Study of Adhesion of Resin Materials by Molecular Simulation

OGASAWARA, Miki* TACHIOKA, Masaaki*

ABSTRACT

Molecular simulation is a technology for evaluating the various properties of materials based on their molecular structure by using a computer. It has received attention as a method for speeding up the development of products. Semiconductor modules are being employed to an expanding range of applications such as industrial equipment and electric vehicle. In order to ensure high reliability, importance is placed on the adhesion of materials and resin. Against a backdrop of this, we implemented a study using molecular simulation for analyzing auxiliary agents for improving adhesiveness. We evaluated 2 types of adhesion assistants and elucidated molecular level mechanisms related to adhesion with aluminum.

1. Introduction

Molecular simulation is a technology for evaluating various properties of materials based on their molecular structure using a computer. It has been increasingly applied in recent years not only for the evaluation of materials that have already been launched on the market, but also as a prediction technique for enhancing the performance of or for adding new functionality to materials. As products are designed to have enhanced performance and to be more complex, predicting the properties of materials in advance can reduce the number of prototyping iterations and accelerate the development of highly reliable products. As a result, molecular simulation has been introduced not only in universities but also in companies as a technology for improving the reliability of products and shortening the development period.

Molecular simulation can also be used as a technology for complementing the molecular- or atomic-level analysis technologies such as transmission electron microscopes (TEMs) or atomic force microscopes (AFMs) to provide theoretical support for the analysis results.

This paper describes a way to effectively use molecular simulation for the adhesion analysis of resin materials of resin mold semiconductor modules such as small-capacity intelligent power modules (IPMs), All-SiC modules and automotive power modules.

2. Semiconductor Modules

2.1 Characteristics and challenges

Semiconductor modules are used in power converters and are being applied to an increasingly wide range of fields such as industrial equipment, electric vehicles and home appliances[1]. The semiconductor modules for these power converters must be highly reliable. Power cycle capability, which is an indicator of thermal fatigue based on the estimated temperature change in products during actual operation, is one of the items the market places importance on to prove reliability. As shown in Fig. 1[2], a semiconductor module consists of many components. Separation of or cracks in the components may cause a deterioration of its power cycle capability. To prevent this, it is important to improve the adhesion between the components. Because of its low resistance and high thermal conductivity, aluminum has been used for the bonding wires in semiconductor modules or as a material for insulating aluminum substrates. It has, however, a low adhesion to epoxy resin used for molding so that a certain countermeasure must be taken. In order to make practical use of modules that are more reliable than conventional products in the future, we need to select new materials with higher reliability in terms of adhesion and other properties, not only by using experience but also by taking a scientific approach.

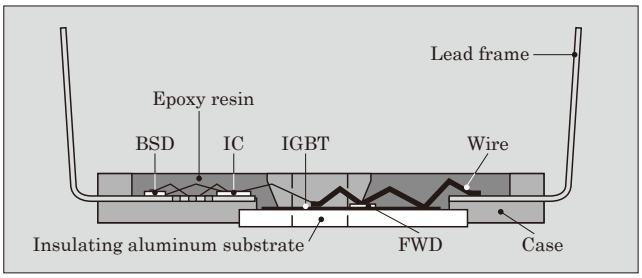


Fig.1 Structure of epoxy resin mold semiconductor module

2.2 Factors affecting adhesiveness

Although adhesiveness may be determined by many factors, particularly important ones are the an-

* Corporate R&D Headquarters, Fuji Electric Co., Ltd.

chor effect; mechanical properties including elastic modulus, linear expansion coefficient and glass transition temperature; and the chemical bonding between the module components and resin.

Among these, chemical bonding directly joins the components and resin in immediate contact and so it can have a major effect on improving adhesion. Consequently, in addition to the anchor effect and mechanical properties which have been focused on for a long time, attention is being placed on improving adhesion through chemical bonding. Since the strength of chemical bonding is determined by the molecular structures of materials, an effective way to enhance it is to carry out analysis using molecular simulation.

3. Molecular Simulation

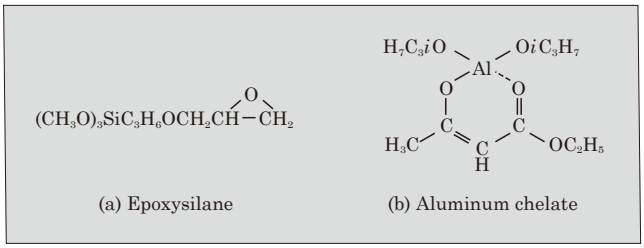
Molecular simulation is a general term for a process that is conducted to analyze the phenomenon that results from the molecular structures of materials. In a molecular simulation, it is necessary to select an appropriate method in accordance with the phenomenon to be analyzed. For example, since the elastic modulus of macromolecules is determined by the element and bonding type of the atoms composing molecules, it is effective to use a molecular dynamics simulation by using atoms as structural units. The first-principles calculation used in this paper is a method of non-empirical calculation using electrons around atoms as structural units. It is used as a method of analyzing chemical reactions or band structures where the motion of electrons controls the material properties. It is characterized by its calculation method just specifying molecular structure based on the Schrödinger equation of quantum mechanics without using experimental data. Consequently, its greatest advantage is that calculation is possible without a real material.

The flow of the first-principles calculation consists of creating a molecular structure and performing a geometry optimization. The geometry optimization repeats the optimization of atomic coordinates and electron state alternately and finishes when a specified convergence condition is satisfied. From the calculation result, a stable molecular structure and the energy of the system in that state can be obtained. In addition, the band structure and various physical property values can be obtained by analyzing the breakdown of the energy.

4. Evaluation

4.1 Adhesion assistants

There are 2 techniques to improve the adhesion of chemical bonding: One is to change the molecular structure of the base material resin and the other is to use additives. This paper focuses on additives, which are adhesion assistants in this case, and evaluates their effect on the chemical bonding with aluminum.



(a) Epoxysilane (b) Aluminum chelate

Fig.2 Molecular structures of adhesion assistants

The adhesion assistants we selected are: Epoxysilane, which is a silane coupling agent; and aluminum chelate, which is a chelate agent. We evaluated and compared their adhesiveness in a calculation and experiment. Figure 2 shows the molecular structure of the adhesion assistants.

4.2 Mechanism

Epoxysilane and other silane coupling agents are generally mixed into resin after the alkoxyl group in the molecules is hydrolyzed. The hydroxyl group that results from the hydrolyzation forms hydrogen bonds with the hydroxyl group on the surface of the aluminum. Then heat is applied to form strong covalent bonds (see Fig. 3). On the other hand, aluminum chelate and other chelate agents are mixed into resin without hydrolyzation. This causes a dealcoholization reaction between an alkoxyl group such as C_3H_7O and the hydroxyl group on the surface of the aluminum, which results in covalent bonding (see Fig. 4).

It can be presumed that both epoxysilane and aluminum chelate enhance the adhesion between the aluminum and epoxy resin by forming covalent bonds

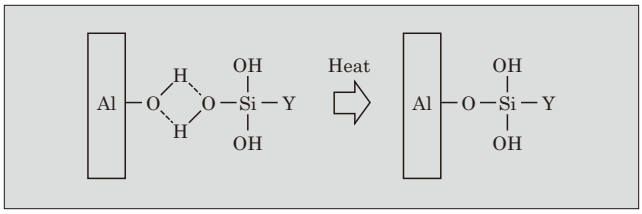


Fig.3 Reaction of a silane coupling agent

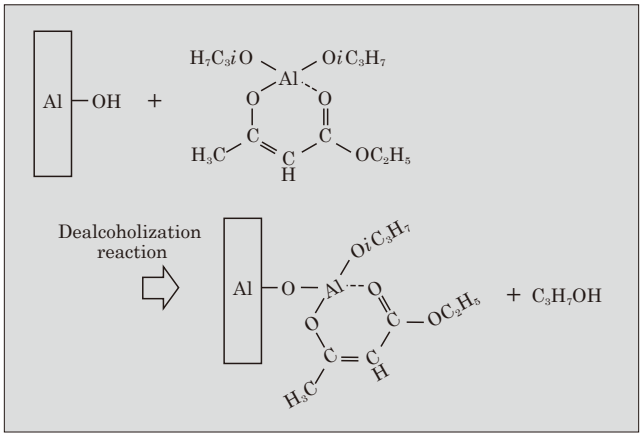


Fig.4 Reaction of aluminum chelate

with aluminum.

4.3 Calculation flow

The calculation flow is shown in Fig. 5. In order to simulate the oxide film on the surface of aluminum, we performed a geometry optimization of alumina crystal, then cut a (100) surface so that oxygen is on the surface, and terminated the oxygen on the topmost surface with hydrogen to create a hydroxyl group. To increase the calculation efficiency, we used only the molecular structure of the adhesion assistants at the section contributing to adhesion. We performed the geometry optimization for the adhesion assistants and aluminum individually and used the obtained structure to create the adhesion structures shown in Fig. 3 and Fig. 4. After performing the geometry optimization of the adhesion structures, we used the obtained structures to create structures where the adhesion assistants were dissociated from the aluminum, and then performed the geometry optimization again. We set the index of adhesiveness to be the difference between the energy of the adhesion structure and that of the dissociation structure (dissociation energy). For the calculation, we used DMol^3 *1, which is a density-functional calculation program.

4.4 Calculation result

Figure 6 shows the molecular structures after the geometry optimization was performed for the adhesion assistants. As expected in advance, we confirmed that they form tetrahedral structures with silicon or aluminum at the center. We then used the structures in Fig. 6 to create structures after the adhesion shown in Fig. 3 and Fig. 4. Figure 7 shows the molecular structures after the geometry optimization was performed for cases where the aluminum and epoxysilane adhered and dissociated. In the adhesion structure, the silicon of epoxysilane or the aluminum of aluminum chelate bonded to the oxygen of alumina and stabilized. Furthermore, the oxygen of epoxysilane or aluminum chelate got closer to the aluminum of alumina, showing an interaction.

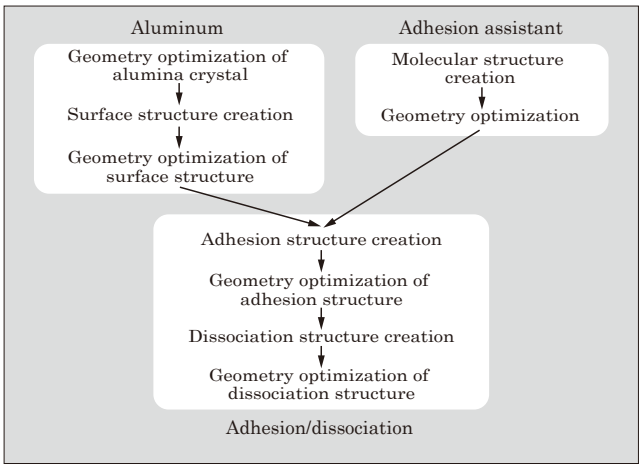


Fig.5 Calculation flow

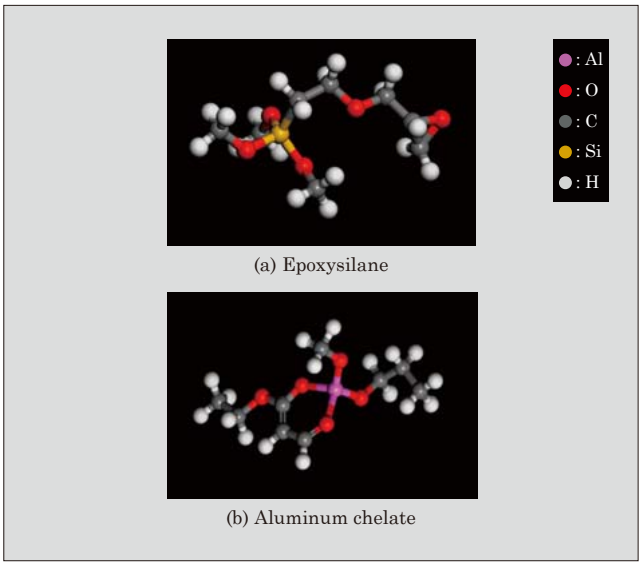


Fig.6 Molecular structures after geometry optimization

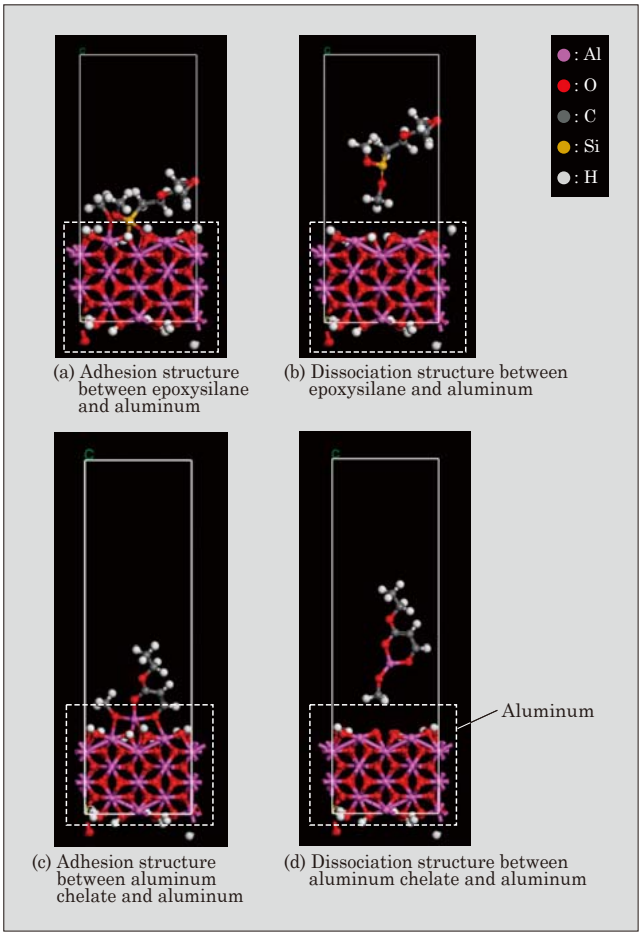


Fig.7 Molecular structures after geometry optimization of epoxysilane/aluminum chelate and aluminum

*1: DMol^3: Part of the Materials Studio software environment. Materials Studio is a trademark or registered trademark of Dassault Systèmes S.A.

Table 1 Dissociation energy

Item	Dissociation energy (eV)
Epoxysilane	4.81
Aluminum chelate	7.29

Table 1 shows the resulted dissociation energy values obtained from the energy difference between the adhesion structure and dissociation structure. A high dissociation energy means larger energy is needed when the object dissociates from the adhered state. From the calculation, we can expect that when epoxysilane and aluminum chelate are compared, aluminum chelate will require more dissociation energy, suggesting higher adhesiveness.

4.5 Measuring the adhesion force

(1) Measurement condition

In the experiment, we added fused silica to an acid anhydride curing agent containing bisphenol A epoxy resin, alicyclic epoxy resin and imidazole catalyst, and mixed them before adding epoxysilane or aluminum chelate.

The adhesion force was measured with the method described below. The shape of the test piece is shown in Fig. 8. A 10 mm square aluminum substrate was washed with ethanol and dried. Then a special mold was secured on the substrate surface and filled with epoxy resin. After the resin had cured under specified conditions, the mold was removed. We fixed the aluminum substrate to the obtained test piece, brought a load-applying jig into contact with the resin part, made it push the resin part in a direction parallel to the substrate surface and measured the maximum breaking load. The maximum breaking load values per unit bonding area of 5 test pieces were averaged and the result was assumed to be the adhesion force.

(2) Comparison of the measurement result with the calculation result

Figure 9 shows the dissociation energy obtained with the calculation and the adhesion force obtained in the experiment. Not only the calculation result but also the experiment result showed that aluminum chelate had a stronger adhesion force, or was harder to dissociate, than epoxysilane. This revealed that a molecular-level mechanism was involved with the difference in adhesion forces.

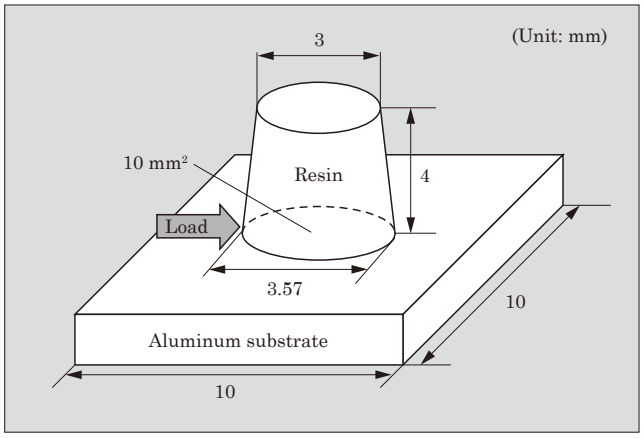


Fig.8 Test piece for adhesion force measurement

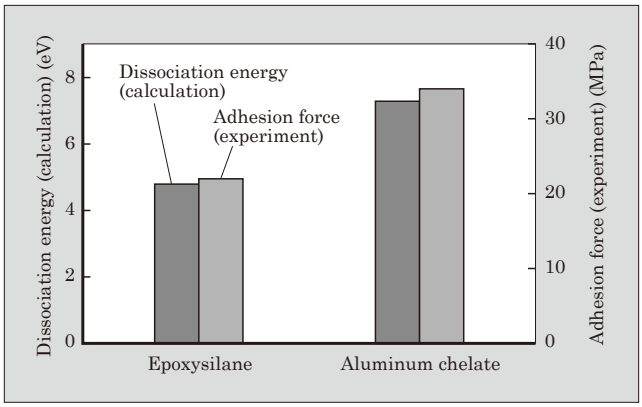


Fig.9 Comparison between calculation result and experiment result

5. Postscript

This paper has described the effective use of molecular simulation for the adhesion analysis of resin materials of resin mold semiconductor modules. It revealed that a molecular-level mechanism was involved with the performance of adhesion assistants that enhance the adhesion between module components and resin. We intend to identify the conditions required for auxiliary agents to give higher adhesion by analyzing the cause of different dissociation energy values between epoxysilane and aluminum chelate and their bonding density with components. We will then apply the result to guidelines for selecting auxiliary agents and contribute to enhancing the reliability of semiconductor modules.

Part of this study was carried out in cooperation with Prof. KOYAMA, Michihisa of the Frontier Energy Research Division of Inamori Frontier Research Center, Kyushu University; and Prof. MURAKAMI, Yasushi of the Faculty of Textile Science and Technology, Shinshu University. We would like to express our deep appreciation for their cooperation.

References

(1) Horio, M. et al. "New Power Module Structure with Low Thermal Impedance and High Reliability for SiC Devices". PCIM Europe 2011, 37 (2011), p.229-234.

(2) Ikeda, Y. et al. "A study of the bonding-wire reliability on the chip surface electrode in IGBT". 2010, Proc. of ISPSD, p.289-292.

Fuji Electric

Innovating Energy Technology