Original Papers

Design of Ceramic Materials with Strong Adhesion to B-DNA with an Efficient Materials Informatics Technology

by

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Appropriate ceramic materials with strong adhesion to B-DNA, which is an eco-friendly (biodegradable and biocompatible) organic material considered to be used for electronics devices, were selected by using a combination of an orthogonal array and a response-surface method. In this technology, at the first stage, the important factors that significantly influence the adhesion strength were selected from various factors that characterize ceramic materials by using an orthogonal array with molecular dynamics simulations. As a result, the short-side and long-side lattice constants ($a$ and $b$) were selected from four ceramic-material factors ($a$, $b$, the surface energy, $S$, and the cohesive energy, $C$). At the second stage, the adhesion strength was described as a function of the selected important factors by using a response-surface method. From this function, the optimal solution (the best values for $a$ and $b$) that made the adhesion strength maximum was obtained. The best values for $a$ and $b$ were obtained as 0.340 nm and 0.589 nm, respectively. At the third stage, the best ceramic material whose lattice constants were equal to the best values ($a = 0.340$ nm and $b = 0.589$ nm), which are B-DNA's lattice constants, was selected by use of the simulation results of lattice constants. As a result, $ZrO_2$/$CaO/HiO_2$, $HiO_2$/$CaO/SrO$ and $CaO/SrO/HiO_2$, whose lattice constants were $a = 0.340$ nm and $b = 0.589$ nm, were selected as the best ceramic materials with the strongest adhesion to B-DNA. The results show that lattice matching is important in the adhesion between B-DNA and ceramics.

Key words:

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

1 Introduction

In these days, environmentally friendly materials such as biodegradable plastics and biocompatible materials are considered to be used for electronics packaging, following the trend concerning the sustainable development goals (SDGs). When these materials are used in electronics devices, the materials with strong adhesion to the eco-friendly materials have to be selected to prevent the adhesive fracture. So, the author tried to design the best materials with strong adhesion to the eco-friendly materials by using materials-informatics (MI) technology based on a combination of an orthogonal array[1] with the response-surface method[2]. In this paper, B-form deoxyribonucleic acid (B-DNA) was used as an example biodegradable and biocompatible material.

Recently, B-DNA has been considered to be employed as an anisotropic conductive film[3] and as a substrate for biocompatible flexible devices[4]. It is well-known that B-DNA is easier to get than A-DNA and Z-DNA and that a lot of B-DNA can be easily gotten from Salmon testes[5] with low cost. However, it is not clear whether B-DNA has strong adhesion to another material. So, the purpose of this study is the selection of ceramic materials with strong adhesion to B-DNA. Generally, 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 materials informatics techniques, which can select an appropriate material by using information technology (for example, response-surface methods[6] and machine learning) with computer simulation or experimental data. However, the information technology sometimes needs a long time to obtain results because it usually uses a lot of data and parameters (materials factors). For example, in Ref. 2), a response-surface method was applied to optimize materials properties by use of a lot of data, which needed much time to analyze. So, by combining an orthogonal array[1] with the response-surface method[2], the author has developed a materials informatics (MI) technology for efficiently selecting an inorganic material with strong adhesion to an organic material (DNA or a resin). This paper describes the application of this technology to the selection of a ceramic material that has strong adhesion to B-DNA.

In the technology that the author has developed, at the first stage, the important factors that significantly influence the adhesion strength are selected from ceramic-material factors such as lattice constants and surface energy that characterize ceramic materials by using an orthogonal array[1] and molecular dynamics simulations[5]. At the second stage, by using a response-surface method[2], the adhesion strength is described as a function of the selected important factors, and the most appropriate values (optimal solutions) of the factors that make the adhesion strength maximum are obtained. At the third (final) stage, appropriate ceramic materials whose factors are close to the most appropriate values are selected.

In this study, the author used B-DNA as an example because B-DNA is considered to be used in electronics devices[3, 4] alongside another eco-friendly organic materials, which was described in another paper. Then, the best ceramic materials with strong adhesion to B-DNA were selected.

2 Material-Design Technology

2.1 Material-Design Technology Made of Three Stages

The basic idea of material design in the author's technology shown in Fig. 1 is to select a material whose

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factors $A$, $B$, $C$, \ldots are close to the most appropriate values $A_0$, $B_0$, $C_0$, \ldots that optimize an objective material property, $P$, by describing the property as a function of material factors (i.e., $F(A, B, C, \cdots)$). In this study, the objective material property ($P$) that the author wants to optimize is the adhesion to B-DNA, and the factors $A$, $B$, $C$, \ldots that the author focuses on are the lattice constants (geometrical factors), the surface energy, and the cohesive energy of a ceramic material (energetic factors). Although other factors such as surface steps, oxygen defects, and interface roughness generally influence the adhesion, these factors are neglected in this paper because the application devices of this paper are thin-film devices in which few defects and little interface roughness exist.

To describe the material property ($F$) as a function of material factors $A$, $B$, $C$, \ldots, a number of data of experiments or simulations to interpolate are needed. If too many factors are used, a lot of data are needed for interpolation and it takes too much time to obtain the function $F(A, B, C, \cdots)^2$. So, the author uses orthogonal array analysis$^3$ to select only the important, dominant 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 stages. At the first stage, by using the orthogonal-array sensitivity analysis$^1$ with molecular dynamics simulations$^5$, the important material factors that significantly influence an objective material property are selected from material factors (the lattice constants, the surface energy, and the cohesive energy) that characterize ceramic materials. In the sensitivity analysis, the results of molecular dynamics simulations of the objective material property that is paid attention to are used as input data. At the second stage, 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$^2$ with the simulation results, which are also used at the first stage. 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) stage, the materials (ceramic materials, in this paper) whose factors are close to the most appropriate values are selected.

### 2.2 Simulations Used at the First and Second Stages

As shown in Fig. 1, molecular dynamics simulations are used in the first and second stages. So, the method of the simulations is explained in this section. In this paper, B-DNA (Fig. 2), whose interbase spacing is 0.34 nm, is used because B-DNA is considered to be used in electronics devices for the reason that B-DNA has strong mechanical strength. The simulation model of B-DNA is shown in Figs. 2 and 3. Figure 2 shows an overview of B-DNA, where the schematic structures of bases (Guanine, Cytosine, Adenine, and Thymine) are shown. Figure 3 shows the details of the lattice structure of B-DNA, and the lattice constants. The simulation model that the author used in this study is an interface between B-DNA (Figs. 2 and 3) and a ceramic multilayer, as shown in Fig. 4. By using the ceramic multilayer made up of atomic-scale thin films shown in Fig. 4, instead of using a single ceramic material, it was possible to control the lattice constants of the top layer shown in Fig. 5 almost freely. This simulation model was made by using “Materials Studio®” software from Dassault Systemes BIOVIA. Twelve B-DNA molecules (three layers of four molecules), one of which is shown in Fig. 3, were used as the B-DNA film model.
Next, the size of the ceramic-multilayer model shown in Fig. 4 is explained in this paragraph. From the past molecular dynamics simulations\(^6\) it was found that the adhesion strength between organic and inorganic materials was almost independent of the thickness when the thickness was larger than 2 nm. So, in this study, the author set the thickness of the ceramic layer at 3 nm. The thickness of Ceramics 1, 2, and 3 in Fig. 4 was set at 1 nm. These values were determined to make it easy to control the lattice constants of the top layer of the ceramic multilayer. The sizes of the ceramics in the \(x\) and \(y\) directions are set at 10 nm and 10 nm, which are large enough for attachment of twelve B-DNA molecules (three layers of four molecules).

In this study, the adhesion strength was evaluated by calculating the adhesive fracture energy\(^5\) that was defined as the difference between the area density of potential energy of the B-DNA/ceramics-attached state (Fig. 4) and that of the B-DNA/ceramics-detached state. The fracture energy was calculated by using molecular dynamics with a universal force field\(^6\).\(^7\). The temperature was kept at 20°C by using a velocity-scaling method\(^8\).

As described in Refs. 6) and 7), 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.

\[
P = P_b + P_\alpha + P_\beta + P_{\text{vdw}} + P_{\text{ele}}
\]  

Here, bond stretching \(P_b\), bond angle bending \(P_\alpha\), dihedral angle torsion \(P_\beta\), and inversion \(P_{\text{ele}}\) terms are valence interactions. On the other hand, van der Waals \(P_{\text{vdw}}\) terms and electrostatic \(P_{\text{ele}}\) terms are nonbonded interactions. The universal force field expressed by Eq. (1) was employed in this study because the results obtained with this force field were confirmed to agree well with the results obtained with first principle quantum-mechanics simulations (density-functional-theory simulations, DFT) by using the software, Dmol3, from Dassault Systemes BIOVIA. The comparison among the lattice constants and surface energy obtained from molecular dynamics (MD) simulation with the universal force field (UFF), DFT, and experiment is shown in Table 1. The experimental values of lattice constants of this work in Table 1 were obtained by using X-ray diffraction (XRD). The experimental values of surface energy of this work were obtained by measuring contact angles\(^9\) with a contact angle meter (PCA-1, Kyowa Interface Science Co., Ltd.). Half of the data in Table 1 are not the results of this work, and they are shown in Refs. 10)-16). Furthermore, another comparison is shown in Table 4 in Section 2.4, where experimental values are shown in parentheses. As shown in this table, the relative differences between the results of MD with UFF and those of experiment are within 10%. Because the purpose of this study is not to simulate interface adhesion very accurately but to select appropriate materials, the author thinks that the accuracy of MD with UFF, whose relative difference with experiment is within 10%, is sufficient.
Table 1 Comparison among molecular dynamics (MD) simulation with universal force field (UFF), density functional theory (DFT), and experiment.

|            | MD with UFF | DFT (this work) | DFT (references) | Experiment (this work) | Experiment (references) |
|------------|-------------|-----------------|------------------|------------------------|-------------------------|
| B-DNA's interface spacing (nm) | 0.340 | 0.341 | 0.34(10) | 0.34 | 0.34(10) |
| Lattice constant of the side of GeO2 cubic unit cell (nm) | 0.55478 | 0.5476 | 0.5475(10) | 0.5438 | 0.5398(10) |
| Lattice constant of the side of MgO cubic unit cell (nm) | 0.4263 | 0.4261 | 0.4265(10) | 0.4237 | 0.4185(10) |
| Surface energy of GeO2 (J/m²) | 1.318 | 1.412 | 1.41(10) | 1.32 | 1.21(10) |
| Surface energy of MgO (J/m²) | 1.231 | 1.371 | 1.37(10) | 1.24 | 1.12(10) |

2.3 Material Factors Used at the First Stage

In this section, the material factors of ceramics are explained. The author focused on four factors (the short-side and long-side lattice constants a and b, the surface energy, S, and the cohesive energy, C) of the ceramic multilayer, and then investigated which factors significantly influence the adhesion strength. The lattice constants (a and b) are defined at the top surface of the ceramic multilayer, and as a function of the important material deposition (PVD). For example, by using PVD, the author described the adhesion strength on the four ceramic factors. When ceramic films are deposited by using physical vapor deposition (PVD). For example, by using PVD, the author obtained single-orientation films such as cubic ZrO2(111), cubic HfO2(111), cubic CaO(111), hexagonal Al2O3(0001), and cubic SrO(111) films. The short-side and long-side lattice constants (a and b) are defined at the crystal planes of the top ceramic layer, as shown in Fig. 5. On the ceramic layer, B-DNA is placed parallel to the surface so that the structure is energetically stable.

The surface energy of the ceramics, S, which is the energy density required to create a surface from bulk, was defined as half of the difference between the area density of potential energy of the surface-absent state and that of the surface-created state, where two surfaces are created by separating the surface-absent state. S was calculated by using molecular dynamics with a universal force field(5, 7).

The cohesive energy, C, is defined as the difference between the potential energy of the free atoms and that of the atoms of a solid.

2.4 Orthogonal Array Used at the First Stage

At the first stage of the material-design technology (Fig. 1), the important material factors (ceramic factors) that significantly influence the objective material property (adhesion strength) are selected by clarifying the dependence of the adhesion strength on the four ceramic 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 2) are needed to clarify the important factors on which the adhesion strength strongly depends(1). Here the author set Level 1 (small values), Level 2 (middle values), and Level 3 (large values) of the four factors at the regions shown in Table 3. The author set these levels so that each level has about one third of the ceramic-material simulation samples by using the results of molecular dynamics simulations. By looking into the data of molecular dynamics simulations, the author was able to find nine ceramic multilayers that correspond to the nine sets of factors shown in Table 2. These nine ceramic multilayers are shown in Table 4. 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 ceramic multilayers shown in Table 4 (i.e., Table 2), the sensitivity(1) for the adhesive fracture energy(5) between the ceramic multilayer and B-DNA was calculated.

By applying sensitivity analysis(1) based on orthogonal arrays to the fracture-energy data calculated for the nine ceramic multilayers in Table 4 (i.e., Table 2), the sensitivity of Level j of the i-th factor, Wj is given by

\[ W_j = 10 \log [(P_{j} - Q_{j})/n], \]

where

\[ P_j = (D_{i1} + D_{i2} + \cdots + D_{i8})/n \]

and

\[ Q_j = (D_{i1}^2 + D_{i2}^2 + \cdots + D_{i8}^2 - P_j)/(n-1). \]

Here, Dij 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 2 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: Surface energy S | 4th factor: Cohesive energy C |
|-----------|----------------------------------|--------------------------|------------------|------------------|
| 1 Level 1 | Level 1                           | Level 1                  | Level 1          | Level 1          |
| 2 Level 1 | Level 1                           | Level 2                  | Level 2          | Level 2          |
| 3 Level 1 | Level 2                           | Level 1                  | Level 2          | Level 3          |
| 4 Level 1 | Level 2                           | Level 2                  | Level 2          | Level 3          |
| 5 Level 1 | Level 2                           | Level 3                  | Level 2          | Level 1          |
| 6 Level 1 | Level 3                           | Level 2                  | Level 1          | Level 2          |
| 7 Level 1 | Level 3                           | Level 3                  | Level 2          | Level 2          |
| 8 Level 1 | Level 3                           | Level 1                  | Level 3          | Level 2          |
| 9 Level 1 | Level 3                           | Level 3                  | Level 2          | Level 1          |

Table 3 Factors and levels for ceramic multilayers.

|                | 1st parameter: Short-side lattice constant a (nm) | 2nd parameter: Long-side lattice constant b (nm) | 3rd parameter: Surface energy S (J/m²) | 4th parameter: Cohesive energy C (10⁵ J/m³) |
|----------------|--------------------------------------------------|---------------------------------------------|----------------------------------------|------------------------------------------|
| Level 1 (small)| <0.3                                             | <0.5                                       | <3.0                                   | <6.0                                    |
| Level 2 (middle)| ≤0.35                                           | ≤0.55                                      | ≤3.0                                   | ≤6.0                                    |
| Level 3 (large)| ≤0.4                                           | ≤0.65                                      | ≤3.5                                   | ≤9.0                                    |
According to the sensitivity-analysis method\(^1\) based on orthogonal arrays, the factors whose increase from Level 1 to Level 3 significantly influences the sensitivity, \(W_i\) are important in maximizing the adhesion strength, and they are selected as important factors at the first stage of the material-design technology (Fig. 1). At the second stage 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 2 and 4 by use of a response-surface method.

### 2.5 Response-Surface Method at the Second Stage

At the second stage 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\(^2\), 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. 6. 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 with B-DNA is described as a function of the important material factors (ceramic-multilayer factors). By using this function, the most appropriate values of material factors that maximize the adhesion strength can be determined. At the third (final) stage, appropriate materials (ceramic multilayers) whose factors are close to the most appropriate values are selected.

### Table 4 Nine ceramic multilayers corresponding to Table 1 (values in parentheses are experimental).

| Ceramics | 1st parameter: Short-side lattice constant \(a\) (nm) | 2nd parameter: Long-side lattice constant \(b\) (nm) | 3rd parameter: Adhesive fracture energy \(G\) (10\(^{-5}\) J/mol) |
|----------|---------------------------------|---------------------------------|----------------------|
| VO/MgO/CuO | 0.2871 (0.2674) | 0.4981 (0.4976) | 5.972 (2.556) |
| VO/NiO/RuO \(_2\) | 0.2972 (0.2866) | 0.6221 (0.6277) | 3.873 (3.686) |
| VO/ZnO/TiO \(_2\) | 0.5674 (0.5668) | 0.7877 (0.7884) | 5.183 (5.177) |
| SrO/NiO/MnO \(_3\) | 0.5828 (0.5832) | 0.6984 (0.6976) | 3.665 (3.856) |
| SrO/CeO \(_3\)/CuO | 0.5835 (0.5832) | 0.6283 (0.6279) | 5.218 (5.224) |
| SrO/BaO/SnO \(_2\) | 0.5631 (0.5626) | 0.7878 (0.7883) | 5.681 (5.759) |
| K \(_2\)O/NiO/MnO \(_3\) | 0.4554 (0.4547) | 0.4893 (0.4977) | 5.169 (5.174) |
| K \(_2\)O/ZnO/IrO \(_3\) | 0.4553 (0.4548) | 0.6284 (0.6276) | 2.591 (2.586) |
| K \(_2\)O/RhO \(_2\)/BaO | 0.4582 (0.4546) | 0.7882 (0.7876) | 3.687 (3.892) |

Fig. 6 Schematic view of interpolation with Kriging method.

### 3 Material-Selection Results and Discussions

The calculated adhesive fracture energy data corresponding to the L9 orthogonal array (Table 4) are shown in Table 5. Figure 7 shows the sensitivity, \(W_i\) calculated by using the fracture energy data (Table 5) and Eqs. (2), (3), and (4). From Fig. 7 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 surface energy and the cohesive energy). Thus, the short-side and long-side lattice constants \((a, b)\) were selected as important, dominant factors at the first stage of the material-design technology shown in Fig. 1.

At the second stage of Fig. 1, the author described the adhesive fracture energy as a function by interpolating the nine data in Table 5 with the Kriging method. The obtained function is shown in Fig. 8. The ideally most appropriate values of the important factors (the short-side and long-side lattice constants, \(a\) and \(b\) ) are obtained as \(a = 0.340\) nm and \(b = 0.586\) nm.

### Table 5 Calculated adhesive fracture energy.

| Ceramics | 1st parameter: \(a\) | 2nd parameter: \(b\) | 3rd parameter: \(S\) | Adhesive fractur | 4th parameter: \(G\) (10\(^{-5}\) J/mol) |
|----------|-----------------|-----------------|-----------------|----------------|----------------------|
| VO/MgO/CuO | Level 1 | Level 1 | Level 1 | 0.223 |
| VO/NiO/RuO \(_2\) | Level 1 | Level 2 | Level 1 | 0.245 |
| VO/ZnO/TiO \(_2\) | Level 1 | Level 3 | Level 3 | 0.204 |
| SrO/NiO/MnO \(_3\) | Level 2 | Level 1 | Level 2 | 0.256 |
| SrO/CeO \(_3\)/CuO | Level 1 | Level 3 | Level 3 | 0.331 |
| SrO/BaO/SnO \(_2\) | Level 2 | Level 3 | Level 2 | 0.276 |
| K \(_2\)O/NiO/MnO \(_3\) | Level 3 | Level 1 | Level 3 | 0.189 |
| K \(_2\)O/ZnO/IrO \(_3\) | Level 3 | Level 2 | Level 3 | 0.221 |
| K \(_2\)O/RhO \(_2\)/BaO | Level 3 | Level 2 | Level 1 | 0.176 |

Fig. 7 Results of sensitivity based on the orthogonal array.
The atomic configurations of the B-DNA/VO/ZnO/TiO₂ interface, whose adhesive fracture energy (0.204 J/m²) is smaller than that of the B-DNA/ZrO₂/CaO/HfO₂ interface are shown in Fig. 10. This figure shows that most of negatively charged oxygen atoms of B-DNA can not be seen through near the centers of the six-membered rings of the top ceramic layer (VO). Accordingly, negatively charged oxygen atoms of B-DNA are not positioned at energetically stable sites in Fig. 10 in spite of high surface energy and high cohesive energy. So, the accumulation of atomic interaction at the interface between B-DNA and VO/ZnO/TiO₂ is smaller than that at the interface shown in Fig. 9.

![Fig. 9 Coherent B-DNA/ZrO₂/CaO/HfO₂ interface.](image)

![Fig. 10 Incoherent B-DNA/VO/ZnO/TiO₂ interface.](image)

![Fig. 11 Semi-coherent B-DNA/SrO/CoO interface.](image)
Thus, the accumulation of atomic interactions caused by the lattice-matched state at the interfaces between B-DNA and three multilayers (ZrO$_2$/CaO/HfO$_2$, HfO$_2$/CaO/SrO and CaO/SrO/HfO$_2$) was found to lead to the strong adhesion.

The atomic configuration of the interface between B-DNA and SrO/CeO$_2$/CoO is shown in Fig. 11. In this figure, almost all the negatively charged oxygen atoms are seen through near the centers of the six-membered rings of SrO, but are not seen through at the centers of the six-membered rings. Thus, lattice matching in Fig. 11 is not as perfect as that in Fig. 9, but is much better than that in Fig. 10. This is the reason that SrO/CeO$_2$/CoO has strong adhesion to B-DNA, as shown in Table 5. The film made of single ceramic material (CaO, HfO$_2$, ZrO$_2$, or SrO) has almost the same adhesion with B-DNA as SrO/CeO$_2$/CoO although figures are not shown.

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 with a scratch tester, CSR-02 made by Rheosa 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\(^{17-19}\). However, these advanced methods were very difficult to apply to fairly strong surfaces such as the interface between B-DNA and ZrO$_2$/CaO/HfO$_2$. Accordingly, a simple scratch-testing method that was applicable to the strong B-DNA/ZrO$_2$/CaO/HfO$_2$ interface was employed. In the scratch testing, a diamond indenter with a tip radius of 5 \(\mu\)m makes the dynamic indentations. During the measurement, load is gradually increased with a zig-zag trajectory, and when it reaches a critical load, fracture occurs at the interface, as shown in Fig. 12. The adhesion strength is determined by measuring the critical load, \(L\), at which the adhesive fracture occurs.

The author used 0.5-mm-thick B-DNA films attached on the ceramics for the scratch test. The molecular structure of B-DNA is shown in Fig 3. For the ceramics, the author used the five ceramic multilayers (ZrO$_2$/CaO/HfO$_2$, VO/MgO/CoO, SrO/BaO/SrO, SrO:NiO/MnO$_2$, and K$_2$O/NiO/MnO$_2$), four of which are listed in Table 5. These ceramic multilayers were deposited on silicon substrates 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 scan of the X-ray diffraction (XRD) analysis, the author selected the specimens that have only significant diffraction peaks showing single orientation. The DNA films were made as followed\(^{20, 21}\). The author mixed an aqueous solution of DNA from Salmon testes with an aqueous solution of a cationic amphiphile, N,N,N-trimethyl-N-(3,6,9,12-tetraethyldodecyl)ammonium bromide\(^{20}\). The precipitated DNA-lipid polynion complex (1:1 ratio of phosphate anion to cationic amphiphile) was collected and solubilized in chloroform/ethanol (4:1 v/v). The author cast the solution (40 mg/mL, 4 wt. %) on the prepared ceramic film, and evaporated the solvent slowly under saturated solvent vapor at 25°C. In order to stabilize the molecular structure of the B-DNA/ceramics interface, the specimens were kept at 25°C for 120 hours, and were cooled to 20°C in 120 hours. By repeating this procedure, the specimens were obtained.

By carrying out the scratch test, the adhesive fracture energy, \(D\), obtained from molecular dynamics simulations and the critical load, \(L\), obtained from the scratch test of the interfaces between B-DNA films and ceramic multilayers are compared in Fig. 13. Although linear relationship is seen in Fig. 13, the reason has not been clarified because complicated non-elastic deformation occurs at the interface in the scratch test. So, the absolute-evaluation method has not been completely established. However, the adhesion-simulation method is considered to be effective for relatively evaluating adhesion strength, and to be useful for selecting appropriate materials. In reality, from the results shown in Fig. 13, it is experimentally confirmed that the ZrO$_2$/CaO/HfO$_2$ multilayer, which has been selected by using our material-design technology (Fig. 1), has the strongest adhesion to B-DNA, and the usefulness of this technology was confirmed.

5 Summary

A materials-informatics technology for efficiently designing a ceramic material with strong adhesion to organic materials with a combination of an orthogonal array and a response-surface method was used to design appropriate ceramics with strong adhesion to B-DNA. In this technique, at the first stage, important factors that significantly influence the adhesion strength with B-DNA were selected from various factors that characterize ceramics by use of an orthogonal array with molecular dynamics simulations. At the second stage, 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 best values of the important factors that made the adhesion strength maximum were obtained. At the third stage, the best ceramic materials whose important factors were close to the most appropriate values were selected. By carrying out these procedures on the B-DNA/ceramics adhesion, 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, dominant factors from four ceramic-multilayer factors (the lattice constants, \(a\), \(b\), the surface energy, \(S\), and the cohesive energy, \(C\)).

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 best values for \(a\) and \(b\) that made the adhesion strength maximum were obtained as 0.340 nm and 0.589 nm, respectively. This result shows that lattice matching is important in the adhesion strength because the best values are equal to the lattice constants of B-DNA.

3) Three multilayers (ZrO\(_2\)/CaO/HfO\(_2\), HfO\(_2\)/CaO/SrO and CaO/SrO/HfO\(_2\)), whose lattice constants were \(a = 0.340\) nm and \(b = 0.589\) nm (the best values), were selected as the best ceramics with the strongest adhesion to B-DNA. Representative simulation results were confirmed by scratch testing. Thus, the accumulation of atomic interactions caused by lattice matching at the interfaces between B-DNA and the three multilayers (ZrO\(_2\)/CaO/HfO\(_2\), HfO\(_2\)/CaO/SrO and CaO/SrO/HfO\(_2\)) was found to lead to the strong adhesion. Thus, the effectiveness of this technology was confirmed.

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