Efficient Optimum Design of Metal with Strong Adhesion to Ceramics with a Combination of Orthogonal Array and Response-Surface Method

by

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A technology for efficiently designing an appropriate metal material with strong adhesion to a ceramic material was developed by using a combination of an orthogonal array and a response-surface method, and it was applied to the interface adhesion between metals and an example ceramic, alumina (\(\text{Al}_2\text{O}_3\)) in nanoscale thin-film devices. In this optimum-design technology, at the first step, important factors that significantly influence the adhesion strength were selected from various factors that characterize metal materials by using an orthogonal array with molecular simulations. As a result, the short-side and long-side lattice constants \(a\) and \(b\) were selected from four metal-material factors \((a, b, \text{the electronegativity, } E, \text{and the surface energy density, } S)\). At the second step, the adhesion strength was described as a function of the selected important factors by using a response-surface method. From this function, the ideally most appropriate values for \(a\) and \(b\) that made the adhesion strength maximum were obtained. The obtained optimum values for \(a\) and \(b\) agreed well with the lattice constants of the ceramic (alumina). At the third step, the most appropriate metal material whose lattice constants were close to the optimum values, which were the lattice constants of the ceramic (alumina), was selected by use of the molecular simulation results of lattice constants. As a result, a Pd alloy with Ni, whose lattice constants were almost the same as the optimum values, was selected as the most appropriate metal material with the strongest adhesion to the ceramic (alumina).

Key words:

Adhesion strength, Metal materials, Ceramic, Response-surface method, Molecular simulation, Orthogonal array

1 Introduction

Recently, high-permittivity ceramic materials such as alumina (\(\text{Al}_2\text{O}_3\)) and hafnia (\(\text{HfO}_2\)) are used to improve the performance and reliability of nanoscale thin-film devices (for example, GaN power devices\(^1\) and sensors). Because the devices are expected to be used at places of high temperatures and high humidity in the upcoming IoT (Internet of Things) era, the interface adhesion between ceramics and metal materials needs to be strong to realize the sufficient device reliability. However, it is difficult to select an appropriate material that has strong adhesion to another material by using a conventional trial-and-error approach. So, recently many researchers have paid attention to a materials-informatics technique that can select an appropriate material by using a response-surface method\(^2\)\(^,\)\(^3\) with computer simulation and experimental data. However, although the response-surface method can determine the best material, it needs a long time to obtain results because it uses a lot of data to clarify the dependence of objective material property on material factors when the number of factors is large\(^2\). This problem is called ‘Problem 1’ in this paper.

On the other hand, an orthogonal array\(^3\)\(^,\)\(^4\) was useful in selecting important factors that significantly influence objective material property from various material factors such as lattice constants and surface energy density by using a small amount of data. In the paper\(^6\), the author showed that the lattice mismatches were important factors for adhesion strength between metals and resins and that reducing the lattice mismatches was effective for improving the adhesion strength. In that case, the author was able to determine the best metal material because the adhesion strength is a monotonically decreasing function of lattice mismatches. However, the orthogonal array would not have been able to determine the best material if the adhesion had not been a monotonic function. Generally, an orthogonal array is not able to determine the best material, that is, the optimum solution, if a material property is not a monotonous function of parameters. This problem is called ‘Problem 2’ in this paper.

In order to solve Problems 1 and 2 described above, by combining an orthogonal array\(^1\)\(^,\)\(^2\) with the response-surface method\(^2\), the author has developed a technology for efficiently determining the best material by using only important selected factors. In the previous papers\(^6\)\(^,\)\(^5\), the metal and ceramic with strong adhesion to a resin were selected by using this efficient technology. In those papers, this technology was found to be effective for maximizing the adhesion to resins, which have small surface energy density (smaller than 0.05 J/m\(^2\))\(^6\). However, it is not clear whether this technology can be applied to the adhesion between metals and ceramics, both of which have large surface energy density (larger than 0.1 J/m\(^2\))\(^6\). So, in this paper, the author will clarify whether this technology can be applied to the selection of a metal material that has strong adhesion to a ceramic (alumina). Furthermore, the author will also clarify whether the surface energy density is an important factor for the adhesion between metals and ceramics, while the surface energy density is not an important factor for the adhesion between resins and metals\(^4\) and for the adhesion between resins and ceramics\(^5\). In the field of thin-film electronics
devices, metal materials are used as electrodes while ceramics are often used as insulating materials. When the adhesive fracture occurs at the interface between metal materials and the ceramics in electronics devices, mechanical or electrical failures are caused. So it is important to select appropriate metal materials with strong adhesion to ceramics.

In the technology that the author has developed, at the first step, the important factors that significantly influence the adhesion strength are selected from metal-material factors such as lattice constants and surface energy density that characterize metal materials by using an orthogonal array and molecular simulations. At the second step, by using a response-surface method, the adhesion strength is described as a function of the selected important factors, and the most appropriate values of the factors that make the adhesion strength maximum are obtained. At the third (final) step, appropriate metal materials whose factors are close to the most appropriate values are selected.

In this study, the author used alumina (Al₂O₃) as an example of ceramic because alumina is often used in electronics devices. Then, the best metal material with strong adhesion to alumina was selected by using the optimum design method.

2 Optimum Design Technology for Selecting Materials

2.1 Overview of Optimum Design Technology

The basic idea of material design in the author’s technique shown in Fig. 1 is to select a material whose factors A, B, C, ⋯ that optimize an objective material property, F, by describing the property as a function of material factors (i.e., F(A, B, C, ⋯)). In this study, the objective material property, F that the author wants to optimize is the adhesion to a ceramic material, and the factors A, B, C, ⋯ that the author focus on are the lattice constants (geometrical crystal factors), the electronegativity (an electric factor), and the surface energy density (an energetic factor) of a metal material.

Although other factors such as misfit dislocations and interface roughness generally influence the adhesion, these factors are neglected in this paper because this paper’s application devices are nanoscale thin-film devices in which few defects and little interface roughness exist.

To describe the material property F as a function of material factors A, B, C, ⋯, a number of data of experiments or simulations to interpolate are needed. If too many factors are used, many data are needed for interpolation and it takes too much time to obtain the function F(A, B, C, ⋯). So the author uses orthogonal-array analysis to select only the important factors that strongly influence the adhesion (objective material property).

The overview of the material-design technology is shown in Fig. 1. This figure shows that the method consists of three steps. At the first step, by using the orthogonal-array sensitivity analysis with molecular simulations, the important material factors that significantly influence an objective material property are selected from material factors (the lattice constants, the electronegativity, and the surface energy density) that characterize metal materials. In the sensitivity analysis, the results of molecular simulations of the objective material property that is paid attention to are used as input data. At the second step, the objective material property, which is the adhesion in this paper, is described as a function of the selected important factors by using a response-surface method with the molecular-simulation results that are also used at the first step. By using this function, the most appropriate values of the factors that optimize the objective material property, which is adhesion strength in this paper, are determined. At the third (final) step, the materials (metal materials, in this paper) whose factors are close to the most appropriate values are selected.

Fig. 1 Overview of material-design technology.
alumina (Al₂O₃) layer seen in the [001] direction is shown in Fig. 2. The molecular-simulation model that the author used in this study is an interface between alumina and a metal film, as shown in Fig. 3. This simulation model was made by using “Materials Studio®” software from Dassault Systemes BIOVIA. The sizes of alumina in this model (Fig. 3) are set at 3.2 nm, 3.4 nm, and 1.8 nm in the x, y, and z directions, respectively while those of metals are set at 2.8 nm, 2.9 nm, and 1.6 nm in the x, y, and z directions, respectively. These sizes are considered to be large enough to calculate the adhesion strength because from the past molecular-dynamics simulations⁷⁻⁹ it was found that the adhesion strength between the ceramic and metal materials was almost independent of the sizes when the size in each direction was larger than 1.5 nm, as shown in Chapter 5.

In this study, the adhesion strength was evaluated by calculating the adhesive fracture energy⁶⁻⁹ that was defined as the difference between the area density of potential energy of the ceramic/metal attached state (Fig. 3(a)) and that of the ceramic/metal detached state (Fig. 3(b)). The fracture energy was calculated by using molecular dynamics with a universal force field¹⁰, and the temperature was kept at 20°C by using a velocity-scaling method¹¹. As described in Ref. 10, the universal force field used in molecular-dynamics simulations is determined based on the element, its hybridization, and its connectivity. As explained in these references, the potential energy of this force field is expressed as a sum of valence or bonded interactions and nonbonded interactions in the following equation.

\[ P = P_R + P_s + P_\omega + P_{\text{el}} + P_{\text{cl}} \]  

Here, bond stretching (\( P_R \)), bond angle bending (\( P_s \)), dihedral angle torsion (\( P_\omega \)), and inversion terms (\( P_{\text{el}} \)) are valence interactions. On the other hand, van der Waals (\( P_{\text{el}} \)) terms and electrostatic (\( P_{\text{cl}} \)) terms are nonbonded interactions. The universal force field expressed by Eq. (1) was employed in this study because the results obtained from this force field with the effect of atomic charges were confirmed to agree well with the results obtained with first-principle quantum simulations (density-functional-theory simulations) by using the software, Dmol3, from Dassault Systemes BIOVIA. As shown in Table 4 in Chapter 3, the difference between the results of molecular-dynamics simulations and those of the first principle quantum simulations were smaller than 1%.

The electrostatic (\( P_{\text{el}} \)) terms in Eq. (1) are long-range Coulomb interactions induced by the partial charges. So, the atoms were kept free to move, and no periodic boundary conditions are set so that long range electrostatic forces from the replica molecular models induced by the periodic boundary conditions do not influence real molecular models.

![Fig. 4 Lattice constants of the bottom layer of metal whose crystal planes are fcc(111), hcp(0001), or bcc(110).](image)

### 2.3 Material Factors Used at the First Step

In this section, the material factors of metals are explained. The author focused on four factors (the short-side and long-side lattice constants, \( a \) and \( b \), the electronegativity, \( E \), and the surface energy density, \( S \)) of the metal film, and then investigated which factors significantly influence the adhesion strength. The short-side and long-side lattice constants \( a \) and \( b \) are defined at the crystal planes of the bottom metal layer, as shown in Fig. 4. The lattice constants of alumina are also defined at the top oxygen surface in the way similar to metals (Fig. 4), as shown in Fig. 5. In this study, the \( xy \)-plane in Figs. 4 and 5 was set parallel to the crystal plane of highest atomic density, which is the energetically stable crystal plane. This plane appeared at the surface when films were deposited by using physical vapor deposition (PVD). For example, by using PVD, the author obtained single-orientation films such as hexagonal Al₂O₃(001) and cubic HfO₂(111), whose X-ray diffraction profile is shown in Ref. 13). In case of metals, the crystal planes of highest atomic density such as face-centered-cubic (fcc) Pt(111), hexagonal-close-packed (hcp) Ti(0001), and body-centered-cubic (bcc) Mo(110) were observed to appear at the surface by using PVD. The lattice constants \( a \) and \( b \) in Figs. 4 and 5 are defined at these surfaces.

The initial \( xy \) coordinates of the atom at the center of the bottom metal layer were set at the same coordinates as those of the oxygen atom at the center of the top Al₂O₃ layer while the initial \( z \) coordinate of the bottom metal-layer atom was set so that the distance between the bottom metal layer and the top oxygen layer in the \( z \) direction was the same as the interplanar spacing in the metal. By adopting these initial
positions, large interatomic force to cause the lattice disorder did not occur, and the single-crystal structure observed in experiments (Chapter 4) was obtained in simulations.

Electronegativity, $E$, is defined as the ability of an atom to attract electrons towards itself, and is shown in Ref. 12.

The surface energy density of the metals, $S$, which is the energy density required to create a surface from bulk, is defined as half of the difference between the area density of potential energy of the surface-connected state (Fig. 6(a)) and that of the surface-separated state (Fig. 6(b)). The surface energy density, $S$ was calculated by using molecular dynamics with a universal force field(10).

Fig. 5 Oxygen-atom configuration of the top (001) surface in alumina and interface lattice constants.

2.4 Orthogonal Array Used at the First Step

At the first step of the material-design technology (Fig. 1), the important material factors (metal factors) that significantly influence the objective material property (adhesion strength) are selected by clarifying the dependence of the adhesion strength on the four metal factors. When we investigate the dependence, we usually change the value of one factor with the other three factors fixed. However, it is time-consuming to clarify the dependence by using this method. Accordingly, the author used the orthogonal-array design methodology(9), which is known to be effective for efficiently designing macro-scale structures such as propeller fans and diaphragms. In this methodology, when there are four material factors, only nine simulations or experiments shown in an L9 orthogonal array (see Table 1) are needed to clarify the important factors on which the adhesion strength strongly depends(9). Here the author set Level 1 (small values), Level 2 (medium values), and Level 3 (large values) of the four factors at the regions shown in Table 2. The author set these values of levels so that each level has about one third of single-element metals. By looking into the data of molecular dynamics simulations, the author was able to find nine metal films that correspond to the nine sets of factors shown in Table 1. These nine metal films are shown in Table 3. When it is impossible to set three levels for each factor, the orthogonal array cannot be used. In such case, the first stage in Fig. 1 has to be skipped, and all the factors have to be dealt with at the second stage, where more data than those of orthogonal array are needed for interpolation. By using the nine metal films shown in Table 1 (i.e., Table 3), the sensitivity(3) for the adhesive fracture energy(7-9) between the metal film and the ceramic was calculated. By applying sensitivity analysis(3) based on orthogonal arrays to the fracture-energy data calculated for the nine metal films in Table 1 (i.e., Table 3), the sensitivity of Level $j$ of the $i$-th factor, $W_{ij}$ is given by:

$$W_{ij} = 10 \log [(P_i - Q_j)/n]$$

where

$$P_i = (D_{a1} + D_{a2} + \cdots + D_{ax})/n$$

and

$$Q_j = (D_{b1} + D_{b2} + \cdots + D_{bx})/n - (n - 1).$$

Here, $D_{ak}$ is the $k$-th fracture-energy datum that belongs to Level $j$ of the $i$-th factor, and $n$ is the number of the data that belong to Level $j$ of the $i$-th factor.

Table 1: L9 orthogonal array in the case of four factors.

| Condition | 1st factor: Short-side lattice constant $a$ | 2nd factor: Long-side lattice constant $b$ | 3rd factor: Electronegativity $E$ | 4th factor: Surface energy density $S$ |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1         | Level 1 | Level 1 | Level 1 | Level 1 |
| 2         | Level 1 | Level 2 | Level 2 | Level 2 |
| 3         | Level 1 | Level 3 | Level 3 | Level 3 |
| 4         | Level 2 | Level 1 | Level 2 | Level 2 |
| 5         | Level 2 | Level 2 | Level 3 | Level 1 |
| 6         | Level 2 | Level 3 | Level 1 | Level 2 |
| 7         | Level 3 | Level 1 | Level 3 | Level 2 |
| 8         | Level 3 | Level 2 | Level 1 | Level 3 |
| 9         | Level 3 | Level 3 | Level 2 | Level 1 |

Table 2: Factors and levels for metal films.

| Condition | 1st factor: Short-side lattice constant $a$ (nm) | 2nd factor: Long-side lattice constant $b$ (nm) | 3rd factor: Electronegativity $E$ | 4th factor: Surface energy density $S$ (J/m$^2$) |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Level 1   | $a < 0.280$ | $b < 0.450$ | $E < 1.60$ | $S < 0.5$ |
| Level 2   | 0.280 $\leq a < 0.310$ | $0.450 \leq b < 0.480$ | $1.60 \leq E < 1.9$ | $0.5 \leq S < 2.0$ |
| Level 3   | 0.310 $\leq a < 0.480$ | $b < 0.480$ | $1.9 \leq E < 2.0$ | $2.0 \leq S$ |
Table 3 Nine metal films corresponding to Table 1 (L9), where Levels 1, 2, and 3 are shown in Table 2.

| Metal | 1st factor: a | 2nd factor: b | 3rd factor: E | 4th factor: S |
|-------|---------------|---------------|---------------|---------------|
| Be    | 0.227         | 0.393         | 1.57          | 0.497         |
| Zn    | 0.286         | 0.464         | 1.65          | 0.508         |
| Pt    | 0.277         | 0.480         | 2.28          | 2.47          |
| V     | 0.303         | 0.428         | 1.63          | 2.25          |
| Sn    | 0.281         | 0.459         | 1.96          | 0.473         |
| Ti    | 0.295         | 0.511         | 1.54          | 1.89          |
| Mo    | 0.315         | 0.445         | 2.16          | 1.98          |
| Nb    | 0.330         | 0.467         | 1.50          | 3.06          |
| In    | 0.324         | 0.563         | 1.78          | 4.42          |

According to the sensitivity-analysis method\(^3\) based on orthogonal arrays, the factors whose increase from Level 1 to Level 3 significantly influences the sensitivity \(W_0\) are important in optimizing the adhesion strength, and they are selected as important factors at the first step of the material-design technology (Fig. 1). At the second step in Fig. 1, the adhesion strength is described as a function of the selected factors by interpolating the nine fracture-energy data corresponding to the L9 orthogonal array in Tables 1 and 3 by use of a response-surface method.

2.5 Response-Surface Method

At the second step of the material-design technology (Fig. 1), a response-surface method is used to describe the objective material property (adhesion strength) as a function of the important factors selected by use of the orthogonal-array analysis explained in Section 2.4. In this study, the author employed a response-surface method\(^4,5\), so called Kriging method, which is often used in geostatistics and mechanical structure design. The schematic view of one-dimensional data interpolation by use of the Kriging method is shown in Fig. 7. In this method, the function curve is made so that all the data points used for interpolation are on the curve. The basic idea of the Kriging method is to predict the value of a function at a given point by computing a weighted average of the known values of the function in the neighborhood of the point. The theory derives a best linear unbiased estimator, based on assumptions on covariances, and is mathematically related to regression analysis. By using the Kriging method, the adhesion strength is described as a function of the important material factors (metal films). By using this function, the most appropriate values of material factors that maximize the adhesion strength can be determined. At the third (final) step, appropriate materials (metal films) whose factors are close to the most appropriate values are selected.

3 Material-Selection Results

The calculated adhesive fracture energy data corresponding to the L9 orthogonal array (Table 3) are shown as \(D\) in Table 4. In this table, the results of the first principle quantum simulations are also shown as \(F\). The relative difference between \(D\) and \(F\) is confirmed to be smaller than 1%. Figure 8 shows the sensitivity, \(W_0\) calculated by using the fracture energy data (Table 4) and Eqs. (2), (3), and (4). From Fig. 8 it is found that the adhesive fracture energy (adhesion strength) strongly depends on the 1st and 2nd factors (the short-side and long-side lattice constants), while the fracture energy does not strongly depend on the 3rd and 4th factors (the electronegativity, and the surface energy density). Thus, the short-side and long-side lattice constants, \(a\) and \(b\), were selected as important factors at the first step of the material-design technology shown in Fig. 1.

Table 4 Calculated adhesive fracture energy data corresponding to Table 3 (L9).

| Metal | 1st factor: a | 2nd factor: b | 3rd factor: E | 4th factor: S | \(D\) (J/m²) | \(F\) (J/m²) |
|-------|---------------|---------------|---------------|---------------|-------------|-------------|
| Be    | 1.089         | 0.894         |               |               |             |             |
| Zn    | 0.569         | 0.467         |               |               | 0.569       | 0.467       |
| Pt    | 1.42          | 1.43          |               |               | 1.42        | 1.43        |
| V     | 0.743         | 0.745         |               |               | 0.743       | 0.745       |
| Sn    | 1.02          | 1.02          |               |               | 1.02        | 1.02        |
| Ti    | 0.874         | 0.877         |               |               | 0.874       | 0.877       |
| Mo    | 0.618         | 0.621         |               |               | 0.618       | 0.621       |
| Nb    | 0.845         | 0.848         |               |               | 0.845       | 0.848       |
| In    | 0.726         | 0.729         |               |               | 0.726       | 0.729       |
At the second step of Fig. 1, the author described the adhesive fracture energy as a function by interpolating the nine data in Table 4 with the Kriging method. The obtained function is shown in Fig. 9. The ideally most appropriate values of the important factors (the short-side and long-side lattice constants, \(a\) and \(b\)) are obtained as \(a=0.275\) nm and \(b=0.476\) nm by using the gradient of the obtained function. Because these values are the same values of alumina’s lattice constants shown in Fig. 5, it is found that the lattice matching between the metal film and the ceramic (alumina) is the most important in increasing the adhesion strength between them.

At the third (final) stage of Fig. 1, the appropriate materials (metal films) whose factors are close to the most appropriate values \((a=0.275\) nm and \(b=0.476\) nm, which are alumina’s lattice constants) are selected. The author selected a Pd-21at.%Ni film because the molecular simulation showed that the lattice constants of this alloy film [\(a=0.275\) nm and \(b=0.476\) nm] are the same as alumina’s lattice constants. In the Pd-21at.%Ni film, Ni atoms are randomly positioned at fcc-Pd-lattice sites. This uniform structure was obtained by using physical vapor deposition (PVD). By calculating the adhesive fracture energy defined in Section 2.2, the value for the Pd-21at.%Ni film was obtained as 1.69 \(\text{J/m}^2\), which is higher than all the values shown in Table 4. To clarify the reason that Pd-21at.%Ni has strong adhesion to the ceramic, the author visualized the atomic configuration of the interface between the ceramic (alumina) and Pd-21at.%Ni, as shown in Fig. 10. Because Fig. 10 shows that almost all oxygen atoms of the top alumina (Al₂O₃) layer can be seen through near the centers of triangles made of metal atoms (Pd or Ni atoms at triangular lattice points) and that the configuration of the oxygen atoms are in harmony with metal atoms, the accumulation of atomic interactions caused by this harmony is considered to lead to the strong adhesion. The configuration of Zn/Al₂O₃ interface whose adhesive fracture energy (1.56 \(\text{J/m}^2\)) is also large has similar harmony and regularity to Fig. 10, as shown in Fig. 11.

On the other hand, the atomic configuration of the Mo/Al₂O₃ interface whose adhesive fracture energy (0.618 \(\text{J/m}^2\)) is smaller than those of the Pd-21at.%Ni/Al₂O₃ and Zn/Al₂O₃ interfaces is shown in Fig. 12. This figure shows that oxygen atoms can not be seen through near the centers of triangles made of metal atoms. The harmony seen in Fig. 10 is not seen in Fig. 12. So metal atoms are not positioned at energetically stable sites in Fig. 12 in spite of high surface energy. Accordingly, the accumulation of atomic interaction at the Mo/Al₂O₃ interface is smaller than that at the interface shown in Figs. 10 and 11. Thus, the accumulation of atomic interactions caused by the lattice matching seen at the Pd-21at.%Ni/Al₂O₃ and Zn/Al₂O₃ interfaces (Figs. 10 and 11) is confirmed to lead to the strong adhesion.

Fig. 8 Results of calculated sensitivity.

Fig. 9 Function obtained with a response-surface method (Kriging method).

Fig. 9 Function obtained with a response-surface method (Kriging method).

Fig. 10 Configuration at Pd-21at.%Ni/Al₂O₃ interface.

Fig. 11 Configuration at Zn/Al₂O₃ interface.
4 Comparison between Simulations and Experiments

To confirm the effectiveness of the molecular-dynamics simulation technique described in Chapters 2 and 3, the author conducted a scratch test on the film-laminated structure (scratch tester: CSR-02 made by Rhesca Co., Ltd.) and compared the test results with the simulation results. Recently, more advanced methods for measuring adhesion strength have been proposed in a number of research papers. However, these advanced methods were very difficult to apply to fairly strong interfaces such as the interface between alumina and Zn. Accordingly, a simple scratch-testing method that was applicable to the Zn/Al2O3 interface was employed. In the scratch testing, a diamond indenter with a tip radius of 5 μm makes the dynamic indentations. During the measurement, load is gradually increased and when it reaches a critical load, adhesive fracture occurs at the interface. The adhesion strength is determined by measuring the critical load, L, at which the adhesive fracture occurs.

The author used 0.1-μm-thick alumina films deposited on silicon substrates by using physical vapor deposition (PVD) for the scratch test. For the metals, the author used the five metal films (Pd-21at.%Ni, Zn, Pt, Ti, and Mo), four of which are listed in Table 4. These metal films were deposited on the alumina film by using physical vapor deposition (PVD), and the thickness of each film was set at the same as that used in the simulations by controlling the deposition time. By using the 0-20 scheme of the X-ray diffraction (XRD) analysis, the author selected the specimens with the single diffraction peak that shows single-orientation films, which were obtained when the deposition temperature was from 20°C to 200°C. An example result of the XRD for Pt/Al2O3 (Fig. 13) shows the single orientation of Pt and Al2O3. Because the author did not observe the spectrum profile that showed the presence of oxygen-terminated alumina and lattice defects in the results of X-ray photoelectron spectroscopy (XPS), almost the same structure as the simulation model was considered to be obtained in this experiment.

The adhesive fracture energy, D, obtained from molecular simulations and the critical load, L, obtained from the scratch test of the interfaces between the alumina film and metal films are compared in Fig. 13. Because the linear relationship can be seen between simulations and experiments, the adhesion calculation method is found to be effective for determining the adhesion strength. Furthermore, from the results shown in Fig. 13, it is experimentally confirmed that the Pd-21at.%Ni film, which was selected by using our material-design technology (Fig. 1), has the strongest adhesion to the ceramic (alumina). Thus, our technique for selecting appropriate materials with a combination of an orthogonal array and a response-surface method is considered to be effective for selecting a metal material that has strong adhesion to the ceramic (alumina).

5 Discussions

In this paper, the application of a materials design technology to nanoscale thin-film devices is discussed. Figure 15 shows an example of the size dependence of the adhesive fracture energy for the Pt/Al2O3 interface, where the sizes of Pt and Al2O3 are varied with the sizes in the x, y, and z directions kept equal. The adhesive fracture energy was almost independent of the material sizes when the size in each direction was larger than 1.5 nm, as shown in Fig. 15. However, when the size of the materials is larger than the nanoscale, the effect of factors such as misfit dislocations and interface roughness, which are neglected in this paper, must be taken into account in addition to a, b, c, and S. So, more than four factors must be used. In this case, an L9 orthogonal array is not enough to analyze the sensitivity, and an L18 or L36 orthogonal array, where 18 or 36 simulation data are needed instead of 9 data, must be used. The application to these issues will be reported in another paper.

6 Summary

A technique for efficiently selecting a metal material with strong adhesion to a ceramic with a combination of an orthogonal array and a response-surface method was used to
select an appropriate metal that has strong adhesion to alumina in nanoscale thin-film devices. In this technique, at the first step, important factors that significantly influence the adhesion strength to the ceramic were selected from various factors that characterize metals by use of an orthogonal array with molecular simulations. At the second step, the adhesion strength was described as a function of the selected important factors by using a response-surface method (Kriging method). From this function, the most appropriate values of the important factors that made the adhesion strength maximum were obtained. At the third step, the most appropriate metal materials whose important factors were close to the most appropriate values were selected. By carrying out these procedures on an example ceramic (alumina), which is often used in GaN power devices, the following results were obtained.

1) By using the sensitivity analysis based on an orthogonal array, the short-side and long-side lattice constants, \( a \) and \( b \) were selected as the important factors from four metal-film factors (the lattice constants, \( a \), \( b \), the electronegativity, \( E \), and the surface energy density, \( S \)).

2) By describing the adhesive fracture energy as a function of the important factors (the short-side and long-side lattice constants, \( a \) and \( b \)), the ideally most appropriate values for \( a \) and \( b \) that made the adhesion strength maximum were obtained as the values that agreed well with the lattice constants of the ceramic (alumina).

3) The most appropriate metal film whose lattice constants were the optimum values, which were almost the same as the lattice constants of the ceramic (alumina), was selected. As a result, a Pd alloy with Ni was selected as the most appropriate metal with the strongest adhesion to a ceramic (alumina).

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