### Effects of the Complexed Moisture in Metal Acetylacetonate on the Properties of the No-Flow Underfill Materials

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ABSTRACT: A potential no-flow (compression filling of encapsulant) underfill encapsulant for simultaneous solder joint reflow and underfill cure has been reported by the authors. The encapsulant is based on a cycloaliphatic epoxy/organic anhydride/Co(II) acetylacetonate system. The key of this no-flow encapsulant is the use of a latent metal acetylacetonate catalyst that provides the solder reflow prior to the epoxy gellation and fast cure shortly after the solder reflow. However, most of the metal acetylacetonates can easily absorp moisture as their ligand. Therefore, it is of practical importance to understand the effect of the complexed water on the properties of the no-flow material before and after cure. In this paper, differential scanning calorimetry, thermal gravimetric analysis, thermal mechanical analysis, dynamic mechanical analysis, and Fourier transform infrared spectrometry were used to validate the existence of complexed moisture in the Co(II) acetylacetonate. The effects of the complexed water on the curing profile, glass transition temperature, and storage modulus of the cured no-flow underfill material were studied. A possible catalytic mechanism of the metal acetylacetonate in the cycloaliphatic epoxy/anhydride system was subsequently discussed and proposed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 103-111, 1999

Key words: epoxy and anhydride; metal chelate catalyst; no-flow underfill; flip-chip

### **INTRODUCTION**

Flip-chip technology is the key interconnect packaging technology in developing high-density, large I/O, and high-performance semiconductor devices.<sup>1-3</sup> Due to the thermal coefficient of expansion (TCE) mismatch between silicon IC chip (2.5 ppm/°C) and substrate (18–24 ppm/°C for FR-4 PWB) during temperature cycling in normal operation, reliability becomes an issue.<sup>4-7</sup> The recent development of high-performance filled epoxy or cyanate ester-based underfill encapsulants has extended the technology to a variety of organic substrate materials, but the process is tedious, time-consuming, and expensive.<sup>8,9</sup> The noflow underfilling process was developed to overcome these disadvantages.<sup>10,11</sup> The no-flow process of the underfill encapsulant implies compressing the underfill between the flip-chip integrated device and the substrate. However, because conventional underfill encapsulants that rely on capillary action to draw the underfill between the chip and substrate cure at a temperature prior to the solder joint reflow and cannot provide solder fluxing, these underfills are not suitable for the no-flow underfilling process. In our prior work, a potential metal acetylacetonatecatalyzed epoxy/anhydride-based no-flow underfill encapsulant was developed.<sup>12-14</sup> The curing peak temperature of the no-flow underfill encapsulant is generally >200 °C, which can better fit the eutectic Sn/Pd solder reflow profile. However, the proper curing profile of the base formulation

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Name of Chemicals	Structure of Chemicals	Usage Quantity (parts by weight)
Cycloaliphatic epoxy resin		100
Curing hardener		30-100
Curing catalysts	Aged Co(II) acetylacetonate Anhydrous Co(II) acetylacetonate Co(II) acetylacetonate hydrate	0.1-1 0.1-1 0.1-1

Table I	<b>Chemical Ing</b>	redients in tl	he No-Flow	Underfills for	r Flip-Chi	o Applications

is only one of the necessary requirements for a successful no-flow underfill. Stability and compatibility with other additives of the base formulation are also important. Because these base formulation properties are directly related to the catalyst used, its stability and compatibility with other additives of the metal acetylacetonate catalyst are necessary to design a successful no-flow underfill material. Metal acetylacetonates were used as a catalyst in the bisphenol A/anhydride system by other researchers who reported a possible catalytic mechanism.<sup>15</sup> But the proposed mechanism was based on very limited evidence and speculative. Since then, no systematic work on the catalytic behaviors of the metal acetylacetonate in the epoxy/anhydride system has been done, and little knowledge of aspects is known. This situation motivated us to systematically study the catalytic behaviors of metal acetylacetonate in the epoxy/anhydride system, aiming at optimizing the developing no-flow underfills. Most of the metal acetylacetonates are hygroscopic and can slowly absorb air moisture; therefore, we have first studied the effects of the complexed water in Co(II) acetylacetonate on the curprofile of the epoxy/anhydride/Co(II) ing acetylacetonate system and the physical and mechanical properties of the cured underfills. An alternative catalytic mechanism of the metal acetylacetonate in the epoxy/anhydride underfill system is subsequently discussed and proposed.

### EXPERIMENTAL

#### Materials

Table I lists the chemical structures of epoxy resin, hardener, and catalysts used in the experiments. The epoxy resin is 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate provided by Union Carbide under the trade name ERL-4221D and used as received. The molecular weight and epoxide equivalent weight of the epoxy resin is  $252.3 \text{ g mol}^{-1}$  and 133 g, respectively. The hardener (or crosslinker) is hexahydro-4methylphthalic anhydride (HMPA) purchased from Aldrich Chemical Company, Inc., and used as received. HMPA molecular weight is 168.2 g  $mol^{-1}$ , and its purity is > 97%. Aged Co(II) acetylacetonate, anhydrous Co(II) acetylacetonate, and Co(II) acetylacetonate hydrate were used as curing catalysts for this study. Their concentrations are also listed in Table I. The KBr for the preparation of the Fourier transform infrared spectrometry pallets was purchased from Aldrich Chemical Company and used as received.

#### Preparation of the Epoxy/Anhydride/Co(II) Acetylacetonate System

A specified quantity of hardener was added into the epoxy resin, and the mixture was stirred for 15 min at 60°–70°C. Then, a specified quantity of catalyst was added into the mixture and stirred for additional 30 min at  $60^{\circ}$ -70°C until the catalyst was homogeneously dissolved. Formulations were then stored in a freezer at  $-40^{\circ}$ C.

# Differential Scanning Calorimetry (DSC) Studies on Curing Profile

To study the curing profile and glass transition temperature  $(T_g)$  of the prepared system, a modulated DSC instrument (by TA Instruments, model 2920) was used. A sample of  $\sim 10$  mg of an underfill that had been equilibrated to room temperature from  $-40^{\circ}\mathrm{C}$  was placed into a hermetic DSC sample pan. The sample was then heated in the DSC cell at 5°C min^{-1} to  $\sim 300^{\circ}\mathrm{C}$  to obtain the curing profile.

# Thermal Mechanical Analysis (TMA) Studies on TCE and $T_g$

Measurement of TCE and  $T_{\mbox{\scriptsize g}}$  of a cured system was performed on a TMA instrument (by TA Instruments, model 2940). A specimen for TMA was made by placing a liquid system into an aluminum pan  $(1\frac{1}{2}$ -inch diameter), transferring the pan to an 80°C preheated convective oven, and then heating it to 250°C at 3°C min<sup>-1</sup>. Then, the specimen was isothermally cured in the 250°C oven for an additional 15 min. The sample was then removed from the oven and cooled to room temperature. A diamond saw was used to cut the cured sample into strips, with dimensions of  $\sim 5$  $\times$  5  $\times$  2 mm. After placing the specimen in the TMA instrument, it was heated from room temperature to  $\sim 250^{\circ}$ C at a rate of 5°C min<sup>-1</sup>. The TCE was obtained from the slope of the plot of thermal expansion versus temperature. The inflection point of thermal expansion was defined as TMA  $T_g$ .

### Dynamic Mechanical Analysis (DMA) Studies on Dynamic Mechanical Properties

The preparation of a specimen used for DMA testing was the same as for the TMA testing, and the experiments were performed on a DMA instrument (by TA Instruments, model 2980). However, the dimension of the specimens for DMA is  $\sim 32$  $\times 11 \times 3$  mm. Measurement was performed in single cantilever mode under 1-Hz sinusoidal strain loading. Storage moduli (E'), loss moduli (E''), and loss tangent (tan  $\delta$ ) were calculated by the instrument's software.

## Thermal Gravimetric Analysis (TGA) Studies on Decomposition Temperature

The weight losses of the three Co(II) acetylacetonates were studied by a TGA instrument (by TA Instruments, model 2050). A sample of ~ 40 mg of aged Co(II) acetylacetonate, anhydrous Co(II) acetylacetonate, or Co(II) acetylacetonate hydrate was placed into a platinum TGA sample pan. The sample was then heated in the TGA furnace at 10°C min<sup>-1</sup> to ~ 600°C under N<sub>2</sub> purging (N<sub>2</sub> flow rate: 77 mL min<sup>-1</sup> in the vertical direction and 12 mL min<sup>-1</sup> in the horizontal direction). The instrument automatically calculates the weight loss percentage within a selected temperature range.

# FTIR Studies on the Existence of Water Molecules in Co(II) Acetylacetonates

A Nicolet FTIR spectrometer (model 205) was used to detect the existence of water molecules in the metal acetylacetonates. An FTIR pallet was prepared with  $\sim 5-10$  wt % metal acetylacetonate ground with FTIR grade KBr in a mortar. The pallet was then placed in the infrared sample holder. The infrared signal was automatically collected by the instrument and analyzed by the instrument's software.

### **RESULTS AND DISCUSSION**

### Effect of Moisture on Curing Profile

An aged Co(II) acetylacetonate (stored at an ambient condition for >15 years) was first used at the beginning of the development of the no-flow underfill encapsulant. The curing profile of the aged Co(II) acetylacetonate-catalyzed epoxy/anhydride system shows two curing peaks, as indicated in Figure 1. A small peak appears at 165.36°C, and a larger peak appears at 210.22°C. To further elucidate the reaction nature of these two peaks, a well-defined anhydrous Co(II) acetylacetonate and Co(II) acetylacetonate hydrate were each mixed with the same cycloaliphatic epoxy and anhydride mixture at the same weight ratio. The curing profiles for these two systems are also shown in Figure 1. The system catalyzed by anhydrous Co(II) acetylacetonate only shows one noticeable exothermic peak at 222.74°C. But, the system catalyzed by Co(II) acetylacetonate hydrate shows two similar peaks to those of the system catalyzed by the aged Co(II) acetylacetonate. A small peak appears at 165.36°C, and a



**Figure 1** Curing profiles of the cycloaliphatic epoxy/anhydride system catalyzed by aged, anhydrous, and hydrated Co(II) acetylacetonates, respectively. The added amount of the catalyst is 0.4 wt % of the epoxy/anhydride mixture.

larger peak appears at 216.48°C. However, there are some differences between the curing profiles for the Co(II) acetylacetonate hydrate-catalyzed system and for the aged Co(II) acetylacetonate-catalyzed system. The small peak at 165.36°C has lower exothermic heat for the Co(II) acetylacetonate hydrate-catalyzed system than that for the aged Co(II) acetylacetonate-catalyzed system. The larger peak shifts to lower temperature for the aged Co(II) acetylacetonate-catalyzed system, compared with the Co(II) acetylacetonate hydrate-catalyzed system.

Figure 2 shows the FTIR spectra for these three Co(II) acetylacetonates. The peak at  $\sim 3500$  cm<sup>-1</sup> indicates that all these Co(II) acetylaceto-

nates contain some complexed water. But, the peak intensity could not be used as a measurement of the quantity of the complexed water in each Co(II) acetylacetonate due to the varied concentration of Co(II) acetylacetonate in KBr and varied thickness of the prepared pallet. Figure 3 shows the TGA diagrams of the aged, anhydrous, hydrated Co(II) acetylacetonates. All three Co(II) acetylacetonates show two weight-loss steps. The first weight-loss step (step 1) appears at the temperature range from 70° to 100°C, and the second weight-loss step (step 2) appears at the temperature range from 190° to 230°C. However, aged Co(II) acetylacetonate and Co(II) acetylacetonate hydrate lose much more weight in step 1 than



**Figure 2** FTIR spectra of aged, anhydrous, and hydrated Co(II) acetylacetonates, respectively.



Figure 3 TGA diagram of aged, anhydrous, and hydrated Co(II) acetylacetonates.

anhydrous Co(II) acetylacetonate. So, the step 1 weight loss mainly results from the loss of the complexed water. The existence of step 1 for anhydrous Co(II) acetylacetonate implies that the anhydrous Co(II) acetylacetonate actually contains a trace quantity of complexed water. This is also supported by the absorbance peak at 3500  $cm^{-1}$  in the FTIR diagram of the anhydrous Co(II) acetylacetonate. The theoretically calculated number of coordinated water per Co(II) acetylacetonate molecule for the aged, hydrated and anhydrous Co(II) acetoacetonates is 2.62, 2.07, and 0.47, respectively. Considering the curing profiles, as shown in Figure 1, TGA data indicate that the complexed water can cause the small curing peak at  $\sim 165^{\circ}$ C and shift the large curing peak to lower temperatures (from 222.74°C to 210.22°C). The more complexed the water presence, the more obvious the above effects. The TGA diagram also shows that, in step 2, all three Co(II) acetylacetonates show a large quantity of weight loss [69.6%, 70.2%, and 69.0% for aged, anhydrous, hydrated Co(II) acetylacetonate, respectively]. Similar weight-loss values in step 2 for the three Co(II) acetylacetonates can be explained by the combination of two different weight-loss mechanisms: vaporation and decomposition. The vaporation process seems to be related to the melting of Co(II) acetylacetonate (165°-170°C) and can be seen by the deposited Co(II) acetylacetonate on the wall of the waste gas outlet glass tube. Because there is > 15% residue after heating to 600°C, the decomposition of Co(II) acetylacetonate must take place during the heating. The decomposed fragments of the Co(II) acetylacetonate can be the acetylacetonate ligand and metal oxide.

### Effects of Complexed Water on TCE, TMA $T_{g'}$ and Storage Modulus

Because Co(II) acetylacetonate can slowly absorb air moisture to expand its coordination from 4 to 5 or 6, the investigation of the effects of the complexed water molecules on the TCE,  $T_g$  and storage modulus of the cured underfill shows its importance from the flip-chip application point of view. Figures 4 through 6 are the curves of TCE versus added amount of anhydride, using anhydrous and hydrated Co(II) acetylacetonates for



**Figure 4** Effect of the added amount of anhydride on TCE of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.1 wt % of the mixture of epoxy/anhydride for both catalysts.



**Figure 5** Effect of the added amount of anhydride on TCE of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.4 wt % of the mixture of epoxy/ anhydride for both catalysts.

comparison. Within experimental error, these curves indicate that the TCE decreases with the increase in anhydride concentration (especially at the low anhydride concentration region) for both anhydrous and hydrated Co(II) acetylacetonatecatalyzed systems at the three studied catalyst concentrations. Given the same anhydride and catalyst concentration, TCE of the cured samples are basically the same for anhydrous and hydrated Co(II) acetylacetonates. That is, the complexed water itself does not noticeably affect the TCE of the cured samples. Figures 7 through 9 are the curves of TMA  $T_g$  versus an added amount of anhydride, using anhydrous and hydrated Co(II) acetylacetonates for comparison. These curves indicate that  $T_g$  increases with the



**Figure 6** Effect of the added amount of anhydride on TCE of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.8 wt % of the mixture of epoxy/ anhydride for both catalysts.



**Figure 7** Effect of the added amount of anhydride on TMA  $T_g$  of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.1 wt % of the mixture of epoxy/anhydride for both catalysts.

increase anhydride concentration for both anhydrous and hydrated Co(II) acetylacetonate-catalyzed systems. These results are consistent with our prior work.<sup>3</sup> When the catalyst concentration is < 0.4%, given the same anhydride concentration, the complexed water does not show its effect on  $T_g$  within the experimental error. The  $T_g$  difference becomes noticeable (as big as 50°C; see Fig. 9) only for the formulations with a high catalyst concentration (0.8% percentage) and a high anhydride concentration. The reason for this difference is not clear at this time. Figures 10 through 12 show the effects of the anhydride concentration on the room temperature storage modulus of the cured samples. Considering the mea-



**Figure 8** Effect of the added amount of anhydride on TMA  $T_g$  of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.4 wt % of the mixture of epoxy/anhydride for both catalysts.



**Figure 9** Effect of the added amount of anhydride on TMA  $T_g$  of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.8 wt % of the mixture of epoxy/anhydride for both catalysts.

surement error, there is no noticeable effect of anhydride on this property. Moreover, the modulus difference between the anhydrous Co(II) acetylacetonate-catalyzed system and Co(II) acetylacetonate-catalyzed system is minimal.

# Catalytic Mechanism of Co(II) Acetylacetonate in the Epoxy/Anhydride System

Figure 13 is the DSC heating curve. It indicates that there is no noticeable reaction occurs between cycloaliphatic epoxy and anhydride, or between cycloaliphatic epoxy and anhydrous Co(II) acetylacetonate at a temperature below 200°C. However, Figure 14 shows that the reaction between anhydride and anhydrous Co(II) acetylac-



Figure 10 Effect of the added amount of anhydride on storage modulus of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.1 wt % of the mixture of epoxy/anhydride for both catalysts.



**Figure 11** Effect of the added amount of anhydride on storage modulus of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.4 wt % of the mixture of epoxy/anhydride for both catalysts.

etonate does occur at a temperature as low as 100°C and peak at 144.90°C. These results indicate that the first step of the curing reaction of the Co(II) acetylacetonate-catalyzed epoxy/anhydride system is the reaction between Co(II) acetylacetonate and anhydride. Then, the reaction intermediate further opens the epoxy and anhydride rings, resulting in crosslinking of the entire system. But how does Co(II) acetylacetonate react with anhydride and then initiating the curing reaction of the epoxy/anhydride system? Based on the studies on bisphenol A/anhydride/metal acetvlacetonate system, Smith<sup>15</sup> proposed that the decomposition fragments of metal acetylacetonate is the most likely active species responsible for the initiation of polymerization in epoxy/ anhydride resins. They pointed out further that the more likely initiation mechanism is the one



**Figure 12** Effect of the added amount of anhydride on storage modulus of the cured samples. Anhydrous and hydrated Co(II) acetylacetonates were used for comparison. The added amount is 0.8 wt % of the mixture of epoxy/anhydride for both catalysts.



**Figure 13** DSC heating curves of cycloaliphatic epoxy/anhydride and cycloaliphatic epoxy/anhydrous Co(II) acetylacetonate.

involving an electron transfer between carboxylic anhydride and the liberated metallic cations to give a reactive initiating species, which is described in eqs. (I) and (II) in Figure 15. However, this initiation mechanism cannot explain our experimental results: (1) either  $\text{Co}^{2+}$  or  $\text{Co}^{3+}$  acetylacetonate shows the same catalytic reactivity; (2) the characteristic green color of  $\mathrm{Co}^{3+}$  did not change before and after curing; (3) the characteristic red color of  $Co^{2+}$  turned into  $Co^{3+}$ , with its characteristic green color; and (4)  $K^+$  and Na<sup>+</sup> acetylacetonate show the same catalytic activity in the epoxy/anhydride system, but K<sup>+</sup> and Na<sup>+</sup> are very difficult to be reduced. The coordination ligands of hydrated Co(II) acetylacetonate include acetylacetonate anion and water ligand. Since the

water ligand can be released during heating, there is no special reason to believe the acetylacetonate anion cannot be released from the Co(II) acetylacetonate complex during heating. Therefore, we proposed an alternative initiation mechanism herein to explain the experimental results that we have obtained, which can be schematically shown in eqs. (I) and (II) in Figure 16. The acetylacetonate anion ligand is first released from the Co(II) acetylacetonate when it is heated to exceed its melting temperature (165°-170°C). The enolate form of acetylacetonate anion can then effectively attack the carbonyl carbons of the anhydride and form a carboxylic anion that can further open the epoxy ring of epoxy resins or another anhydride molecule to initiate anionic



Figure 14 DSC heating curve of anhydride/anhydrous Co(II) acetylacetonate.



Figure 15 Electron transfer initiation mechanism proposed by Smith.<sup>15</sup>

polymerization and finally form a crosslinked network.

#### **CONCLUSIONS**

Co(II) acetylacetonate can slowly absorb air moisture. The complexed water can cause a small curing peak in the epoxy/anhydride system at  $\sim 165$ °C and shift the main curing peak to a lower temperature by 8°–15°C, depending on the quantity of the complexed water. More coordinated water shifts the large curing peak to lower temperature. However, the coordinated water does not have any noticeable effects on TCE, TMA  $T_g$  [except in the high Co(II) acetylacetonate anhydride concentration region], and room temperature storage modulus of the cured Co(II) acetylacetonate-catalyzed epoxy/anhydride system. The



**Figure 16** Anionic initiation mechanism proposed by our lab.

most possible initiation mechanism in the Co(II) acetylacetonate-catalyzed epoxy/anhydride underfill system is the initial dissociation of the Co(II) acetylacetonate complex and formation of the acetylacetonate anion at 165°–170°C. The enolate form acetylacetonate anion is a very strong base and can effectively attack the carbonyl carbons of the anhydride and form a carboxylic anion. The carboxylic anion can further open the epoxy ring or another anhydride molecule to initiate anionic polymerization and form a crosslinked epoxy network.

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