Adhesion Analysis of Resin/Resin Interface by Molecular Dynamics Simulation*

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Abstract

Nanotechnology devices with strong adhesion strength are required due to the miniaturization and reduction of the thickness of electronic equipment. In this paper, a technique for using a molecular dynamics simulation to analyze the adhesion of the interface between adhesive and polyimide, that is the resin/resin interface, has been proposed. It is difficult to make the resin/resin interface when we perform a simulation because the structure of resin is complicated and the resin doesn’t have a regular configuration. We made it possible to performed adhesion analysis of resin/resin interface by establishing a method for modeling the interface. We calculated the adhesion energy at the interface between three candidate adhesives (polyamide-imide, phenoxy resin, polymethyl methacrylate) and polyimide in order to evaluate the adhesion strength at the interface. The adhesion energy obtained from the molecular dynamic simulation increased in the order of polyamide-imide/polyimide > phenoxy resin/polyimide > polymethyl methacrylate/polyimide. This order agrees with the experimental result. We also showed that the adhesive with high adhesion strength had more atomic pairs in which the distance between an adhesive carbon atom and a polyimide carbon atom was less than 5 Å and interacted with the polyimide more. Our simulation method is effective for selecting the best material with the highest adhesion strength.

Key words: Adhesion Strength, Adhesion Energy, Molecular Dynamic Simulation, Interface, Resin, Thin Film

1. Introduction

Nanotechnology devices such as the semiconductor packages, magnetic recording media, and optical disks, used in electronic equipment have a laminate structure comprised of different materials. Maintaining high adhesion strength at the interface between the different materials is difficult. Adhesives made from resins are used to improve the adhesion strength. Recently, the problem of flaking at the interface has been growing due to the miniaturization and reduction of the thickness of electronic equipment. Adhesion strength can be measured with a peel strength test(1). However, quantitative measurement is difficult because the resin material is soft, and the effect of deformation is large(2). Therefore, using a computer simulation to evaluate the adhesion strength of a material is efficient.

Molecular dynamics simulation is a method for calculating the properties of the interface at the atomic or molecular scale level. It provides a step-by-step numerical solution for the classical equations of motion. The molecular dynamics methods for determining the adhesion strength of metal/metal(3)-(6), resin/metal(7), and resin/ceramics(8) interfaces have been carried out. In these methods, adhesion strength is determined by calculating adhesion energy. Adhesion energy is defined as the difference between the total potential energy of the material-connected state and that of the material-separated state.
In this research, we analyzed the adhesion at the interface between adhesive and polyimide by using a classical molecular dynamics simulation. The adhesive and the polyimide were both resins, meaning that the interface between the two was a resin/resin interface. The method for predicting the adhesion strength with adhesion energy has not been applied to the resin/resin interface. The structure of resin is complicated and the resin does not have a regular configuration like metal and ceramics. Therefore, it is difficult to make the resin/resin interface when we perform a simulation. We made it possible to perform adhesion analysis of resin/resin interfaces by establishing a method for modeling the interface.

Three kinds of adhesives, polyamide-imide, phenoxy resin, and polymethyl methacrylate, were used as an example, and we calculated the adhesion energy between these adhesives and the polyimide to evaluate the adhesion strength at the interface. By comparing the results of the adhesion energy, we were able to select the best adhesive with the highest adhesion strength.

Furthermore, we calculated the number of atomic pairs in which the distance between an adhesive carbon atom and a polyimide carbon atom was less than 0.5 nm in order to evaluate the relationship between the adhesion strength and the interaction at the interface. We show from the results that the adhesive with a high adhesion strength had more carbon-carbon atomic pairs and interacted with the polyimide more. This result showed that the characteristics of adhesion were related to the atomic scale adhesion mechanism at the interface.

2. Adhesion analysis at the interface

Fig. 1 shows an example of the laminate structure of a semiconductor device. Adhesives made from resins are used to improve the adhesion strength at the interface between the different materials. We analyzed the adhesion at the interface between an adhesive and a polyimide by using a classical molecular dynamics simulation. We calculated the adhesion energy to evaluate the adhesion strength at the interface. Three kinds of adhesives, polyamide-imide, phenoxy resin, and polymethyl methacrylate, were used as examples. The molecular structure of the polyimide and the adhesives is shown in Figs. 2 and 3. The polymerization degree \( n \) of the polyimide, polyamide-imide, and phenoxy resin used for the simulation was two, while that of polymethyl methacrylate was ten. “Discover” was used for the molecular dynamics simulations. “Discover” is a module within “Materials Studio”\(^{(9)}\), which is a simulation software from Accelrys, Inc. “COMPASS”\(^{(10)}\) was used as a force field.

![Fig. 1 Example of the laminate structure of a semiconductor device](image-url)
3. Modeling method of adhesive/polyimide interface

Fig. 4 shows the modeling method for the adhesive/polyimide interface. The interfaces of resin materials, such as those between an adhesive and polyimide, are rough and not regular, so it is difficult to make a clear interface between the adhesive and polyimide. Therefore, we first optimized the structures of the adhesive and polyimide individually on the Cu layer (Fig. 4(a)). The adhesive and polyimide were then arranged flatly for the interaction of the adhesive and Cu or the polyimide and Cu (Fig. 4(b)). Next, we stuck the adhesive and polyimide together and eliminated the Cu layer (Fig. 4(c)). After that, we optimized the structures at the interface. To optimize the structures quickly, the temperature was gradually lowered from 600 to 500 to 400 K. We performed structure optimization at each temperature and finally got the optimized structure at room temperature (Fig. 4(d)). During the structure optimization process, the total potential energy varies with time. The system is considered to reach equilibrium when the total potential energy converged.

A strong point of this modeling method was that we were able to make a separated structure with the two materials at the interface and get an optimized structure quickly because we optimized the structure at a high temperature, and the molecules moved energetically.
In a classical molecular dynamics simulation, optimized structures at the interface like those in Figs. 4(b) and (d) are obtained by calculating Newton’s equation of motion,

\[ m_i \frac{d^2 r_i}{dt^2} = -\frac{\partial U_T}{\partial r_i} \]

where \( m_i \), \( r_i \), and \( U_T \) are the atomic mass, atomic position of the \( i \)-th atom, and total potential energy, respectively.

The functional forms used in the COMPASS force field can be written as:

\[
U_T = \sum_b \left[ k_2 (b-b_0)^2 + k_3 (b-b_0)^3 + k_4 (b-b_0)^4 \right] + \\
\sum_\theta \left[ k_1 (1-\cos \theta) + k_2 (1-\cos 2\theta) + k_3 (1-\cos 3\theta) \right] + \\
\sum_\phi \left[ k_2 \phi^2 + \sum_{b,b'} k(b-b_0)(b'-b'_0) + \\
\sum_{b,b'} k(b-b_0)(\theta-\theta_0) + \sum_{b,b'} (b-b_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] + \\
\sum_{\theta',\theta} (\theta-\theta_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] + \\
\sum_{\theta',\theta} k(\theta'-\theta_0')[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] + \\
\sum_{\theta',\theta} k(\theta'-\theta_0')[\theta'-\theta'_0] \cos \phi + \sum_{i,j} q_i q_j r_{ij} + \\
\sum_{i,j} \varepsilon_{ij} \left[ 2 \left( \frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left( \frac{r_{ij}^0}{r_{ij}} \right)^6 \right] 
\]

The functional can be mainly divided into bond interaction terms and nonbond interaction terms. The bond interaction terms represent internal coordinates of bond (\( b \)), angle (\( \theta \)), torsion angle (\( \phi \)), and out-of-plane angle (\( \chi \)), and the cross-coupling terms include combinations of two or three internal coordinate. The nonbond interactions include a Lennard-Jones 9-6 function for the van der Waals terms and a Coulombic function for an electrostatic interaction.

The Lennard-Jones 9-6 parameters (\( \varepsilon_{ij}^0 \) and \( r_{ij}^0 \)) are given for like atom pairs. For unlike atom pairs, a 6th order combination law\(^{11}\) is used to calculate the off-diagonal parameters:

\[
r_{ij}^0 = \left( \frac{(r_i^0)^6 + (r_j^0)^6}{2} \right)^{1/6} 
\]

\[
\varepsilon_{ij}^0 = 2 \sqrt{\varepsilon_i \varepsilon_j} \left( \frac{(r_i^0)^3 \cdot (r_j^0)^3}{(r_i^0)^6 \cdot (r_j^0)^6} \right) 
\]

The number of molecules for the polyimide, polyamide-imide and phenoxy resin used for the simulation was twenty, and the number for the polymethyl methacrylate was eight. The total number of atoms for the adhesive/polyimide interface was about 4000. We adopted the NVT ensemble for the molecular dynamics simulation. The whole number of
calculated steps was 30,000 (30 ps).

The optimized structures from the molecular dynamics simulation are shown in Fig. 5. Only one molecule of the adhesives or the polyimides at the interface is represented by ball atoms. Fig. 5 shows that the polyamide-imide and the polyimide were arranged flatly next to each other, that a benzene ring was standing in the case of the phenoxy resin/polyimide interface, and that the polymethyl methacrylate was arranged spherically in the case of the polymethyl methacrylate/polyimide interface. We think that the structure of polyamide-imide and that of polyimide are similar to each other in terms of the presence of benzene rings and the interface was flatly because polyamide-imide and polyimide tried to interact more strongly among benzene rings. Phenoxy resin also has benzene rings, but the structure is not similar to polyimide and it is soft compared with polyamide-imide, so it is considered that the benzene ring was standing. Polymethyl methacrylate does not have benzene rings and soft, so tends to agglomerate spherically.

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(a) Initial structure of adhesive or polyimide/Cu interface
(b) Optimized structure of adhesive or polyimide/Cu interface
(c) Stick adhesive and polyimide together
(d) Optimized structure of adhesive/polyimide interface

Fig. 4 Modeling method for the adhesive/polyimide interface
4. Results of the adhesion energy

We calculated the adhesion energy between the adhesive and the polyimide by using the optimized structures. As shown in Fig. 6, the adhesion energy ($E_{ad}$) is defined as the difference between the total potential energy of the material when connected ($E_{co}$) and when separated ($E_{se}$) (i.e., $E_{ad} = E_{se} - E_{co}$). The optimized structure shown in Fig 5 is used as material-connected state. The material separated state is obtained by eliminating the interatomic potentials between the adhesive and the polyimide in material-connected state. When the adhesion energy is high, the adhesion strength is high.

The adhesion energy obtained from the molecular dynamic simulation and the peel strength measured with the peel strength test are compared in Fig. 7. The peel strength is represented by an arbitrary unit normalized to the quantity of polyamide-imide in the logarithmic scale. The details of the peel test is shown in § 6. Both simulation and experimental results in Fig. 7 show that polyamide-imide had the highest adhesion strength and polymethyl methacrylate had the lowest adhesion strength. In the case of polyamide-imide, the area contacting with the polyimide layers in the atomic level was large, and many of the polyamide-imide and polyimide atoms interacted because the polyamide-imide was arranged flatly, as shown in Fig. 5 (a). That is why polyamide-imide has the highest adhesion strength. In contrast, polymethyl methacrylate had the lowest adhesion energy because the polymethyl methacrylate was arranged spherically and had few atom contacts with the polyimide, as shown in Fig. 5 (c).
5. Evaluating the relationship between flatness and interaction

Resin materials such as adhesive and polyimide are mainly made of carbon atom, and the interaction between an adhesive carbon atom and a polyimide carbon atom is the largest and most important of all atomic pairs at the interface. Therefore, to evaluate the relationship between the adhesion strength and the strength of the interaction at the interface, we calculated the number of atomic pairs in which the distance between an adhesive carbon atom and a polyimide carbon atom was less than 0.5 nm (Fig. 8).

As shown in the formula (2), the Lennard-Jones 9-6 function was used for the atomic interactions acting between the \(i\)-th and \(j\)-th atoms for the van der Waals force in the COMPASS force field. The interaction energy which is shown as the Lennard-Jones 9-6 function between carbon and carbon is shown in Fig. 9. The reason we calculated the number of C-C pairs in which the distance between the two atoms was less than 0.5 nm was that we thought that when the distance between two atoms is more than 0.5 nm, the potential energy between the two atoms is less than 50% of maximum value, so the interaction between the two atoms is small.
The adhesion energy and the number of C-C pairs in which the distance between two atoms was less than 0.5 nm are compared in Fig. 10. This graph shows that C-C pairs increased in the adhesive with high adhesion energy. This means that the adhesive with high adhesion strength had more C-C pairs and interacted with the polyimide more because the adhesive was arranged flatly at the atomic level.

Fig. 8 Simple sketch of a C-C pair

![Fig. 8 Simple sketch of a C-C pair](image)

Fig. 9 Interaction energy between carbon and carbon

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Fig. 10 Comparison between the number of C-C pairs and adhesion energy

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6. Comparison between simulation and experimental results

The peel test was carried out in the following way. Three kinds of adhesives, polyamide-imide, phenoxy resin, and polymethyl methacrylate, were attached on polyimide substrates. The thickness of the adhesives is 20µm, and that of the polyimide substrate is 200µm. The width and length of the specimens are 5 mm and 200 mm, respectively. The peeling force was applied to the edge of the adhesives, as shown in Fig. 11, and the adhesive film was pulled away from the polyimide substrate at a 90° angle at a peel rate of 50 mm/min. The peel strength was determined by measuring the peeling force. For each adhesive material, we carried out 10 peel tests, and averaged the measured results.

The averaged values of measured peeling forces for polyamide-imide, phenoxy resin, and polymethyl methacrylate were 15.8, 1.05, and 0.216 (10^2 N/m), respectively. In Fig. 7, these values are shown by using an arbitrary unit normalized to the quantity of polyamide-imide in the logarithmic scale. Although the order of peel strength (polyamide-imide/polyimide > phenoxy resin/polyimide > polymethyl methacrylate/polyimide) agrees with that of the simulation, the ratio of the experimental result of polyamide-imide (15.8×10^2 N/m) to that of phenoxy resin (1.05×10^2 N/m) is very high, compared with the simulation result. We think that the reason for this disparity between the simulation and experimental results is due to the plastic deformation in the peel test. While the plastic deformation is not taken into account in the simulation, it can not be neglected in the peel test. In particular, when the adhesion strength is quite strong (for example, at the polyamide-imide/polyimide interface), the contribution of the plastic deformation is likely to be very large in the peel test. On the other hand, when the adhesion strength is rather week (for example, at the phenoxy-resin/polyimide and polymethyl-methacrylate/polyimide interfaces), the contribution of the plastic deformation is likely to be small in the peel test. Therefore, in order to compare the simulation result with experiment, we need to use another experimental method that cause less plastic deformation such as nano-indentation methods and bending tests. We will report such work in the next paper.
Summary

We analyzed the adhesion at the interface between an adhesive and a polyimide (resin/resin interface) by using a classical molecular dynamics simulation. Three kinds of adhesives, polyamide-imide, phenoxy resin, and polymethyl methacrylate, were used as examples, and we calculated the adhesion energy between these adhesives and polyimide to evaluate the adhesion strength at the interface. The following results were obtained.

1. By using Cu layer before making resin/resin interface, we have established a method for modeling resin/resin interfaces, where resin does not have a regular configuration.
2. The adhesion energy obtained from the molecular dynamics simulation showed that the adhesion energy increased in the order of polyamide-imide/polyimide > phenoxy resin/polyimide > polymethyl methacrylate/polyimide.
3. The order of adhesion strength (polyamide-imide/polyimide > phenoxy resin/polyimide > polymethyl methacrylate/polyimide) agrees with that of the peel strength test.
4. The adhesive with high adhesion strength had more atomic pairs in which the distance between an adhesive carbon atom and a polyimide carbon atom was less than 0.5 nm.
5. The adhesive that was arranged flatly had the highest adhesion strength because the number of C-C atomic pairs had increased, and many of the adhesive and polyimide atoms interacted.
6. We were able to predict and select the material with the highest adhesion strength efficiently by using the molecular dynamics simulation. We also found that the characteristics of adhesion are related to the atomic scale structure at the interface, and it is expected that the results obtained from the simulation will be effective in future material design.

References

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