Surface Mounting Process Using Hybrid Resin Sheet Including Self-Organizable Solder Particles

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To ensure the robustness of surface-mount technology, underfill resin should be applied between the chip device and the substrate. However, this application process is time consuming. Therefore, a novel chip surface-mounting process using hybrid resin containing solder particles is proposed to shorten the underfill application process. The hybrid resin consists of semicured thermoset epoxy resin containing a reducing reagent, Sn–Bi solder particles, and thermoplastic polyester thin resin film. Viscosity and reduction ability of the hybrid resin were investigated via various techniques. The semicured epoxy resin fabricated at lower temperature showed better bondability. Acetic acid was effective in reducing the oxide film on the solder particles. The coalescence behavior of molten solder particles depended on both the reduction reaction and the viscosity of epoxy resin at the bonding temperature. The epoxy resin with low viscosity was mounted on the substrate via an overcoat of the polyester film. A conductive path covered with the resin formed between the chip resistor and the substrate via the hybrid resin. [doi:10.2320/matertrans.MD201204]

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1. Introduction

Surface-mount devices such as ball grid arrays and chip-scale packages are becoming increasingly popular for reducing the size of packaging in the growing trend of downsizing electronic devices. Flip chip assembly consists of the following steps: aligning the solder ball and connectors on the external circuitry, performing reflow soldering to obtain bumps, underfilling with an electrically insulating resin, and curing the resin. One important step in the flip chip process is underfilling, in which an underfill agent is applied in the clearance space between chip parts and the printed circuit board to ease the stress and to hold the parts in place. The conventional underfill process uses epoxy resins that are deposited after solder bump reflow. Most current underfill encapsulants are deposited on the edge of the assembled package. This allows the capillary phenomenon to draw the underfill into the gap between the chip and the substrate of the assembled package to complete the encapsulation process. The underfilling process also requires a curing stage. Although many improvements have been made to reduce the number of steps required, underfilling and curing remain time-consuming stages in the production of surface-mount technology. Therefore, a no-flow underfilling process for flip chip assembly has been developed.¹–³ In this process, first, the underfill epoxy resin is dispensed on a substrate with pads. The chip with solder bumps is held to face the pads in the resin, and cures completely in a typical reflow profile. The no-flow underfilling process leads to a significant reduction in the steps and time required.

On the other hand, Ohta et al. propose a self-organization assembly process using a novel thermoset resin including tiny solder particles.⁴–⁹ The molten solder particles in the thermoset resin coalesce spontaneously in the highly fluid resin at elevated temperature to form conductive paths between electrodes and terminal pads (see Fig. 1). The resin for the self-organization assembly process has high fluidity even at room temperature to give sufficient mobility to solder particles. Therefore, it must be treated and stored carefully to maintain the appropriate properties, and it is difficult to premount on a substrate. We have therefore developed a hybrid resin containing solder particles for the chip surface-mounting process that is easy to store and can be premounted on a substrate, similar to the no-flow resin.¹–³

To realize the process, the resin properties must be optimized. Figure 2 shows the requirements for the resin. At room temperature, the resin should have high viscosity,
that is, low fluidity, to be able to be premounted in position on the substrate. The viscosity of the resin should be decreased to give some degree of mobility to the solder particles when it is heated beyond the melting point of the solder particles. Otherwise, the solder particles will not clump together. At the same time, oxide film on the solder particles must be reduced to enable coalescence. The resin is cured successively after the formation of a conductive path to encapsulate the path. Therefore, resin properties such as the viscosity and the reduction ability of the solder particles, not only at elevated temperature but also at room temperature, are important factors.

The objective of this study was to clarify the requirements for the resin so as to establish a novel surface-mounting process. A hybrid resin containing solder particles was designed in terms of viscosity and reduction ability for solder particles.

## 2. Experimental Procedures

### 2.1 Materials

Two types of thermoset epoxy resins were used as an underfill resin matrix. Table 1 lists the properties of the resins, and Fig. 3 shows the viscosity of the resins as a function of the temperature, measured by a coaxial-cylinder rotational viscometer. Resin-A (bisphenol-A epoxy resin, EP-4100E, ADEKA Co., Ltd.) contained no hardener or reduction reagent. Hardener reagent was added to epoxy resin-A with a mass percentage of 3. Resin-B (XB1007, Fujikura Kasei Co., Ltd.) showed lower viscosity than resin-A at high temperature. Thermoplastic phenoxy and polyester resins were also used. The softening temperatures of phenoxy and polyester resin were 393 and 395 K, respectively. The solder particles used were Sn–58 mass percentage Bi alloy with an average diameter of 21 µm (Senju Metal Industry Co., Ltd.). The melting point of the solder was 411 K. The geometries of the substrate and chip resistor are shown in Fig. 4. There are two copper (Cu) lands on the substrate, and both ends of the chip have metal plating.

### 2.2 Fabrication of resin sheet

The Sn–Bi solder particles were stirred in the epoxy resin at room temperature. The volume fraction of solder particles was 5%. Formic acid or acetic acid was added to the epoxy resin as the reducing agent. The acid solution to epoxy resin-A had a mass percentage of 20. Epoxy resin-A without a reducing agent was prepared for reference. Epoxy resin-A containing solder particles was applied on the plate in uniform thickness. At this stage, epoxy resin-A showed low viscosity. The epoxy resin-A applied on the glass plate was held at various temperatures from 298 to 383 K in air atmosphere to fabricate a semicured resin sheet. The heating time was 600 s. The thickness of the resin-A sheet was 55 µm. Hereafter, the heat-treated resin-A is referred to as “semicured resin”. Similarly, the thermoplastic polyester and phenoxy resin thin films were fabricated at 358 K for 600 s. The thickness of each thermoplastic resin film was 13 µm.

### 2.3 Bonding process

The bonding process involves a reflow and curing process at the same time. The semicured thermoset resin-A sheet including solder particles was inserted between a chip and a substrate (see Fig. 5(a)). In addition, resin-B and resin-A with low viscosity were covered with thermoplastic resin film to hold them in position on the substrate (see Figs. 5(b) and 5(c)), hereafter referred to as the “hybrid resin”. The specimens were kept at 453 K for 60 s to form a conductive path covered with the resin between the chip and the substrate. The heating profile in the bonding process is shown in Fig. 6. In some cases, preheating for 80 s was carried out at
393 K, which was lower than the melting point of the solder particles, to promote the reduction reaction.

2.4 Evaluation
Cross sections of the bonds were observed using optical microscopy. Since the viscosity of semicured resin cannot be measured by a viscometer, the hardness was measured by a ball-on-disk-type wear tester to evaluate the viscosity of semicured epoxy resin-A fabricated at various temperatures. The ball was SUS304 stainless steel with a diameter of 4.8 mm. The load was 50 gf, and the wear speed was 3.1 mm/s. The width of the wear track was measured by a stereoscope. To evaluate the viscosity of the resin during the bonding process, gravitational sedimentation of the solder particles in the resin was observed by the stereoscope, and the sedimentation velocity was measured.

3. Results and Discussion
3.1 Hardness of semicured epoxy resin-A
High viscosity at room temperature is required to hold the semicured epoxy resin-A in position on the substrate. Ball-on-disk wear tests were carried out as a simple method for evaluating the viscosity or hardness of the semicured epoxy resin-A without solder particles. The width of the wear track corresponded to the hardness. Figure 7 shows the width of the ball track on the semicured epoxy resin-A fabricated at various temperatures. The change in hardness after the exposure durations of 86.4 and 172.8 ks at room temperature was also evaluated. Because semicured resin fabricated below 323 K still showed very low viscosity, which was similar to that of the as-received resin-A, the wear ball sunk completely into the epoxy resin, and the track width could not be estimated accurately. The epoxy resin fabricated at 358 K was harder than the as-received resin, but remained soft to some degree, which indicated low viscosity. As the fabrication temperature increased, the width of the ball track decreased. The wider track indicated a reduction in hardness. When the fabrication temperature was 383 K, only a thin wear track was observed. The epoxy resin also gradually hardened with further exposure at room temperature, which indicated that curing proceeded even at room temperature in the air atmosphere.

3.2 Resoftening of semicured epoxy resin-A
The semicured epoxy resin-A must be resoftened and must show low viscosity when heated to the bonding temperature; otherwise, the solder particles cannot coalesce (see Fig. 2). When the epoxy resin had high fluidity, the solder particles settled out in the softened epoxy resin. The sedimentation of solder particles in the resin was observed when the semicured resin-A was heated to 373 K. Figure 8 shows the sedimentation velocity of solder particles in the resoftened resin-A was measured at 373 K.
to ensure the mobility of solder particles during the bonding process.

Semicured epoxy resin-A after exposure in the air atmosphere showed a lower sedimentation velocity than the as-fabricated resin. This was because curing proceeded isothermally even at room temperature.

### 3.3 Effect of reducing agent

In the self-organization assembly process, the reduction of surface oxide film on the solder particles is a significant factor, in addition to sufficient mobility of the particles in the resin, in ensuring that the particles coalesce, as shown in Fig. 2. It has also been reported that the movement of solder particles in the resin is driven by the Marangoni effect due to the unevenness of interfacial energy, which results from the inhomogeneous distribution of oxide film on molten solder particles. Thus, some amount of surface oxide film on solder particles is necessary to obtain driving force for movement. On the other hand, surface oxide film must be reduced for the particles to coalesce. As described in the preceding section, the solder particles are able to move in the semicured epoxy resin-A fabricated at a low temperature. To reduce oxide films, some types of carboxylic acids such as formic and acetic acid were added in epoxy resin-A during the fabrication process. It is known that carboxylic acid (nR-COOH) reduces metallic oxides according to the following reaction.

\[
nR\text{-COOH} + \text{MO} \rightarrow (n\text{-R-COO})\text{n} + \text{H}_2\text{O} \quad (1)
\]

Figure 9 shows the cross sections of bonds between a chip and a substrate using epoxy resin-A including solder particles and acetic acid or formic acid. When the epoxy resin contained no acid, each solder particle retained its original spherical shape, which indicated that no coalescence occurred, although some clusters formed. On the other hand, a conductive path formed between the chip and the Cu land by the addition of acetic acid, and the conductive path was covered with the cured resin. Although some wandering solder particles remained near the surface of the resin, these particles were also fully covered with the cured epoxy resin. Thus, they were not a significant issue. According to eq. (1), formic acid can reduce tin oxide. Isaka et al. reported that tin oxide is reduced by formic acid and H₂, O₂ and H₂O gas evolved at 423 K. However, in our study, the Sn–Bi solder particles did not coalesce when formic acid was added, and many large voids formed in the resin, as shown in Fig. 9(c). The formic acid was probably decomposed according to the reaction in eq. (2) at high temperature.

\[
\text{HCOOH} \rightarrow \text{H}_2\text{O} \uparrow + \text{CO} \uparrow \quad (2)
\]

Therefore, the reduction ability of formic acid was degraded at 453 K, and the evolved CO and water vapor caused the formation of voids.

### 3.4 Effect of cover film

A lower fabrication temperature appears to be more desirable for the resoftening process, as described in section 3.2. However, the semicured resin-A fabricated at low temperature showed low viscosity and resembled sol at room temperature. The resin with low viscosity could not be held in position on the substrate at room temperature. Thus, semicured epoxy resin-A fabricated at 363 K was covered with the thermoplastic resin film to hold it on the substrate (see Fig. 5(b)). Because the thermoplastic resin was in a solid state at room temperature, the spread of the thermoset epoxy resin-A with low viscosity was inhibited by the film. The sedimentation of solder particles in epoxy resin-A covered with the thermoplastic resin film was observed at 413 K. Figure 10 shows the sedimentation velocity of solder particles in the double-layered resin sheet. The sedimentation velocity of particles in epoxy resin-A covered with the thermoplastic resin film was smaller than that in the monolayer epoxy resin sheet. In particular, the solder particles hardly moved through the overcoat of phenoxy resin film. The phenoxy resin probably reacted with the epoxy resin-A, which accelerated the curing. On the other hand, the polyester resin film had no significant effect on the viscosity of the epoxy resin-A layer. Because some solder
particles were stuck in the overcoat polyester film, the average sedimentation velocity was lower than that in epoxy resin-A without the overcoat film. The polyester resin film is a candidate overcoat film to protect and to hold in position on the substrate this epoxy resin with low viscosity.

3.5 Viscosity

Viscosity of the resin is a significant factor, in addition to the oxide film, in optimizing the design of hybrid resin sheets. In the case of the self-organization assembly process, it has been reported that a preheating process carried out below the melting point of solder particles is necessary to promote the reduction of oxide film on solder particles.11) Figure 11 shows the cross sections of bonds using polyester/epoxy-A hybrid resin containing acetic acid under temperature profiles with and without preheating. The solder particles did not coalesce under the temperature profile with preheating. Although oxide films could be reduced during the preheating process, the movement of solder particles was inhibited owing to an increase in the viscosity. On the other hand, most of the solder particles coalesced under the temperature profile without preheating. The oxide film on solder particles might be reduced during the heating process to melting point by using an adequate reducing agent such as acetic acid. Therefore, the preheating process is not always necessary from the viewpoint of viscosity. A lower viscosity may be better for forming a conductive path. However, there may be a threshold for forming a conductive path fully covered with the resin. Figure 12 shows the cross section of bonds using resin-B that exhibited lower viscosity than resin-A at the bonding temperature and contained a reducing reagent for tin oxide. A conductive path formed between the chip and the substrate, and no residual wandering solder particles were observed. However, the conductive path was not fully covered with the cured resin-B, because most of the resin ran out owing to low viscosity at the bonding temperature, as shown in Fig. 3.

Figure 13 shows the cross sections of bonds formed using a polyester resin/epoxy/resin-B/polyester resin hybrid sheet containing acetic acid. The middle epoxy resin-A layer was semicured at various temperatures. The lower semicuring temperature showed better bondability because the viscosity of the resin was low. The middle epoxy resin layer that was semicured at 308 K showed superior bondability, which indicated the formation of a conductive path fully covered with the resin.
The most important factor was balancing the viscosity and the reduction ability of the resin as a function of the temperature profile. Further studies are necessary to optimize these features.

4. Conclusions

A feasibility study of a novel soldering process using a hybrid resin was carried out. The following conclusions were obtained.

1. The semicured epoxy resin that was fabricated at a lower temperature showed lower viscosity in the subsequent heating stage during bonding.

2. The thermoplastic polyester resin held epoxy resin-A with low viscosity in position on the substrate and did not prohibit the mobility of molten solder particles to enable them to coalesce at an elevated temperature during bonding. The hybrid resin sheet containing solder particles allowed a conductive path covered with resin to form at the same time.

3. Acetic acid showed better reduction of tin oxide film on solder particles than did formic acid.

4. Both high viscosity at room temperature and low viscosity at the bonding temperature are required for the resin to successfully form bonds. Further work is necessary to optimize the viscosity both at room temperature and at high temperature during bonding. Optimizing the reduction ability of solder particles is also important to enable them to coalesce and form a conductive path.

REFERENCES