On the Possibility of Valence Control of Aluminum Oxide for Electronics Applications

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Aluminum oxide, including crystalline Al_2O_3 and amorphous AlO_x, is usually regarded as an insulator. If its conductivity is controlled by donor and acceptor doping, it can be used for various electronics applications as a wide-gap semiconductor or a transparent conductive oxide. In search for shallow donors and acceptors, the energy levels introduced by various impurities are calculated for corundum Al_2O_3 by the first-principles calculation based on the density-functional theory. Density of states is calculated for a supercell consisting of 120 atoms including one impurity atoms. According to the results, group VII elements (F, Cl, Br, I) can act as a shallow donor, and group II elements (Mg, Zn, Ca) can act as a shallow acceptor. Thus there is a possibility that both n- and p-type aluminum oxides are fabricated by proper doping and applied for electronics.

Keywords: aluminum oxide; semiconductor; doping; valence control; first-principles calculation

INTRODUCTION

Group III-oxides are indispensable in the modern electronics. In_2O_3 is the most popular transparent conducting oxide (TCO) and has been widely used for electrodes in display devices and solar cells.[1] Ga_2O_3 has recently attracted much attention as a wide-gap semiconductor and is regarded as promising for application to UV sensors and power devices. Alloy semiconductor $(Al_xGa_{1-x})_2O_3$ has also been investigated because it can constitute various heterostructure devices based on Ga_2O_3.[2] On the other hand, Al_2O_3 has been considered to be an insulator, not semiconductor or conductor. Sapphire single crystals have been used for the substrate of GaN-based devices. Al_2O_3 thin films have been used as the insulating layer in MOS devices. Amorphous AlO_x films have widely been used for passivating surfaces of semiconductor devices. In all of those popular applications, aluminum oxide acts as an insulator. Electrical conduction in Al_2O_3 is usually considered to be dominated by the Frenkel mechanism, typical for dielectric materials: free carriers are basically absent, and minimum current can flow owing to electric-field-assisted emission of electrons from taps which have deep energy levels.[3] An exceptional case is resistive memory devices where an aluminum oxide film is employed as a bi-stable conducting material.[4,5]

Thus, so far, aluminum oxide has not been considered as a semiconductor, though Ga_2O_3 and even $(Al_xGa_{1-x})_2O_3$ have proven to be useful in various semiconductor device applications. If aluminum oxide is successfully used as a semiconductor, it can have tremendous merits. Al_2O_3 has a larger band gap than Ga_2O_3, and thus may have larger breakdown field strength. The growth of single-crystalline sapphire is well established, and sapphire wafers are available at low cost. Moreover, aluminum is the most abundant metal element in the earth crust, in contrast to indium, which is a rear earth element with much less mineral abundance. Therefore, if In_2O_3-based TCO is replaced with aluminum oxide-based TCO, we would have virtually unlimited mineral resource for TCO. It is known that nonstichiometric AlO_x has a smaller band gap than crystalline Al_2O_3.[6] Thus we may be able to modify the band gap of aluminum oxide by controlling O/Al ratio as we can do for conventional alloy semiconductors.

For any application in semiconductor electronics, the valence control is essential. In_2O_3 is inherently conductive owing to the native defects (oxygen vacancy), and its resistivity is much reduced by Sn-doping, which makes indium-tin-oxide (ITO) an excellent TCO. Tin is also a fairly good donor for Ga_2O_3.[1] However, for aluminum oxide, the valence control by impurity doping does not seem to be investigated, because aluminum oxide has not been regarded as a semiconductor. The energy levels of native defects (vacancies and interstitials) have been investigated theoretically, and it is generally agreed that the dominant native defects form deep energy levels within the band gap.[7-9] The energy levels have been calculated for some impurities, such as C and Cr.[10-14] It seems that so far attention is mainly focused on transition metal elements because natural sapphire often contains such metal elements and is colored by them.

In this work, the first principles calculation is performed to obtain energy levels of various impurities in corundum Al_2O_3, in search for shallow donors and acceptors. According to the classical semiconductor theory, group IV elements and group II elements are expected to act as a donor and an acceptor, respectively, when they substitute Al. On the other hand, group VII elements and group V elements may become a donor and an acceptor, respectively, when they occupy the oxygen site. In addition to those elements, several transition metals are also examined. The impurity elements considered in this work are listed in Table I. We focus on nontoxic and abundant elements because elemental abundance and nontoxicity is one of the major merits of aluminum oxide. The calculation results indicate that several elements will act as a shallow impurity. Thus n-type and p-type aluminum oxides may be fabricated by a proper doping, and therefore there is possibility that aluminum oxide can be used for various electronic devices and even for TCO.

In the next section, the calculation procedure is given. In the third section, the results are given for 1) native defects (vacancies), 2) potential donors, 3) potential acceptors, and 4) transition metals.

CALCULATION PROCEDURE

The matrix material is corundum Al_2O_3, whose unit cell consists of 12 Al atoms and 18 O

atoms. For the supercell calculation for the defect/impurity level, a 120 atom cell (2x2x1) is considered. To introduce a vacancy, an Al or O atom was removed. For the doping, one Al or O atom was replaced with an impurity element. The first-principles calculation based on the density functional theory (DFT) and the plane-wave pseudo-potential method was performed using the PHASE code (Center for Research on Innovative Simulation Software, Univ. Tokyo). For the exchange and correlation interactions, the generalized gradient approximation (GGA) by Perdewe-Burkee-Ernzerhof was adopted.[15] It is known that the band gap is underestimated by the DFT calculation based on GGA; the calculated band gap is 6.0 eV for the defect-free Al_2O_3, smaller than the experimental value (8.7 eV). The whole lattice of the supercell with an impurity or a defect was allowed to relax, to minimize the total energy. In this work, the density of states (DOS) is calculated for the neutral state, and possibility of n- or p-type conduction is discussed on the basis of DOS.

RESULTS

Vacancies

Figure 1 shows DOS for the supercell (a) without any defect, (b) with an O vacancy, and (c) with an Al vacancy. The origin of the horizontal (energy) scale corresponds to the highest occupied level, i.e., the Fermi level at 0K, for all the figures in this paper. The O vacancy introduces the energy level at 2.3 eV higher than the valence band top E_v ($E_v + 2.3$ eV) as shown in Fig.1 (b). This level is occupied by two electrons. The level is so far from the conduction band bottom E_c that one cannot expect the O vacancy to act as a donor. On the other hand, the Al vacancy introduces levels near E_v, and the Fermi level is located within those levels, as shown in Fig. 1 (c). Thus, unoccupied levels are introduced near E_v, i.e., the Al vacancy is expected to act as a shallow acceptor. Those results for the vacancies agree well with the previously reported first-principle DFT calculation.[7]

At thermodynamical standard conditions, oxygen is gas whereas aluminum is solid, and thus experimentally Al-rich conditions are more readily created than O-rich conditions. Therefore one can expect that O vacancies are introduced more dominantly than Al vacancies. Thus, although Al vacancies may act as an acceptor, p-type conduction due to Al vacancies

will be difficult to realize in actuality.

Potential donor impurities

Group VII elements at the oxygen site are expected to be a donor. In fact, fluorine is a good donor for SnO_2, and F-doped SnO_2 (FTO) is widely used as TCO. Figure 2 shows DOS for (a) F- and (b) Cl-doped Al_2O_3. In Fig.2 (a), the Fermi level is located within the conduction band; there is one electron in the conduction band. The corresponding state is not localized at the F atom but spreads over the cell. Thus the F atom is thought to donate a conduction electron. The results for Cl are similar to those for F, as shown in Fig. 2 (b). The Fermi level is also located within the conduction band for Br- and I-doped Al_2O_3. Thus, all the group VII elements (F, Cl, Br, I) are expected to act as a shallow donor.

Figure 3 shows DOS for (a) Sn-, (b) Si-, and (c) C-doped Al_2O_3. Group IV element at the Al site may be able to donate an electron. In fact, Sn is the common dopant for In_2O_3 and Ga_2O_3. However, for Al_2O_3, Sn introduced half-filled energy level at about 1.7 eV away from E_c, as shown in Fig.3 (a). Thus one cannot expect that Sn will act as an effective donor in Al_2O_3. (For Sn, the effects of the lattice relaxation are significant. With a rigid lattice, Sn is expected to introduce levels considerably closer to E_c.) The level introduced by Ge is almost the same ($E_c - 1.6$ eV) and thus is also too deep to act as a donor. On the other hand, the energy level introduced by Si doping is only 0.6 eV away from E_c. The states are half-filled and localized around the Si atom. Thus, at room temperature, Si may partially be ionized and donate electrons to the conduction band, although the ionization ratio would be rather small. In contrast, C is expected to introduce energy levels near the mid gap ($E_v + 3$ eV). Formation of such deep levels was predicted in the previous theoretical work also.[10,11] (Experimentally, C doping is known to enhance thermo-luminescence involving oxygen vacancies, but the mechanism is not well understood.[16]) Thus, among the group IV elements, only Si would have a relatively shallow donor level.

Potential acceptor impurities

First we consider group II elements at an Al site as a potential acceptor. Figure 4 shows

DOS for (a) Zn- and (b) Mg-doped Al_2O_3. Zn introduces partially (3/4) filled energy levels at $E_v + 0.3$ eV, i.e., there is one unoccupied state near E_v. Thus, Zn is thought to act as an acceptor. In the case of Mg doping, there is one non-localized, unoccupied state at the valence band top. Thus, according to the calculation results, Mg acts as a shallow acceptor. The results for Ca are similar to those of Mg, and thus Ca is also expected to be a shallow acceptor.

Substitution of oxygen with a group V element is another possibility of acceptor doping. DOS for Al_2O_3 doped with N and P are shown in Fig. 5. N at the O site introduces several localized states with energy levels near E_v. An unoccupied state is located at $E_v + 0.6$ eV, and thus this level may be able to act as an acceptor with a large ionization energy. P introduced 1/2-filled states at $E_v + 2.6$ eV, along with occupied states around $E_v + 1.5$ and $E_v + 1.9$ eV. Sb and As introduce similar but slightly deeper levels. (The levels tend to be deeper for a heavier element.) Thus, among the group V elements, N may be regarded as a deep acceptor, while the levels of P, As, and Sb are too deep to accept an electron from the valence band.

Transition metals

The energy levels associated with the transition metal elements are summarized in Table II. Most of the transition metals examined introduce deep mid-gap levels. For example, in the case of Fe, there are 5/6-filled states at $E_v + 2.0$ eV and empty states at $E_c - 1.7$ eV. For V, Cr, Mn, Fe, Co, and Ni, the empty (occupied) states are more than 2.0 eV apart from the valence (conduction) band edge, and thus those elements are not expected to act as a donor or an acceptor. The energy level of Cu is relatively close to E_v ($E_v + 1.0$ eV) and 2/4-filled. Thus it may be regarded as a deep acceptor level. The level associated with Ti is relatively shallow, i.e., located around $E_c - 1.4$ eV and partially (1/6) filled, but it is still too deep to donate an electron to the conduction band.

DISCUSSION

The qualitative conclusions drawn from the calculation results are summarized in Table III. Here the levels are tentatively classified depending on the ionization energy E_a: shallow levels

with $E_a < 0.5$ eV, deep levels with $0.5 < E_a < 1.0$ eV, and mid-gap levels with $E_a > 1.0$ eV. E_a is defined as the energy difference from E_c for the potential donor (occupied) level, and the energy difference from E_v for the potential acceptor (unoccupied) level. According to the results, n-type conduction may be realized by doping of group VII elements and Si, and p-type conductivity by group II elements and N, Cu.

The calculation method adopted in this work has the following limitations.[17]

a) The calculation is based on DFT within GGA, and the band gap is significantly underestimated.

b) The defect energy level is determined from DOS of the neutral cells, and thus change in the local atomic structure depending on the defect charge state is not taken into account.

c) The supercell approach is adopted, and thus the energy level can be influenced by artificial (electronic and elastic) interactions between the defects.

The errors in the energy levels due to b) and c) are difficult to predict. On the other hand, since the band gap is underestimated because of a), the ionization energy of the impurity may be underestimated. Then one may regard the present calculation as an initial quick screening of possible useful dopants. Considering the tendency of underestimation, the levels classified as deep or mid-gap levels are expected to be actually deep. For the "shallow levels" in Table III, the conclusions need to be checked by a more sophisticated calculation, e.g., that using hybrid-functionals,[18] and also by experimental investigation.

The solid solubility of the impurities is not discussed in this work. Since each impurity is considered as a dopant for the valence control, its content is supposed to be low ($<10^{19}$ cm^{-3}). In addition, various non-equilibrium techniques are available for the film deposition, such as atomic-layer deposition. Therefore, the solubility would not be a serious problem in the actual doping. From the view point of thermodynamics, the self-compensation is another problem. For example, for an acceptor-type defect, the effective formation energy is reduced by the energy difference from the Fermi level and the defect level. Thus, if the Fermi level is shifted upward by donor doping, the defect formation energy is reduced. As noted above, the O vacancy has a level in the lower half of the band gap. That level is occupied, and the O vacancy is a donor-type defect. Its formation energy is reduced by the acceptor doping, but

since the O vacancy level is rather close to E_v (E_v + 2.3 eV), the reduction of the formation energy is small. Therefore, according to the calculation results, the self-compensation due to the O vacancy will not be significant. The Al vacancy is expected to be a shallow acceptor, and thus its formation energy is significantly reduced by the donor doping. However, formation of Al vacancies will be thermodynamically unfavorable under usual preparation conditions as discussed in the previous section. Thus, one may expect that self-compensation due to the vacancies will not be serious problem for both the n- and p-type doping.

As noted in the introduction, amorphous nonstoichiometric AlO_x has a smaller band gap than stoichiometric Al_2O_3. The energy levels of the O vacancy were calculated for amorphous Al_2O_3 on the basis of DFT.[19,20] According to the calculation results, the level of neutral O vacancy is located at E_v + 2.6 eV,[19] E_v + 2.5 eV,[20] rather close to the level of O vacancy in crystalline Al_2O_3 (E_v + 2.3 eV). There is also an experimental work which showed that O vacancy levels are similar in crystalline and amorphous Al_2O_3.[21] Therefore, one may expect that structural disorder and non-stoichiometry would not drastically change the energy levels of the defects and impurities. Thus the qualitative conclusion of this work would not be completely altered for amorphous AlO_x. Then amorphous AlO_x with proper doping may be used for thin film devices and electrodes.

CONCLUSION

The possibility of valence control of aluminum oxide has been investigated theoretically. In search for shallow donors and acceptors, the energy levels introduced by vacancies and impurities are calculated by the first-principles DFT calculation based on GGA. According to the results, group VII elements can act as a shallow donor, and group II elements can act as a shallow acceptor. If conductivity is controlled by doping of those impurities, electronic devices can be fabricated based on crystalline Al_2O_3 or amorphous AlO_x. Heavily doped n-type AlO_x may even be applied for TCO electrodes. All the conclusions are yet to be confirmed experimentally, since so far no attempt has been made to utilize aluminum oxide as a semiconductor. The present results indicate that it is worth attempting to control conductivity of aluminum oxide by impurity doping for various electronics applications.

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Fig. 1 DOS for corundum Al_2O_3 (a) without defect, (b) with an O vacancy, and (c) with an Al vacancy. The origin of the horizontal (energy) scale is the highest occupied level, i.e., the Fermi level at 0K.

Fig. 2 DOS for (a) F-doped and (b) Cl-doped Al_2O_3.

Fig. 3 DOS for (a) Sn-doped, (b) Si-doped, and (c) C-doped Al_2O_3.

Fig. 4 DOS for (a) Zn-doped and (b) Mg-doped Al_2O_3.

Fig. 5 DOS for (a) N-doped and (b) P-doped Al_2O_3.

Table 1 Native defects and impurities for which energy levels are calculated in this work.

category		element
native defects		O vacancy , Al vacancy
potential donors	group VII	F, Cl, Br, I
	group IV	C, Si, Ge, Sn
potential acceptors	group II	Mg, Zn, Ca
	group V	N, P, As, Sb
transition metals		Ti, V, Cr, Mn, Fe, Co, Ni, Cu

Table 2 Summary of the results for the transition metal elements (energy levels with respect to the nearer band edge in eV).

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
unoccupied		E_c–0	E_c–0.5	E_c–1.3	E_c–1.7	E_c–2.7	E_v+2.1	
partially occupied	E_c–1.4	E_c–2.2	E_c–3.0	E_v+2.5	E_v+2.0		E_v+2.0	E_v+1.0
occupied						E_v+1.3		

Table 3 Classification of the defects and impurities based on the energy levels calculated.

character		element
shallow ($E_a < 0.5$ eV)	donor	F, Cl, Br, I
	acceptor	Mg, Zn, Ca, Al vacancy
deep (0.5 eV $< E_a <$ 1.0 eV)	donor	Si
	acceptor	N, Cu
mid-gap level ($E_a > 1.0$ eV)		O vacancy, C, Ge, Sn, P, As, Sb Ti, V, Cr, Mn, Fe, Co, Ni

Fig 1 (a)
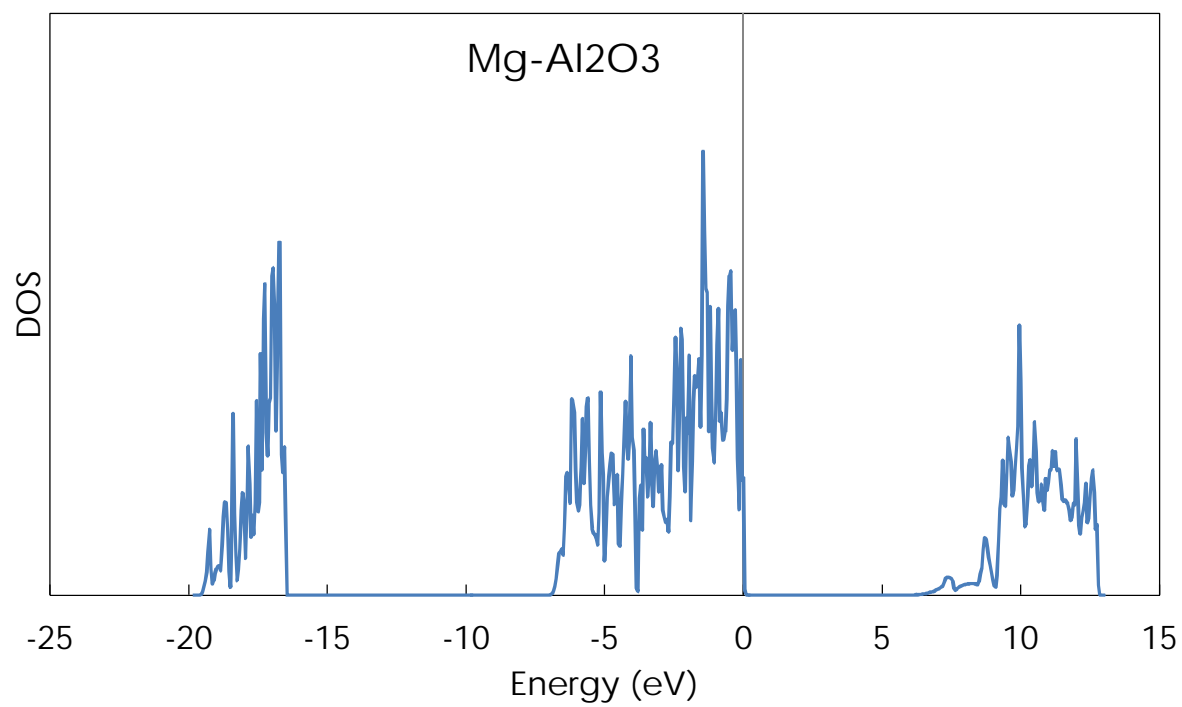

Fig 1 (b)

Al vacancy-Al2O3

Fig 1 (c)

F-Al2O3

Fig 2 (a)

Cl-Al2O3

Fig 2 (b)

Fig 3 (a)

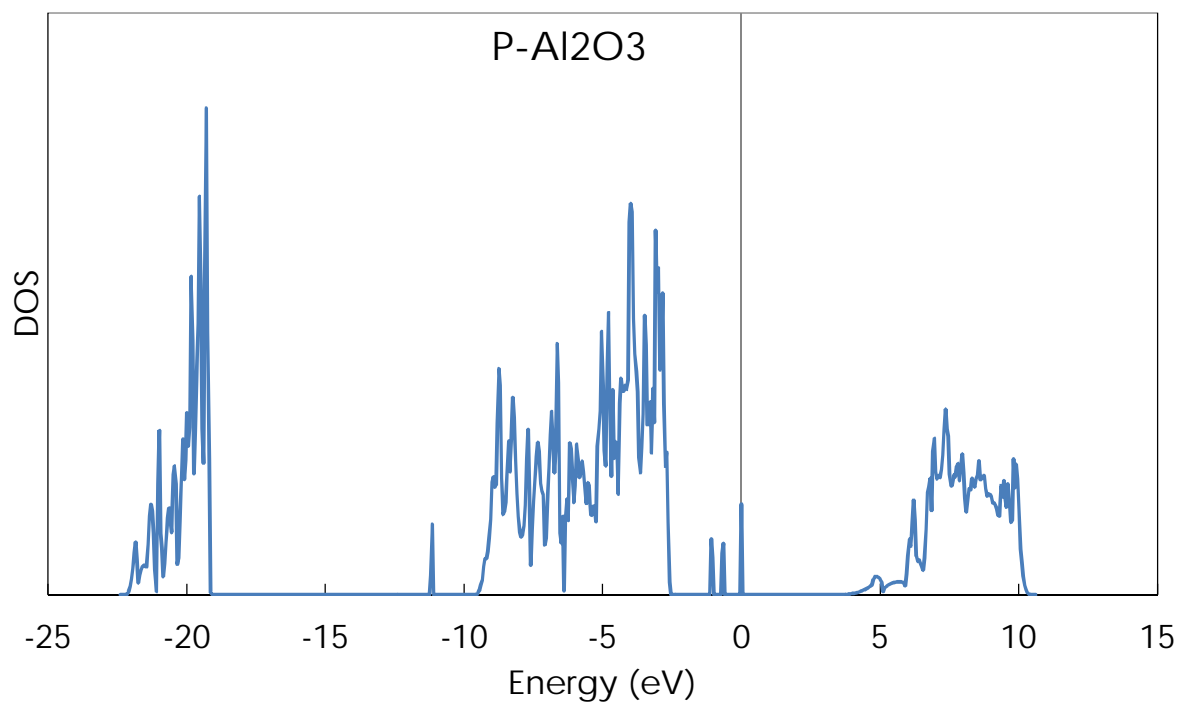Fig 3 (b)

17

C-Al2O3

Fig 3 (c)

Fig 4 (a)

Fig 4 (b)

19

Fig 5 (a)

Fig 5 (b)