Electron-Transport Characteristics through Aluminum Oxide (100) and (012) in a Metal–Insulator–Metal Junction System: Density Functional Theory—Nonequilibrium Green Function Approach

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ABSTRACT: Al2O3 is commonly used in modern electronic devices because of its good mechanical properties and excellent electrical insulating property. Although fundamental understanding of the electron transport in Al2O3 is essential for its use in electronic device applications, a thorough investigation for the electron-transport mechanism has not been conducted on the structures of Al2O3, especially in nanometer-scale electronic device settings. In this work, electron transport via Al2O3 for two crystallographic facets, (100) and (012), in a metal–insulator–metal junction configuration is investigated using a density functional theory-based nonequilibrium Green function method. First, it is confirmed that the transmission function, T(E), decreases as a function of energy in (E − E_F) < 0 regime, which is an intuitively expected trend. On the other hand, in the (E − E_F) > 0 regime, Al2O3(100) and Al2O3(012) show their own characteristic behaviors of T(E), presenting that major peaks are shifted toward lower energy levels under a finite bias voltage. Second, the overall conductance decay rates under zero bias are similar regardless of the crystallographic orientation, so that the contact interface seemingly has only a minor contribution to the overall conductance. A noteworthy feature at the finite bias condition is that the electrical current drastically increases as a function of bias potential (>0.7 V) in Al2O3(012)-based junction compared with the Al2O3(100) counterpart. It is elucidated that such a difference is due to the well-developed eigenchannels for electron transport in the Al2O3(012)-based junction. Therefore, it is evidently demonstrated that at finite bias condition, the contact interface plays a key role in determining insulating properties of Al2O3–Pt junctions.

1. INTRODUCTION

Because integrated circuits in modern electronics are composed of lots of nanometer-scale electronic components such as transistors, capacitors, and resistors on a very small silicon substrate, good insulation is a critical factor for the reliable operation of the devices. Metal oxide has been widely used as an insulating material. In particular, crystalline aluminum oxide (alumina, Al2O3) has been proven as a versatile insulating material for various applications. First of all, Al2O3 has been used as an effective insulating barrier in capacitor applications,1 which is mainly due to its high resistivity, stable dielectric strength, relatively high thermal conductivity (κ = 30−35 W/mK),2 and a high-fracture toughness (3.37 MPa m1/2).3 In addition, Al2O3 has excellent surface properties suitable for broad range of applications including a good corrosion resistance to a wide range of chemistries. For example, hydroxylated γ-Al2O3 shows catalytic activity for water dissociation.4 Al2O3 has mixed bonding characteristics composed of ionic and covalent bonding, a large band gap energy, and concomitantly low concentration of both ionic defects and electronic carriers.5 These intrinsic characteristics are crucial in determining various electronic phenomena at the interfaces in device applications. Two-dimensional MoS2 thin-film growth on α-Al2O3, for example, shows a considerable enhancement of charge mobility at the interface. In this case, the α-Al2O3 substrate is known to suppress the Coulomb scattering of the charge carriers or changes in phonon dispersion, which enhances the charge mobility of the device.6,7 It should be noted that, despite the wide use of Al2O3 in diverse research fields, its electronic structure per se is usually less known than that of pure or mixed metals. The reason is mostly due to (1) the readily formed defective surface structures that alter original electronic properties and (2) experimental difficulties
in measuring its electronic transport properties like many other metal oxides. In that context, we investigate the electron-transport properties of Al\textsubscript{2}O\textsubscript{3} in two major crystallographic directions using density functional theory-based nonequilibrium Green function (DFT-NEGF) method\textsuperscript{8–12} to achieve fundamental understanding of the electron-transport mechanisms through the system. Recently, the NEGF coupled DFT methodology has successfully explored strong orbital overlap and the electron and phonon scattering to investigate thermoelectric transport at the Al\textsubscript{2}/\textsubscript{Pt} interface\textsuperscript{13}. For the study, we utilize the DFT-NEGF to a model system configured as metal–insulator–metal (Pt–Al\textsubscript{2}O\textsubscript{3}–Pt) to investigate the electron scattering in nanometer-thick dielectric transport channels at the interfaces in these models, and thereby, clarify the transport mechanism through the dielectric media in nanometer scale.

Considering modern electronic device development often requires nanometer-scale architectures where understanding atomistic structures of the materials and their electronic properties become crucial to accomplish desirable device performance,\textsuperscript{14} the propagation of electronic state with an equilibrium state.\textsuperscript{15} A challenge in this problem, however, is that the electron transport in a multiple-component system takes place via many-body electronic energy states.\textsuperscript{16–18} Because it has been known that the given single-electron based scattering theory\textsuperscript{19} would not be sufficiently accurate, especially at the interface between electron reservoir and contact region, a method such as the DFT-NEGF approach can be employed to accurately describe electron transport via interface by taking into account the many-body electronic interaction within the self-consistent framework of the Kohn–Sham Hamiltonian in the nonequilibrium state.

In this study, the variation of electronic structure and corresponding difference in electron transmission at Pt–Al\textsubscript{2}O\textsubscript{3}–Pt junction system are investigated as a function of bias voltage, using the DFT-NEGF formalism described above. Thereby, the conductance of the junction systems with two different Al\textsubscript{2}O\textsubscript{3} crystallographic directions, (100) and (012) in various thicknesses are thoroughly characterized in: (1) zero-bias limit and (2) finite-bias voltage limit.

2. RESULTS AND DISCUSSIONS

2.1. Structural Property of Al\textsubscript{2}O\textsubscript{3}. The systems were built using Al\textsubscript{2}O\textsubscript{3}(100) and (012) crystallographic facets for the contact interface as shown in Figure 1a. The Al\textsubscript{2}O\textsubscript{3}(100) facet has the same surface morphology with the Al\textsubscript{2}O\textsubscript{3}(010) due to crystallographic symmetry. Thus, the two surfaces such as Al\textsubscript{2}O\textsubscript{3}(100) and Al\textsubscript{2}O\textsubscript{3}(012), were used to construct the junction systems, which are denoted by A100 and A012, respectively. The surface facets were prepared by cleaving the surface along the crystallographic directions without any atomic defect or dangling bond. Therefore, aluminum-top or oxygen-top surfaces are generated in each facet at the contact interface, such as on-top, hollow, bridge sites (Supporting Information Figure S1a). Individual contributions to the electronic structure of oxygen atoms at each site, however, is why this study pays attention to length dependence of the Al\textsubscript{2}O\textsubscript{3} phase to the electron transport by keeping the contact geometry constant for different lengths.

2.2. Electron Transmission. 2.2.1. Bias-Dependent Shift of Major Peak Positions. The DFT-NEGF calculations were performed for various thicknesses of the Al\textsubscript{2}O\textsubscript{3} phase (2–6 nm) to obtain transmission spectra \( T(E) \) under the zero and finite applied bias (\( V_b \)) conditions. Figure 1b compares the transmissions of A100 and A012 in logarithmic scale as a function of electron energy. The transmission spectra show their characteristic features under the applied biases. The values of \( T(E) \) of both systems are monotonously decreased in the regime of \( (E - E_F) < 0 \) for all thickness conditions, while \( T(E) \) shows characteristic features depending on the crystallographic orientation of Al\textsubscript{2}O\textsubscript{3} phases in the regime of \( (E - E_F) > 0 \). \( T(E) \) of A100 is relatively flat compared with that of A012. One noticeable feature observed in Figure 1b is that the major peak positions are dependent on the Al\textsubscript{2}O\textsubscript{3} phase orientation (for instance, \( E_F + 1.26 \text{ eV} \text{ for A100 and } E_F + 0.84 \text{ eV} \text{ for A012})

Table 1. Atomic Distances between Pt and O and between Pt and Al Atoms at Pt–Al\textsubscript{2}O\textsubscript{3} Junctions

| atomic distance | Pt(111)/Al\textsubscript{2}O\textsubscript{3}(100) (Å) | Pt(111)/Al\textsubscript{2}O\textsubscript{3}(012) (Å) |
|----------------|--------------------------------|--------------------------------|
| Pt–O           | ≈1.92                          | ≈2.15                          |
| Pt–Al          | ≈2.00                          | ≈2.43                          |

Figure 1. (a) Junction systems using the Al\textsubscript{2}O\textsubscript{3}(100) and Al\textsubscript{2}O\textsubscript{3}(012) in contact with Pt(111) facet; (b) evolution of transmission spectra for the systems based on Al\textsubscript{2}O\textsubscript{3}(100) and Al\textsubscript{2}O\textsubscript{3}(012) as a function of the thickness of Al\textsubscript{2}O\textsubscript{3} phase. For each thickness, three bias potentials are applied, namely, 0 V (black), 0.5 V (blue), and 1.0 V (red). The transmission spectra are shifted by Fermi energy.
at \( V_b = 0 \) V. Another feature is that the major peaks are shifted toward \( E_F \) with increasing \( V_b \) (from 0.0 to 1.0 V) by \( \sim V_b/2 \) regardless of the thickness. To be more precise, the major peak at zero-bias condition is split into two parts as \( V_b \) is applied, and each split peak corresponds to each electrode, where one peak is shifted by \( +V_b/2 = \mu_L - E_F \) and another peak is shifted by \( -V_b/2 = \mu_R - E_F \). According to eq 4, only the latter one is affected by the bias window and, consequently, influences the electrical current. Therefore, the peak shifting downward is in major concern. Table 2 summarizes the positions of major transmission peaks at each applied bias, showing that the peak positions are shifted toward lower energy as the applied bias increases, whereas their relative peak intensities with respect to that of Fermi level remain nearly constant, regardless of the thickness variation of Al2O3 phase. Considering both distinct A100 and A012 phases providing the same degree of major peak shift by \( eV_b/2 \) that is comparable to the chemical potential shift of the electrode, it is inferred that the shifted peaks are originated from the contact part of the Pt–Al2O3 junction, rather than from the structural difference of crystallographic phases. This also shows that, in addition to the cross-sectional area and length dependency of the resistance in macroscopic scale, the contact interface between electrode (Pt) and material (Al2O3) becomes an important factor \(^{20,21} \) in nanometer-scale devices because the dimension of the interface is not ignorable.

2.2.2. Thickness Dependency. \( T(E) \) in Figure 1b demonstrates the thickness dependency of the conductance. For given \( V_b \) values, the \( T(E) \) decreases exponentially while the major peak position remains unchanged even as the Al2O3 becomes thicker. Particularly, it is clear from \( T(E = E_F, V_b = 0 \) V) that the conductance decreases by around three order of magnitude as the thickness increases by 1 nm. This indicates that the Al2O3 essentially acts as a good insulator.

2.3. Conductance within Zero-Bias Limit. 2.3.1. Length Scaling of Conductance at Zero-Bias Limit. In order to quantitatively investigate the effect of the Al2O3 surface facet at the interface with Pt(111) on the conductance of the system, the thickness dependency of the zero-bias conductance \( G = T(E = E_F, V_b = 0 \) V) is analyzed as shown in Figure 2a. The exponential decay of conductance is observed as a function of the thickness \( L \), supposing that the Al2O3 phase is an insulating thin film sandwiched between two Pt electrodes in the metal–insulator–metal junction. This means that electrons can penetrate the insulator via quantum tunneling. Here, the thickness dependency of the electron tunneling can be characterized using a simplified Simmons equation \(^{22,23} \) for the metal–insulator–metal junction as presented by

\[
G = G_C e^{-\beta L}
\]

where \( \beta \) denotes the tunneling decay rate of the conductance with the barrier thickness \( L \), and \( G_C \) is an effective contact conductance that can be obtained by extrapolating from the trends down to \( L = 0 \), and here, the unit is expressed in terms of \( G_C \). Assuming a rectangular potential barrier of the tunneling junction with the average height of \( \phi \), \( \beta \) is written as\(^{24} \)

\[
\beta = \frac{4\pi}{\hbar} \sqrt{2m\phi}
\]

Table 2. Positions of the Concerning Transmission Peaks for the A100 and A012 System at Zero, 0.5, and 1.0 V of Applied Bias

| thickness of Al2O3 (nm) | A100 | A012 |
|-------------------------|------|------|
|                         | 0 V  | 0.5 V | 1.0 V | 0 V  | 0.5 V | 1.0 V |
| 2                       | 1.255| 1.015| 0.755| 0.835| 0.595| 0.355|
| 3                       | 1.255| 1.015| 0.755| 0.835| 0.585| 0.345|
| 4                       | 1.255| 1.015| 0.755| 0.835| 0.585| 0.345|
| 5                       | 1.255| 1.015| 0.755| 0.835| 0.585| 0.335|
| 6                       | 1.255| 1.015| 0.755| 0.835| 0.585| 0.335|

The position is measured in the unit of eV.
where \( m \) is the mass of electron and \( h \) is the Planck constant.

The conductance of the junction system, calculated by eq 1, is governed by two factors: (1) the contact interface between Pt phase and Al\(_2\)O\(_3\) phase and (2) the intrinsic transport properties of Al\(_2\)O\(_3\). The effective contact conductance \( G_c \) is mainly determined by the characteristics of the contact interface, for which it is found that \( G_{c,100} = 0.0243 \, G_0 \) and \( G_{c,012} = 0.0216 \, G_0 \) for A100 and A012, respectively. This comparison of \( G_c \) indicates that the contact interface of A100 is tighter than that of A012 at the atomic level, which is consistently confirmed by observing the shorter bond lengths for Pt–Al and Pt–O as summarized in Table 1. However, it should be noted that it provides only a minor contribution to differentiating the conductance since the difference of \( G_c \) between A100 and A012 is not significant. This is also presented in the tunneling decay rate \( \beta \) that depends on the internal atomic and electronic structure of Al\(_2\)O\(_3\). As shown in Figure 2a, A100 gives higher decay rate (0.78/Å) than A012 (0.74/Å), which indicates that Al\(_2\)O\(_3\) provides slightly more insulation in A100 compared with A012. Based on the contact conductance and the tunnel decay rate, therefore, Al\(_2\)O\(_3\) demonstrates a similar insulating property in the junction system, regardless of the channel length at \( L < 7 \) nm as well as the crystallographic direction.

### 2.3.2. Insulating Electronic Structure of Al\(_2\)O\(_3\)

To investigate the detailed electronic structures of the junction system, the projected density of states (PDOS) are analyzed as a function of (1) the position in the electron-transport direction (\( z \)) and (2) electron energy (\( E \)). Figure 2b,c shows the PDOS contour of each system with the thickness of 2 nm as an example which has the highest conductance among the junction systems in this study. The second Pt layers at the Pt–Al\(_2\)O\(_3\) interface is located at the origin of position axis. From the PDOS plots, it is observed that the density of states has higher intensity at 0–5 Å (region I) and 20–25 Å (region II), indicating that PDOS at the interface (yellow and green) is slightly stretched out into the Al\(_2\)O\(_3\) phase for both A100 and A012 systems. In contrast, the Al\(_2\)O\(_3\) phase (dark blue) has very low PDOS between the electrodes. Along with the zero-bias conductance, which rapidly decreases as the thickness increases, this PDOS analysis substantiates the excellent insulating characteristics of the Al\(_2\)O\(_3\), even for such a thin thickness as 2 nm.

### 2.3.3. Electronic Structure Dependence of Transmission Functions

In Figure 3a,b, the zero-bias transmission spectrum, \( T(E,0 \, \text{V}) \) and PDOS for distinct positions (\( z \)) along the transport direction in A100 and A012 systems with 2 nm thickness are compared with each other in order to investigate the electron-transport mechanisms. As mentioned above, the major peak at zero-bias locates at \( E = E_{p,0V} = E_p + 1.26 \, eV \) and \( E_p + 0.84 \, eV \) for A100 and A012 systems, respectively. By analyzing PDOS as a function of the position in \( z \)-axis direction, (i) at the contacting top surface layer of the Al\(_2\)O\(_3\) at Pt–Al\(_2\)O\(_3\) interface (\( z = z_0 = 1.96 \, \text{Å} \) for A100 and 2.25 Å for A012); (ii) at 3 Å above the Al\(_2\)O\(_3\) surface-most layer (\( z = z_0 + 3 \, \text{Å} \)); (iii) at 8 Å above the Al\(_2\)O\(_3\) surface-most layer with (\( z = z_0 + 8 \, \text{Å} \)), we find several interesting features.

First, the PDOS has a negligible contribution to the major transmission peak at \( E_{p,0V} = E_p + 1.26 \, eV \) in A100 system as indicated by arrows in Figure 3a, as the position in \( z \)-axis direction moves into Al\(_2\)O\(_3\) phase (A → B → C). The absence of PDOS peak means that the A100 system has no dominant hybridized energy state influencing \( T(E) \). On the other hand, it is found that the major transmission peak for A012 system at \( E_{p,0V} = E_p + 0.84 \, eV \) in Figure 3b is correlated with a residing DOS peak at \( E_{p,0V} \) even up to 8 Å distance from the Al\(_2\)O\(_3\) top surface layer which belongs to the mid position of channel. From this result, it is inferred that the Pt–Al\(_2\)O\(_3\) hybridization states propagate into Al\(_2\)O\(_3\) phase in the A012 system, which enables a resonant quantum tunneling through the system.

By integrating the density of state over the energy range \( E_{p,0V} = 0.05 \, eV < E < E_{p,0V} + 0.05 \, eV \), local density of states (LDOS) at around the major peak position \( E_{p,0V} \) can be visualized in real space as presented in Figure 3c,d for A100 and A012, respectively. As implied from the PDOS above, the electronic states are highly localized at the interfacial atoms for A100 system, whereas the A012 system shows the protruding states toward the Al\(_2\)O\(_3\) phase. This indicates that the strong
transmission peaks at the junctions originate from the electronic hybridizations at Al₂O₃−Pt interface. In particular, atomic arrangement of Al₂O₃ in A012 system mediates relatively well-connected DOS features along the transport direction at the interface with Pt than that in A100 system.

2.4. Conductance within Finite-Bias Condition.  

2.4.1. I−V Characteristics. For further understanding of the material response to applied biases, the current−voltage characteristics were investigated for A100 and A012 systems using eq 4, especially focusing on the two smaller thicknesses (L = 2 nm and L = 3 nm). The finite-bias conductance is defined as \( G = I/V_b \) and \( \mu_L = E_F - eV_b/2 \) for left electrode and \( \mu_R = E_F + eV_b/2 \) for right electrode which define the bias window, \( \mu_L \approx \mu_R \). (c,d) Eigenchannels for the four energy states (\( E_F, E_{P,0V}, E_{P,0.5V}, E_{P,1V} \)). A100 shows no eigenchannels at left electrode region at \( E_{P,1V} \), while A012 shows well-developed eigenchannels on both electrode regions and even at the Al₂O₃ phase region at \( E_{P,1V} \).

Figure 4. I−V characteristics of the both systems with two different thicknesses: (a) \( L = 2 \) nm and (b) \( L = 3 \) nm. A012 system demonstrates a sudden increase of the conductance at higher bias region (>0.7 V), whereas A100 system shows linear increase of current with nearly a constant conductance up to 1.0 V.

Figure 5. (a,b) \( T(E) \) for each device with respect to bias voltages, where purple lines indicate the chemical potentials \( \mu_L = E_F + eV_b/2 \) for left electrode and \( \mu_R = E_F - eV_b/2 \) for right electrode which define the bias window, \( \mu_L \approx \mu_R \).

2.4.2. Transmissions and Eigenchannels. In order to elucidate the mechanism for the bias-dependent conductance, we investigate the evolution of major peak of \( T(E) \) and the corresponding eigenchannels as a function of bias voltages. By revisiting bias-dependent transmission functions for A100 and A012 systems in Figure 5, we clarify the direct origin of the conductance change with respect to the applied bias. At \( V_b = 0 \) V in Figure 5a,b, distinct transmission peaks are found at
$E_{p,0} = E_F + 1.26 \text{ eV}$ for the A100 system and $E_{p,12} = E_F + 0.84 \text{ eV}$ for the A012 system. When $V_b$ increases to 1.0 V, the transmission peaks shift to lower energy levels by $eV_b/2 = 0.5 \text{ eV}$, so that the peak becomes located at $E_{p,12} \approx E_{p,0} - eV_b/2 = E_F + 0.93 \text{ eV}$ for A100 and $E_F + 0.36 \text{ eV}$ for A012. Please note that the major transmission peak stems from the contact part of the Pt–Al2O3 junction because the extent of peak shift ($eV_b/2$) is exactly the same as that of chemical potential shift ($\mu_L/R = E_F \pm eV_b/2$) of the electrode. Considering the integration range (or bias window) of eq 4 for an applied bias, $\mu_L(E_F - eV_b/2) < \mu_L(E_F + eV_b/2)$, the major peak in A100 stays outside of the bias window ($E_F - 0.5 \text{ eV} < E < E_F + 0.5 \text{ eV}$ for $V_b = 1.0 \text{ V}$), while that in A012 comes into the integrating bias range. Estimating from the extent of peak shift, such a peak of A012 starts involving to electrical current at $V_b \approx 0.7 \text{ V}$, entailing a significant conductance change from $G_{3012}$ to $G_{31012}$. In addition to the shift, the $T(E)$ peak intensity of A100 under the zero-bias is found to diminish down to nearly zero when the bias ($V_b = 1.0 \text{ V}$) is applied. However, the peak of A012 is also weakened but still intense under the bias condition. The presence of the intense peak from A012 implies that its well-connected electronic states form solid electron transmission channels under the bias condition, while such electronic channels are easily disconnected as a result of external bias in the case of A100.

Therefore, in order to understand such electron transmission channels at various applied bias, the eigenchannel for each system is analyzed. Please note that the eigenchannel is a set of particular scattering states with a well-defined transmission probability, which is calculated using the NEGF approach.25 Figure 5c,d presents the eigenchannels for three different energy levels: $E_F$ at zero-bias, $E_{p,0}$, $E_{p,12}$, and $E_{p,12}$. As the bias voltage is increased, the connectivity of eigenchannel is gradually weakened. It is observed that there is a finite disconnection of eigenchannels for the electron transmission at $E_F$ within zero-bias condition. However, there is a striking difference in the distribution of the eigenchannels between A100 and A012 systems. At zero-bias condition, the strong transmission peak at $E_{p,0}$ is observed due to a well-connected eigenchannel throughout the device for both systems, while at the bias of 1 V, the overall features of eigenchannel at $E_{p,12}$ are greatly different from those at $E_{p,0}$. The eigenchannels of the A100 system are not found at the left electrode region at the bias of 1 V, which means that the scattering states contributing to electron transmission at the peak in equilibrium are now disconnected from the electrodes as the bias is applied. On the contrary, A012 system shows well-established eigenchannels throughout both electrode regions and even in Al2O3 phase at the peak position within the bias. It explains the different trend in major $T(E)$ peak evolution with respect to bias voltages, where the peak diminishes for A100 system but remains intense for A012 system under a finite applied bias.

### 3. CONCLUSIONS

In this study, the electron-transport characteristics of the Al2O3 phase in a few nanometer thickness is investigated using the DFT-NEGF method. In the Pt–Al2O3–Pt junction configuration, two different crystallographic orientations of the Al2O3 phase such as Al2O3(100) and Al2O3(012) are selected to scrutinize the orientation-dependency of the electron transport, which are denoted as A100 and A012, respectively.

The transmission spectra $T(E)$ are calculated for various thicknesses of the Al2O3 phase. At $(E - E_F) < 0$, $T(E)$ is monotonously decreased for both systems, while at $(E - E_F) > 0$, A100 and A012 have their own characteristic behavior of $T(E)$. It was found that each A100 and A012 has the major $T(E)$ peak at $E_F + 1.26 \text{ eV}$ and $E_F + 0.84 \text{ eV}$, respectively, under zero-bias condition, while such major peaks are shifted toward a lower energy level under a finite applied bias. By analyzing the conductance decay rate from $T(E)$, it is found that the overall conductance decay rates are similar to each other under zero-bias condition, regardless of the crystallographic orientation. Although A100 has a tighter contact interface between the Pt phase and Al2O3 phase, it has only a minor contribution to the overall conductance.

Even though both systems show distinctive electron transmission spectra, they have a similar thickness dependency in the conductance whose magnitude is decreased by around 3 orders of magnitude with respect to 1 nm the thickness increase of Al2O3 phase. Electron transmission spectrum also changes as a function of applied bias such that the major peaks in those transmission spectra are shifted toward lower energy level as the applied bias is increased. A noteworthy feature from the $I$–$V$ characteristics induced by the spectral shift is that the A012 system shows a significant change in conductance at 0.7 V in comparison with A100. For instance, the conductance of A012 is jumped at 0.7 V from $7.95 \times 10^{-12}$ S at low bias region $(0.1-0.7 \text{ V})$ to $47.63 \times 10^{-12}$ S for high bias range $(0.7-1.0 \text{ V})$, whereas that of A100 is just slightly increased from $4.44 \times 10^{-12}$ to $5.76 \times 10^{-12}$ S at 0.7 V. The fundamental reason for such drastic change is elucidated using the eigenchannels analysis, demonstrating that the eigenchannels for electron transmission were developed better throughout the A012 compared to the A100, which enhanced the conductance in nanoscale. This feature strongly presents that, unlike what we have observed from zero-bias limit, the contact interface plays an important role in nonequilibrium electronic transport within finite bias condition. We expect that this work will shed a light on the critical role of nanoscale contact in understanding and designing the behavior of nanometer-scale junction devices.

### 4. MODELING AND COMPUTATIONAL DETAILS

The crystalline Al2O3 phase has a space group of R3c, presenting electrically insulating property. Although it has been expected in general that the crystalline Al2O3 phase holds such insulating property even in a few nanometer thickness, the electron transport via the electronic structures of Al2O3 with a few nanometer thickness has not been thoroughly studied. Thus, in order to achieve its fundamental understanding, surface-cleaved Al2O3 systems are systematically modeled with various thicknesses ranging from 2 to 6 nm in the metal–insulator–metal configuration as shown in Figure 1a. In the systems, the two regions are defined: (i) left and right electrode regions configured by crystalline Pt phase and (ii) central scattering region configured by the insulating Al2O3. Pt(111) is modeled as an electrode surface with six layers. The dimension of the systems are $4.76 \times 12.99 \times 12.83 \text{ Å}$ and $4.81 \times 5.37 \times 14.13 \text{ Å}$ to accommodate Al2O3(100) and Al2O3(012), respectively. A noteworthy point is that the crystalline phase of Al2O3 has relatively large band gap of ~4.3 eV while the amorphous phase has a smaller band gap of ~3.2 eV, meaning that the crystalline phase of Al2O3 is more advantageous for better insulating property in integrated circuit devices.
All calculations are performed using generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof functional\textsuperscript{27} with norm-conserving pseudopotentials to describe the electron–ion interactions.\textsuperscript{28} Double-\(\zeta\)-polarization-quality numerical atomic orbital basis set optimized for corresponding GGA pseudopotentials is employed.\textsuperscript{29} A single \(k\) point shifted off from \(\Gamma\) point is sampled normal to the electrode-surface direction, so that the Brillouin zone is sampled with \(5 \times 5 \times 1\) and \(6 \times 2 \times 1\) Monkhorst–Pack \(k\)-point mesh with spin polarization for the electronic density of states and local charge density distribution, respectively, for both configurations.

We use TranSIESTA code\textsuperscript{8} for NEGF calculations and TBtrans for the transmission function calculations and current–voltage (I–V) characteristics. In the DFT-NEGF method, a transmission function \(T(E)\) is expressed in terms of a single Green function and spectral density function, which describes the coupling between device components\textsuperscript{9}

\[
T(E, V_b) = \text{Tr}[G_L(E, V_b)G(E, V_b)\Gamma_R(E, V_b)G^\dagger(E, V_b)]
\]

(3)

where \(\Gamma\) and \(G\) are a spectral density function and a Green function, respectively, and \(V_b\) is the bias voltage. Using the transmission function of eq 3, the steady-state electronic current is given by\textsuperscript{32,33}

\[
I(V_b) = \frac{2e^2}{h} \int dE (f_L(E) - f_R(E)) T(E, V_b)
\]

(4)

where \(h\) is the Planck’s constant and \(f\) is the Fermi–Dirac distribution function. Bias voltage \(V_b\) is defined as \((\mu_L - \mu_R)/e\), and \(\mu_{L/R}\) is the electrochemical potential of left/right electrode. In symmetric junctions, \(\mu_{L/R} = E_F \pm eV_b/2\) where \(E_F\) is the Fermi energy level of the system. Thus, the Fermi–Dirac distribution function is given as \(f = 1/[1 + \exp(E - E_F)/KT]\), and it can be rewritten with respect to left/right electrode as \(f_{L/R}(E) = 1/[1 + \exp(E - \mu_{L/R})/KT]\). For the current, \(I_0(V_b)\), linearly depending on applied finite bias, the conductance is simply defined as the slope of \(I-V\) relation

\[
G = \frac{1}{R} = \frac{\Delta I}{\Delta V_b}
\]

(5)

Here, please note that, in the limit of zero-bias (\(V_b \approx 0\) V) and zero-temperature (\(T \approx 0\) K), the conductance in Landauer formalism is given by\textsuperscript{32,33}

\[
G = \frac{1}{R} \left| \frac{dI}{dV_b} \right|_{V_b=0} = G_0 \frac{dE_F}{dV_b}
\]

(6)

where \(G_0 = 2e^2/h \approx 7.75 \times 10^{-5}\) S is defined as the quantum conductance. Therefore, \(T(E_F)\) simply stands for the conductance \(G\) in the unit of \(G_0\) at the condition of zero-bias and zero-\(T\) limits.

In this study, the transmission is normalized by the contact surface area for direct comparison between two insulating surfaces. To calculate surface Green functions for each electrode, we perform DFT calculations using 30 \(k\)-points for the calculation of scattering states along the surface-normal direction of Pt(111) surface, which provides highly converged transmission data. Considering the conductance data, we focus on the low-voltage coherent tunneling limit, for which the usual adiabatic approximation can be invoked and the coupling between the charge transport and the molecular vibration is negligible.

## ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04011.

Atomic contact configuration (PDF)

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**Notes**

The authors declare no competing financial interest.

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