Technology for Designing Metal Film with Strong Adhesion to Hydrocarbon-Chain-Based Soft Resin by Use of Orthogonal Array and Molecular Simulation

by

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A technology for efficiently designing a multilayer metal film with strong adhesion to a soft resin was developed by combining a molecular simulation with an orthogonal array. In this technique, the adhesion strength of the interface between the metal film and resin is evaluated by calculating the adhesive fracture energy by use of a molecular-dynamics simulation. The most significant factor in the adhesion strength can be found by using an orthogonal array. This paper describes an application of this technique to the design of a metal film with strong adhesion to a soft resin made of hydrocarbon chains. By carrying out a sensitivity analysis with the orthogonal array, the mismatches among four metal-film factors (the short-side and long-side lattice mismatches with the resin $\Delta a$ and $\Delta b$ values, the surface energy density, $G$, and the cohesive energy, $H$ of an atomic-layer laminated metal film) were found to be the most dominant factors in the adhesion strength. The author also found that reducing the mismatches is effective for increasing the adhesion strength. The results of molecular-dynamics simulations showed that a copper/cobalt/nickel-laminated film is the most appropriate structure with strong adhesion to the hydrocarbon-chain-based resin.

Key words:

Adhesion strength, Metal film, Resin, Molecular simulation, Orthogonal array

1 Introduction

In atomic-scale nanotechnology devices such as future biomechanics devices, semiconductor packages, magnetic recording media, and optical disks, the interface adhesion between thin films made up of different materials is becoming more and more important. When the interface between the different materials is not stable, adhesive fractures occur at the interface. Selecting appropriate materials is one of the keys to preventing these adhesive fractures. In semiconductor packages, for example, it is well known that the adhesion of electro-plated nickel-interconnection films to chromium underlayers is very good. However, it is very time-consuming to find such appropriate-material pairs by using an experimental trial-and-error approach. On the other hand, the orthogonal-array design methodology (1-4) has often been used to efficiently design macro-scale structures such as propeller fans and diaphragms (1). However, this methodology has rarely been applied to materials design or materials selection because material parameters such as lattice constants and atomic radii cannot be continuously changed. So, the author applied the orthogonal-array design methodology to materials design by changing the material parameters almost continuously by use of combinations of atomic-scale thin films.

In this study, a molecular-dynamics simulation and an orthogonal array were used to design a multilayer metal film that has strong adhesion to a soft resin made of hydrocarbon chains (alkyl chains), which are chains of bonded -CH2-elements. The adhesion strengths of the interfaces between the metal film and the resin were evaluated by using molecular dynamics simulations, which have been found effective in determining the adhesion strength (5-10). The purpose of this study is to clarify the dependence of the adhesion strength on four metal-film factors (the short-side and long-side lattice mismatches with the resin $\Delta a$ and $\Delta b$ values, the surface energy density, $G$, and the cohesive energy, $H$, of the metal film), and to find effective methods of strengthening the adhesion. In the field of optimization design, those factors are sometimes called descriptors or explanatory variables, and the design based on such factors is called a descriptor-based design. This paper describes the descriptor-based design of a multilayer metal film with strong adhesion to a hydrocarbon-chain-based resin, which is softer than benzene-ring-chain resins, reported in the previous papers (9, 10).

2 Analysis Method

2.1 Simulation Model

As shown in Fig. 2, the simulation model that the author used in this study is an interface between a soft resin made of hydrocarbon chains (Fig. 1) and an atomic-layer laminated metal film. This simulation model was made by using...
“Materials Studio®” software from Dassault Systemes BIOVIA. Sixteen resin molecules (four layers of four molecules), one of which is shown in Fig. 1, were used as the resin film model. There are 2,112 atoms in the resin molecules. Because past molecular-dynamics simulations have found the adhesion strength between the resin and the metal film to be almost independent of the total number of metal layers when that number was more than seven, the number was set at eight. The metal film was formed by using three metal species, Metal 1 (two atomic layers), Metal 2 (three atomic layers), and Metal 3 (three atomic layers), as shown in Fig. 2. The sizes of the metals in the x and y directions are set at 15a and 15b, where the short-side lattice constant, a, and the long-side lattice constant, b, are shown in Fig. 3. Accordingly, the number of atoms in a multilayer metal is 3,600.

2.2 Control Factors of Metal Film

In this section, the control factors (that is, the descriptors or explanatory variables) of the multilayered metal film are explained. The author changed the values of four factors (the short-side and long-side lattice mismatches with the resin, $\triangle a$ and $\triangle b$ values, the surface energy density, $G$, and the cohesive energy, $H$) of the metal film by changing the three metal species (Metal 1, Metal 2, and Metal 3), and then investigated how the adhesion strength depends on these factors. Here, the short-side lattice mismatch was defined as the difference between the top layer’s short-side lattice constant, $a$, in the metal film (Fig. 3), and the second nearest-neighbor distance between the carbon atoms of the hydrocarbon chains (alkyl chains) in the resin (Fig. 1), that is, 0.246 nm. The long-side lattice mismatch was defined as the difference between the top layer’s long-side lattice constant, $b$, in the metal film (Fig. 3) and the length that is $3^{1/2}$ times as long as the second nearest-neighbor distance between the carbon atoms of the benzene ring in the resin (Fig. 1), that is, 0.427 nm. From these definitions, the short-side lattice mismatch, $\triangle a$, is calculated as the absolute value of $100(a-0.246)/0.246$. The long-side lattice mismatch, $\triangle b$ is calculated as the absolute value of $100(b-0.427)/0.427$. In this study, the x-y plane in Fig. 2 is set parallel to the crystal planes of the highest atomic density, which are the (111), (001), and (110) planes for the face-centered-cubic (fcc), hexagonal-close-packed (hcp), and body-centered-cubic (bcc) structure metals, respectively. These crystal planes are energetically stable and are experimentally found to be most likely to appear at the surfaces when metal films are deposited by using physical vapor deposition (PVD).

The surface energy density of the metal film, $G$, 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-connected state (Fig. 4) and that of the surface-separated state (Fig. 5). The cohesive energy of the metal film was defined as the energy required to break the film into isolated atoms. The surface energy density, $G$, and cohesive energy, $H$, were calculated by using molecular-dynamics simulations with a universal force field. As described in Refs. 11) and 12), this force field is determined based on the element, its hybridization, and its connectivity. To clarify the dependence of the adhesion strength on the four factors, the author changed and...
controlled the four factors (the short-side and long-side lattice mismatches with the resin, the surface energy density, and the cohesive energy) by changing the three metal species, and the author tried to find the most appropriate metal set (Metal 1, Metal 2, and Metal 3). The numbers of layers of the three metal species Metal 1, Metal 2, and Metal 3 in Fig. 2 were set at two, three, and three, respectively, because from the past molecular-dynamics simulations, these numbers of layers were found to be the most convenient to easily control the four factors. In this study, the adhesion strength was evaluated by calculating the adhesive fracture energy which was defined as the difference between the area density simulations with the universal force field and cohesive energy data calculated for the nine metal films, the sensitivity and the signal-to-noise ratio of the adhesive fracture energy becomes largest. Thus, reducing the short-side and long-side lattice mismatches and increasing the surface energy and cohesive energy (5.1×10^5 J/mol) of this film are fairly high. In this case, the sensitivity of Level j of the i-th factor, S_i,j is given by

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

where

\[ P_{i,j} = (D_{i,j} + D_{i,j+1} + \cdots + D_{i,n})/n \]

and

\[ Q_{i,j} = (D_{j,j} + D_{j,j+1} + \cdots + D_{j,n})/n. \]

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

The signal-to-noise ratio of Level j of the i-th factor, R_{i,j} is given by

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

Consequently, the author used the orthogonal-array design methodology, 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 control factors, only nine simulations or experiments shown in an L9 orthogonal array (see Table 1) are needed to clarify the dependence of the adhesion strength on these factors. Here the author set Level 1 (small values), Level 2 (middle values), and Level 3 (large values) of the four factors at the values shown in Table 2. By using the calculated data of 27,000 candidates of the three metal species (Metal 1, Metal 2, and Metal 3) shown in Appendix, the author was able to find nine metal films that correspond to the nine parameter sets shown in Table 1. These nine metal films are shown in Table 3. In Appendix the details of how Level (small), Level 2 (middle), and Level 3 (large) of the four factors were set at the values shown in Table 2 and how the nine metal films in Table 3 were selected are described. By using these nine metal films, the sensitivity and the signal-to-noise ratio for the adhesive fracture energy between the metal film and the resin were calculated. By applying Taguchi’s method for orthogonal arrays to the fracture-energy data calculated for the nine metal films, the sensitivity of Level j of the i-th factor, S_{i,j} is given by

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

where

\[ P_{i,j} = (D_{i,j} + D_{i,j+1} + \cdots + D_{i,n})/n \]

and

\[ Q_{i,j} = (D_{j,j} + D_{j,j+1} + \cdots + D_{j,n})/n. \]

The signal-to-noise ratio of Level j of the i-th factor, R_{i,j} is given by

\[ R_{i,j} = 10 \log [(P_{i,j} - Q_{i,j})/(n Q_{i,j})]. \]
simulations with the universal force field 11), 12). In the of potential energy of the resin/metal-attached state (Fig. 2) molecular-dynamics simulations5)-10), these numbers of layers of Metal 2, and Metal 3. The numbers of layers of the three author tried to find the most appropriate metal set (Metal 1, cohesive energy) by changing the three metal species, and the mismatches with the resin, the surface energy density, and the sensitivity of Level 3 19% 19% 2.7 J/m2 5.7 J/m2.

2.3 Orthogonal-Array Design Methodology

When we investigate the dependence of the adhesion strength on the factors1)-4). Here the author set Level 1 (small values), Level 2 (middle values), and Level 3 (large values) of the four factors were set at the values shown in Table 2 and how the signal-to-noise ratio 1)-3) for the adhesive fracture energy 6)-8) is given by 1)-3) for orthogonal arrays to the orthogonal-Array Design Methodology

Table 1  L9 Orthogonal array.

| Condition | 1st factor: Short-side lattice mismatch | 2nd factor: Long-side lattice mismatch | 3rd factor: Surface energy density | 4th factor: Cohesive energy |
|-----------|----------------------------------------|---------------------------------------|-----------------------------------|---------------------------|
| 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 3                                | Level 1                               | Level 3                           | Level 3                   |
| 4 Level 2 | Level 1                                | Level 2                               | Level 2                           | Level 3                   |
| 5 Level 2 | Level 2                                | Level 3                               | Level 1                           | Level 3                   |
| 6 Level 2 | Level 3                                | Level 1                               | Level 2                           | Level 3                   |
| 7 Level 3 | Level 1                                | Level 2                               | Level 3                           | Level 2                   |
| 8 Level 3 | Level 2                                | Level 3                               | Level 1                           | Level 2                   |
| 9 Level 3 | Level 3                                | Level 2                               | Level 3                           | Level 1                   |

Table 2  Control factors and levels for metal films.

| 1st factor: Short-side lattice mismatch | 2nd factor: Long-side lattice mismatch | 3rd factor: Surface energy density | 4th factor: Cohesive energy |
|----------------------------------------|---------------------------------------|-----------------------------------|---------------------------|
| Level 1 5.0%                          | 5.0%                                  | 1.5 J/m2                          | 5.7×10^7 J/mol            |
| Level 2 12%                           | 12%                                   | 2.1 J/m2                          | 4.7×10^7 J/mol            |
| Level 3 19%                           | 19%                                   | 2.7 J/m2                          | 5.7×10^7 J/mol            |

Table 3  Nine metal films corresponding to Table 1 (L9), where Levels 1, 2, and 3 are shown in Table 2.

| Metal 1/Metal 2/Metal 3 | 1st factor: Short-side lattice mismatch | 2nd factor: Long-side lattice mismatch | 3rd factor: Surface energy density | 4th factor: Cohesive energy |
|------------------------|----------------------------------------|---------------------------------------|-----------------------------------|---------------------------|
| Co/Ni/Rh               | Level 1                                | Level 1                               | Level 1                           | Level 1                   |
| Cu/Pt/Co              | Level 2                                | Level 2                               | Level 2                           | Level 2                   |
| Mn/Au/Ag              | Level 3                                | Level 3                               | Level 3                           | Level 3                   |
| Ru/Ag/Pt              | Level 2                                | Level 1                               | Level 2                           | Level 3                   |
| Pd/Co/Ti              | Level 2                                | Level 2                               | Level 3                           | Level 1                   |
| Ti/Ni/Mo              | Level 3                                | Level 1                               | Level 2                           | Level 3                   |
| Al/Ni/Ag              | Level 3                                | Level 2                               | Level 1                           | Level 2                   |

According to Taguchi’s method1)-3) for orthogonal arrays, the conditions in which $S_p$ and $R_p$ are the largest are effective for strengthening the adhesion between the metal film and the resin with the deviation of adhesion kept small.

3 Analysis Results

The data of the adhesive fracture energy, $D$, calculated from molecular dynamics are shown in Table 4. Figure 7 shows the sensitivity, $S_p$, calculated by using the fracture energy data (Table 4) and Eqs. (1), (2), and (3). Figure 8 shows the signal-to-noise ratio, $R_p$, calculated by using the fracture energy data from Table 4 and Eqs. (2), (3), and (4). From these figures it is found that when the 1st and 2nd factors (the short-side and long-side lattice mismatches) are smallest and when the 3rd and 4th factors (the surface energy density and cohesive energy) are largest, the sensitivity and signal-to-noise ratio of the adhesive fracture energy becomes largest. Thus, reducing the short-side and long-side lattice mismatches and increasing the surface energy and cohesive energy are effective for strengthening the adhesion with the deviation of adhesion kept small. By changing the three metal species (Metal 1, Metal 2, and Metal 3), the author searched for the metal set that satisfies the condition that the 1st and 2nd factors (the short-side and long-side lattice mismatches) are small and the 3rd and 4th factors (the surface energy density and cohesive energy) are large. By carrying out 10 trial molecular-dynamics simulations, the author found that the lattice mismatches can be reduced by using Cu, Ni, and Co, because the lattice constants, $a$ and $b$, of these metals are close to those of the resin. Among 27 permutations of these three metals (Cu, Ni, and Co), the Cu/Co/Ni film was found to best satisfy the optimum condition. Both the short-side and long-side lattice mismatches of the Cu/Co/ Ni film are small (0.8%), and the surface energy (2.3 J/m²) and the cohesive energy (5.1×10^7 J/mol) of this film are fairly high. In this case, the adhesive fracture energy is obtained as 0.269 J/m², which is higher than those of the nine metal films in Table 4.

Table 4  Calculated adhesive fracture energy data corresponding to Table 1 (L9).

| Metal 1/Metal 2/Metal 3 | 1st factor: Short-side lattice mismatch | 2nd factor: Long-side lattice mismatch | 3rd factor: Surface energy density | 4th factor: Cohesive energy |
|------------------------|----------------------------------------|---------------------------------------|-----------------------------------|---------------------------|
| Co/Ni/Rh               | Level 1                                | Level 1                               | Level 1                           | Level 1                   |
| Cu/Pt/Co              | Level 2                                | Level 2                               | Level 2                           | Level 2                   |
| Mn/Au/Ag              | Level 3                                | Level 3                               | Level 3                           | Level 3                   |
| Ru/Ag/Pt              | Level 2                                | Level 1                               | Level 2                           | Level 3                   |
| Pd/Co/Ti              | Level 2                                | Level 3                               | Level 3                           | Level 1                   |
| Ti/Ni/Mo              | Level 3                                | Level 1                               | Level 2                           | Level 3                   |
| Al/Ni/Ag              | Level 3                                | Level 2                               | Level 1                           | Level 2                   |

Fig. 7 Results of calculated sensitivity.
The cohesive energy depends on the surface energy. In this paper, the author focused on the four factors (the surface energy, the lattice mismatch, the adhesion strength, and the cohesive energy) that have been introduced in the previous section. The surface energy is defined as the energy required to increase the surface area of a material. The lattice mismatch is defined as the difference between the lattice constants of two materials. The adhesion strength is defined as the energy required to separate two materials. The cohesive energy is defined as the energy required to break a bond within a material.

Irregularity caused by the large lattice mismatch ($\beta = 19\%$) is considered to lead to the weaker adhesion ($D = 0.172 \text{ J/m}^2$) compared to the lattice mismatch ($D = 0.269 \text{ J/m}^2$). So the lattice mismatches are considered to be the dominant factors in the adhesion strength.

In this study, the initial orientation of the resin was set so that the large-side lattice constant is in the $y$ direction. Even when the initial orientation of the resin was set at different orientations, the orientation of the resin was found to finally converge to the same orientation as that in Figs. 9 and 10 at $20^\circ \text{C}$ because this orientation makes the system energetically most stable.

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 Rhesa 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 hydrocarbon-chain-resin/Cu interface. Accordingly, a simple scratch-testing method that was applicable to the hydrocarbon-chain-resin/Cu interface was employed. A schematic view of the scratch testing apparatus is shown in Fig. 11. A diamond indenter with a tip radius of $5 \mu \text{m}$ makes the dynamic indentations. During the measurement, load is gradually increased and when it reaches a critical load, adhesive fracture occurs at the interface. An example of the surface profile after this test is shown in Fig. 12. The adhesion strength is determined by measuring the critical load, $L_c$, at which the adhesive fracture occurs.

The author used $0.01$-mm-thick hydrocarbon-chain resin films deposited on atomic-layer laminated metal films for the scratch test. The molecular structure of the resin films is the same as that in Fig. 1. For the metal films, the author used the four laminated films (CoNi/Rh, Mn/Au/Ir, TiNi/Mo, and Al/Au/Ag) listed in Table 4, and the best film (Cu/CoNi). These films were deposited on silicon substrates by using physical vapor deposition (PVD). The deposition times were controlled so that the thicknesses of Metal 1, Metal 2, and Metal 3 were the same as those in the simulations, specifically, two atomic layers (0.4 nm) for Metal 1, three atomic layers (0.6 nm) for Metal 2, and three atomic layers (0.6 nm) for Metal 3. By using the 0-20 scheme of the X-ray diffraction (XRD) analysis, the author selected the specimens where the diffraction peaks corresponding only to the planes of the highest atomic density were significantly observed.
The adhesive fracture energy, $D$, obtained from molecular dynamics and the critical load, $L$, obtained from the scratch test of the interfaces between hydrocarbon-chain resin films and laminated metal films (Al/Au/Ag, Ti/Ni/Mo, Mn/Au/Ir, Co/Ni/Rh, and Cu/Co/Ni) are compared in Fig. 13. The ratios of $D_{Al/Au/Ag}$, $D_{Ti/Ni/Mo}$, $D_{Mn/Au/Ir}$, $D_{Co/Ni/Rh}$, and $D_{Cu/Co/Ni}$ (where $D_X$ denotes the corresponding fracture energies) are $1 : 1.33 : 1.65 : 1.95 : 2.66$. On the other hand, the ratios of $L_{Al/Au/Ag}$, $L_{Ti/Ni/Mo}$, $L_{Mn/Au/Ir}$, $L_{Co/Ni/Rh}$, and $L_{Cu/Co/Ni}$ (where $L_X$ denotes the corresponding critical loads) are $1 : 1.31 : 1.66 : 1.98 : 2.61$. Because these ratios agree well with each other, the adhesion-calculation method is found to be effective for determining the adhesion strength.

In this study, to find optimum metal films such as a Cu/Co/Ni film, the author carried out nine simulations for an L9 orthogonal array and carried out another ten trial simulations and 27 simulations corresponding to 27 permutations for three metal species (Cu, Ni, and Co). Thus, the total number of simulations was 48. If the orthogonal-array design methodology had not been used, 27,000 ($=3^9$) simulations of adhesion strength would have been needed because there are 30 species of metals and because 3 species of metals for Metal 1, Metal 2, and Metal 3 have to be selected. So the orthogonal-array design methodology is considered to be effective for efficiently selecting appropriate materials for nanotechnology devices.

5 Discussions

In the papers, the author described that the lattice mismatches were dominant factors for increasing the adhesion strength at hard-material interfaces such as metal/metal, metal/benzene-ring-chain-resin, and ceramics/benzene-ring-chain-resin interfaces. In this paper, it is found that the lattice mismatches are important even in the adhesion of soft materials such as benzene-ring-free resins made of hydrocarbon chains (alkyl chains), which are chains of bonded -CH$_2$- elements. Accordingly, the author think that the reduction of the lattice mismatches can be used as a generalized design guideline for improving the adhesion strength.

In this paper, the author focused on the four factors (the short-side and long-side lattice mismatches with the resin $\Delta a$ and $\Delta b$ values, the surface energy, $G$, and the cohesive energy, $H$). The short-side and long-side lattice mismatches were focused on because geometrical mismatches between metals and resins are considered to be important factors in adhesion strength. On the other hand, the surface energy density, $G$, and the cohesive energy, $H$, were focused on because these factors are considered to be related to the bond energy between atoms. In bulk metals that have close-packed structures such as a face-centered-cubic (fcc) structure or a hexagonal close-packed (hcp) structure, the long-side lattice mismatch depends on the short-side lattice mismatch, and the cohesive energy depends on the surface energy. In multilayered nano-scale films, however, those four factors can be independently controlled by selecting appropriate metal species (Metal 1, Metal 2, and Metal 3). This is why multilayered metals corresponding to an L9 orthogonal array could be selected, as shown in Table 3.

It is difficult to confirm the effectiveness of molecular simulations because the adhesive fracture energy cannot be
easily measured by experiments. The results of scratch tests include plastic deformation effects while the adhesive fracture energy calculated from molecular dynamics does not include these effects. So it is considered that the proportional relationship between the results of molecular dynamics and those of the scratch tests shown in Fig. 12 was obtained because the plastic-deformation energy increased in proportion to the increase in the adhesive fracture energy.

This paper describes the results for 20°C, and does not describe the temperature dependence. However, the author confirmed that the ratios of $D_{Al/Ag/Ag}$, $D_{Ti/Ti/Ti}$, $D_{Mo/Al/Al}$, $D_{Co/Co/Co}$, and those of $L_{Al/Al/Al}$, $L_{Ti/Ti/Ti}$, $L_{Mo/Al/Al}$, $L_{Co/Co/Co}$ did not depend on the temperature. Accordingly, the Cu/Co/Ni film is considered to be the most effective for obtaining strong adhesion to resins.

6 Summary

A molecular-dynamics simulation and an L9 orthogonal array were used to design a multilayer metal film that has strong adhesion to a soft resin made of hydrocarbon chains (alkyl chains). A sensitivity analysis with the orthogonal array produced the following results.

1) Among four factors (the short-side and long-side lattice mismatches with the resin $\Delta a$ and $\Delta b$, values, the surface energy, $G$, and the cohesive energy, $H$, of an atomic-layer laminated metal film) the mismatches were found to be the dominant factors in determining the adhesion strength.

2) Reducing the lattice mismatches and increasing the surface energy and cohesive energy are effective in strengthening the adhesion with the deviation of adhesion kept small.

3) A copper/cobalt/nickel-laminated film is an appropriate structure that has strong adhesion to the hydrocarbon-chain-based resin.

Appendix

In this appendix the details of how Level 1 (small), Level 2 (middle), and Level 3 (large) of the four factors (the lattice constants $a$ and $b$, the surface energy, $G$, and cohesive energy, $H$, of multilayer metal films (Metal 1/Metal 2/Metal 3) were set at the values shown in Table 2 and how the nine parameter sets shown in Table 1 (the $L_9$ orthogonal array) were used to design a multilayer metal film that has strong adhesion to resins. By using the calculated data of 27,000 metal films, the author looked for nine metal films that correspond to the nine parameter sets shown in Table 1 (the $L_9$ orthogonal array). As a result, the author found that nine metal films in Table 5 have the values close to Level 1, Level 2, and Level 3 of the four factors in the $L_9$ orthogonal array. As shown in Table 5, the values of the four factors are a little different from those of Level 1, Level 2, and Level 3. However, the differences are so small that they can be neglected by using two significant figures. Because the purpose of use of orthogonal arrays is not to obtain quantitative dependence of adhesion on the four parameters but to obtain qualitative tendency, the use of two significant figures is considered to be appropriate. Therefore, by rounding off the values in Table 5 to two significant values, Table 5 can be used as the $L_9$ orthogonal array. In this way, Table 3 was obtained from Table 5.

Fortunately, in this study the author was able to find nine metal films that have the nine parameter sets in the $L_9$ orthogonal array. However, there are cases that nine material sets that correspond to $L_9$ can not be found. In such cases, different methods such as response-surface methods and data-mining methods are needed.
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Table 5 Values for nine multilayer films in Table 3.

| Metal 1/Metal 2/Metal 3 | 1st factor: \( \Delta_a \) (%) | 2nd factor: \( \Delta_b \) (%) | 3rd factor: \( G \) (J/m²) | 4th factor: \( H \) (10⁻¹J/m²) |
|-------------------------|-----------------|-----------------|-----------------|-----------------|
| Co/Ni/Rh                | 5.016           | 5.016           | 1.537           | 3.743           |
| Cu/Pt/Pt                | 5.044           | 12.27           | 2.148           | 4.733           |
| Mn/Au/Ir                | 5.037           | 19.08           | 2.738           | 5.719           |
| Ru/Co/W                 | 12.04           | 5.046           | 2.127           | 5.743           |
| Pt/Co/Os                | 12.29           | 12.29           | 2.744           | 3.708           |
| Rh/Ti/Al                | 12.38           | 19.37           | 1.515           | 4.723           |
| Ti/Ni/Mo                | 19.45           | 5.038           | 2.719           | 4.716           |
| Ag/Pt/Mo                | 19.28           | 12.43           | 1.548           | 5.725           |
| Al/Au/Ag                | 19.46           | 19.46           | 2.118           | 3.731           |

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