# Thermal Behavior of Silver Paste to Improve Reliability and Image Quality of LCoS Panel

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## Abstract

*Silver paste curing process is very important in LCoS panel manufacture because incomplete curing process will cause poor bonding strength and increase resistance. The imperfection situation results in poor reliability and the variation of the common voltage, respectively. The change of the common voltage causes image flicker. According to Kinetics, we acquire activation energy by using dynamic DSC and compare two kinds of silver paste. From the result of isothermal DSC, we get optimum curing parameters to solve the flicker problem caused of incomplete curing of the silver paste.*

## 1. Introduction

There are many kinds of conducting paste widely used in attachment process. In terms of curing mechanism, thermal curing and photo curing is two common types of silver paste. Thermal curing type paste is used in the attachment between the cell and the package while UV light used in the photo curing type silver paste will result in the degradation of liquid crystal. In addition, high curing temperature is harmful to the package and other components, so low curing temperature type of silver paste is preferred in LCoS panels.

Silver paste devised to air-drying is convenient but it will take much time for curing. How long the silver paste takes to cure completely depends on the thickness and the depositing method. The curing process can be sped up by slightly heating. The highest curing temperature is limited because the silver paste becomes deteriorated. Curing process must be executed carefully since incomplete curing process causes poor bonding strength between a package and a panel. Incomplete curing process also results additional resistance that varies common voltage. The change of common voltage causes image flicker.

All of these problems result in bad reliability of our product. And we focus study on the kinetic behavior of low curing temperature silver paste in order to obtain the relationship between curing time and temperature. We hope optimize the curing parameters to avoid unnecessary heating and time consumption.

## 2. Theory

The Arrhenius equation is based on the collision theory. The theory supposes that particles must collide both with the correct orientation and with sufficient kinetic energy, if the reactants are to be converted into products. According to Arrhenius equation:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \qquad (1)$$

where *A:* the pre-exponential factor, *E*a: the activation energy, *T:* the absolute temperature, and *R:* the gas constant. The equation assumes that A and *E*a are independent of temperature. All kinetic studies assume that the isothermal rate of conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rate constant, *k*, and a temperature-independent function of the conversion, α:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (2)$$

Assuming that there is no connection between A, Ea and f( $\alpha$ ), we combine (1) and (2) , and replace dt by using heating rate, $\beta$=d*T*/d*t*:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-Ea}{RT}\right)} f(\alpha) \qquad (3)$$

Integral function of conversion , G( $\alpha$ ), integration from an initial temperature, $T_0$, to inflection temperature, T, corresponding to $\alpha_0$ to $\alpha$, gives:

$$G(\alpha) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} e^{\left(\frac{-E_a}{RT}\right)} dT \qquad (4)$$

If initial temperature is low, we can assume that reaction rate is very small, $\alpha_0$=0, and there is no reaction between 0 and T0. Replaced T0 by 0 in the integral [1]. We have:

$$G(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} e^{\left(\frac{-E_a}{RT}\right)} dT \qquad (5)$$

According to Ozawa method, and then we integrated Eq(5) by using the Doyle approximation [2] [3]. The result is as:

$$\log\beta = \log(\frac{AE_a}{G(\alpha)R}) - 2.315 - 0.457\frac{E_a}{RT} \quad \text{.........................(6)}$$

The activation energy can be calculated by plotting log $\beta$ versus 1000/T without a knowledge of reaction order because the slope of the line is -0.457Ea/R. Slope will be -1.052 by plotting ln $\beta$ versus 1000/T.

## 3. Experiment

### 3.1 Equipment

Dynamic Scanning Calorimetry (DSC) is an instrument that can measure some fundamental property in some materials. Fig. 1 is the schematic diagram of DSC equipment. The application of DSC is very important. The main functions of DSC are as following. First, it can measure the reactive temperature of chemical materials. Generally speaking, there is endothermic or exothermic change during the chemical reaction. By measuring the change of endothermic or exothermic temperature, we can determine the temperature range and enthalpy of the chemical reaction. Second, it can determine the phase transition temperature. When phase transition happens, the property of materials will change, including specific heat. During the heating process, comparing the calorie of test materials with that of reference materials will have difference, and the system will increase or decrease heat flow to keep temperature of test materials the same with that of reference materials. From the difference of heat flow that system supply to test material, we can determine the phase transition temperature of the materials.

Dynamic DSC is widely used for studying chemical crosslinking reactions. Typically, the curve features an exothermal peak. We draw one tangent line along base line, so the curve and tangent line form a closed area. The area is proportional to the reaction enthalpy. Isothermal DSC experiments are used in several studies to calculate various kinetic parameters. In the experiment, we use both methods to analyze the property of two kinds of paste [4][5].

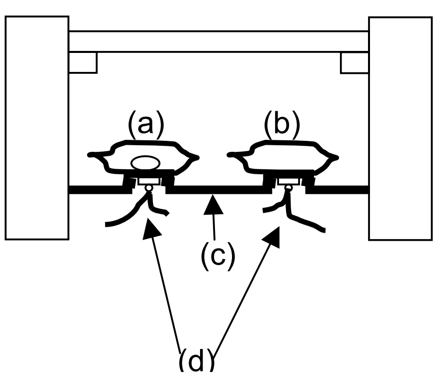



**Fig. 1 Schematic diagram of DSC equipment.**
**(a) Sample in Al cell (b) References just Al cell (c) Heater (d) Thermal couples.**

### 3.2 Experiment process

The silver paste (5.5±0.3mg) was filled in sealed aluminum pans with a pin-hole in the lid. Besides, the paste is stored in a refrigerator to prevent further curing.

All measurements were carried out on a Perkin-Elmer differential scanning calorimeter, Model DSC-7. The information of DSC-7 is listed in Table. 1. Dynamic scans were performed at heating rates of 1, 2.5, 5, and 10$^o$C/min, respectively. The performed temperature range in paste EN4072 is from 100$^o$C to 200$^o$C, while in 2030SC is from 50$^o$C to 150$^o$C. Isothermal runs were accomplished with 2030SC at 60, 70 and 80$^o$C for 5hrs.

**Table. 1 Information about DSC-7**

| | |
|---|---|
| Equipment | Perkin-Elmer DSC-7 |
| Temperature range | 40$^o$C to 400$^o$C |
| Heating rate | 5~40$^o$C/min |
| Environmental gas | $N_2$ |
| Gas flow rate | 20 m/s |

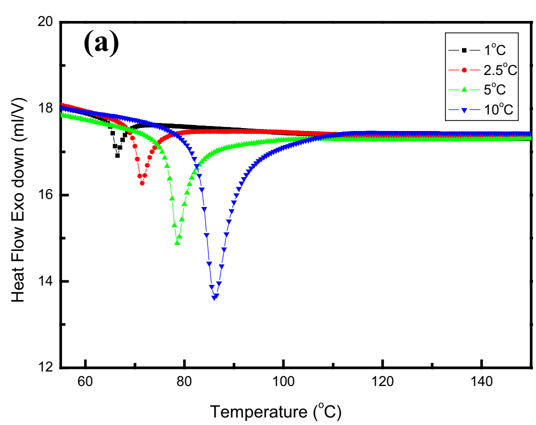
## 4. Result

By the dynamic and isothermal DSC experiment, we get the tendency of heat flow during the silver paste curing process; the higher the heating rate, the higher the reaction temperature. The enthalpy of one material is high means that the reactive rate is increasing. When the curve crosses peak temperature, the curve will return to the base line, and the reaction is finished. [6]

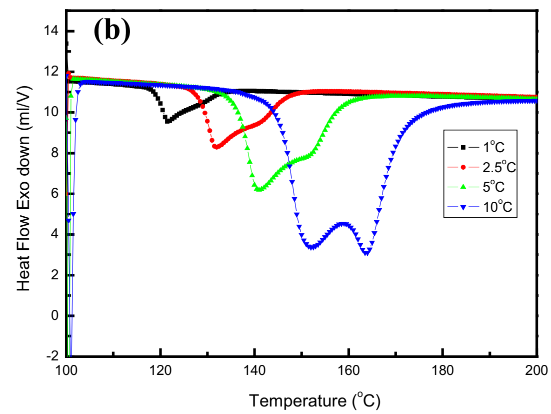
Two kinds of silver paste, i.e. 2030SC and EN4072, are used in the experiment. The result is showed in Fig. 2(a) and (b). The DSC curve of 2030SC has one obvious peak appeared between 66℃ and 86℃. The range of reactive temperature will change with different heating rates. From equation (10), we get the diagram of ln $\beta$ vs. 1/T ( $\beta$ : heating rate.) The active energy of silver paste 2030SC is calculated from this diagram, and the result is showed in Table. 2. Fig. 2(b) shows DSC curve of EN4072, and there are two peaks in the curve. As the heating rate increases, two reactive peaks separate apparently. The smallest reactive temperature of EN4072 is above 120℃ and occurred with heating rate in 1$^o$C/min. The active energy of EN4072 also showed in Table. 2.

From the result of DSC curves, we can understand that the curing reaction of EN4072 will happen in the high temperature. This situation indicates that reaction needs more energy to let the molecules have crosslink phenomenon and then the silver paste starts the curing reaction. The clean point of liquid crystal is 90℃, so the curing temperature of silver paste must below this temperature and 2030SC is more suitable in the LCoS process. In order to get the shortest curing time and optimum curing parameters, we do the DSC constant temperature experiment. The result is shown as Fig. 4. If the reactive temperature is lower, the curing time will be longer. When the curing temperature is 60℃, the complete curing time is about 100 minutes and that means the curve will be back to baseline. Applying 80℃ curing temperature can find the reaction is quite violent on initial 20 minutes. On the 40th minute, the curve will be back to baseline and the curing reaction is almost complete. Considering the manufacture process, the liquid crystal arrangement and the curing time, the suitable silver paste curing condition is applying 80℃ operator temperature with 1 hour tact time.

Fig. 5 shows conductance of silver paste 2030SC at 80℃ curing environment. Electric conductivity will increase with time and become stable. From the result we find the electric conductivity is stable after 55 minutes. Comparing with Fig. 3 and Fig. 4, we generalize the optimum curing parameters, and get the silver paste which has more stable electric conductivity under the condition. In the manufacture process, if the silver paste is not curing completely, the panel can not pass the thermal shock test. Without curing completely, the silver paste will have high electric resistance and the common voltage in the ITO side of the panel will be changed. When the driving voltage inverts on every frame, image will be flicker if common voltage shifts. Therefore the electric resistance will become more stable if the silver paste is curing completely. Meanwhile, the common voltage shift problem and flicker can be solved.




| | $T_p$ (℃) | ΔH ( J/g) |
|---|---|---|
| 1 ℃ | 66.45 | 19.26 |
| 2.5 ℃ | 70.29 | 20.34 |
| 5 ℃ | 78.58 | 29.27 |
| 10 ℃ | 86.16 | 19.18 |




| | $T_{p1}$ (℃) | $T_{p2}$ (℃) | ΔH ( J/g) |
|---|---|---|---|
| 1 ℃ | 121.65 | - | 152.03 |
| 2.5 ℃ | 131.83 | 140.992 | 148.7 |
| 5 ℃ | 140.92 | 151.71 | 151.008 |
| 10 ℃ | 151.33 | 163.49 | 152.403 |

**Fig. 2 Dynamic DSC scans for (a) 2030SC and (b) EN4072 silver paste.**

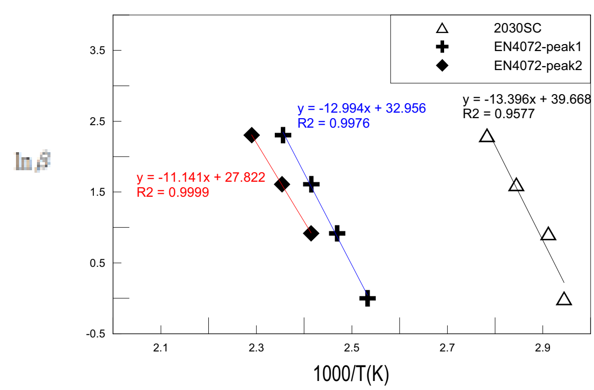



**Fig. 3 Plots of ln β versus 1000/T by using the Ozawa's equation.**

**Table. 2 Activation energy of reaction to 2030SC and EN4072 silver paste.**

| | $Ea_1$ (KJ/mole) | $Ea_2$ (KJ/mole) |
|---|---|---|
| 2030 SC | 105.89 | - |
| EN 4072 | 102.71 | 88.06 |

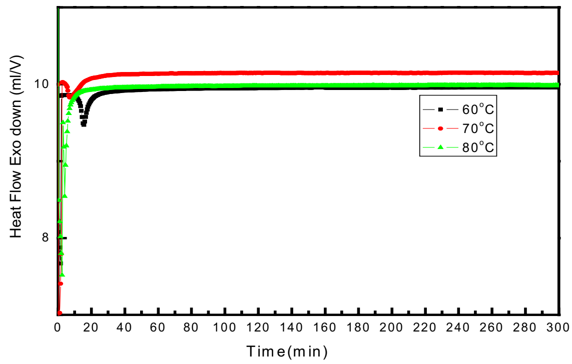



**Fig. 4 Isothermal DSC scans for 2030SC silver paste.**

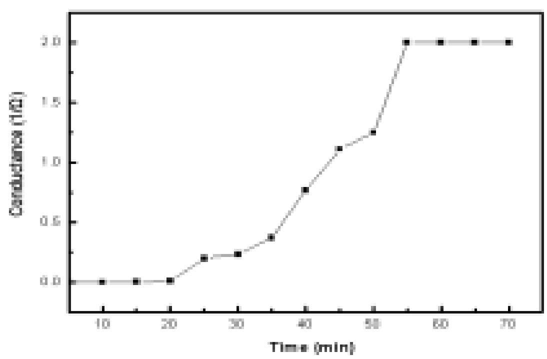



**Fig. 5 Conductance varies with time for 2030SC silver paste at 80℃.**

## 5. Conclusion

The experiment proved that the curing temperature of silver paste 2030SC is lower than that of silver paste EN4072. The 2030SC activation energy (Ea) was calculated to equal 105.89 KJ/mole. EN4072 had two reaction peaks and the activation energy is 102.71 KJ/mole(Ea1) and 88.06 KJ/mole(Ea2) respectively. We concluded from the result of isothermal DSC vs. conductivity experiment that the reaction heat (ΔH) and conductivity of 2030SC will not increase with time under 80℃ 55 minutes curing conditions.

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