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Modification of Frit Surface by Thermal Treatment for a Transparent Dielectric in Plasma Display Panel

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Many studies have been conducted to replace lead based materials with non-lead materials in the Plasma Display Panel (PDP) industry, because of the environmental problems posed by the former. One of the problems encountered in wet milling is the elution of the alkaline components of the frits, which are added to improve the thermal properties of the components of PDP. The purpose of our study is to investigate quantitatively the improvement of the frit surface afforded by thermal treatment. After making frits with an average particle size of 2–3 μm through wet milling, they were heat treated at different temperatures below the glass transition temperature of the glass. Using DTA, XRD, FT-IR and FE-SEM, we studied the improvement of the frit surface by examining the weight loss, images of the frit surface, the crystalline phases and the hydroxyl content.

Keywords: frit; frit surface; FT-IR; wet milling

INTRODUCTION

Frits have been widely used as component materials, such as transparent dielectrics, barrier-ribs, sealing materials and electrode materials, in plasma display panel (PDP), sealing materials in liquid crystal display (LCD)-back light units, and dielectrics in the field emission display (FED) industry. In the fabrication of displays, frit is used in the form of a paste or slurry with a vehicle, with the result

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that the mixing condition is important for controlling the reliability of the quality. For example, in PDP, pores in the transparent dielectrics lower the transparency and breakdown voltage, as well as reducing the bonding strength of the sealing materials. The frit used for display materials is mostly composed of glass based on the PbO system. Especially, glasses based on the PbO system have been used for transparent dielectrics, because of their high transmittance and easy control of their thermal properties [1,2]. However, materials containing PbO cause a chemical reaction with the acid or alkaline in waste water, thereby resulting in the pollution of the ground and water [1,2]. Recently, many studies on the Bi_2O_3, B_2O_3 and P_2O_5 glass systems have been conducted in order to replace PbO based glasses with PbO free glasses [1–4].

The transmittance of transparent dielectrics is mainly influenced by the thickness and the surface illuminance of the film, the presence of bubbles, the hydroxyl contents and the reaction between water and glass frit. When replacing lead based glasses with lead free glasses, it is difficult to obtain a high transmittance, due to the yellowing and discoloration phenomena caused by the reaction with the milling solution and the elution of the alkaline components added to improve the thermal properties [5]. Nowadays, lead free glass contains a large amount of alkali ions, in order to lower its melting temperature. Thus, the alkali ions in the glass composition of the frit are easily leached into milling solutions such as water and alcohol, and these leaching alkali ions cause the formation of a leaching layer on the frit surface. A recent survey suggested that the transparency of dielectrics can be improved by controlling the composition of the frit, the frit size and distribution, and the firing temperature [6].

The purpose of this research is to examine the surface condition of the frits at several stages, viz. after wet milling and through various heat treatment steps, in order to reveal the contaminants present on the frit surface. In this study, we selected the Bi_2O_3–B_2O_3–ZnO–BaO BaO glass system as the lead free glass and conducted heat treatment to remove the impurities formed during wet milling. After making frits with an average particle size of 2–3 μm through wet milling, they were heat treated at temperatures below the glass transition temperature. Using DTA, XRD, FT-IR and FE-SEM, we studied quantitatively the improvement of the frit surface.

EXPERIMENTAL

The bismate glass system with the analyzed composition, $40Bi_2O_3$–$18H_3BO_4$–$20ZnO$–$12BaCO_3$–$5Na_2CO_3$–$3SiO_2$–$2Al_2O_3$ (mol%), was

employed in the present study. The batches were well mixed and melted in alumina crucibles at 1100°C for 30 min. The melts were poured into a stainless roller to make glass cullet and pulverized to an average particle size of 106 μm using a sieve with a mesh size of 140. After the wet milling process using a planetary mono mill, the frit was pulverized to a size of 2∼3 μm. After milling, the frit was dried in an IR oven for 24 h and heat-treated at temperatures of 200 and 400°C for 1 h.

The thermal properties and weight loss of the frit were observed with TG-DTA (Thermogravimetric-Differential thermal analyzer, Thermo Plus TG8120, Rigaku, Japan). The glass transition temperature (Tg) and the weight loss between 100°C and 400°C were determined by heating the 45 μm (325 mesh) glass frit to 1200°C at a heating rate of 10°C/min. The frits heat-treated at 200°C and 400°C after wet milling were examined under the same conditions. After wet milling, the heat-treated frit was analyzed to identify the possible formation of new crystalline phases using XRD (X-ray diffraction, APD system, PANalytical, Netherlands). To observe the changes of the heat-treated frit surface, FEG-SEM (field emission gun-scanning electron microscope, S-4200, HITACH, Japan) was used. Using the PSA (particle size analyzer, LS230 & N4PLUS, Coulter, USA), the particle size of the frits after wet milling was determined after the heat treatment at different temperatures.

The hydroxyl content of the frit after wet milling and the frits heat-treated at 200°C and 400°C were determined by FT-IR (Fourier transform-Infrared spectroscopy, IRPrestige-21, Shimadzu, Japan). A pellet with a thickness of 2 mm was made at a specific ratio of KBr to glass frit. The spectra were recorded by IR absorbance in the range of 400∼4000 cm^{-1}. The analyzed peaks were separated using a Gaussian function in the PeakFit^{TM} (Jandel) program. To measure the hydroxyl contents, it was quantified using the Beer-Lambert law. The equation is as follows [12,14].

$$A = \varepsilon CL$$

where C: concentration of water (mol/L), A: maximum height of optical absorbance band (unit-less) or the area under the band (cm^{-1}), ε: molar extinction coefficient or molar absorptivity (L/mol · cm), L: path length of light through the sample (cm).

RESULTS AND DISCUSSION

As results of TG-DTA, the weight loss of the frits heat-treated at 200°C and 400°C for 1 h after wet milling are shown in Figure 1. The glass

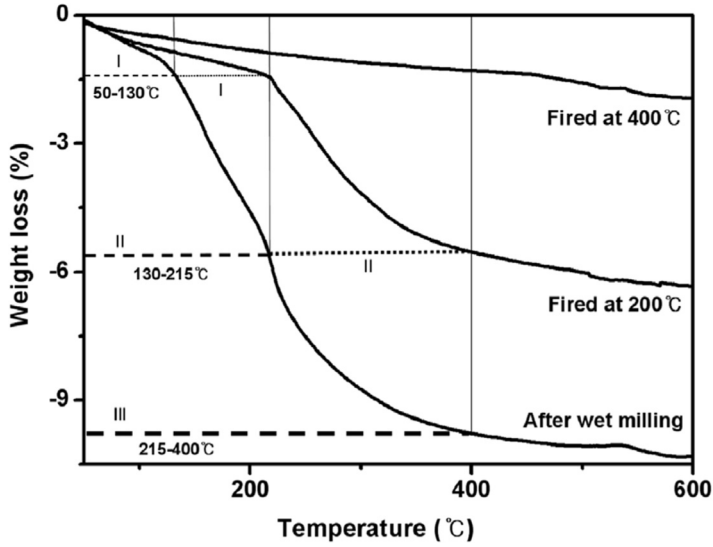

FIGURE 1 TG curves of the frits heat treated at 200–400°C after wet milling.

transition temperature (Tg) is found to occur at 417°C by DTA. Weight losses of 10.2% in the frit after wet milling, 6.0% in the frit heat-treated at 200°C and 1.4% in the frit heat-treated at 400°C are observed until 400°C, which is below the Tg. These results show that the hydroxyl content in the frit decreases with increasing heat treatment temperature. The weigh losses observed in the TG analysis correspond to three different steps after wet milling, viz. the vaporization of water at around 130°C (I), the first hydrate formation step in the temperature range of 130∼215°C (II) and the second hydrate formation step in the temperature range of 215∼400°C (III), which result in a total decrease of the hydroxyl content of 10% after the heat treatment at temperatures below the glass transition temperature (Tg).

According to the results shown in Figure 1, a minimum of two hydrates are formed on the surface of the frits during wet milling. The results of the XRD analysis for the formation of new crystalline phases and the phase changes in the frits brought about by the heat treatment are shown in Figure 2. The crystalline phases, $Na_3(AlSiO_4)_3(H_2O)$ and $Ba(OH)_2(H_2O)_8$, were observed in the frits examined after milling, due to the hydration reaction between the milling solution (distilled water) and the frits. The surface of the as-received sample (frits) is generally very clean and smooth (Figure 3), but we found a hydrate layer on the surface of the frits examined after wet milling, due to

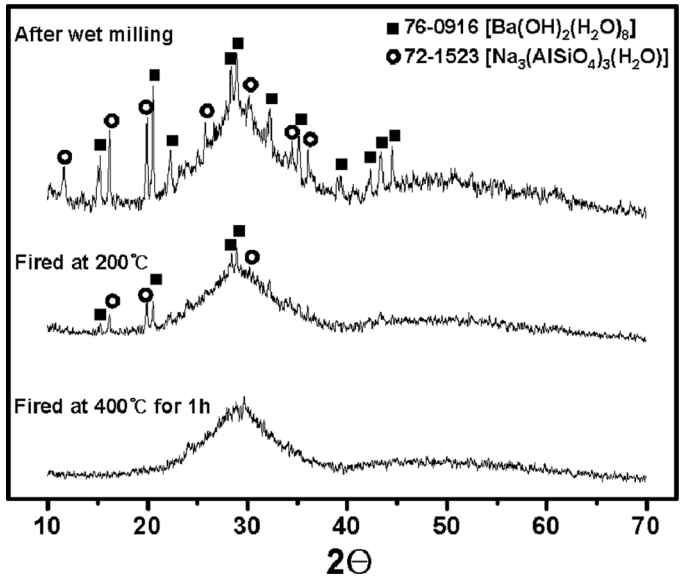

FIGURE 2 XRD patterns of frits after wet milling and heat treated frits.

ion exchange [7]. According to a previous study, it is expected that the Ba and B components in the frits are easily leached and deposited on the surface of the frits [6]. The hydroxyl group (−OH) is separated from the hydrate or the hydrate layer formed on the frit surface during the heat treatment. However, it is found that the frits heat-treated at 400°C were in a nearly amorphous state.

The surface morphologies of the frits after wet milling and the frits heat-treated at 200°C and 400°C are shown in Figure 3. No hydrate or hydroxide was observed on the surface of the frits made by dry milling. On the other hand, some hydrates were formed on the surface of the frits after wet milling, due to their reaction with water. The particle size of the frits decreased following the heat treatment. The reason for this is that the hydrates were separated from the surface of the frits. The particle size (d_{10}, d_{50}) of the frits after wet milling decreases with increasing heat treatment temperature (Table 1). The specific surface area of the frits has a slight tendency to increase with increasing temperature. However, when heat-treated at 400°C, the particle size (d_{90}) increases and the specific surface area decreases, due to the cohesion of the particles.

To determine the free hydroxyl group (−OH) concentration in the frits after wet milling, the FT-IR peaks were separated using a

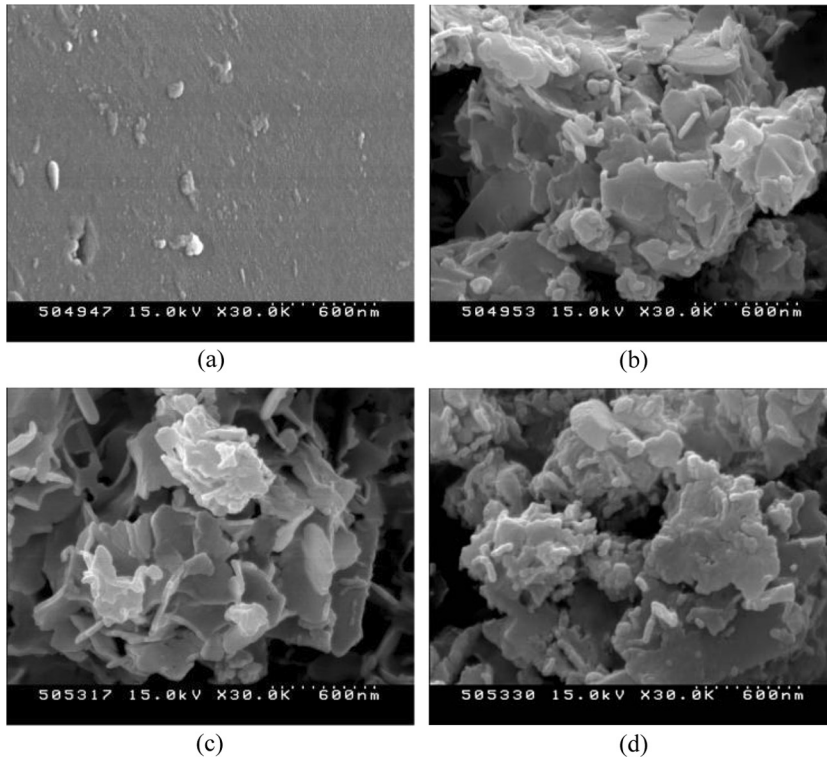

FIGURE 3 SEM images of frits treated by (a) dry milling, (b) wet milling, (c) fired at 200°C for 1 h, and (d) fired at 400°C for 1 h after wet milling in water solution.

Gaussian function, as shown in Figure 4. A peak in a specific wavelength range, which is not found in sample (a), viz. the frits made by sieving, is observed in the spectra of the sample after wet milling. Peak (II) at $3519 \pm 3520\,\mathrm{cm}^{-1}$ corresponds to the Si−OH (silanol)

TABLE 1 Particle Size (d_{10}, d_{50}, d_{90}) and Specific Surface Area of Frits with Heat Treatment

Conditions	After wet milling	Fired in air at 200°C	Fired in air at 400°C
d_{10} (μm)	0.63	0.61	0.26
d_{50} (μm)	3.49	2.99	2.82
d_{90} (μm)	9.67	7.16	7.56
Specific surface area (m^2/g)	24	26	21

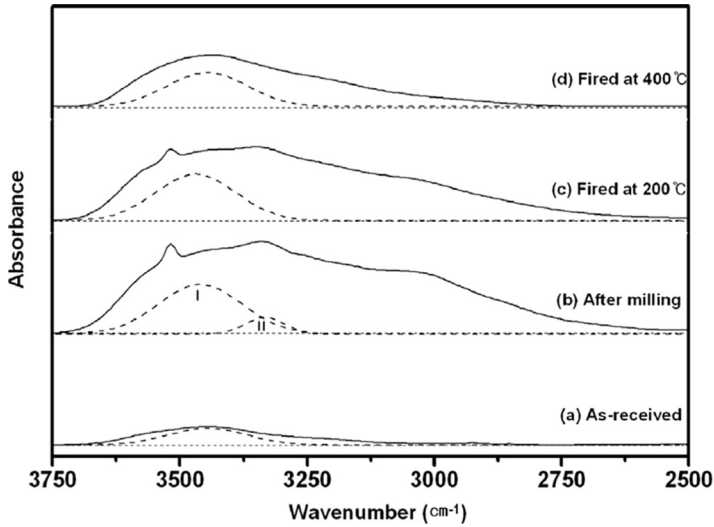

FIGURE 4 Spectral deconvolution of the IR spectrum of the frits in terms of the Gaussian components: (a) as-received, (b) after wet milling, (c) fired at 200°C for 1 h and (d) fired at 400°C for 1 h. (-): experimental data, (–): individual spectral components.

group resulting from the chemical reaction between the SiO_2 within the glass compositions and the milling solution (H_2O) during wet milling. It is observed that the Si-OH band disappears in the spectra of the heat-treated frits.

The formation mechanism of the Si−OH band is explained as follows [8–10] Assuming that the frit surface has Si−OH, B−OH and Al−OH bonds, in water, the frit surface reacts with H_2O to form hydroxyl bonds, as shown in Eqs. (1)–(6),

$$\mathrm{Si{-}OH} + \mathrm{H_2O} = \mathrm{Si{-}O^-} + \mathrm{H_3O^+} \tag{1}$$

$$\mathrm{Si{-}OH} + \mathrm{H_2O} = \mathrm{Si{-}OH_2^+} + \mathrm{OH^-} \tag{2}$$

The oxides of alkali and alkaline earth ions in the frits (Si−O−Si, $\mathrm{Si{-}O^-\cdots R^+}$, $\mathrm{Si{-}O^-\cdots R^{2+}}$) are reactive in water and are dissolved to release OH^-, which increases the pH of the solution.

$$(\mathrm{Si{-}O^-\cdots R^+})_{\mathrm{glass}} + \mathrm{H_2O_{sol}} = \mathrm{Si{-}OH_{glass}} + \mathrm{R^+_{sol}} + \mathrm{OH^-_{sol}} \tag{3}$$

$$(\mathrm{Si{-}O^-\cdots R^{2+}})_{\mathrm{glass}} + \mathrm{H_2O_{sol}} = \mathrm{Si{-}OH_{glass}} + \mathrm{R^{2+}_{sol}} + \mathrm{OH^-_{sol}} \tag{4}$$

TABLE 2 The Hydroxyl Content Obtained Using TG-DTA and the Beer-Lambert Law Using the Extinction Coefficient (77.5 L/mol · cm)

Hydroxyl content	As-received	After wet milling	Fired at 200°C	Fired at 400°C
TG-DTA (%)	0	10.2	6.0	1.4
FT-IR (%)	0.03	0.1	0.09	0.06
FT-IR (ppm)*	332	975	910	676

*Hydroxyl content (ppm) calculated using the Beer-Lambert law with the extinction coefficient.

For the calculation of the hydroxyl content (ppm unit), $A = \varepsilon CL$ is applied.

$$C_{ppm_{OH}} = \left(\frac{A}{L}\right)\left(\frac{1}{\varepsilon}\right)\left(\frac{1\,L_{glass}}{1000\,\mathrm{cm}^3}\right) \times \left(\frac{17\,\mathrm{g}}{1\,\mathrm{mol}_{OH}}\right) \times \left(\frac{1000\,\mathrm{mg}}{1\,\mathrm{g}}\right).$$

Later, after a certain amount of time in water, when the pH reaches 9, the following reaction occurs

$$(\mathrm{Si{-}O{-}Si}) + \mathrm{OH}^- = \mathrm{Si{-}OH_{glass}} + \mathrm{Si{-}O^-_{glass}} \tag{5}$$

or

$$(\mathrm{Si, B, Al})\mathrm{OH} - \mathrm{H}^+ + \mathrm{Na}^+ = (\mathrm{Si, B, Al})\mathrm{OH}^-\mathrm{Na}^+ + \mathrm{H} \tag{6}$$

Peak (I) at $\sim 3500\,\mathrm{cm}^{-1}$ indicates the presence not of hydrogen-bonded but of free hydroxyl groups (−OH) [8–12]. The absorption coefficient of the frits after wet milling has a tendency to increase rapidly compared to that of sample (a). The hydroxyl contents of the frits calculated by the Beer-Lambert law are shown in Table 2 in units of ppm and percentage (%), as compared to the weight loss determined by TG-DTA (Fig. 1). These were calculated using absorption coefficients of O−H group (70 and $77.5 \pm 1.51\,\mathrm{L/mol \cdot cm}$) as obtained from the literature [12–15]. The as-received sample has a hydroxyl content of 0.03% (332 ppm), which is created during the glass production process. The hydroxyl content of the frits is increased after wet milling and decreased by the heat treatments at 200°C and 400°C.

CONCLUSIONS

After wet milling, the hydroxyl content in the frits was 0.1% and crystalline phases such as $Na_3(AlSiO_4)_3(H_2O)$, $Ba(OH)_2(H_2O)_8$ and $BaAl_2O_4$ were created on the surface of the frits, due to the hydration between the milling solution (distilled water) and the frits during the

wet milling. However, the hydroxyl content in the frits after wet milling decreased to 0.06% following the heat treatment. Moreover, the surface of the frits heat treated at elevated temperature was clear and consisted of an amorphous phase that denotes the improvement of the frit surface by the thermal treatment. We consider that the heat-treated frits can have good reactivity with a vehicle that can form a dielectric with a high transmittance.

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