Spherical Shape PbO–B₂O₃–SiO₂ Glass Powders Prepared by Flame Spray Pyrolysis

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Micron-sized PbO–B₂O₃–SiO₂ glass powders were directly prepared by high temperature flame spray pyrolysis. The flow rates of fuel and carrier gas in the flame spray pyrolysis were critical to the control of morphologies of PbO–B₂O₃–SiO₂ glass powders. The optimum flow rate of fuel gas to prepare the PbO–B₂O₃–SiO₂ glass powders with spherical shape and micron-size was 20 L/min. The powders prepared at low flow rates of carrier gas had bimodal size distributions with nanometer and micron sizes. The number of the nanometer size powders increased with decreasing the flow rate of carrier gas. When the flow rate of carrier gas was 30 L/min, the prepared powders had spherical shape and micron size. The transmittances of the dielectric layers were higher than 90% regardless of the flow rates of carrier gas when the dielectric layers were sintered at temperatures between 520 and 580°C.

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1. Introduction

Glass powders are widely used as dielectric layers and fillers in various types of displays and ceramic capacitors.^{1)–3)} Especially, plasma display panels (PDPs) use various types of glass powders for barrier ribs and dielectric layers of front and back panels. Dielectric layers are formed using the screen printing process. The characteristics of the dielectric layers formed from the glass powders are affected by mean sizes and morphologies of the powders.⁴⁾ The glass powders formed by the conventional melting process have irregular morphology and rough surface.^{5)–7)} The dielectric layers formed from the screen printing method using glass powders with irregular morphologies have rough surface and pores with large size, which cause voids after sintering.⁸⁾

Flame spray pyrolysis is different from spray pyrolysis in energy source.^{9)–12)} High temperature flame, which is used in flame spray pyrolysis instead of electrical furnace, causes melting of powders to be spherical and dense. However, high temperature flame often causes evaporation of some components and improper phase generation, and that limits the application of flame spray pyrolysis.⁹⁾

In this study, PbO–B₂O₃–SiO₂ glass powders were directly prepared by flame spray pyrolysis. The temperature of the diffusion flame and the residence time for the powders inside the diffusion flame were controlled by changing the amounts of fuel and carrier gases. In order to see whether flame spray pyrolysis is an applicable technique for the production of glass powders, the characteristics of dielectric layers formed from the prepared glass powders were investigated.

2. Experiments

Glass powders with a 70 mass% PbO–20 mass% B₂O₃–10 mass% SiO₂ composition were directly prepared by flame spray pyrolysis. The system of flame spray pyrolysis has a droplet generator, flame nozzle, quartz reactor, powder collector, and blower. A 1.7 MHz ultrasonic spray generator is used to generate droplets, which are carried into the high-temperature diffusion flame by oxygen, as the carrier gas. Droplets and powders evaporate, decompose, and melt inside the diffusion flame. Propane as the fuel and oxygen as the oxidizer create the diffusion flame. The flame nozzle has five

concentric pipes. Droplets generated from the precursor solution are supplied to the diffusion flame through the center pipe by different flow rates of carrier gas. The temperatures of the diffusion flame and the residence time for the powders inside the diffusion flame are controlled by changing the amounts of fuel, oxidizer, and carrier gases. The spray solutions were obtained by adding Pb(NO₃)₂ (Junsei, 99.5%), H₃BO₃ (Kanto, 99.5%), and tetraethyl orthosilicate (TEOS, Aldrich, 98%) to distilled water. The overall solution concentration was 0.34 mol/L. The glass transition temperature (*T_g*) of the prepared glass powders was studied using differential scanning calorimetry (DSC). The crystal structures of the powders were studied using X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The morphologies of the powders were investigated using scanning electron microscopy (SEM). The transparency of the dielectric layer formed from the prepared glass powders was measured using a spectrophotometer within a visible light range.

3. Results and discussions

In the flame spray pyrolysis, the flow rates of fuel and carrier gas affect the morphologies of the prepared powders by changing the temperature of diffusion flame and residence time of the powders inside the high temperature flame. Especially, PbO–B₂O₃–SiO₂ glass powders have low melting and evaporation temperatures. Therefore, the control of the flow rates of fuel and carrier gases in the flame spray pyrolysis is critical to the control of morphologies of PbO–B₂O₃–SiO₂ glass powders. **Figure 1** shows the SEM photographs of the PbO–B₂O₃–SiO₂ powders prepared by flame spray pyrolysis at different flow rates of fuel and carrier gases. The flow rates of oxygen used as carrier gas were changed from 10 to 40 L/min. The flow rates of propane used as fuel gas were changed from 2 to 3 L/min. The flow rate of oxygen used as oxidizer was fixed at 30 L/min. The powders prepared at low flow rates of carrier gas below 20 L/min had bimodal size distributions with nanometer and micron sizes when the flow rate of propane was 2 L/min. The number of the nano-sized powders increased with decreasing the flow rate of carrier gas. In other words, the number of nanometer size powders increased with increasing the residence time of the powders inside the diffusion flame. In the flame spray pyrolysis, one micron-sized powder was formed from one micron-sized droplet. On the

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Fig. 1. SEM photographs of the glass powders prepared at different flow rates of fuel-oxidizer-carrier gases. (a) 2-30-10, (b) 2-30-20, (c) 2-30-30, (d) 2-30-40 and (e) 3-30-30

other hand, the nano-sized powders were formed by the chemical vapor deposition (CVD) process. Some of the materials evaporated inside the high temperature diffusion flame. Nano-sized powders were formed by CVD process from the evaporated materials through nucleation and growth mechanisms. In the case of high flow rate of carrier gas as 40 L/min, the precursors were not completely decomposed because of insufficient residence time for the powders inside the high temperature diffusion flame. The incomplete decomposition of precursors formed the powders with large size and irregular morphology. When the carrier gas flow rate was 30 L/min, the prepared powders had spherical shape and micron size. However, the increase of the flow rate of fuel gas increased the number of the nano-sized powders as shown in Fig. 1(e).

Figure 2 shows the XRD spectra of the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ powders prepared by flame spray pyrolysis at various flow rates of carrier gas. The $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ powders prepared at high flow rates of carrier gas above 30 L/min had crystalline phase of $\text{Pb}(\text{NO}_3)_2$, in which transition to the glass phase did not completely occur because of short residence time of powders inside the high temperature diffusion flame. On the other hand, the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ powders prepared at low flow rates of carrier gas below 20 L/min had broad peaks in the XRD spectra. The broad peaks at around 28° in the XRD spectra represent the character of glass materials. The TG/DSC curves of the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass powders prepared by flame spray pyrolysis were investigated. The flow rates of the fuel, oxidizer and carrier gases were each 2, 30, and 20 L/min. In the DSC curve, the glass transition temperature (T_g) of the glass powders was 395°C . In the TG curve, the weight loss of the glass powders was 1.04% at temperatures below 500°C .

The micron-sized $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass powders (Fig. 1(c)) prepared by flame spray pyrolysis were mixed with an organic vehicle that consisted of ethyl cellulose, α -terpineol,

Fig. 2. XRD spectra of the glass powders prepared at different flow rates of fuel-oxidizer-carrier gases.

and butyl carbitol acetate (BCA). The glass paste was screen-printed onto the soda-lime glass substrate. The printed glass substrate was dried at 120°C for 30 min. The screen-printed glass substrate was fired by 2 steps, at first temperature of 400°C for 10 min at a heating rate of $7^\circ\text{C}/\text{min}$ and in the second temperature of 580°C for 6 min at a heating rate of $7^\circ\text{C}/\text{min}$. **Figure 3** shows the SEM photographs of surfaces and cross-sections of the dielectric layers formed from the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass powders. The dielectric layers formed from the glass powders prepared by flame spray pyrolysis had a smooth surface and no void inside the layers regardless of the flow rates of carrier gas. **Figure 4** shows the transmittance patterns of the dielectric layers formed from the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass powders prepared by flame spray pyrolysis. The transmittances of the dielectric layers were higher than 90%

Fig. 3. SEM photographs of the cross-sections of the dielectric layers at different flow rates of fuel-oxidizer-carrier gases. (a) 2-30-10, (b) 2-30-20, (c) 2-30-30 and (d) 2-30-40

Fig. 4. Transparencies patterns of the dielectric layers sintered at 560°C temperature.

Fig. 5. Transmittances patterns of the dielectric layers sintered at different temperatures.

within a visible range, regardless of the flow rates of carrier gas. In Figs. 1, 2 and 4, the morphologies and crystal structure of the powders did not affect the transmittances of the dielectric layers at sintering temperature of 580°C. The transmittances of the dielectric layers sintered at different temperatures were affected by the flow rates of carrier gas as shown in Fig. 5. The transmittances of the dielectric layers were higher than 90% regardless of the flow rates of carrier gas when the dielectric layers were sintered at temperatures between 520 and 580°C. However, the transmittances of the dielectric layers sintered at low temperatures were affected by the preparation conditions of the powders. In the sintering temperature at

500°C, the dielectric layers formed from the powders prepared by flame spray pyrolysis at low flow rate of carrier gas had lower transmittances than those of the powders prepared at high flow rate of carrier gas. The composition change of the powders obtained by flame spray pyrolysis at low flow rate of carrier gas by evaporation of some components decreased the transmittances of the dielectric layers at low sintering temperatures. The long residence time of the powders inside the high temperature diffusion flame at low flow rate of carrier gas caused the evaporation of volatile components such as Pb and B.

The dielectric layers formed from the powders prepared by

flame spray pyrolysis at flow rates of carrier gas as 10 and 40 L/min had a number of voids inside the layers at sintering temperature of 480°C. The hollow structure of the powders prepared by flame spray pyrolysis at high flow rate of carrier gas as 40 L/min produced the voids inside the dielectric layer after sintering at low temperature. On the other hand, the composition change of the powders obtained by flame spray pyrolysis at low flow rate of carrier gas produced the voids inside the dielectric layer.

4. Conclusion

The characteristics of the PbO-B₂O₃-SiO₂ glass powders prepared by flame spray pyrolysis were investigated. The temperature of the diffusion flame and the residence time for the powders inside the diffusion flame were controlled by changing the amounts of fuel and carrier gases. In the flame spray pyrolysis, the flow rates of fuel and carrier gases affect the morphologies of the prepared powders by changing the temperature of diffusion flame and residence time of the powders inside the high temperature flame. The morphologies and crystal structure of the powders obtained by flame spray pyrolysis did not affect the transmittances of the dielectric layers at sintering temperature of 580°C. However, the transmittances of the dielectric layers sintered at low temperatures

below 500°C were affected by the preparation conditions of the powders.

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