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Preparation of Pb-based glass powders by spray pyrolysis using a filter expansion aerosol generator

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$PbO-B_2O_3-SiO_2$ glass powders were directly prepared by a filter expansion aerosol generator (FEAG) process. Glass powders were formed by melting and cooling processes of the powders inside the hot wall reactor which was maintained at a low pressure. The powders prepared at temperatures below 800 °C had a spherical shape and submicrometre size. One glass powder was formed from one droplet at preparation temperatures below 800 °C. On the other hand, the powders prepared at a temperature of 900 °C had a bimodal size distribution with nanometre and submicrometre size. The mean size of the glass powders prepared by the FEAG process at a temperature of 800 °C was 320 nm. In the DSC curve, the glass transition temperature (T_g) of the glass powders was 411.5 °C. The transparencies of the dielectric layers formed from the glass powders obtained by the FEAG process were higher than 90% within the visible light range at annealing temperatures above 500 °C.

Key words: glass powder, spray pyrolysis, dielectric material.

Introduction

Pb-based glass powders are the materials of choice for most commercial dielectric operations and commercially used as transparent dielectric layers in Plasma Display Panel (PDPs) [1]. Most of there glass powders are generally formed by a melting process. The glass powders formed by a conventional melting process have an irregular morphology, a rough surface and large size. Dielectric layers developed from the glass powders are formed by a screen printing process. The properties of dielectric layers formed by the screen printing process are affected by the characteristics of the glass powder such as its morphology, mean size, size distribution and composition.

Spray pyrolysis is one of the more promising processes for the preparation of improved ceramic and metal powders [2-8]. Glass powders with amorphous phases have also been prepared by spray pyrolysis. Koo et al. reported the characteristics of $PbO-B_2O_3-SiO_2$ glass powders a spherical shape and fine size obtained by spray pyrolysis [9]. The dielectric layers formed from these fine-sized glass powders with a spherical shape had a high transparency at low firing temperatures. In particular, in the spray pyrolysis process, one glass powder is formed from one droplet. Therefore, the mean sizes and size distributions of the glass powders prepared by spray pyrolysis are affected by the spray generators. In a previous study, an ultrasonic spray generator has been used in the preparation of glass powders because the ultrasonic spray generator can generate relatively homogeneous droplets with a size of several micrometre [9].

Kang and Park proposed a new spray generator, the filter expansion aerosol generator (FEAG) process that can be applied to the preparation of powders and films by spray pyrolysis [10]. In the study described in this paper, $PbO-B_2O_3-SiO_2$ glass powders were directly prepared by spray pyrolysis using the FEAG process. The morphology, mean size, size distribution and thermal properties of $PbO-B_2O_3-SiO_2$ glass powders prepared by the FEAG process were investigated. The characteristics of dielectric layers formed from the prepared $PbO-B_2O_3-SiO_2$ glass powders were also investigated.

Experimental Procedure

Glass powders with a 70 wt% PbO-20 wt% B_2O_3-10 wt% SiO_2 composition were directly prepared by the FEAG process. Figure 1 shows a schematic diagram of the FEAG process. Details of the filter expansion aerosol generator (FEAG) process have appeared elsewhere [10, 11]. In the FEAG process, the solutions are atomized into fine-sized droplets and delivered into a hot-wall reactor maintained at a low pressure. As the droplets stream passes through the reactor, the solvent evaporates and the metal salts decompose into individual oxide powders and phase change from solid powders to molten glasses occurs. Finally, molten glasses are converted to the individual glass powders by rapid quenching. The spray solutions were obtained by adding $Pb(NO_3)_2$ (Junsei, 99.5%), H_3BO_3 (Kanto, 99.5%), and tetraethyl orthosilicate (TEOS, Aldrich, 98%) into

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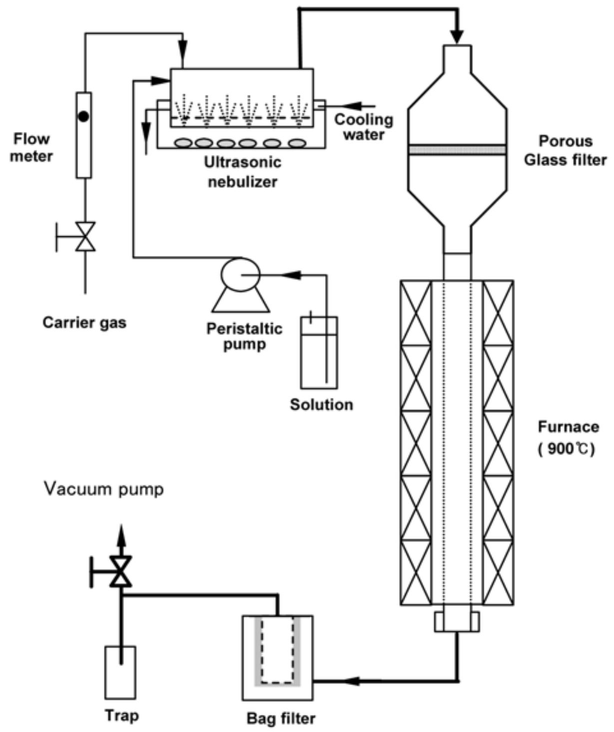


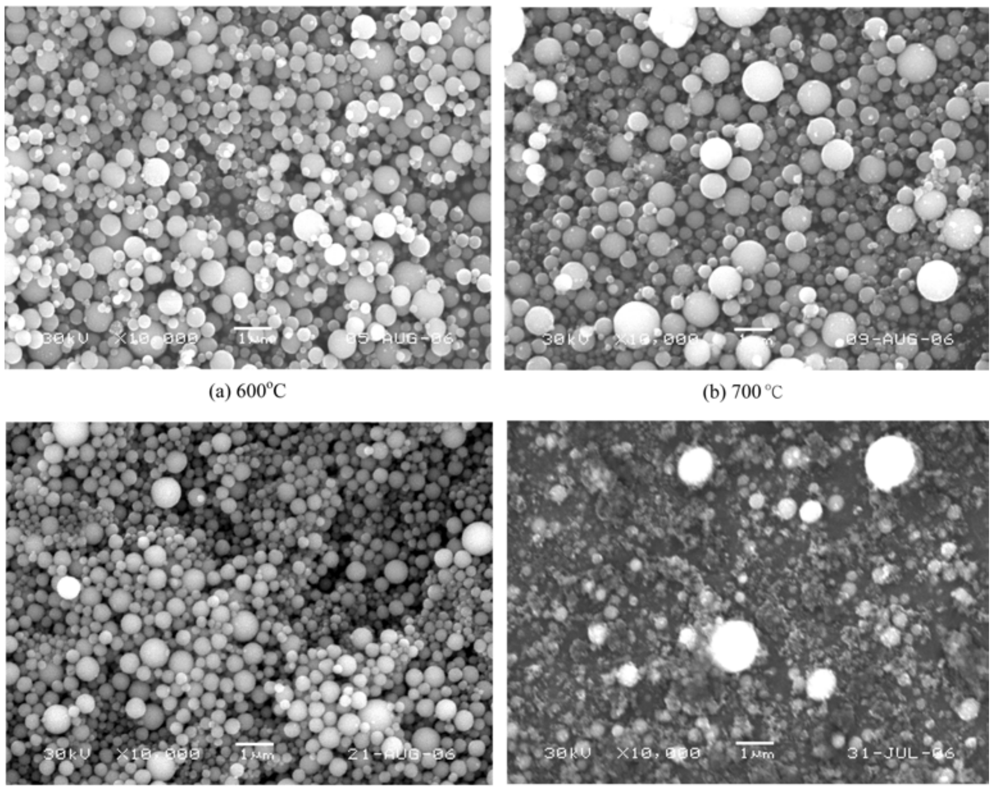
Fig. 1. A schematic diagram of the FEAG process.

distilled water. The overall solution concentration was 0.5 M. The preparation temperatures in the FEAG process were varied from 600 to 900°C.

The thermal properties of $PbO-B_2O_3-SiO_2$ glass powders obtained by the FEAG process were studied using a differential scanning calorimeter (DSC). The morphologies and size distributions of the glass powders were investigated using scanning electron microscopy (SEM). The glass paste was screen-printed onto the soda-lime glass substrates. The printed glass substrates were dried at 120°C for 30 minutes. The dried glass substrates were fired at temperatures between 480 and 580°C for 10 minutes at a heating rate of 5 K·minute^{-1}. The transparency of the dielectric layer formed from the prepared glass powders was measured using a spectrophotometer within the visible light range.

Results and Discussions

Glass powders could be formed by the melting and cooling processes of the powders inside the hot wall reactor in the spray pyrolysis unit. Therefore, the preparation temperature is an important variable in the preparation of glass powders by spray pyrolysis. The Pb-based glass powders were prepared by the FEAG process at various preparation temperatures. Figure 2 shows SEM photographs of the Pb-based glass powders prepared at different temperatures. The morphologies of the glass powders were affected by the preparation temperature. The powders prepared at temperatures below 800°C had a spherical shape and submicrometre size. One glass powder was formed from one droplet at



(a) 600°C (b) 700 °C

(c) 800 °C (d) 900 °C

Fig. 2. SEM photographs of glass powders prepared by the FEAG process at the temperatures indicated.

preparation temperatures below 800°C. On the other hand, the powders prepared at a temperature of 900°C had a bimodal size distribution with nanometre and submicrometre sizes. One submicrometre-sized powder was formed from one droplet by the drying, decomposition and melting processes. However, the nano-sized powders were formed by a chemical vapor deposition (CVD) process. Evaporation of the glass powders occurred at a preparation temperature of 900°C. Nano-sized powders were formed from the evaporated vapors by the CVD process. In previous studies the effects of the preparation temperature on the morphology of the Pb-based glass powders were different in the ultrasonic spray pyrolysis and the FEAG processes [9]. In the ultrasonic spray pyrolysis, the powders prepared at temperatures below 700°C had hollow and non-spherical morphologies. The powder did not melt at preparation temperatures below 700°C. The mean size of the powders prepared by the FEAG process was smaller than that of the powders prepared by the ultrasonic spray pyrolysis. Therefore, in the FEAG process, melting of the glass powder occurred at a lower preparation temperature than that of the ultrasonic spray pyrolysis process. Additionally, the powders prepared by the ultrasonic spray pyrolysis at temperature of 1,000°C had completely spherical shapes, clean surfaces, and dense morphologies. In the FEAG process, nano-sized glass powders were formed at a lower preparation temperature than in the ultrasonic spray pyrolysis process. In the FEAG process, evaporation of the glass powders occurred even at low preparation temperatures because of its low pressure operation condition. Figure 3 shows the size distribution of Pb-based glass powders prepared by the FEAG process at a temperature of 800°C. The prepared glass powders had a fine size and narrow size distribution. The mean size of the glass powders prepared by the FEAG process was 320 nm. The fine-sized glass powders were prepared by the FEAG process from the droplets with a fine size.

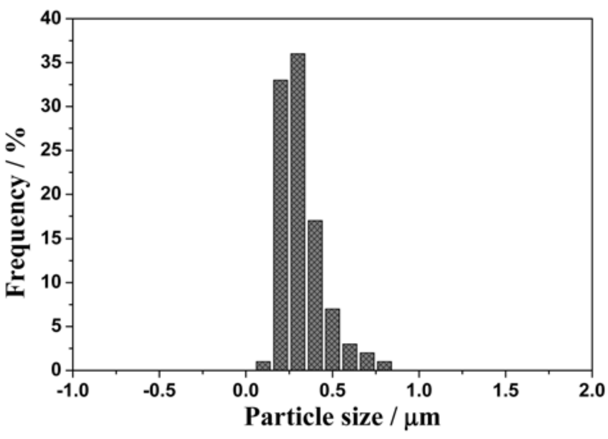


Fig. 3. Size distribution of Pb-based glass powders prepared by the FEAG process at 800 °C.

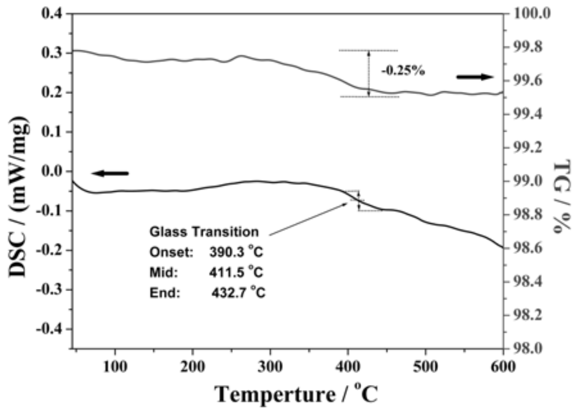


Fig. 4. TG/DSC curves of the glass powders prepared by the FEAG process at 800 °C.

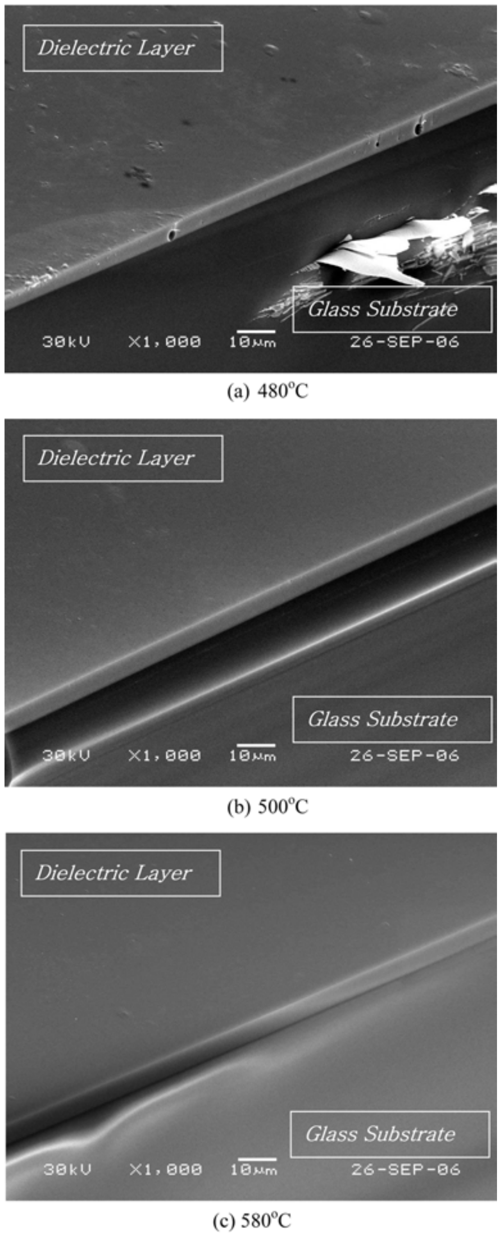


Fig. 5. Cross sections of the dielectric layers formed from the glass powders on substrate at the temperatures indicated.

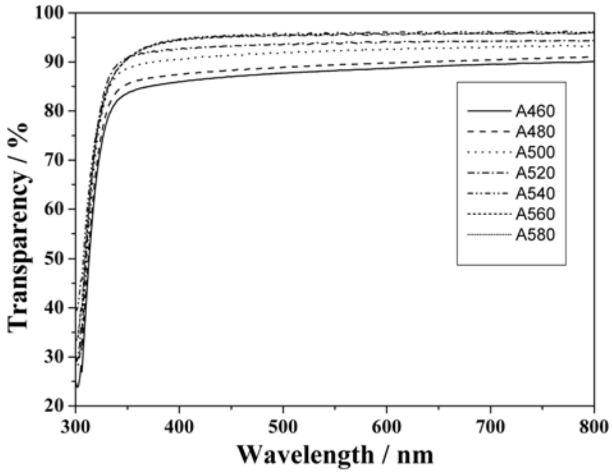


Fig. 6. Transparencies of the dielectric layers formed from the glass powders. (A460 refers to annealing the layer at 460 °C, etc.)

Figure 4 shows the thermo gravimetric/differential scanning calorimeter (TG-DSC) curves of the Pb-based glass powders prepared by the FEAG process at a temperature of 800°C. In the TG curve, the weight loss of the glass powders was 0.25 wt%. The composition of the glass powders prepared by the FEAG process was homogeneous because of the micro-scale reaction inside the fine-sized droplets. Therefore, the weight loss of the glass powders in the TG curve was as low as 0.25 wt%. In the DSC curve, the glass transition temperature (T_g) of the glass powders was 411.5°C.

Figure 5 shows SEM photographs of the dielectric layers formed from the Pb-based glass powders obtained by the FEAG process at temperature of 800°C. The screen-printed glass substrates were annealed at temperatures between 460 and 580°C for 10 minutes at a heating rate of 5 K·minute^{-1}. The dielectric layer annealed at temperature of 480°C had a rough surface because of voids inside the layer. However, the dielectric layers annealed at temperatures of 500 and 580°C had clean surfaces and dense inner structures. Figure 6 shows the transparency patterns of the dielectric layers formed from the glass powders obtained by the FEAG process at different annealing temperatures. The transparencies of the dielectric layers formed from the glass powders obtained by the FEAG process were higher than 90% within the visible light range at annealing temperatures above 500°C. The transparencies of the dielectric layers annealed at temperatures of 460 and 480°C were slightly decreased because of voids inside the layers.

Conclusions

The optimum preparation temperature of Pb-based glass powders with a spherical shape and submicrometre size in the FEAG process was investigated. The effects of the preparation temperature on the morphology of the Pb-based glass powders were different in the ultrasonic spray pyrolysis and the FEAG processes. Fine-sized glass powders were prepared by the FEAG process because the mean size of the droplets formed by the FEAG process had a fine size. Therefore, in the FEAG process, melting of the glass powder occurred at a lower preparation temperature than that in ultrasonic spray pyrolysis process. The fine-sized Pb-based glass powders with spherical shape obtained by the FEAG process formed transparent dielectric layers with good surface properties and high transparencies.

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