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Ceramics International 36 (2010) 1171–1176
CERAMICS INTERNATIONAL
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Short communication

Size-controlled Bi-based glass powders prepared by spray pyrolysis as inorganic additives for silver electrode

Jung Hyun Kim, Hye Young Koo, Dae Soo Jung, You Na Ko, Yun Chan Kang *

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

Received 9 October 2009; received in revised form 9 November 2009; accepted 26 November 2009
Available online 4 January 2010

Abstract

Bi-based glass powders as additive for silver conducting pastes were prepared by spray pyrolysis. The glass powders formed from the spray solution with low concentration of 0.025 M had bimodal size distribution with nanometer and submicron sizes. However, glass powders with spherical shape and narrow size distribution were prepared from the spray solutions with concentrations of 0.05 and 0.5 M. The mean size of the glass powders increased from 0.34 to 0.7 μm when the concentrations of the spray solutions changed from 0.05 to 0.5 M. The glass transition temperature of the glass powders with the mean size of 0.34 and 0.70 μm were 382 and 396 °C, respectively. The glass layers fired at 450 °C had clean surfaces irrespective of the mean size of the glass powders. Silver conducting films were formed by melting of the silver powders irrespective of the mean sizes of the glass powders at firing temperatures between 400 and 500 °C. The specific resistances of the silver conducting films change from 3.13 to 4.03 μΩ cm according to the mean size of the glass powders at a firing temperature of 500 °C.

Keywords: A. Powders: gas phase reaction; A. Powders: chemical preparation

1. Introduction

Silver thick films for making electrical contacts in solar cells, hybrid circuits, and other devices are formed from a conducting paste containing Ag powders, glass powders, and organic vehicles [1–3]. The electrical properties of silver conducting films are affected by the characteristics of silver and glass powders. Silver powders for conducting films with low resistivity should have high crystallinity, high density, low impurity, and spherical shape. Glass powders for conducting films with low resistivity and high adhesion strength should have appropriate softening temperature [4–7]. Requirements of fine-sized silver and glass powders increase with a decrease of width and thickness of silver conducting films. Low firing temperature of silver conducting films also increases the requirement of fine-sized silver and glass powders.

Fine-sized silver powders have been widely studied in various liquid solutions and by gas phase reaction methods [8–13]. Therefore, the effects of mean size of silver powders on the electrical properties of the silver conducting films are well studied. On the other hand, the effects of size of glass powders under submicron sizes on the formation characteristics of silver conducting films are not well studied. Glass powders prepared by the conventional melting process with large size and irregular morphology were mainly used as a permanent binder in the conducting paste. Therefore, the size of the glass powders could not be well controlled in the region of submicron sizes.

Spray pyrolysis, which is one of the gas phase reaction methods, has been applied to the preparation of glass powders resulting in spherical shape and fine size [14–17]. The mean size of the glass powders prepared by spray pyrolysis could be controlled by changing the solution concentration because one glass particle is formed from one droplet by drying, decomposition, melting, and quenching processes.

In this study, Bi-based glass powders as additive for silver conducting pastes were prepared by spray pyrolysis. The mean sizes of the glass powders were changed from 0.34 to 0.7 μm by changing the spray solution concentration. The effects of mean size of Bi-based glass powders on the electrical properties of silver conducting films were investigated.

* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

0272-8842/$36.00
doi:10.1016/j.ceramint.2009.12.018

2. Experimental

Glass powders were directly prepared by high temperature spray pyrolysis. The ZnO–Bi_2O_3–B_2O_3–BaO glass material with glass transition temperature of 382 °C was prepared. The flow rate of air used as a carrier gas was fixed to 20 L/min. The preparation temperature was fixed to 1300 °C. The spray solutions were obtained by adding ZnO (Kanto, 99%), Bi_2O_3 (Junsei, 99%), H_3BO_3 (Kanto, 99.5%), and $Ba(NO_3)_2$ (Junsei, 99%) to distilled water using an appropriate amount of nitric acid. The overall concentration of the solution of glass components was changed from 0.025 to 0.5 M.

The crystal structures of the prepared glass powders were investigated by using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). The morphological characteristics of the prepared glass powders and fired electrodes were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060). The specific resistances of the silver electrodes were measured using a four-point probe method (CMT-SR 1000N, Advanced Instrument Technology).

3. Results and discussion

The morphologies of the glass powders prepared by spray pyrolysis from spray solutions with various concentrations are shown in Fig. 1. The glass powders had spherical shapes and submicron sizes irrespective of concentrations of the spray solutions. The mean size of the glass powders increased with an increase of concentrations of the spray solution. The glass powders formed from the spray solutions with concentrations above 0.05 M had narrower size distributions than those formed from the spray solution with low concentration of 0.025 M. The glass powders formed from the spray solution with low concentration of 0.025 M had bimodal size distribution with nanometer and submicron sizes. Evaporation of some glass components inside the hot wall reactor maintained at 1300 °C occurred because of high evaporation characteristics of fine-sized glass powders. Nano-sized glass powders are formed from the evaporated vapors of glass components by nucleation and growth mechanisms.

Fig. 2 shows the size distributions formed from the spray solutions with concentrations of 0.05 and 0.5 M. The mean size

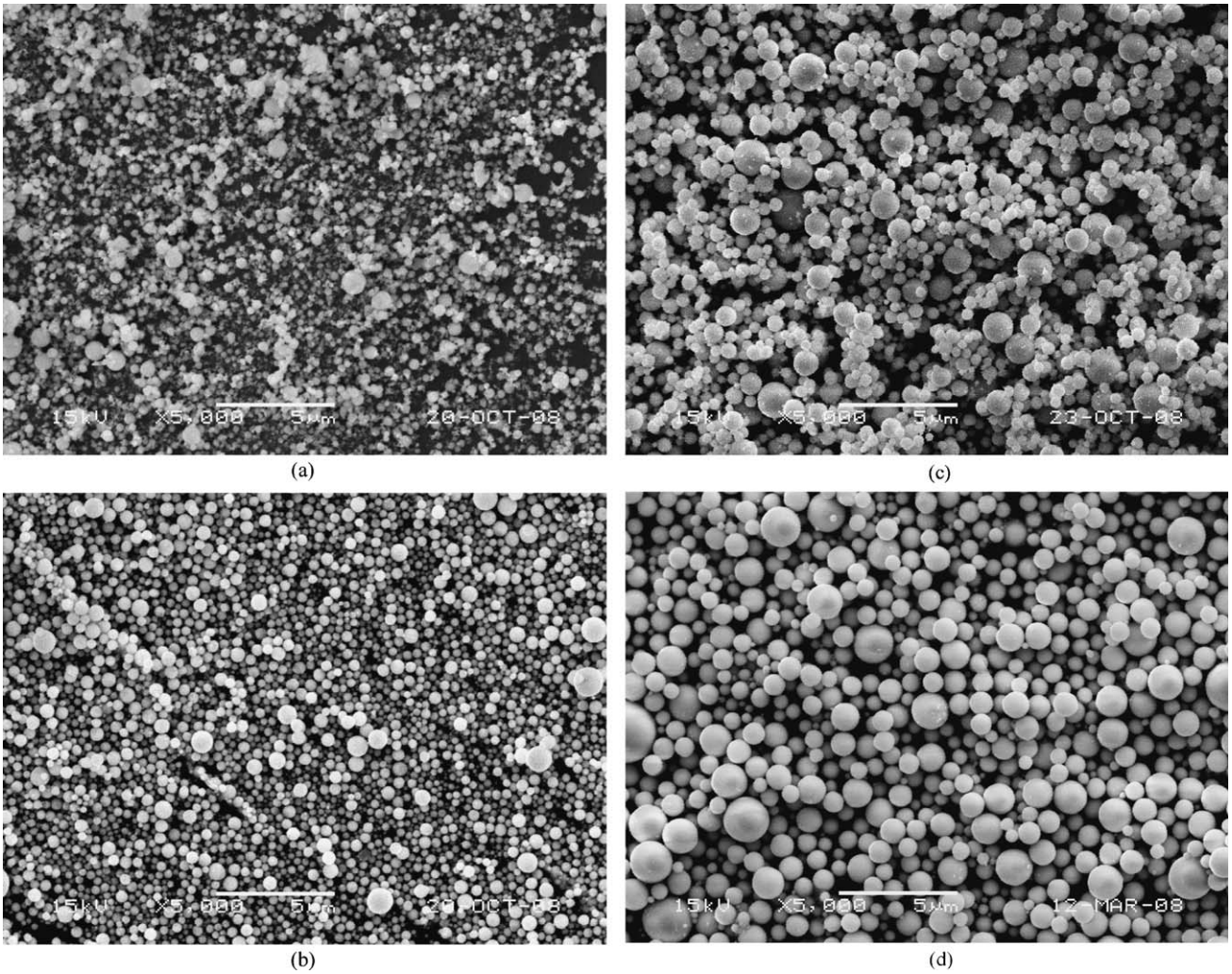


Fig. 1. SEM images of the glass powders prepared from spray solutions with various concentrations. (a) 0.025 M, (b) 0.05 M, (c) 0.1 M and (d) 0.5 M.

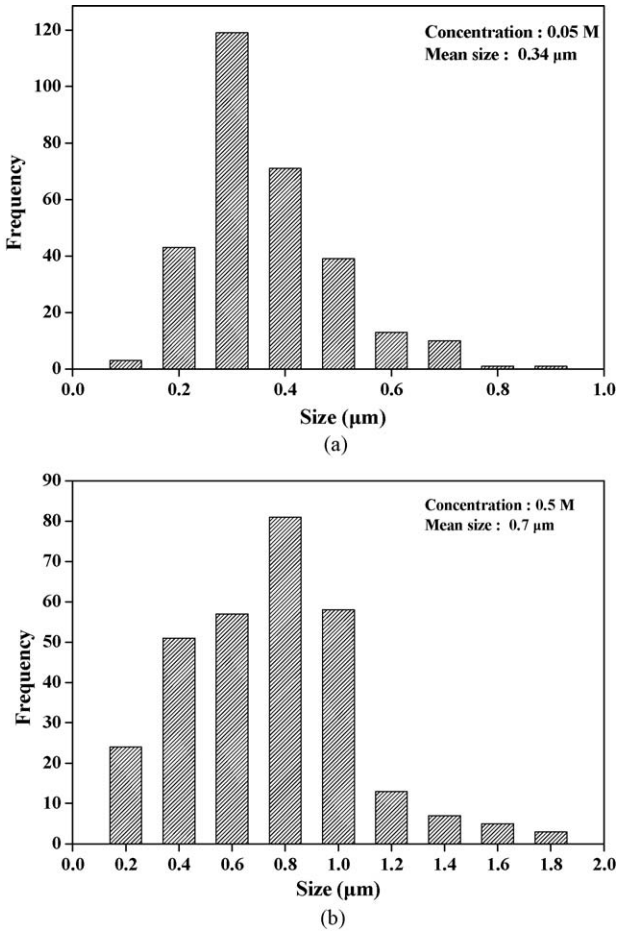


Fig. 2. Size distributions of the glass powders prepared from spray solutions with various concentrations. (a) 0.05 M and (b) 0.5 M.

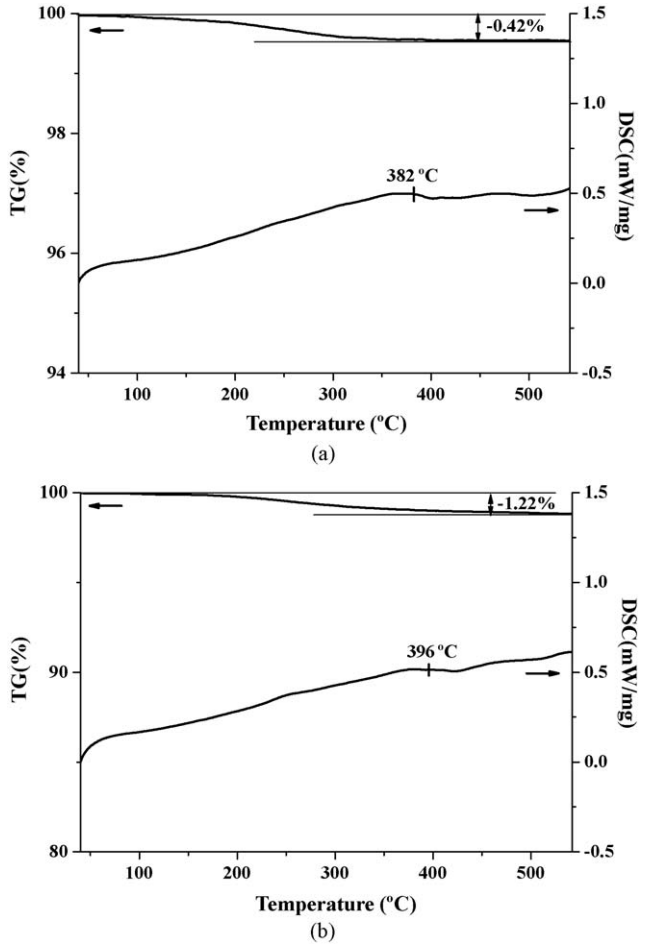


Fig. 4. TG/DSC curves of the glass powders prepared from spray solutions with various concentrations. (a) 0.05 M and (b) 0.1 M.

and geometric standard deviation of the powders formed from the spray solution with concentration of 0.05 M were 0.34 μm and 1.42. However, the mean size and geometric standard deviation of the powders formed from the spray solution with concentration of 0.5 M were 0.70 μm and 1.56.

Fig. 3 shows the XRD patterns of the Bi-based glass powders prepared by spray pyrolysis from spray solutions with various concentrations. The powders prepared by spray pyrolysis had broad peaks at around 28°, characteristic of the glass material, irrespective of the concentrations of the spray solutions. However, some crystal peaks were observed from the XRD patterns of the powders prepared from the spray solutions with low concentrations of 0.025 and 0.05 M. Deviation of compositions of glass powders occurred by evaporation of some glass components when the concentration of the spray solutions was too low, i.e. below 0.05 M.

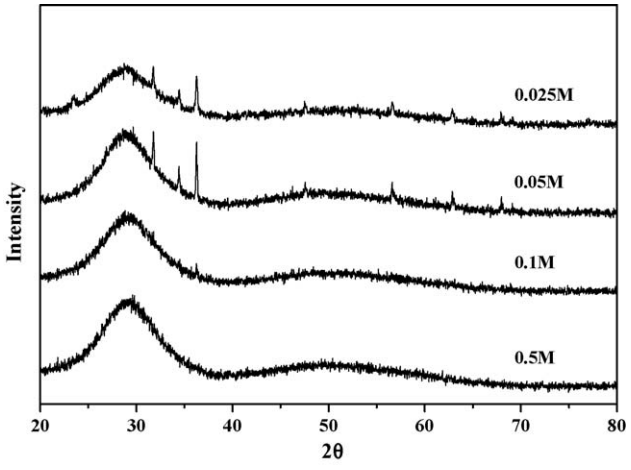
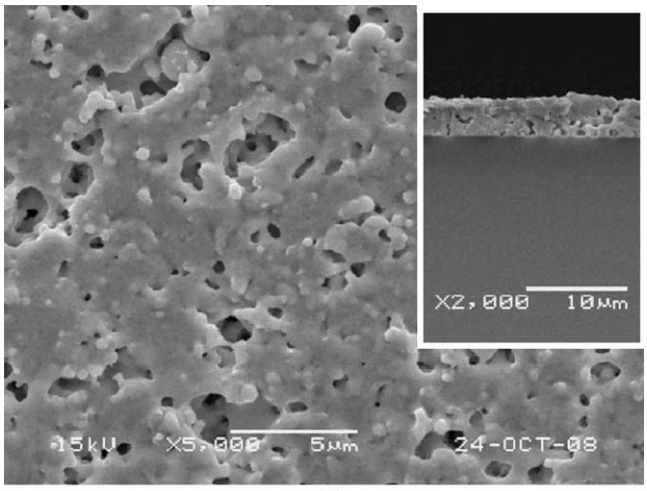


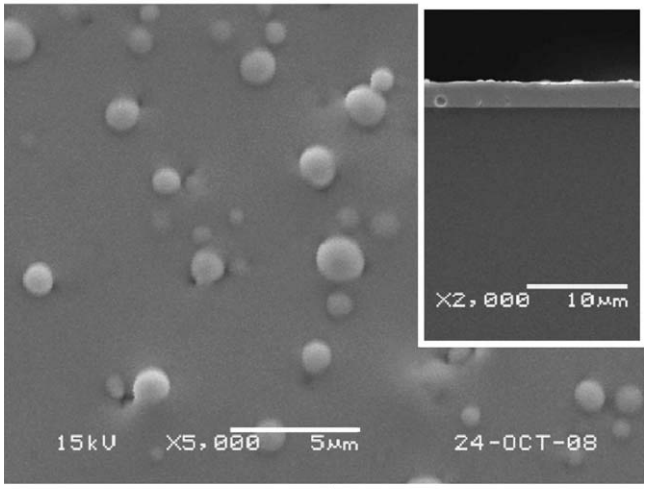
Fig. 3. XRD patterns of the glass powders prepared from spray solutions with various concentrations.

Fig. 4 shows the TG/DSC curves of the glass powders prepared from the spray solutions with concentrations of 0.05 and 0.1 M. The glass transition temperatures of the glass powders formed from the spray solutions with concentrations of 0.05 and 0.1 M were 382 and 396 °C. The exothermic peaks indicating crystallization of the glass materials were not observed in the DSC curves. The weight losses of the glass powders by elimination of adsorbed water molecules were 0.4 and 1.2 wt% in the TG curves.

The firing characteristics of the Bi-based glass powders with different mean size were investigated. The glass powders prepared from the spray solutions with various concentrations were mixed with an organic vehicle that consisted of ethyl

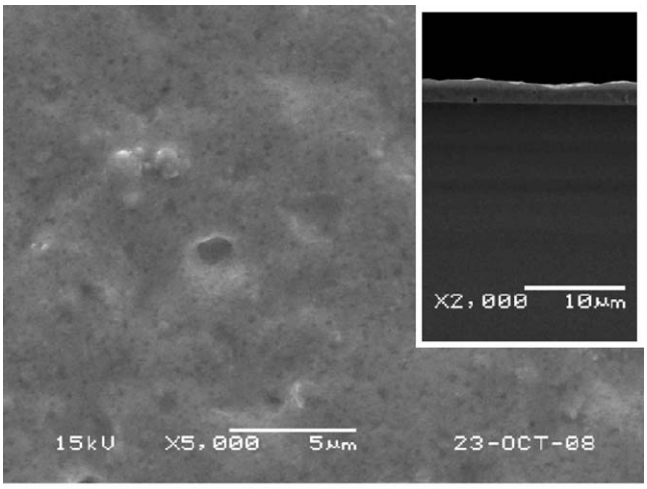


(a)

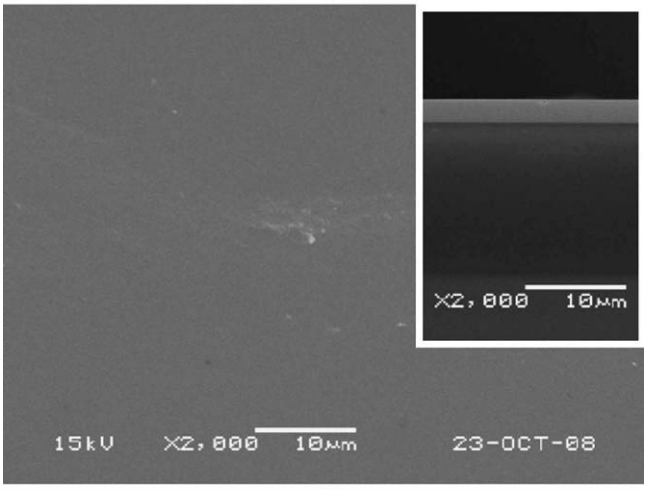


(b)

Fig. 5. SEM images of the glass layers formed from the glass powders obtained from spray solutions with various concentrations at a firing temperature of 400 °C. (a) 0.025 M and (b) 0.5 M.



(a)



(b)

Fig. 6. SEM images of the glass layers formed from the glass powders obtained from spray solutions with various concentrations at a firing temperature of 450 °C. (a) 0.025 M and (b) 0.5 M.

cellulose, α-terpineol, and butyl carbitol acetate (BCA). The paste was screen-printed onto a soda–lime glass substrate. The glass substrate was fired at 400 and 450 °C for 10 min under the same condition. Figs. 5 and 6 show the SEM images of the surfaces and cross-sections of the glass layers fired at 400 and 450 °C. The glass layer formed from the glass powders prepared from the spray solution with low concentration of 0.025 M had porous inner structure and rough surface, in which densification of glass layer by complete melting of the glass powders did not occur. On the other hand, the glass layer formed from the glass powders prepared from the spray solution with high concentration of 0.5 M had clean surface and dense structure. The number of voids inside the glass layers decreased with an increase of the mean sizes of the glass powders. However, melting of the glass powders with large sizes did not occur at a low firing temperature of 400 °C. Complete melting of the glass powders occurred at a firing temperature of 450 °C irrespective of the mean size of the glass powders. Therefore, glass layers had clean surface irrespective of the mean size of the glass powders. However, inner structures of the glass layers were affected by the mean size of the glass powders. The glass layers formed from the glass powders with fine size as shown in Fig. 6(a) had a number of voids inside the layers. On the other hand, the glass layer formed from the glass powders with large size as shown in Fig. 6(b) had dense inner structure without voids.

Silver paste was prepared using the prepared silver powders and the prepared glass powders. The silver powders prepared by spray pyrolysis had spherical shape and non-aggregation characteristics. The mean size of the silver powders was 0.7 μm. Glass content of the paste was fixed to 3 wt% of silver component. The paste was screen-printed onto a soda–lime glass substrate. Fig. 7 shows the SEM images of the surfaces and cross-sections of the silver conducting films fired at 400 °C. Silver conducting films were formed by melting the silver powders irrespective of the mean size of the glass powders. However, the silver conducting films had porous structure

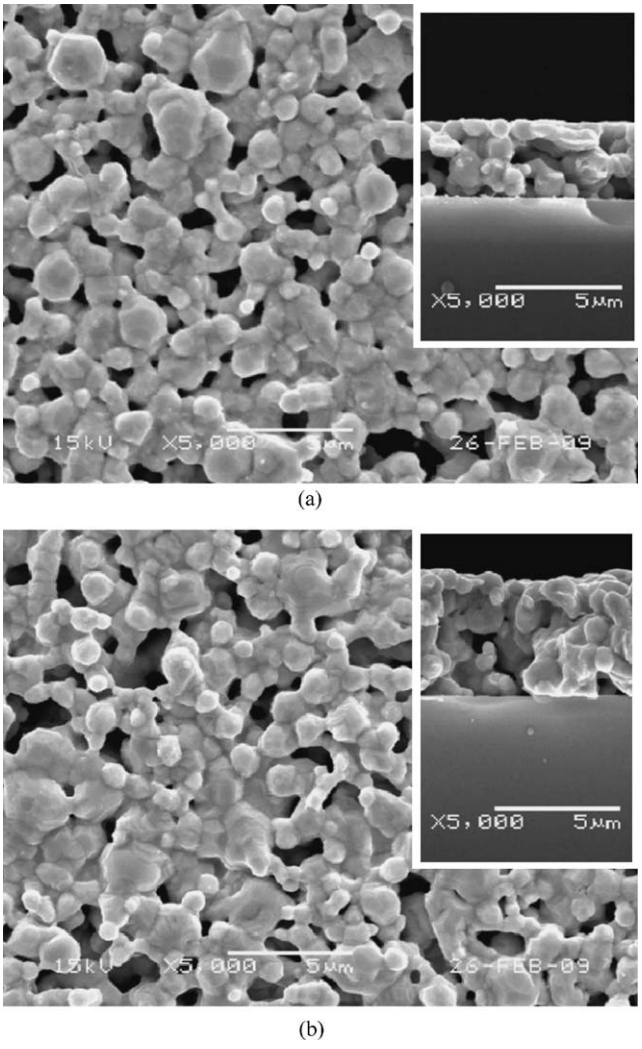


Fig. 7. SEM images of the silver conducting films fired at a temperature of 400 °C. (a) 0.025 M and (b) 0.5 M.

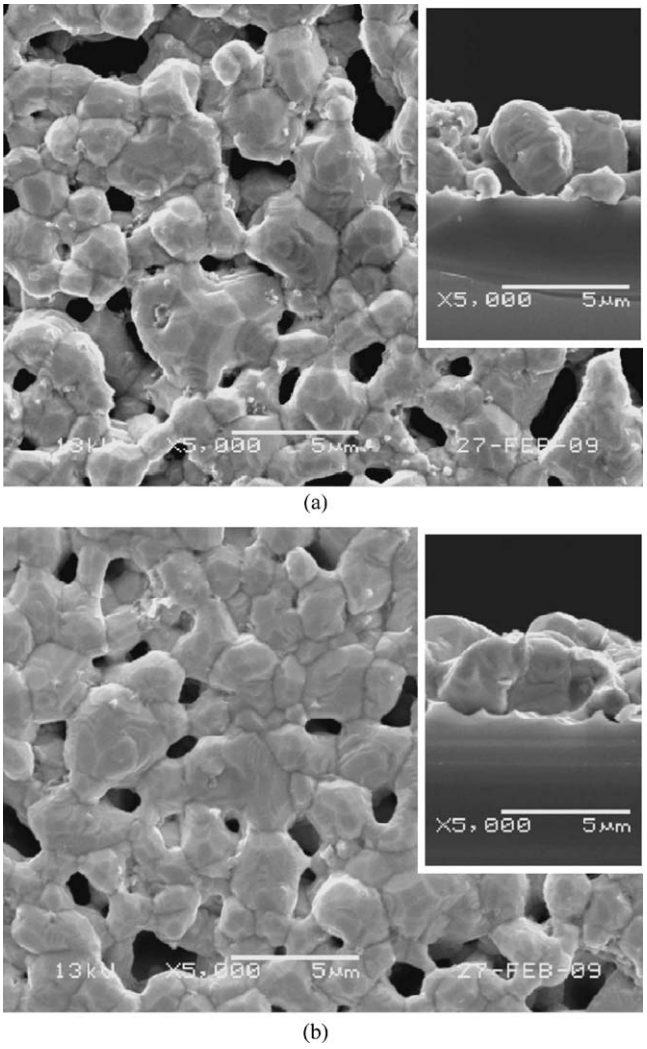


Fig. 8. SEM images of the silver conducting films fired at a temperature of 500 °C. (a) 0.025 M and (b) 0.5 M.

because of low firing temperature. The density of the silver conducting films increased with an increase of the firing temperature. Therefore, the silver conducting films fired at 500 °C as shown in Fig. 8 had dense structure irrespective of the mean size of the glass powders. The adhesion strength of the silver conducting films to the glass substrates estimated from the SEM images of the cross-sections increased with the increase of the firing temperature. The silver conducting films fired at 400 °C had poor adhesion to the glass substrate irrespective of the mean size of the glass powders. On the other hand, the silver conducting films fired at 500 °C had good adhered well to the glass substrate irrespective of the mean size of the glass powders.

Fig. 9 shows the specific resistances of the silver conducting films fired at 400, 450 and 500 °C. The specific resistances of the silver conducting films decrease with the increase of the firing temperature. The specific resistance of the silver conducting films changes from 3.13 to 4.03 μΩ cm according to the mean size of the glass powders at a firing temperature of 500 °C.

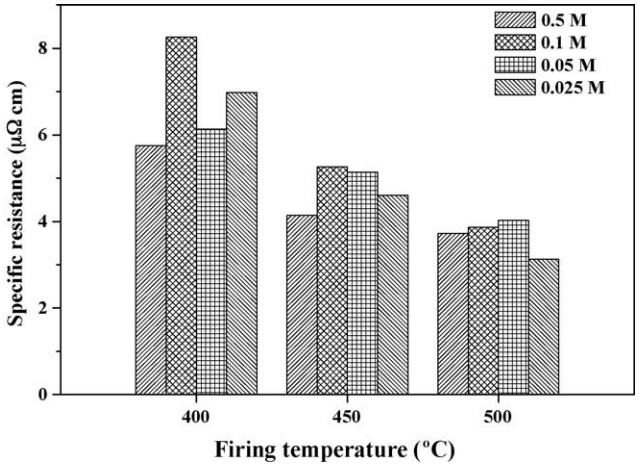


Fig. 9. Specific resistance of the silver conducting films fired at various temperatures.

4. Conclusions

Size-controlled Bi-based glass powders as additive for silver conducting pastes were directly prepared by spray pyrolysis. Firing characteristics of the glass powders were affected by the mean size of the glass powders. However, complete melting of the glass powders occurred at a firing temperature of 450 °C irrespective of the mean size of the glass powders. Silver conducting films are formed at a low temperature of 400 °C by melting the silver powders irrespective of the mean size of the glass powders used as inorganic binder. The specific resistances of the silver conducting films slightly change according to the mean size of the glass powders.

Acknowledgement

This work was supported by Seoul R&BD Program (WR090671).

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