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Calculation of Positron States and Annihilation Parameters in Gamma and Amorphous Al_2O_3

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We calculate positron states and annihilation parameters theoretically in gamma and amorphous Al_2O_3 and compared with those in alpha Al_2O_3. They show systematic variations and are investigated in terms of relationships with microscopic structures and densities. Good correlations of the positron annihilation parameters with the density are observed.

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1. Introduction

Gallium nitride and related compounds attract much attention because of their applicability not only in light-emitting devices but also in power devices. The quality of gate insulator material plays a crucial role for the device performance and Al_2O_3 is a promising candidate. It is thought that deposited Al_2O_3 layers have various structures depending on the preparation method and condition. The positron annihilation spectroscopy is expected to be applied in evaluating their qualities [1, 2]. Recently, we applied slow positron beams in characterizing gate-stack Al_2O_3 layers [3].

In the present study, we construct appropriate structural models of gamma (γ-) and amorphous (a-) Al_2O_3, which are often observed in real insulator layers. Positron states and annihilation parameters (the positron annihilation Doppler broadening S and W parameters as well as positron lifetime τ) therein are calculated and compared with those in alpha (α-) Al_2O_3.

2. Computational details

Structural models of γ-Al_2O_3 are prepared by reference to [4]. The γ-Al_2O_3 crystal has a defect cubic spinel structure. To obtain a stoichiometric Al_2O_3, three cubic cells are needed. An equivalent hexagonal supercell is used in this study. By removing 8 Al atoms, a stoichiometric $Al_{64}O_{96}$ structure is constructed. There are two different crystallographic Al sites in the cubic spinel structure, the octahedral (O) and tetrahedral (T) sites. The theoretical work by Streitz and Mintmire [5] indicated that, although it is energetically favorable when all vacant Al sites are located at O sites, the increase in energy when T sites are occupied with a modest fraction is small. Therefore, we construct 16+16 different structural models by randomly removing 8 Al atoms from the O sites only or from both the O and T sites.

Structural models of a-Al_2O_3 are prepared as follows. 64 Al and 96 O atoms are randomly distributed in cubic cells, whose lattice parameters are determined so that the density is 3.0, 3.3, or 3.5 g/cm^3. First-principles molecular dynamics (MD) calculations are performed for each system using the Langevin thermostat as follows: (1) $T = 3000$ K, $\Delta t = 0.2$ fs, $\zeta = 10$ ps^{-1} for 0–0.5 ps, (2) $T = 3000$ K, $\Delta t = 0.5$ fs, $\zeta = 10$ ps^{-1} for 0.5–2.0 ps, (3) $T = 3000$ K, $\Delta t = 1.0$ fs, $\zeta = 0.01$ ps^{-1} for 2.0–10.0 ps, (4) $T = 1500$ K, $\Delta t = 1.0$ fs, $\zeta = 1$ ps^{-1} for 10.0–14.0 ps, and (5) $T = 1500$ K, $\Delta t = 1.0$ fs, $\zeta = 0.01$ ps^{-1} for 14.0–22.0 ps, where T, Δt, and ζ represent a temperature, a time interval, and a friction parameter, respectively. From MD runs at 1500 K for each density, snapshots at every 1000 steps (1 ps) are extracted and the atomic positions therein are optimized. The obtained structures are reasonable when compared with previous studies [6, 7].

Structural models of defect-free α-Al_2O_3 and a system containing V_5, where two Al sites and three O sites are vacant, are also prepared using an orthorhombic supercell equivalent to $2 \times 2 \times 1$ hexagonal unit cells.

On these structural models, positron states and annihilation parameters S, W, and τ are calculated with our computational code QMAS [8]. The S and W parameters are evaluated using spherically averaged momentum densities. As for the enhancement factor, we use the form $\gamma = 1 + (\gamma_{\mathrm{BN}} - 1)(1 - 1/\varepsilon_\infty)$, where γ_{BN} is the Boroński–Nieminen enhancement factor [9] and ε_∞ is the high-frequency dielectric constant. This form is slightly different from the original semiconductor model [10]. It follows the form in the positron generalized-gradient approximation [11] and is consistent with the scaled positron-electron correlation energy [10]. Further details are described in our recent paper [12]. ε_∞ is set to be 3.0 in the present study.

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3. Results and discussion

Figure 1 represents the calculated positron annihilation parameters in 16 [octahedral sites only (O only)] + 16 [octahedral and tetrahedral sites ($O + T$)] structural models of γ-Al_2O_3. Some of the positron-lifetime results have been already reported in Ref. [3]. Reflecting variations in their structures, the resultant S, W, and τ show finite distributions. The average (S, W, τ) values are (0.4376, 0.01533, 239.0 ps) for the "O only" case and (0.4396, 0.1516, 244.9 ps) for the "$O + T$" case, respectively. Although the differences between the two cases are not large, it seems slightly more likely that vacant sites are closely located from each other in the "$O + T$" case.

In Fig. 2, the calculated positron annihilation parameters for structures optimized from snapshots in MD runs at 1500 K are shown as a function of time. Although fluctuations exist, they show clear dependencies on the density. The calculated τ values for a-Al_2O_3 of the 3.3 or 3.5 g/cm^3 cases as well as those in γ-Al_2O_3 are in good agreement with the values for the shortest component of the experimentally obtained lifetime spectra [3]. The calculated positron annihilation parameters for the defect-free (DF) state and V_5 state in α-Al_2O_3 are listed in Table I. Although the present τ value for the DF state is slightly longer than the experimental value of 143 ps [13], it is still in a reasonable range.

In Fig. 3, the calculated S and τ values for various structures are plotted for comparison. Several corresponding positron density distributions are also shown. Although there is a small but significant separation between γ- and a-Al_2O_3, all the points are on roughly the same line, showing a clear correlation between S and τ. On the other hand, a good negative correlation exists between S and W. As mentioned above, finite distributions

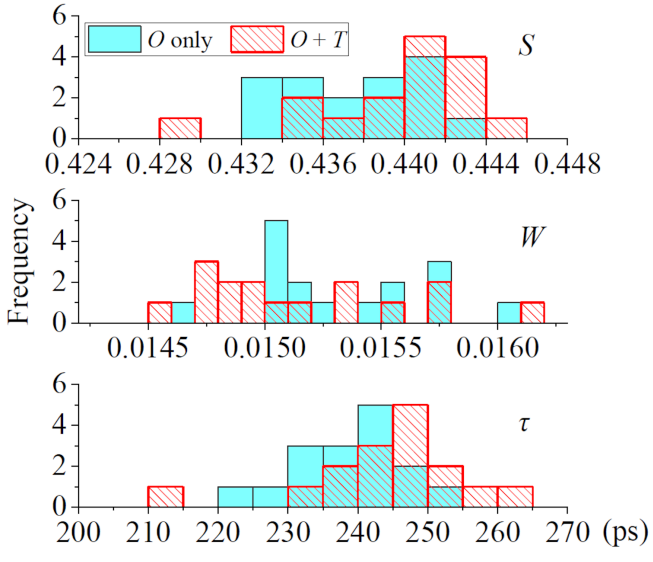

Fig. 1. Frequency distributions of calculated positron annihilation parameters in 16 (octahedral sites only (O only)) + 16 (octahedral and tetrahedral sites ($O + T$)) structural models of γ-Al_2O_3.

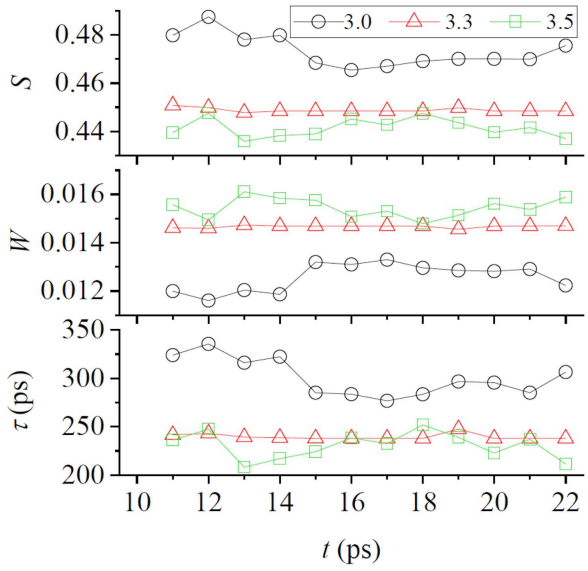

Fig. 2. Calculated positron annihilation parameters for structures optimized from snapshots in MD runs at 1500 K. Numbers in legends represent density values in g/cm^3.

TABLE I

Calculated positron annihilation parameters for the defect-free (DF) state and V_5 state in α-Al_2O_3.

	S	W	τ [ps]
DF	0.411	0.0188	158.9
V_5	0.462	0.0139	287.0

of these parameters are observed for γ- and a-Al_2O_3. To make further quantitative statistical analyses, more data are required. The positron density distribution show large variations from a completely delocalized state to a localized state trapped at an open space.

In Fig. 4, the calculated S, W, and τ are represented as a function of the density ρ. The lower bounds of S and τ as well as the upper bounds of W at respective ρ values for a- and α-Al_2O_3 look to be on the same straight line. If an arbitrary part of the structure is a good representative of the whole structure, it is quite reasonable that the positron annihilation parameters S, W, and τ show clear relationships with ρ. The defect free state of α-Al_2O_3 and some of a-Al_2O_3 structures are thought to fulfill such a condition. Positron distributions therein are delocalized, and the resultant positron parameters are expected to bring average information of the system. The V_5 case of α-Al_2O_3 is completely opposite. The positron distribution is strongly localized, and only information in the vicinity of the vacancy is brought. Therefore, the results for V_5 in Fig. 4 are far off the straight lines. As mentioned above, the structure of γ-Al_2O_3 is characterized by the presence of the cation-site vacancies, although the degree of localization is weaker that that for the V_5 case in α-Al_2O_3. Then, the lower or upper bounds for γ-Al_2O_3 are slightly off the lines.

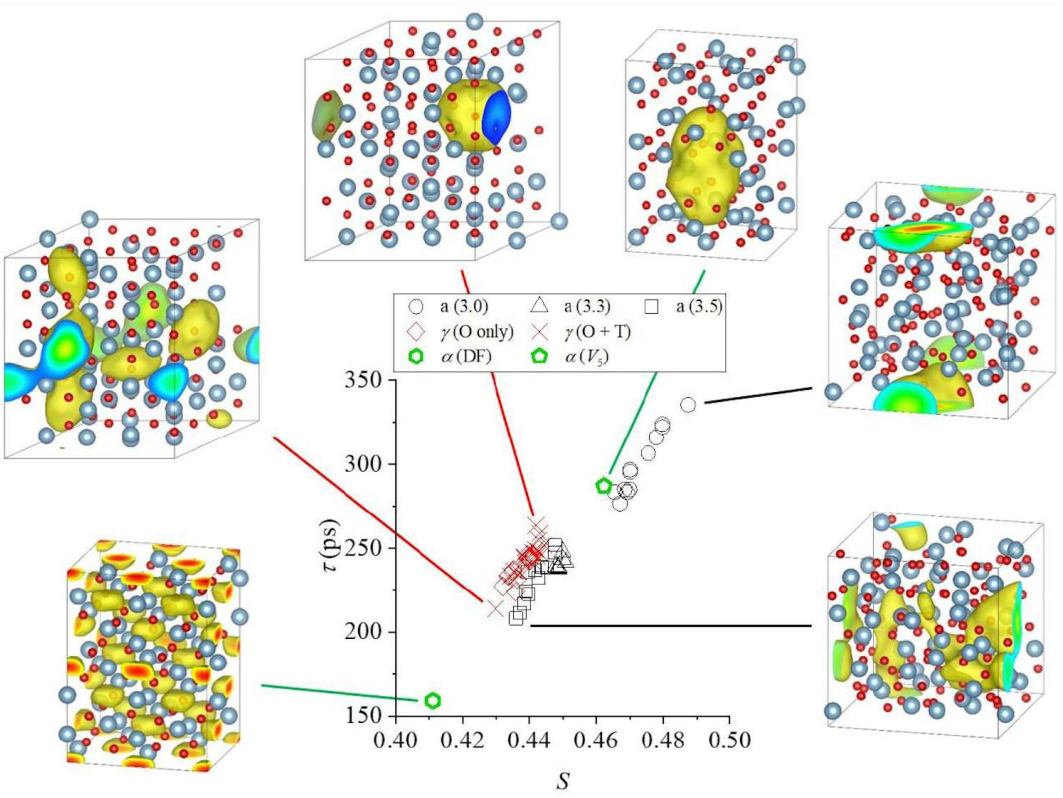

Fig. 3. S and τ in various structures of Al_2O_3 and several corresponding positron density distributions. VESTA [14] was used in drawing a part of figure.

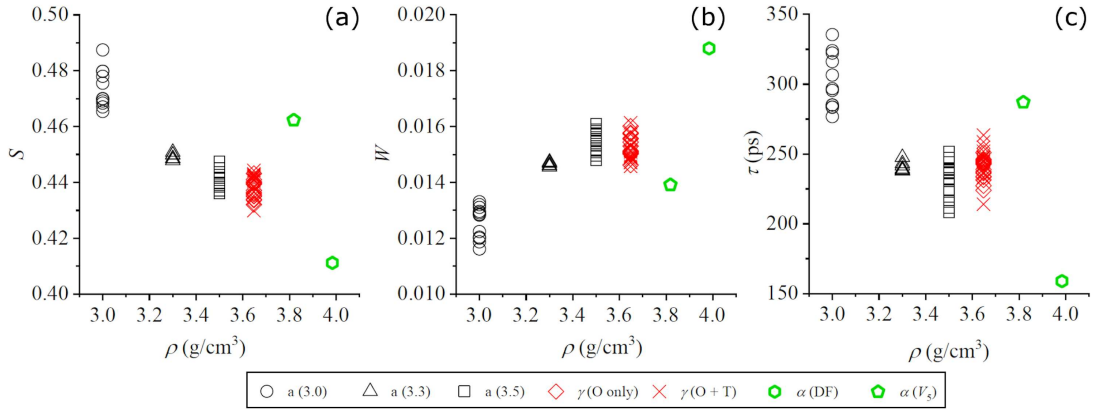

Fig. 4. Calculated S (a), W (b), and τ (c) as a function of ρ.

4. Summary

We have successfully modeled reasonable structures of γ- and a-Al_2O_3. The positron states and annihilation parameters therein are calculated and compared with those in α-Al_2O_3. As for the S, W, and τ values in γ-Al_2O_3 and a-Al_2O_3, finite distributions are observed reflecting variations in their structures. The τ values in γ-Al_2O_3 and a-Al_2O_3 with the density of 3.3 or 3.5 g/cm^3 are in good agreement with the experimental results. The S, W, and τ values in various phases of Al_2O_3 show good correlations with one another. They also show characteristic relationships with the density, which can be applied in characterizing Al_2O_3 insulator layers by the positron annihilation technique.

Since local structures of γ-Al_2O_3 and a-Al_2O_3 have an infinite number of possible configurations, it is important to accumulate further results of calculations. Effects of dopants and/or impurities as well as those of thermal history should be investigated as future issues.

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