A density functional study of vacancy formation in grain boundaries of undoped α -alumina

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Abstract

Recent oxygen permeation experiments of α -alumina have shown that the major diffusion species at grain boundaries, i.e., oxygen and aluminum vacancies, switch over depending on the oxygen partial pressures at high temperatures, namely appearance of the p - n transition. In order to investigate the transition behavior, formation energies of charged oxygen and aluminum vacancies at Al_2O_3 grain boundaries are evaluated by using density functional theory (DFT). The electronic structures affecting the carrier concentrations are assessed for three types of grain boundaries. The ratios of the grain boundary band gaps relative to the bulk value lie in the range of 0.6-0.85 depending on the degree of grain boundary misorientations. From the formation energies we find that, at band gaps around 60% compared to the

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bulk value, the dominant vacancy alters depending on the pressure, consistent with the oxygen permeation experiments. Our results suggest that the band gap narrowing occurring at grain boundaries enhances the creation of oxygen vacancies and conduction electrons, facilitating the observed transition.

Keywords: Alumina, Density functional theory, Vacancies, Grain-boundary diffusion, Oxygen permeation

1. Introduction

Grain boundary (GB) diffusion of intrinsic species in α -alumina is a fundamental and significant phenomenon affecting diffusional creep, sintering processes, and oxidation of alumina-scale-forming alloys, and thus has an important effect on its performance in various applications. In thermal barrier coating systems, the α -alumina scale formed on alumina-forming alloys provides protection against further oxidation, contributing to an increase in the durability of the system at high temperatures [1, 2]. In this context, it is important to control the GB diffusion by addition of reactive elements such as Y, Lu, and Hf, which segregate to GBs. There are, however, unresolved issues concerning GB diffusion in α -alumina even in the undoped case. In this paper, we provide a theoretical basis for understanding the GB diffusion behavior observed in oxygen permeation experiments of undoped α -alumina [3, 4] which were designed to investigate the oxidation process.

In a series of oxygen permeation experiments [3, 4, 5, 6, 7, 8], different oxygen partial pressures imposed on two sides of a sample wafer, labeled $P_{\text{O}_2}^{\text{high}}$ and $P_{\text{O}_2}^{\text{low}}$, induced oxygen permeation at high temperatures from 1750 K to

18 1950 K. Observed surface morphologies around GBs after the permeation
 19 experiments and the associated measured permeabilities were interpreted in
 20 terms of two regimes. When $P_{\text{O}_2}^{\text{high}} = 1$ Pa and $P_{\text{O}_2}^{\text{low}} = 10^{-8} - 10^{-4}$ Pa,
 21 oxygen vacancies formed on the $P_{\text{O}_2}^{\text{low}}$ side through release of oxygen molecules
 22 diffuse to the opposite ($P_{\text{O}_2}^{\text{high}}$) side and contribute to the dissociative reaction
 23 of oxygen molecules on that side. The overall reaction can be expressed in
 24 Kröger-Vink notation as

25 where V is a vacancy and e' is an electron. On the other hand, when $P_{\text{O}_2}^{\text{low}} =$
 26 1 Pa and $P_{\text{O}_2}^{\text{high}} = 10^3 - 10^5$ Pa, aluminum vacancies are created on the $P_{\text{O}_2}^{\text{high}}$
 27 side through an alumina-forming reaction expressed by

28 where $h^{\bullet}$ is a hole, and diffuse to the $P_{\text{O}_2}^{\text{low}}$ side where the opposite reaction
 29 to Eq. (2) occurs, yielding oxygen molecules. GB diffusion coefficients, D_{gb} ,
 30 of O and Al were calculated from the permeation measurements under the
 31 limited P_{O_2} range. These two different regimes indicate that the diffusing
 32 species in GBs alter as a function of ΔP_{O_2} . This switchover has also been
 33 observed in oxygen permeation measurements of Hf-, Lu-, and Y-doped alu-
 34 mina, although the diffusivities are partially suppressed [5, 6, 8]. In order
 35 to understand the suppression mechanism, it is first necessary to understand
 36 the behavior in undoped samples. Although tracer experiments of oxygen
 37 GB diffusion have been performed [9, 10, 11, 12, 13], the dependence on P_{O_2}
 38 is inaccessible and reports of tracer diffusion of aluminum have been limited
 39 to bulk crystals due to experimental difficulties [14, 15].

40 Heuer et al. [16] pointed out the importance of electronic structures for
 41 interpretation of the switchover of the GB-diffusion species, and referred to
 42 the phenomenon induced by P_{O_2} as the p - n transition, since the dominant
 43 electronic carriers are considered to switch between the two regimes as a re-
 44 sult of the reactions in Eqs. (1) and (2). As discussed in their paper, density
 45 functional theory (DFT) calculations of point defect formation energies in
 46 α -alumina [17, 18, 19, 20] are useful to investigate how electronic structures
 47 affect the defect stabilities and GB diffusion. In DFT calculations, following
 48 the widely used formulation proposed by Zhang and Northrup [21], defect
 49 formation energies and related defect concentrations are defined as a func-
 50 tion of oxygen partial pressure and temperature through oxygen chemical
 51 potentials, μ_{O_2} , as well as electron chemical potentials, μ_e . Because migra-
 52 tion barriers are independent of P_{O_2} , the switchover depends only on the
 53 formation energies. To determine the energies using those theoretical calcu-
 54 lations, μ_e must be determined. Although Hine et al. have shown calculation
 55 of μ_e for the Schottky pair [19], reports including contributions of conduc-
 56 tion electrons and holes have yet to be found, required to gauge the effect of
 57 electronic structures quantitatively.

58 In this paper, we investigate the P_{O_2} dependence of defect formation
 59 energies in balance with electronic carriers based on first-principles DFT.
 60 Here, we limit our discussion to the dominant defect types, fully charged
 61 oxygen and aluminum vacancies, i.e., $V_{\text{O}}^{\bullet\bullet}$ and $V_{\text{Al}}^{\bullet\bullet\bullet}$ for clarity and simplicity
 62 [17, 18]. In order to incorporate the electronic character of GBs, we examine
 63 electronic structures of two types of $\Sigma 13$ GBs [22, 23, 24] and a $\Sigma 31$ GB
 64 [25, 26] whose structures in bicrystal samples have been characterized by

high-resolution transmission electron microscopy (HRTEM) and theoretical calculations (including DFT) based on coincident site lattice (CSL) theory.

2. Methodology

2.1. Formation energies

The formation energies of vacancies in α -Al₂O₃ denoted by V_{η}^q , where η is whether O or Al and q is the charge state, are given by [21]

$$E_{\text{f}}^{V_{\eta}^q} = E_{\text{T}}^{V_{\eta}^q} - E_{\text{T}}^{\text{Pristine}} + \mu_{\eta}(P_{\text{O}_2}, T) + q\mu_{\text{e}}. \quad (3)$$

Here, $E_{\text{T}}^{V_{\eta}^q}$ and $E_{\text{T}}^{\text{Pristine}}$ are the calculated total energies of the vacancy and pristine systems, respectively, and μ_{η} and μ_{e} are the chemical potentials of η atoms and electrons, respectively. The atomic chemical potentials are determined by the procedure of Hine *et al.* [18]. When in equilibrium with the surrounding gas, by equating the oxygen chemical potential with half the chemical potential of O₂ gas, i.e., $\frac{1}{2}\mu_{\text{O}_2(g)}$, the formation energies can be connected with temperature and oxygen pressure using the Gibbs free energy of O₂ gas which is calculated using thermochemical data [27] within the ideal gas approximation. The chemical potential under standard conditions, $\mu_{\text{O}_2}^0$, can be obtained from

$$\Delta G_{\text{f}(\text{Al}_2\text{O}_3)}^0 = E_{\text{Al}_2\text{O}_3} - 2E_{\text{Al(s)}} - \frac{3}{2}\mu_{\text{O}_2}^0. \quad (4)$$

Here, $E_{\text{Al}_2\text{O}_3}$ and $E_{\text{Al(s)}}$ are the DFT energies of the bulk alumina and metal aluminum per formula unit, respectively, which are approximately equal to the Gibbs free energies under standard conditions. The formation energy of α -alumina, $\Delta G_{\text{f}(\text{Al}_2\text{O}_3)}^0$, is also taken from experimental results [27]. Under

85 equilibrium conditions, μ_{Al} is given through $E_{\text{Al}_2\text{O}_3} = 2\mu_{\text{Al}} + 3\mu_{\text{O}}$ by neglect-
 86 ing the vibrational contributions to the Gibbs free energy. μ_{e} is measured
 87 with respect to the valence band maximum (VBM), i.e., $\mu_{\text{e}} = \varepsilon_{\text{F}} + \varepsilon_{\text{VBM}}$,
 88 where ε_{F} is the Fermi level. Thus, the formation energies of oxygen and
 89 aluminum vacancies are rewritten as

$$E_{\text{f}}^{V\bullet\bullet} = E_0^{V\bullet\bullet} + \Delta\mu_{\text{O}}(T, P_{\text{O}_2}) + 2\varepsilon_{\text{F}} \quad (5)$$

90 and

$$E_{\text{f}}^{V'''_{\text{Al}}} = E_0^{V'''_{\text{Al}}} - \frac{2}{3}\Delta\mu_{\text{O}}(T, P_{\text{O}_2}) - 3\varepsilon_{\text{F}}, \quad (6)$$

91 where $\Delta\mu_{\text{O}}$ is the oxygen chemical potential with respect to the value at
 92 $T = 2371$ K and $P_{\text{O}_2} = 0.2$ atm. E_0 was obtained from previous DFT
 93 calculations [18].

94 In order to determine the Fermi level, we impose the charge neutrality
 95 condition given by

$$2[V_{\text{O}}^{\bullet\bullet}] + [\text{h}^{\bullet}] = 3[V_{\text{Al}}^{'''}] + [\text{e}']. \quad (7)$$

96 The concentration of vacancies, $[V_{\eta}^q]$, was calculated according to

$$[V_{\eta}^q] = N_{\eta} \exp\left(-E_{\text{f}}^{V_{\eta}^q}/k_{\text{B}}T\right), \quad (8)$$

97 where N_{η} are the concentrations of η lattice sites per volume and the vibra-
 98 tional entropy terms are ignored. The hole and conduction electron densities
 99 are evaluated through

$$[\text{h}^{\bullet}] = N_{\text{v}} \exp(-\varepsilon_{\text{F}}/k_{\text{B}}T) \quad (9)$$

100 and

$$[\text{e}'] = N_{\text{c}} \exp(-(E_{\text{g}} - \varepsilon_{\text{F}})/k_{\text{B}}T), \quad (10)$$

101 where E_g is the band gap and N_v and N_c are the effective densities of states
 102 of valence and conduction bands, respectively. The usage of these formula is
 103 validated when the numerator of the exponential is sufficiently larger than
 104 $k_B T \approx 0.17$ eV for $T = 2000$ K and this is satisfied in our cases due to
 105 the wide band gaps of α -alumina crystals. N_v and N_c are calculated from
 106 $2(m_h k_B T / 2\pi \hbar^2)^{3/2}$ and $2(m_e k_B T / 2\pi \hbar^2)^{3/2}$, respectively, where m_h and m_e
 107 are the effective masses of holes and electrons, respectively, which we calcu-
 108 lated by DFT. Here, the multiplicity factors are taken to be unity because
 109 the bottom of the conduction band and the top of the valence band of α -
 110 alumina are situated at the Γ point of the Brillouin zone, as shown in Fig.
 111 2.

112 2.2. DFT calculation details

113 In DFT calculations, it is well known that the conventional local density
 114 approximation (LDA) and general gradient approximation (GGA) for the
 115 exchange-correlation functional usually underestimate band gaps in the case
 116 of insulators and semiconductors. Because this problem has a large effect on
 117 formation energies of defects with occupied states in the band gap, empirical
 118 corrections for the band gap, e.g., ridged shift of the conduction band and
 119 defect levels in the middle of the band gap to adjust the gap to the experi-
 120 mental value, have been adopted in LDA and GGA studies of intrinsic point
 121 defects in α -alumina [17, 18]. Recently, hybrid density functionals combin-
 122 ing LDA or GGA functionals and non-local Fock exchange components have
 123 been developed to obtain more accurate band gaps, and thus defect forma-
 124 tion energies, resulting in a revision of thermal transition levels in α -alumina
 125 [20]. It is not possible to compare these data directly, however, because the

126 correction methods for the Coulomb interaction between periodic images in
 127 charged defect calculations are different. In this work, our interest is in the
 128 E_0 values in Eqs. (5) and (6). Since $V_{\text{O}}^{\bullet\bullet}$ and V_{Al}''' have no defect levels in
 129 the band gap, the difference in E_0 between the functionals is expected to be
 130 slight, so we adopt the LDA values for E_0 in this study [18].

131 To obtain electronic structures of bulk and GB systems, DFT calculations
 132 have carried out the projector augmented wave (PAW) method [28] based on
 133 plane-wave bases as implemented in VASP [29]. For the exchange-correlation
 134 functional, the Perdew-Burke-Ernzerhof generalized gradient approximation
 135 (PBE-GGA) [30] and HSE06 (after Heyd, Scuseria and Ernzerhof) hybrid-
 136 functional [31] were used. A plane-wave cutoff energy of 500 eV was used
 137 and the Brillouin zone (BZ) was sampled by the Monkhorst-Pack method
 138 [32]. The residual atomic forces in the relaxed structures were lower than
 139 0.01 eV/Å. For bulk α -alumina, the rhombohedral cell was relaxed using a
 140 $5 \times 5 \times 5$ k -point grid. The effective masses were calculated by fitting parabola
 141 around the valence band maximum and conduction band minimum.

142 The preparation of the $\Sigma 13$ and $\Sigma 31$ GB models follows previous re-
 143 ports. The $\Sigma 13$ tilt GB was constructed by rotating one half-crystal by
 144 103.6° around the $[10\bar{1}0]$ axis. From all possible $\Sigma 13$ ($10\bar{1}0$) GBs, two Al-
 145 terminated and O-terminated configurations, labeled G(Al) and G(O) [22],
 146 were selected. The structures are shown in Fig. 1 (a) and (b). The two
 147 GBs in each cell, which contain 120 atoms, are separated by about 15.5 Å. A
 148 $\Sigma 31$ tilt GB was constructed by rotating one half-crystal by 17.9° around the
 149 $[0001]$ axis. We used the structural model shown in Fig. 1 (c), as it repro-
 150 duces the atomic arrangement observed by HRTEM [25, 26]. This contains

620 atoms in the cell with GBs separated by about 13.8 Å. For BZ sampling,
a $3 \times 3 \times 1$ k -point grid and Γ point only were used for the $\Sigma 13$ and $\Sigma 31$
GBs, respectively. The GB structures obtained by relaxing with the GGA
functional were used in HSE06 calculations to minimize the computational
cost.

3. Results and discussion

3.1. Electronic structures of bulk and grain boundaries

The lattice constants of relaxed bulk structures of rhombohedral α -Al₂O₃
were $a = 5.178$ Å and $\alpha = 55.30^\circ$ for GGA and $a = 5.122$ Å and $\alpha = 55.33^\circ$
for HSE06, which are close to experimental values of $a = 5.136$ and $\alpha =$
 55.28° [33]. This may indicate that the trend in GGA to overestimate lattice
constants is improved by use of the HSE06 hybrid functional. The band struc-
tures obtained from GGA and HSE06 calculations are shown in Fig. 2 (a)
and (b), respectively. The band profiles are similar to each other except for
the energy levels of the conduction bands. By virtue of hybridizing the Fock
exchange potential, the bulk band gap according to HSE06, $E_g^B = 8.16$ eV, is
closer to the experimental values of 8.8 to 9.2 eV [34, 35] than $E_g^B = 5.87$ eV
according to GGA. The calculated effective masses show a large anisotropy
only for the valence band maximum, as shown in the inset of Fig. 2 (b).
This is because of bands that exist about 0.1 eV below the maximum at the
 Γ point. We assume a prolate spheroidal shape whose longer axis is in the
 $[111]$ direction (corresponding to the $[0001]$ direction in the hexagonal repre-
sentation) and whose shorter axes are in the $[1\bar{1}0]$ and equivalent orthonor-
mal directions. While GGA gives $m_h^{[111]}/m_0 = 0.70$ and $m_h^{[1\bar{1}0]}/m_0 = 15.08$,

175 HSE06 gives $m_h^{[111]}/m_0 = 0.49$ and $m_h^{[1\bar{1}0]}/m_0 = 10.46$. Average effective
 176 masses for the effective density of states, $(m_h^{[111]}m_h^{[1\bar{1}0]}m_h^{[1\bar{1}0]})^{1/3}$, are $5.42m_0$
 177 for GGA and $3.77m_0$ for HSE06. On the other hand, the minimum of the
 178 conduction band shows almost isotropic behavior. The differences between
 179 $m_h^{[111]}/m_0$ and $m_h^{[1\bar{1}0]}/m_0$ are less than 0.1. The average effective masses are
 180 0.74 for GGA and 0.75 for HSE06, being independent of the functional used.
 181 Although here we use the values of HSE06 for the concentrations of carriers,
 182 our conclusions are unaltered by the use of values obtained using GGA.

183 Figure 3 shows the density of states (DOS) of the three types of GBs
 184 according to HSE06. While the valence bands of the bulk and $\Sigma 13G(Al)$
 185 GB are similar to each other, the highest occupied level of the $\Sigma 13G(O)$ and
 186 $\Sigma 31$ GBs are isolated. The latter are localized states at the GBs as shown in
 187 the example of Fig. 4, in which the isosurface of the partial charge density
 188 corresponding to the peak in the DOS of the $\Sigma 13G(O)$ GB is depicted. At
 189 the $\Sigma 13G(O)$ GB, nearest-neighboring oxygen atoms at the GB plane are
 190 coordinated by three aluminum atoms, less than the four atoms of other
 191 oxygen atoms at the GB and in the bulk-like region. Figure 4 shows that
 192 those oxygen atoms with dangling bonds contribute the localized states in
 193 Fig. 3 (c). This localized character has been seen in a few GBs in ZnO[36].
 194 A similar isolated peak is also found in the $\Sigma 31$ GB DOS (Fig. 3 (d)).
 195 The conduction bands of the GBs are strongly influenced by their atomic
 196 structures, shifting to a lower energy range compared to the bulk, as seen in
 197 Fig. 3. These changes induce a narrowing of the band gap.

198 The band gaps of the GBs relative to that of the bulk crystal are plotted
 199 in Fig. 5 as a function of the grain boundary energy, E_{GB} , for both function-

als. This figure shows that GB band gaps correlate well with the degree of interface coincidence despite the difference in the relative band gaps, E_g/E_g^B , and E_{GB} between the functionals. In HSE06 calculations, the relative band gap of the $\Sigma 31$ GB reaches around 60%, so that this drastic change must affect the defect creation through the electron formation described by Eq. (10). Because the relative band gap of amorphous Al_2O_3 by LDA has a similar value [37] (also shown in Fig. 5), the narrowing of the band gap may be limited to around 60%.

Oxygen permeation experiments have been carried out to measure aluminum diffusion using alumina bicrystals forming $\Sigma 13$ and $\Sigma 31$ GBs [7]. According to these measurements, while the migration in the $\Sigma 13$ GB bicrystal was too small to be observed, Al diffusion coefficients at the $\Sigma 31$ GB were comparable to that in polycrystalline alumina. For the $\Sigma 31$ GB, oxygen GB diffusion coefficients measured by tracer experiments [13] have also proven to be comparable to those of polycrystalline Al_2O_3 reported in the literature [9]. These bicrystal experiments showed that GB diffusivity is closely related to the atomic structures of the interface. Our calculations indicate that the band gap of a GB depends on the interface atomic structure, which will thus affect the defect formation energetics at GBs, as described in the next section.

Experiments based on spatially resolved valence electron energy-loss spectroscopy showed that the interband electronic structure of near- $\Sigma 11$ ($N\Sigma 11$) GB exhibits increased ionicity around the GB, suggesting a reduction of the band gap, although this could not be quantified [38]. First principles calculations of $N\Sigma 11$ GB revealed a low E_{GB} of 1.7 J/m^2 and a band gap reduction

225 of 1.0 eV from a bulk gap of about 6.0 eV to give a relative band gap of 0.83
 226 [39]. These values are similar to those for a $\Sigma 13\text{G}(\text{Al})$ GB in Fig. 5. The ob-
 227 servation that no levels are introduced into the band gap in the $\text{N}\Sigma 11$ GB is
 228 also consistent with the results for $\Sigma 13\text{G}(\text{Al})$ GB in Fig. 3 (b). These results
 229 indicate that the $\text{N}\Sigma 11$ GB is relatively coherent, similar to the $\Sigma 13\text{G}(\text{Al})$
 230 GB.

231 The temperature dependence of band gaps, which is approximated as a
 232 proportional relation at high temperatures, should be considered because the
 233 temperature-induced band gap change in $\alpha\text{-Al}_2\text{O}_3$ is large compared to that
 234 of typical semiconductors such as Si and Ge [34]. Experiments of interband
 235 electronic structures by vacuum ultraviolet spectroscopy over a wide tem-
 236 perature range from 293 K up to 2167 K gave a linear coefficient at high
 237 temperatures of -0.85 meV/K [40], which is much larger than those for Si
 238 (-0.22 meV/K) or Ge (-0.44 meV/K) [41]. Using this value for the coefficient
 239 and $E_g^{\text{B}} = 9.1$ eV for the bulk band gap at 0 K, the gap at 1900 K is reduced
 240 to 7.49 eV or 82%. Although this suggests that GB band gaps will be further
 241 reduced from the calculated values at 0 K, the temperature dependence of
 242 a GB's band gap will be different from that of the bulk crystal and conse-
 243 quently difficult to predict. In this work, we consider the relative band gap
 244 to be a variable in the range of $0.5 < E_g/E_g^{\text{B}} < 1.0$.

245 3.2. Formation energies

246 Formation energies of O and Al vacancies at 1900 K were calculated from
 247 DFT results after determining ε_{F} . In the calculations, the experimental value
 248 of 9.1 eV for E_g^{B} was used for a P_{O_2} range from 10^{-8} to 10^5 Pa. Figure 6 shows
 249 E_{f} and ε_{F} for the cases of $E_g/E_g^{\text{B}} = 1.0$ and 0.6. As seen in Fig. 6 (b), for

250 the case of $E_g/E_g^B = 1.0$, V_{Al}''' is more energetically favorable over the whole
 251 range of P_{O_2} , but for the case of $E_g/E_g^B = 0.6$, the preference of V_{Al}''' or $V_O^{\bullet\bullet}$
 252 formation changes depending on P_{O_2} . The switchover in the type of dominant
 253 vacancy is consistent with the results from oxygen permeation experiments.
 254 The dependence of E_f on E_g is shown in Fig. 7 (c) for both limits of P_{O_2} .
 255 This figure indicates that the switchover appears somewhere in the range of
 256 E_g/E_g^B below 0.65. The results suggest the importance of the narrowing of
 257 the band gap of a GB in connection with the switchover phenomenon because
 258 the band gap reduction of bulk crystals at high temperature is about 0.8, as
 259 mentioned above.

260 The different behavior of Fermi levels in Figs. 6 (a), 7 (a), and 7 (b)
 261 provides some insight into the defect equilibrium. In Figs. 6 (a) and 7
 262 (a), Fermi levels for the Schottky equilibrium, i.e., $2[V_{Al}'''] = 3[V_O^{\bullet\bullet}]$, are also
 263 shown. The different dependence of ε_F on P_{O_2} for large and small band gaps
 264 are found in Fig. 6 (a). Comparison with the Schottky equilibrium indicates
 265 that the defect concentrations can be very different from those predicted from
 266 the most simple Schottky model over a wide range of P_{O_2} , including around
 267 1 atm. This is also seen in Fig. 7 (a), where the Fermi energies are invariant
 268 and higher than those for Schottky equilibrium in the range of $E_g/E_g^B > 0.7$.
 269 This behavior shows that conduction electrons are sufficiently passive to have
 270 no effect on the equilibrium even at such a high temperature. In this range,
 271 the Fermi level is less than half the band gap, as seen in Fig. 7 (b), and
 272 relatively near to the valence band maximum. Thus, in the bulk-like region
 273 with a wide band gap, the defect equilibrium is determined by Al vacancies
 274 and holes, so the Schottky equilibrium is energetically unfavorable. As in

275 Fig. 7 (b), when the band gap is decreased to the range of $E_g/E_g^B < 0.7$, ε_F
 276 lies at about the midpoint of the band gap and the defect formation energies
 277 are no longer constant, resulting in the change of the dominant vacancy.
 278 This is apparently caused by the participation of conduction electrons in the
 279 equilibrium between charged species according to Eq. (10). Because the
 280 increase in the number of electrons induces not only an enhancement of $V_{\text{O}}^{\bullet\bullet}$
 281 formation but also suppression of V_{Al}''' formation (via the decrease in number
 282 of holes), the behavior is relatively complex and seems to be independent of
 283 ε_F for the Schottky equilibrium as seen in Fig. 7 (a). At a constant E_g in
 284 the range of $0.55 < E_g/E_g^B < 0.65$, when P_{O_2} increases from 10^{-8} Pa to 10^5
 285 Pa, ε_F decreases by less than 0.5 eV. The change in ε_F is sensitive to large
 286 changes in the formation energies as a function of P_{O_2} , as illustrated in Fig.
 287 6.

288 Concentrations of charged species for the case of $E_g/E_g^B = 0.6$ and
 289 $T = 1900$ K are plotted in Fig. 8. This figure confirms the switchover
 290 expected from the formation energies of the vacancies, and the electronic
 291 carriers are found to be the dominant charge carriers. At high P_{O_2} , holes are
 292 dominant and seem to enhance the formation of V_{Al}''' ; this tendency is con-
 293 sistent with the dominant reaction forming alumina (Eq. (2)) suggested by
 294 oxygen permeation experiments. In contrast, the enhanced formation of $V_{\text{O}}^{\bullet\bullet}$
 295 appears to be related to the electrons being the dominant carrier in accord
 296 with the reaction in Eq. (1). The transition from p -type conductivity at
 297 high P_{O_2} to n -type conductivity at low P_{O_2} mentioned by Heuer et al. [16]
 298 is, therefore, reproduced. Since the dominant carriers have a strong effect
 299 on the concentrations of vacancies, the effect of segregated dopants at GBs

on the GB diffusion may be interpreted as resulting from the charge balance that also include the charge carriers from acceptors or donors. To probe this phenomenon further, the defect structures and charge states of the dopants at the GBs should be determined.

4. Conclusion

The switchover of the dominant defects in α - Al_2O_3 as a function of P_{O_2} as suggested by oxygen permeation experiments were investigated by calculating the formation energies of charged oxygen and aluminum vacancies using DFT, where the HSE06 hybrid-type functional was used to obtain more reliable band gaps than those obtained using conventional LDA and GGA functionals. Fermi levels were determined assuming charge neutrality between the charged vacancies, holes, and conduction electrons. Examination of the electronic structures of the GBs revealed that the band gap of GBs is reduced by around 60% compared to the bulk value, depending on the degree of interface coherence and/or disorder. Thus, the dependence of the formation energies on the band gap was also examined. It was shown that the formation energies and the Fermi levels exhibit different behavior for wide band gap and narrower band gap structures. For a wide band gap GB (greater than 70% compared to the bulk value) the aluminum vacancies and holes are dominant regardless of P_{O_2} . A crossover in the formation energies of the two types of vacancies appears only when the band gap is reduced to below $\sim 65\%$ and above $\sim 55\%$ of that in the bulk. Our results suggest that the electronic structures relative to not only the vacancy formation but also electronic carriers which are predominant should be discussed to understand

324 the behavior observed in oxygen permeation experiments in α -Al₂O₃.

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Figure 1: Atomic structures of α - Al_2O_3 grain boundary models: (a) $\Sigma 13$ G(Al), (b) $\Sigma 13$ G(O) viewed down the $[10\bar{1}0]$ axis, and (c) $\Sigma 31$ viewed down the $[0001]$ axis. The black circles in panel (d) indicate the network of aluminum atoms observed by transmission electron microscopy overlaid on the $\Sigma 31$ GB model in (c) [25, 26]. Large red and small blue spheres represent oxygen and aluminum atoms, respectively.

Figure 2: Electronic band structures of single-crystal α - Al_2O_3 from (a) GGA and (b) HSE06 calculations. Inset in (b) shows a magnified view of bands around the valence band maximum.

Figure 3: Density of states of (a) bulk crystal, (b) $\Sigma 13G(\text{Al})$, (c) $\Sigma 13G(\text{O})$, and (d) $\Sigma 31$ grain boundaries of $\alpha\text{-Al}_2\text{O}_3$ as a function of energy with respect to the highest occupied level using the HSE06 functional.

Figure 4: Partial charge density of the valence band maximum of a $\Sigma 13\text{G}(\text{O})$ grain boundary shown in Fig.3 (c). The isosurface corresponds to $0.05 \text{ e}/\text{\AA}^3$.

Figure 5: Band gap of $\alpha\text{-Al}_2\text{O}_3$ grain boundaries relative to the bulk gap as a function of grain boundary energy. The horizontal dotted line indicates the calculated value for amorphous Al_2O_3 [37].

Figure 6: (a) Fermi levels and (b) formation energies of oxygen and aluminum vacancies at $T = 1900$ K as a function of oxygen partial pressure for the case of a relative band gap of 1.0 and 0.6 compared to the bulk value. In panel (a), Fermi levels for Schottky equilibrium are also shown.

Figure 7: (a) Fermi levels, (b) Fermi levels divided by band gap, and (c) formation energies of oxygen and aluminum vacancies at $T = 1900$ K as a function of the relative band gap compared to the bulk value for the case of oxygen partial pressure 10^{-8} Pa and 10^5 Pa. In panel (a), Fermi levels for Schottky equilibrium are also shown for 10^{-8} Pa (thin red solid line) and 10^5 Pa (thin red dotted line). In panel (b), the horizontal dotted line indicates half the band gap.

Figure 8: Concentration of oxygen and aluminum vacancies, holes, and electrons in the case of $E_g/E_g^{\text{B}} = 0.6$ and $T = 1900 \text{ K}$. The right vertical scale shows normalized concentration by the volume of bulk Al_2O_3 per formula unit.