 111.3°, 112.1°, and 114.8°. We shall call this cluster "DB110." On the other hand, we constructed 81- and

86-atom a-Si clusters with a fivefold-coordinated Si atom in the vicinity of the center of the clusters, as was done in Ref. 6. We shall call these two clusters "FB81" and "FB86," respectively. The FB81 has the bond-length fluctuation of 1.2% and the bond-angle fluctuation of 7.0%. The bond angles around the fivefold-coordinated Si atom in the FB81 are 79.0°, 83.1°, 88.1°, 88.7°, 101.5°, 102.0°, 112.2°, 115.9°, 131.9°, and 161.9°. The FB86 has the bond-length fluctuation of 1.3% and the bond-angle fluctuation of 7.5%. The bond angles around the fivefold-coordinated Si atom in the FB86 are 77.8°, 85.6°, 91.0°, 96.0°, 96.8°, 100.0°, 103.0°, 110.9°, 146.2°, and 160.2°.

In order to avoid a surface effect in the cluster calculations, we performed the calculations according to Menzel *et al.*[15] as follows: For the basis functions for the defect atom and 38 (29) atoms around it in the DB110 (FB81 and FB86), we adopted the 1s, 2s, 2p, 3s, 3p, and 3d atomic orbitals. On the other hand, the basis functions for the other Si atoms in the DB110 (FB81 and FB86) were limited to the 1s, 2s, and 2p atomic orbitals.

We obtain the electronic structure for the defect models by solving the following equation:

$$\left[-\tfrac{1}{2}\nabla^2+\sum_a V_a(r)\right]\Psi(\mathbf{r})=E\Psi(\mathbf{r}) \;, \tag{2}$$

where $\sum_a$ means the sum over the atoms in the cluster. In order to solve this equation, $\Psi(\mathbf{r})$ is represented as the linear combination of normalized atomic orbitals $\varphi_\mu(\mathbf{r})$'s as follows:

$$\Psi(\mathbf{r})=\sum_\mu C_\mu \varphi_\mu(\mathbf{r}) \;, \tag{3}$$

where $\sum_\mu$ means the sum over the basis functions for the atoms in the cluster. Then, we solve the secular equation,

$$|H_{\mu\nu}-ES_{\mu\nu}|=0 \;, \tag{4}$$

where $H_{\mu\nu}$ and $S_{\mu\nu}$ are the Hamiltonian and overlap matrix elements, respectively, between $\varphi_\mu(\mathbf{r})$ and $\varphi_\nu(\mathbf{r})$. This is the non-self-consistent first-principles calculation. Since a-Si clusters consist of only Si atoms, the charge on each Si atom should be roughly neutral even if we perform the self-consistent calculation. Accordingly, the results obtained by the non-self-consistent calculations should be reliable.

The defect-state wave functions $\Psi_{\mathrm{ds}}(\mathbf{r})$'s calculated for the DB110, FB81, and FB86, which correspond to the dangling- and floating-bond states, respectively, are shown in Table I. The dangling-bond state is strongly localized on the nonbonding sp-hybridized orbital centered on the threefold-coordinated Si atom. This result is similar to those obtained by other methods.[6-10]

On the other hand, the floating-bond states for the FB81 and FB86 are the bonding states between the 3d orbital centered on the fivefold-coordinated Si atom and the sp-hybridized orbitals centered on its first nearest neighbors. The fractions of these orbitals, $|C_\mu|^2$, in the floating-bond state somewhat change according to the bond angles around the fivefold-coordinated Si atom. However, the sum of them is roughly constant for the

TABLE I. Wave functions of the dangling-bond states (DBS) and floating-bond states (FBS) and the isotropic hyperfine interactions with ^{29}Si's at the various sites of these states. $T3$ and $T5$ mean the threefold- and fivefold-coordinated Si atoms, respectively. FNN$_i$ and SNN$_i$ mean the first- and second-nearest neighbors, respectively, of $T3$ and $T5$. C_μ's are the coefficients in Eq. (3) for $\Psi_{\mathrm{ds}}(\mathbf{r})$. $\sum$ means the sum over three 3p atomic orbitals or five 3d ones. $|\Psi_{\mathrm{ds}}(\mathbf{r}_n)|$ (a.u.) and a (G) mean the amplitude (in atomic units) and the isotropic hyperfine interaction (in gauss), respectively, at the ^{29}Si site $\mathbf{r}_n$ of the DBS or FBS.

Cluster	Ψ_{ds}	$\mathbf{r}_n$	$\lvert C_{3s}\rvert^2$	$\sum\lvert C_{3p}\rvert^2$	$\sum\lvert C_{3d}\rvert^2$	$\lvert\Psi_{\mathrm{ds}}(\mathbf{r}_n)\rvert^2$ (a.u.)	a (G)
DB110	DBS	$T3$	0.035	0.384	0.003	0.32	101
		FNN$_1$	0.001	0.006	0.014	0.01	3
		FNN$_2$	0.000	0.005	0.013	0.00	0
		FNN$_3$	0.001	0.005	0.012	0.01	3
		SNN$_1$	0.000	0.002	0.001	0.01	3
		SNN$_2$	0.007	0.019	0.001	0.09	29
		SNN$_3$	0.005	0.032	0.004	0.05	15
		SNN$_4$	0.008	0.025	0.002	0.07	22
FB81	FBS	$T5$	0.003	0.000	0.142	0.03	10
		FNN$_1$	0.007	0.048	0.004	0.10	32
		FNN$_2$	0.017	0.123	0.006	0.28	89
		FNN$_3$	0.009	0.082	0.007	0.15	48
		FNN$_4$	0.015	0.123	0.005	0.24	76
		FNN$_5$	0.002	0.027	0.002	0.03	10
FB86	FBS	$T5$	0.000	0.003	0.172	0.00	0
		FNN$_1$	0.008	0.096	0.009	0.15	48
		FNN$_2$	0.010	0.115	0.005	0.19	60
		FNN$_3$	0.001	0.008	0.002	0.01	3
		FNN$_4$	0.011	0.096	0.006	0.25	79
		FNN$_5$	0.005	0.067	0.005	0.10	32

change of these bond angles as shown in Table I. The previous result of Biswas *et al.*[9] that stated the amplitude on the fivefold-coordinated Si atom of the floating-bond state is vanishingly small, is different from the present one shown in Table I. This difference should mainly originate from the inclusion of the 3*d* atomic orbitals in the basis functions.

If we neglect the spin-polarization effect that will be discussed below, the splitting of the ESR signal is determined by the isotropic hyperfine interactions, a (in gauss), between the unpaired electron in the defect state, $\Psi_{\mathrm{ds}}(\mathbf{r})$, and ^{29}Si nuclei at the various sites. a at ^{29}Si site $\mathbf{r}_n$ is proportional to $|\Psi_{\mathrm{ds}}(\mathbf{r}_n)|^2$ (in atomic units) as follows:[10]

$$a = 317 \times |\Psi_{\mathrm{ds}}(\mathbf{r}_n)|^2 \ . \tag{5}$$

In addition, the anisotropic hyperfine interaction at $\mathbf{r}_n$ originating from the 3*p* component in $\Psi_{\mathrm{ds}}(\mathbf{r})$ is proportional to $|C_{3p_x}|^2 + |C_{3p_y}|^2 + |C_{3p_z}|^2$.

The doublet structure of the *D*-center ESR signal imposes the following conditions on the hyperfine interactions at various sites: (1) The largest value among a's is about 70–75 G, which corresponds to the splitting of the *D*-center ESR signal,[2–4] and only one site per defect state has this value. (2) The next largest value among a's (superhyperfine interaction) is 20–30 G.[2–4] (3) The anisotropic hyperfine interaction at the site with the largest a is 15–20 G.[4] We shall call these the *D*-center conditions.

a's calculated from the dangling- and floating-bond states by using Eq. (5) are also shown in Table I. Both of two floating-bond states do not satisfy the *D*-center condition (2) as shown in Table I. In addition, the anisotropic hyperfine interaction at the site with the largest a is less than 10 G for both the FB81 and FB86, which is too small for the *D*-center condition (3).

In order to examine the extreme configurations for the fivefold-coordinated Si models, we constructed two 42-atom clusters, the FB42-1 and FB42-2. The bond angles around the fivefold-coordinated Si atom in the FB42-1 are three 70.5°, six 109.5°, and 180°. Those in the FB42-2 are three 80°, three 100°, three 117°, and 180°. The FB42-1 is the so-called canonical model.[1] The topology of the FB42-2 is identical to that of the FB42-1. We adopted the 1*s*-3*d* atomic orbitals for the central 18 atoms and the 1*s*-2*p* ones for the others in these clusters as the basis functions. The largest value among a's is 278 G for the FB42-1 and 132 G for the FB42-2. The next largest values among a's are about 60 G for both the FB42-1 and FB42-2. Furthermore, the anisotropic hyperfine interactions at the site with the largest a are less than 10 G for both the FB42-1 and FB42-2. Though these values become somewhat smaller with an increase of the cluster size, these extreme configurations should also not satisfy at least one of the *D*-center conditions.

The results for the four floating-bond models are understood as follows: As mentioned above, the sum of the fractions of the atomic orbitals, $|C_\mu|^2$, on the fivefold-coordinated Si atom and its first nearest neighbors in the floating-bond state is roughly constant for the change of the bond angles around the fivefold-coordinated Si atom. So, the sum of $|\Psi_{\mathrm{ds}}(\mathbf{r}_n)|^2$ at these nuclear sites has also the same tendency. Accordingly, if a floating-bond model satisfies the *D*-center condition (1), then it should not satisfy (2) and/or (3).

On the other hand, the results for the dangling-bond state satisfy the *D*-center condition (2). In addition, the anisotropic hyperfine interaction at the threefold-coordinated Si atom is 18 G, which satisfy the *D*-center condition (3). However, a at the threefold-coordinated ^{29}Si nucleus (101 G) is too large for the *D*-center condition (1). This value is sensitive to the bond angles around the threefold-coordinated ^{29}Si nucleus, which becomes smaller with the increase of these bond angles. So, on the average the bond angles around the threefold-coordinated Si atoms in real *a*-Si may be somewhat larger than those in our DB110. From these facts, we think that the threefold-coordinated Si model can explain the *D*-center ESR signal in *a*-Si.

Recently, Cook *et al.* pointed out that the spin-polarization effect of the valence electrons on the hyperfine interactions is very important.[10] In their results for the model with the threefold-coordinated Si atom, the isotropic hyperfine interaction at the threefold-coordinated ^{29}Si nucleus mainly consists of the contributions from the dangling-bond state (80 G) and the spin-polarization effect of the valence electrons (66 G).

Though the calculation method used in the present work can not estimate this effect, we can qualitatively discuss it as follows: If an up-spin electron in the defect state is localized in a region A, the potential in this region for the up-spin electrons should be lower than that for the down-spin ones due to the exchange interaction with the extra up-spin density. Accordingly, the amplitude in the region A of the up-spin valence states is larger than that of the down-spin ones. This polarization effect should be negligible beyond a certain distance from the region A. Since the wave functions are normalized, these facts suggest that the amplitude of the down-spin valence states should be larger than that of the up-spin ones in the intermediate region. It is clear that the stronger the localization of the defect state is, the larger the spin-polarization effect is.

The isotropic hyperfine interactions should be enhanced at ^{29}Si sites $\mathbf{r}_n$ with large values of $|\Psi_{\mathrm{ds}}(\mathbf{r}_n)|^2$ and/or $|C_{3s}|^2 + \sum |C_{3p}|^2 + \sum |C_{3d}|^2$ shown in Table I by the spin-polarization effect. For the DB110, this enhancement should be remarkably large at the threefold-coordinated Si site, as obtained by Cook *et al.* (66 G),[10] since the dangling-bond state is strongly localized on the threefold-coordinated Si atom. However, the above discussion concerned with the *D*-center conditions is not affected by this effect. For four floating bond models, main enhancements are expected at the fivefold-coordinated Si atom and two or three of its first nearest neighbors. These values are smaller than that at the threefold-coordinated Si atom for the DB110 and should be similar to one another. So, the fact that the fivefold-coordinated Si model does not satisfy at least one of the

D-center conditions does not change the spin-polarization effect. Namely, the above discussion based on the present calculations is not affected by the spin-polarization effect.

In conclusion, from the results calculated for the realistic *a*-Si clusters with the threefold- and fivefold-coordinated Si atoms with use of a first-principles linear combination of the atomic-orbitals method it was found that the *D* center in *a*-Si is not the fivefold-coordinated Si atom but the threefold-coordinated one.

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