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AB INITIO CALCULATIONS FOR DEFECTS IN SILICON-BASED AMORPHOUS SEMICONDUCTORS

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ABSTRACT

We have calculated the ESR hyperfine parameters of threefold-coordinated Si atoms and twofold-coordinated P and N atoms in Si-based amorphous semiconductors using the density functional theory with a local-spin-density approximation. These calculated results have been compared with the observed ESR results.

INTRODUCTION

The hyperfine structure of electron-spin-resonance (ESR) signal as well as the g -value gives us information about the microscopic structure of defects. Various ESR signals with the hyperfine structures have been observed in silicon-based amorphous semiconductors.

The typical ESR signal ($g = 2.0055$) in hydrogenated amorphous silicon (a-Si:H) does not have a hyperfine structure except for weak satellites which are due to the hyperfine interaction with ^{29}Si [1]. The difference between the central and the weak two satellite lines in the ESR signal is attributed to that between the nuclear spins of ^{28}Si and ^{29}Si . Namely, it is thought that the central and weak satellite lines originate from the defects with ^{28}Si and ^{29}Si , respectively, and the microscopic structure of these ESR centers are the same. The isotropic and anisotropic hyperfine parameters (HFP's) have been estimated as follows: $A_{\text{iso}} = 70 \sim 75\text{G}$ and $A_{\text{aniso}} = 15 \sim 20\text{G}$ [1-3]. We have pointed out [4] that this ESR center (D center) is not the fivefold-coordinated Si atom [5] but the threefold-coordinated Si atom (Si_3^0).

In P-doped a-Si:H the ESR signal with the hyperfine splitting of about 250 G has been observed [6-9]. This splitting corresponds to $A_{\text{iso}} = 250\text{G}$ which is due to the hyperfine interaction between the electron and ^{31}P nucleus with the nuclear spin $\frac{1}{2}$. We call this ESR center the $P250$ center. Up to now, three models for the $P250$ center have been proposed: (1) neutral P donor (P_4^0) [6], (2) neutral twofold-coordinated P atom (P_2^0) [7], and (3) neutral weak Si-P bond between threefold-coordinated Si and P atoms [8,10]. Each of these models, however, does not have a definite evidence of it being the origin of this ESR signal.

Several ESR signals have been observed in a-Si $_{1-x}$ N $_x$:H. The typical one is a single line [11,12] and very weak two satellite lines with the hyperfine splitting of about 360 G has also been observed [13]. It is thought that the microscopic structures of these ESR centers are the same and the difference between the ESR signals is due to the same reason as the case of the D centers. The observed HFP's are $A_{\text{iso}} = 364 \pm 4\text{G}$ and $A_{\text{aniso}} = 16.6 \pm 3.4\text{G}$ [13]. We call the ESR center the K center according to Lenahan *et al.* [13].

In addition, a new ESR signal with the hyperfine structure has been observed in a-Si $_{1-x}$ N $_x$:H after uv irradiation [14]. From a comparison with a computer analysis of ^{14}N hyperfine interactions, this ESR center was identified with neutral twofold-coordinated N atom (N_2^0) with the HFP's, $A_{\text{iso}} = 11 \pm 1\text{G}$ and $A_{\text{aniso}} = 12.5 \pm 1\text{G}$ [14]. Most recently, these parameters are modified as follows: $A_{\text{iso}} = 7.0\text{G}$ and $A_{\text{aniso}} = 11.75\text{G}$ [15]. So we call this ESR center the $N7$ center.

In order to clarify whether or not the microscopic models mentioned above are true, we must carry out the calculations of the HFP's for them. Recently we calculated the HFP's for the P_2^0 and the N_2^0 models using the density functional theory and pointed out that the $P250$ center should not be the P_2^0 and the $N7$ center should be the N_2^0 [16].

In this paper, we present the calculations of the HFP's for two kinds of Si_3^0 , P_2^0 and N_2^0 models using the density functional theory with a local-spin-density approximation. The difference between the calculation methods in the previous and the present works is in the freedom of the basis functions and the integration method. The present method is capable of greater precision than the previous one.

CALCULATION METHOD

We obtain the electronic structure for the defect model by solving the Kohn-Sham (KS) equation [17] self-consistently,

$$\left[-\frac{1}{2}\nabla^2 + V_\sigma(\mathbf{r})\right]\psi_\sigma(\mathbf{r}) = E\psi_\sigma(\mathbf{r}), \quad (1)$$

where

$$V_\sigma(\mathbf{r}) = V_{\text{nucl}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}^\sigma(\mathbf{r}). \quad (2)$$

Here σ denotes the spin state, up and down, and the electron density $\rho(\mathbf{r})$ is

$$\rho(\mathbf{r}) = \rho_{\text{up}}(\mathbf{r}) + \rho_{\text{down}}(\mathbf{r}), \quad (3)$$

where

$$\rho_\sigma(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_{\sigma i}(\mathbf{r})|^2. \quad (4)$$

The first and second terms in right-hand side of Eq.(2) are the Coulomb potentials from nuclei and electrons, respectively. The third one is the exchange-correlation potential which is expressed as the functional of $\rho_{\text{up}}(\mathbf{r})$ and $\rho_{\text{down}}(\mathbf{r})$. For the $V_{\text{xc}}^\sigma(\mathbf{r})$ we have employed the expression by Gunnarsson and Lundqvist [18].

In order to solve Eq.(1), the KS orbital $\psi_\sigma(\mathbf{r})$ is represented as a linear combination of Slater-type orbitals (STO's) $\varphi_\mu(\mathbf{r})$ as follows:

$$\psi_\sigma(\mathbf{r}) = \sum_\mu C_{\mu\sigma} \varphi_\mu(\mathbf{r}). \quad (5)$$

In the present calculations we have employed three *s*-type STO's for H atom, six *s*- and 18 *p*-type ones for N atom, eight *s*- and 24 *p*-type ones for Si atom, and eight *s*-, 24 *p*- and 30 *d*-type ones for P atom as $\varphi_\mu(\mathbf{r})$.

The isotropic and anisotropic HFP's for the nucleus X at the site \mathbf{r}_x , a^x and A_{ij}^x , respectively, are calculated from the following formula [19]:

$$a^x = \frac{8\pi}{3} g_e \beta_B g_x \beta_n [\rho_{\text{up}}(\mathbf{r}_x) - \rho_{\text{down}}(\mathbf{r}_x)] \quad (6)$$

$$A_{ij}^x = g_e \beta_B g_x \beta_n \int [\rho_{\text{up}}(\mathbf{r}) - \rho_{\text{down}}(\mathbf{r})] \times \frac{3(r_i - r_{xi})(r_j - r_{xj}) - \delta_{ij}|\mathbf{r} - \mathbf{r}_x|^2}{|\mathbf{r} - \mathbf{r}_x|^5} d\mathbf{r}, \quad (7)$$

where g_e and g_x are the *g*-factors of the free-electron and the nucleus X, respectively, and β_B and β_n are the Bohr and the nuclear magnetons, respectively.

Numerical calculations were carried out using the method by Becke and Dickson [20]. The iterative calculations are finished when the changes of $\rho_\sigma(\mathbf{r})$ at the sampling points become less than 5.0×10^{-4} a.u.

RESULTS AND DISCUSSION

First, in order to confirm that the Si_3^0 is the *D* center, the calculations for the cluster Si_4H_9 shown in Fig.1 were carried out. The calculated HFP's are shown in Table I together with the observed ones. It should be noted that the sign of the HFP's can not be determined by the ESR measurements. The contributions to a^{Si} from the defect KS orbital, the valence and core polarization effects are -70.4 , -53.1 and 14.8 G, respectively. Here we call the KS orbital which is most strongly localized on the defect atom among

the occupied ones the defect KS orbital. The calculated results well reproduce the results obtained by Cook *et al.*[19] in spite of the differences in the calculation method and the cluster size.

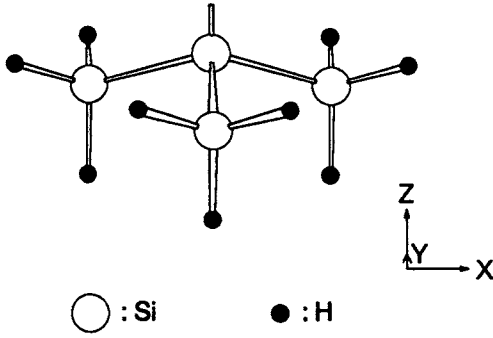


Fig.1. Model cluster for Si_3^0 in a-Si:H. The Si-Si bond length: $d_{\text{Si-Si}} = 2.32$ A. $d_{\text{Si-H}} = 1.48$ A. The bond angles around Si_3^0 : $\angle \text{SiSiSi} = 111.7^\circ$. The bond angles $\angle \text{HSiH}$ around another Si atom are 109.5° . The cluster has C_{3v} point-group symmetry.

Table I. ^{29}Si hyperfine parameters (in units of G) calculated for Si_3^0 in the cluster shown in Fig.1. The observed results are also shown.

Hyperfine parameter	Calculated	Observed [1-3]
a^{Si}	-108.7	70 ~ 75
$A_{xx}^{\text{Si}} = A_{yy}^{\text{Si}}$	28.9	15 ~ 20
A_{zz}^{Si}	-57.8	

The absolute values of the calculated results are greater than the observed ones by about 50% as shown in Table I. It is thought that the calculated defect KS orbital is localized on the Si_3^0 stronger than the actual one since the size of the model cluster used is too small. When the calculations are carried out for larger clusters, the results become somewhat smaller. As a result, the difference between the calculated and observed results becomes smaller. So we think that the D center is the Si_3^0 .

Second, in order to clarify whether or not the P_2^0 is the P_{250} center, the calculations for the cluster PSi_3H_8 shown in Fig.2 were carried out. The calculated HFP's are shown in Table II together with the observed ones. The contributions to a^{P} from the defect KS orbital, the valence and core polarization effects are 0.7, 38.0 and -52.9 G, respectively. The defect KS orbital mainly consists of p_z -type STO's centered on the P_2^0 atom due to its symmetry [16]. So most of a^{P} is the contributions from spin polarization effects.

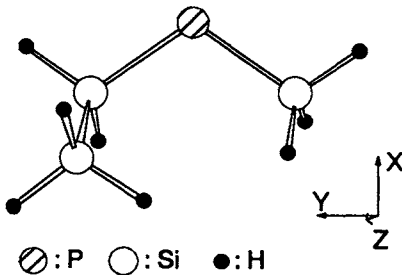


Fig.2. Model cluster for P_2^0 in P-doped a-Si:H. $d_{\text{Si-Si}} = d_{\text{Si-P}} = 2.35$ A. $d_{\text{Si-H}} = 1.48$ A. All bond angles are 109.5° .

Table II. ^{31}P hyperfine parameters (in units of G) calculated for P_2^0 in the cluster shown in Fig.2. The observed results are also shown.

Hyperfine parameter	Calculated	Observed [6-9]
a^{P}	-14.2	~ 250
A_{xx}^{P}	-102.2	
A_{yy}^{P}	-101.1	
A_{zz}^{P}	203.3	

A_{ii}^{P} shown in Table II are nearly equal to those in Ref.16 but a^{P} is not. This reason is as follows: The contribution to a^{P} from the spin polarization effect is calculated as a difference between the up and down spin parts which are nearly equal to each other. As a result, it is very sensitive to the calculation method. However, the fact that the value of a^{P} is too small to explain the observed one is similar for both the present results and those in Ref.16. Accordingly, the P250 center should not be the P_2^0 as pointed out in Ref.16.

In order to clarify whether or not the Si_3^0 bonding with three N atoms is the K' center, the calculations for the cluster SiN_3H_6 shown in Fig.3 were carried out. From the consideration on the chemical bonds, the bond angles around the Si_3^0 were set equal to a value smaller than those in Fig.1, tentatively 102.9° . The calculated HFP's are shown in Table III together with the observed ones. The contributions to a^{Si} from the defect KS orbital, the valence and core polarization effects are -219.2 , -76.5 and 6.6 G, respectively. The calculated a^{Si} in Table III is about 2.5 times that in Table I. This is due to an increase of the s character in the defect KS orbital. The calculated $A_{xx}^{\text{Si}} (= A_{yy}^{\text{Si}})$ agrees with the observed one fairly well. On the other hand, a^{Si} is somewhat smaller than the observed one. a^{Si} is sensitive to the bond angles around the Si_3^0 . The smaller these bond angles are, the larger a^{Si} is. The actual bond angles should be somewhat smaller than those (102.9°) in the cluster used. Since the defect KS orbital is strongly localized on the Si_3^0 , the calculated HFP's scarcely depend on the cluster size in this case. Accordingly, the K' center should be the Si_3^0 bonding with three N atoms.

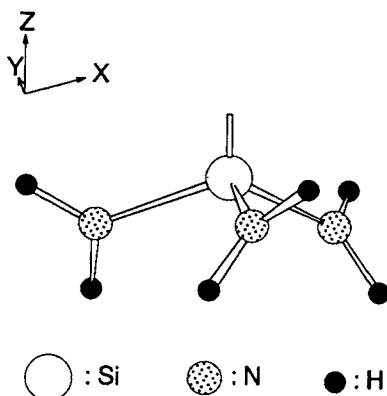


Fig.3. Model cluster for Si_3^0 in a $\text{Si}_{1-x}\text{N}_x\text{:H}$. $d_{\text{Si-N}} = 1.82$ A. $d_{\text{N-H}} = 1.02$ A. $\angle \text{NSiN} = 102.9^\circ$. All bond angles around N atoms are 120° . Each set of two H atoms bonding with a N atom was rotated by 40° around the corresponding Si-N bond from the positions that the plane with these two H atoms and the Si atom is parallel to the z axis. So this cluster has C_3 point-group symmetry, not C_{3v} .

Table III. ^{29}Si hyperfine parameters (in units of G) calculated for Si_3^0 in the cluster shown in Fig.3. The observed results are also shown.

Hyperfine parameter	Calculated	Observed [13]
a^{Si}	-289.1	364 ± 4
$A_{xx}^{\text{Si}} = A_{yy}^{\text{Si}}$	16.6	16.6 ± 3.4
A_{zz}^{Si}	-33.2	

Finally, in order to confirm that the N_2^0 is the $N7$ center, the calculations for the cluster $N_3Si_2H_8$ shown in Fig.4 were carried out. The calculated HFS's are shown in Table IV together with the observed ones. The defect KS orbital mainly consists of the p_z -type STO's on the N_2^0 . The contributions to a^N from the defect KS orbital, the valence and core polarization effects are 0.7, 19.7 and -15.0 G, respectively. These results show the importance of the spin polarization effect. Calculated A_{ii}^N are nearly equal to those calculated in Ref.16. On the other hand, a^N is about one half of that in Ref.16. This difference between a^N 's originates from the sensitivity of a^N to the calculation method as mentioned above. Calculated values agree with the observed ones as shown in Table IV. Accordingly, it is confirmed that the $N7$ center should be the N_2^0 as pointed out in Ref.16.

However, this conclusion does not necessarily mean that these N_2^0 centers are created from N_2^- centers by uv irradiation. It is possible that in N-rich $a-Si_{1-x}N_x:H$ N_2^0 centers are created from $N_4^+-N_3^0$ units by the breaking of the N-N bond due to the capture of an electron [16,21,22]. This mechanism of bond breaking has been generalized and applied to other cases in amorphous semiconductors [23].

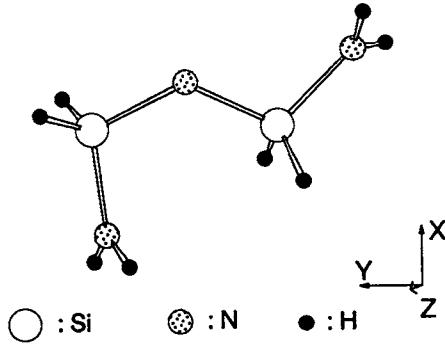


Fig.4. Model cluster for N_2^0 in $a-Si_{1-x}N_x:H$. $d_{Si-N} = 1.74 \sim 1.75$ A. $d_{Si-H} = 1.48$ A. $d_{N-H} = 1.02$ A. Bond angles around Si atoms are $105 \sim 115^\circ$. Bond angles around N atoms are $112 \sim 125^\circ$.

Table IV. ^{14}N hyperfine parameters (in units of G) calculated for N_2^0 in the cluster shown in Fig.4. The observed results are also shown.

Hyperfine parameter	Calculated	Observed [15]
a^N	5.4	7.0
A_{xx}^N	-13.2	$ A_{xx} = A_{yy} $ $= 11.75$
A_{yy}^N	-13.6	
A_{zz}^N	26.8	

CONCLUSION

We presented the results of the calculations of the hyperfine parameters for two kinds of threefold-coordinated Si atoms and twofold-coordinated P and N atoms using the density functional theory with a local-spin-density functional approximation. It is confirmed from these calculations that the D center in $a-Si:H$ is a threefold-coordinated Si atom, the K center in $a-Si_{1-x}N_x:H$ is a threefold-coordinated Si atom bonding with three N atoms, and the $N7$ center in $a-Si_{1-x}N_x:H$ is a twofold-coordinated N atom. On the other hand, the $P250$ center is not a twofold-coordinated P atom. It is found to be very important to take into account the spin-polarization effects in the calculations of isotropic hyperfine parameters.

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