Calculation of Positron States and Annihilation Parameters in Gamma and Amorphous Al$_2$O$_3$

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We calculate positron states and annihilation parameters theoretically in gamma and amorphous Al$_2$O$_3$ and compared with these in alpha Al$_2$O$_3$. 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$_2$O$_3$ is a promising candidate. It is thought that deposited Al$_2$O$_3$ layers have various structures depending on the preparation method and conditions. 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$_2$O$_3$ layers [3].

In the present study, we construct appropriate structural models of gamma ($\gamma$-) and amorphous ($a$-) Al$_2$O$_3$, 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 $\tau$) therein are calculated and compared with those in alpha ($\alpha$-) Al$_2$O$_3$.

2. Computational details

Structural models of $\gamma$-Al$_2$O$_3$ are prepared by reference to [4]. The $\gamma$-Al$_2$O$_3$ crystal has a defect cubic spinel structure. To obtain a stoichiometric Al$_2$O$_3$, 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 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$_2$O$_3$ 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, $\zeta = 10^{-1}$ fs for 0–0.5 ps, (2) $T = 3000$ K, $\Delta t = 0.5$ fs, $\zeta = 10^{-1}$ fs for 0.5–2.0 ps, (3) $T = 3000$ K, $\Delta t = 1.0$ fs, $\zeta = 0.01$ fs for 2.0–10.0 ps, (4) $T = 1500$ K, $\Delta t = 1.0$ fs, $\zeta = 1$ ps for 10.0–14.0 ps, and (5) $T = 1500$ K, $\Delta t = 1.0$ fs, $\zeta = 0.01$ ps for 14.0–22.0 ps, where $T$, $\Delta t$, and $\zeta$ 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 $\alpha$-Al$_2$O$_3$ and a system containing $N_5$, 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 $\tau$ 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 $\gamma = 1 + (\gamma_{\text{BN}} - 1)(1 - 1/\varepsilon_\infty)$, where $\gamma_{\text{BN}}$ is the Borůvský–Nieminen enhancement factor [9] and $\varepsilon_\infty$ 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]. $\varepsilon_\infty$ 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 $\gamma$-Al$_2$O$_3$. Some of the positron-lifetime results have been already reported in Ref. [3]. Reflecting variations in their structures, the resultant $S$, $W$, and $\tau$ show finite distributions. The average $(S, W, \tau)$ values are $(0.4376, 0.01533, 239.0 \text{ ps})$ for the “O only” case and $(0.4396, 0.1516, 244.9 \text{ ps})$ 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 $\tau$ values for $\alpha$-Al$_2$O$_3$ of the 3.3 or 3.5 g/cm$^3$ cases as well as those in $\gamma$-Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ are listed in Table I. Although the present $\tau$ 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 $\tau$ 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 $\gamma$- and $\alpha$-Al$_2$O$_3$, all the points are on roughly the same line, showing a clear correlation between $S$ and $\tau$. On the other hand, a good negative correlation exists between $S$ and $W$. As mentioned above, finite distributions of these parameters are observed for $\gamma$- and $\alpha$-Al$_2$O$_3$. 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 $\tau$ are represented as a function of the density $\rho$. The lower bounds of $S$ and $\tau$ as well as the upper bounds of $W$ at respective $\rho$ values for $\alpha$- and $\alpha$-Al$_2$O$_3$ 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 $\tau$ show clear relationships with $\rho$. The defect free state of $\alpha$-Al$_2$O$_3$ and some of $\alpha$-Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ 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 $\alpha$-Al$_2$O$_3$. Then, the lower or upper bounds for $\gamma$-Al$_2$O$_3$ are slightly off the lines.
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Fig. 3. $S$ and $\tau$ in various structures of Al$_2$O$_3$ and several corresponding positron density distributions. VESTA [14] was used in drawing a part of figure.

Fig. 4. Calculated $S$ (a), $W$ (b), and $\tau$ (c) as a function of $\rho$.

4. Summary

We have successfully modeled reasonable structures of $\gamma$- and $\alpha$-Al$_2$O$_3$. The positron states and annihilation parameters therein are calculated and compared with those in $\alpha$-Al$_2$O$_3$. As for the $S$, $W$, and $\tau$ values in $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$, finite distributions are observed reflecting variations in their structures. The $\tau$ values in $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ with the density of 3.3 or 3.5 g/cm$^3$ are in good agreement with the experimental results. The $S$, $W$, and $\tau$ values in various phases of Al$_2$O$_3$ show good correlations with one another. They also show characteristic relationships with the density, which can be applied in characterizing Al$_2$O$_3$ insulator layers by the positron annihilation technique.

Since local structures of $\gamma$-Al$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ 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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