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Characteristics of Ag powders coated with Pb-based glass material prepared by spray pyrolysis under various gas environments

Jang Heui Yi [a], Hye Young Koo [a], Jung Hyun Kim [a], You Na Ko [a], Yun Chan Kang [a,*], Hye Moon Lee [b], Jung Yeul Yun [b]

[a] Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea
[b] Functional Materials Division, Korea Institute of Materials Science, 531 Changwonadaero, Changwon, Gyeongnam 641-831, Republic of Korea

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Abstract

Ag powders coated with Pb-based glass material for Si solar cell application are directly prepared by spray pyrolysis in various gas environments. Pb-based glass is successfully formed in the composite powders irrespective of gas environment. The composite powders have bimodal size distributions of nanometer and submicron sizes. However, the number of nano-sized powders decreases when the reducing gas was used as the carrier gas. The silver-conducting films fired at 700 and 800 °C have dense structures without pores irrespective of the gas environment in the preparation of the composite powders. Glass materials are uniformly segregated between micron-sized silver grains. The conducting film formed from the composite powders prepared under 20% H_2/Ar atmosphere have sheet resistance of 7.8, 6.8, 5.1 and 5.9 mΩ/sq at firing temperatures of 500, 600, 700 and 800 °C, respectively.

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

1. Introduction

During the preparation of single-crystalline or polycrystalline Si solar cells, a silver electrode is formed on the side with an anti-reflective film. The silver electrode is generally fabricated by the firing of a printed layer formed by a screen-printing method using silver paste containing a silver powder, a glass frit, and a resin binder [1–3]. Silver paste with glass frit having an appropriate softening point can be sintered at 600–800 °C, wetted appropriately, and bonded appropriately to a silicon substrate. In order to improve the power generation characteristics of Si solar cells, it is important to improve the characteristics of the silver electrode.

The characteristics of silver electrode are strongly affected by the properties of silver powders and glass frits. Silver powders with high crystallinity and spherical morphology are preferred for use in the electrode material in Si solar cells. Pb-based glass frits prepared by conventional melting process are used as inorganic binder [4–7]. Fine size glass frits are prepared by repeated milling process in the conventional melting process. Therefore, glass frits obtained by milling process had non-spherical shape.

Silver powders prepared by spray pyrolysis are widely used as conducting powders in Si solar cells because of good electrical properties due to the high preparation temperature of powders. Silver powders prepared by spray pyrolysis had fine size, spherical shape, dense structure, narrow size distribution, high crystallinity and high purity. Glass frits with fine size, spherical shape and narrow size distribution have also been studied in spray pyrolysis [8–11].

In this study, Ag-glass composite powders were directly prepared by spray pyrolysis in various gas environments. Pb-based glass having an appropriate softening point for Si solar cell application was used as the coating material of Ag powders. The effect of gas environment on the formation of Ag-glass composite powders was studied.

2. Experimental method

The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a

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

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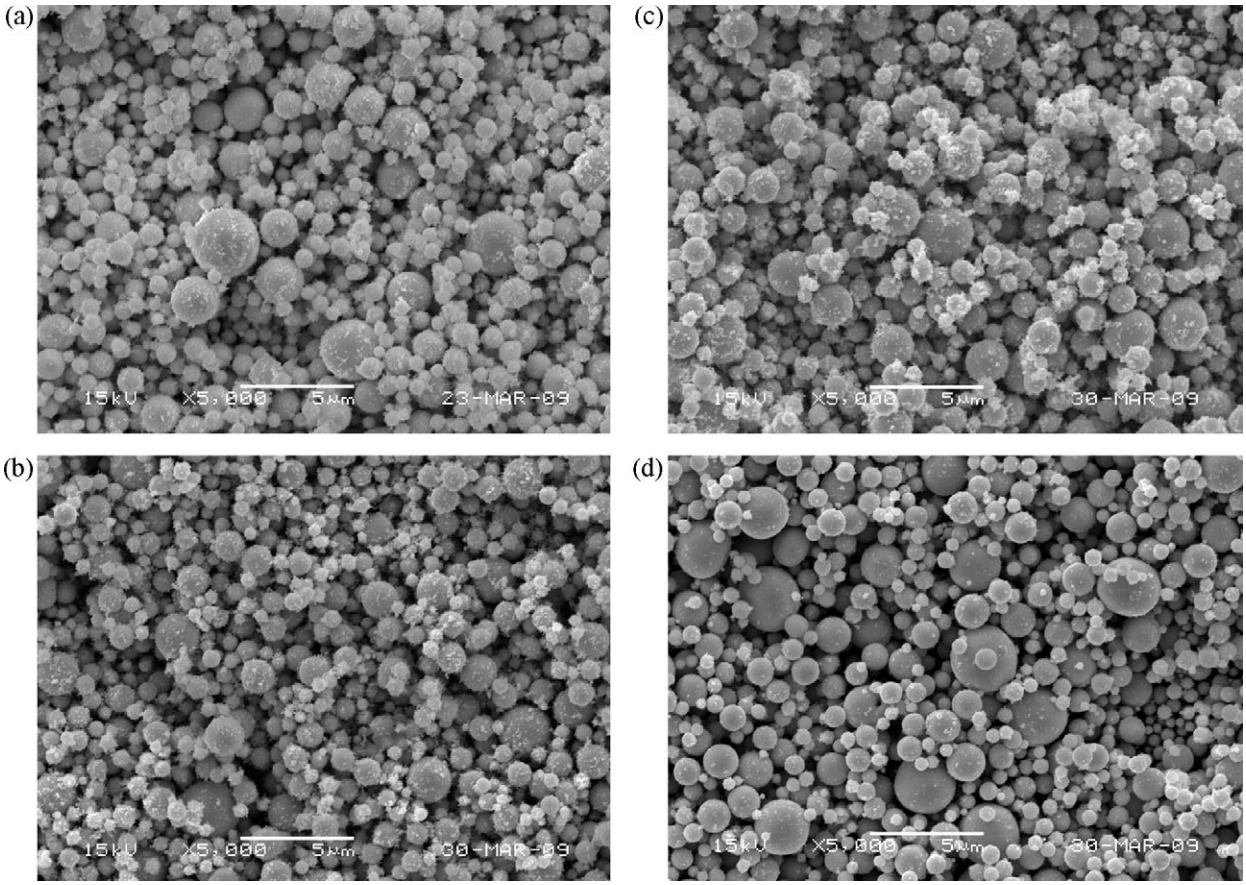

Fig. 1. SEM images of the silver-glass composite powders prepared by spray pyrolysis at various gas environments: (a) Air, (b) Ar, (c) N_2, and (d) 20% H_2/Ar.

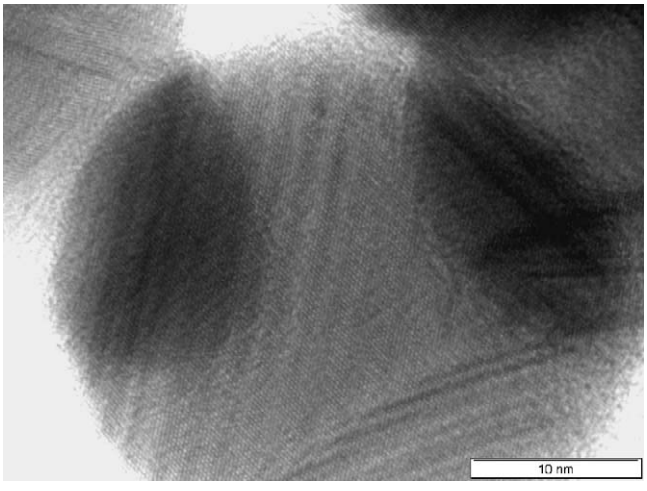

Fig. 2. TEM image of the nano-sized powders prepared by spray pyrolysis.

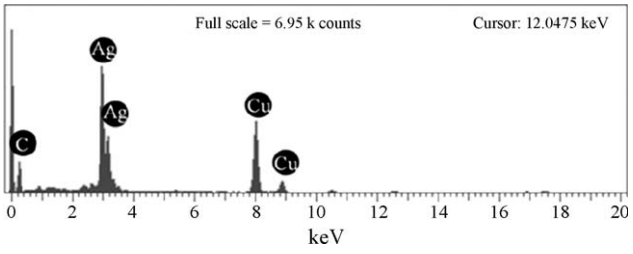

Fig. 3. EDS spectrum of the nano-sized powder prepared by spray pyrolysis.

1000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. The preparation temperature of composite powders was fixed at 1100 °C. The flow rate of air, N_2, Ar, and 20% H_2/Ar used as the carrier gas was fixed at 20 L min^{-1}. The main components of glass material were PbO and SiO_2. Small amount of Al_2O_3, ZrO_2, and P_2O_5 were added. The contents of PbO and SiO_2 were each 62 and 30 mol% of glass composition. Spray solutions were prepared by adding $Pb(NO_3)_2$ (Yakuri,

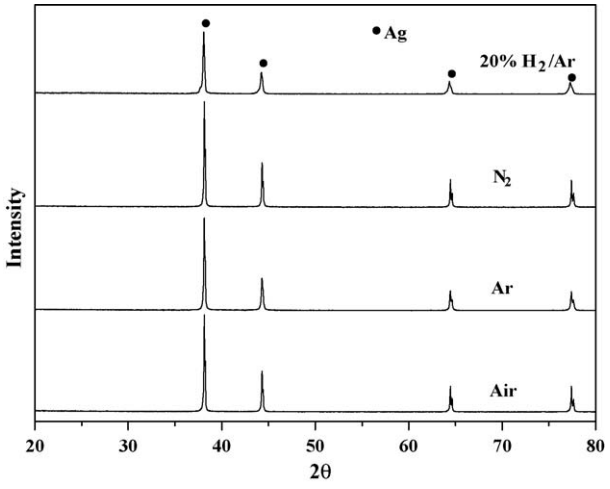

Fig. 4. XRD patterns of the silver-glass composite powders prepared by spray pyrolysis at various gas environments.

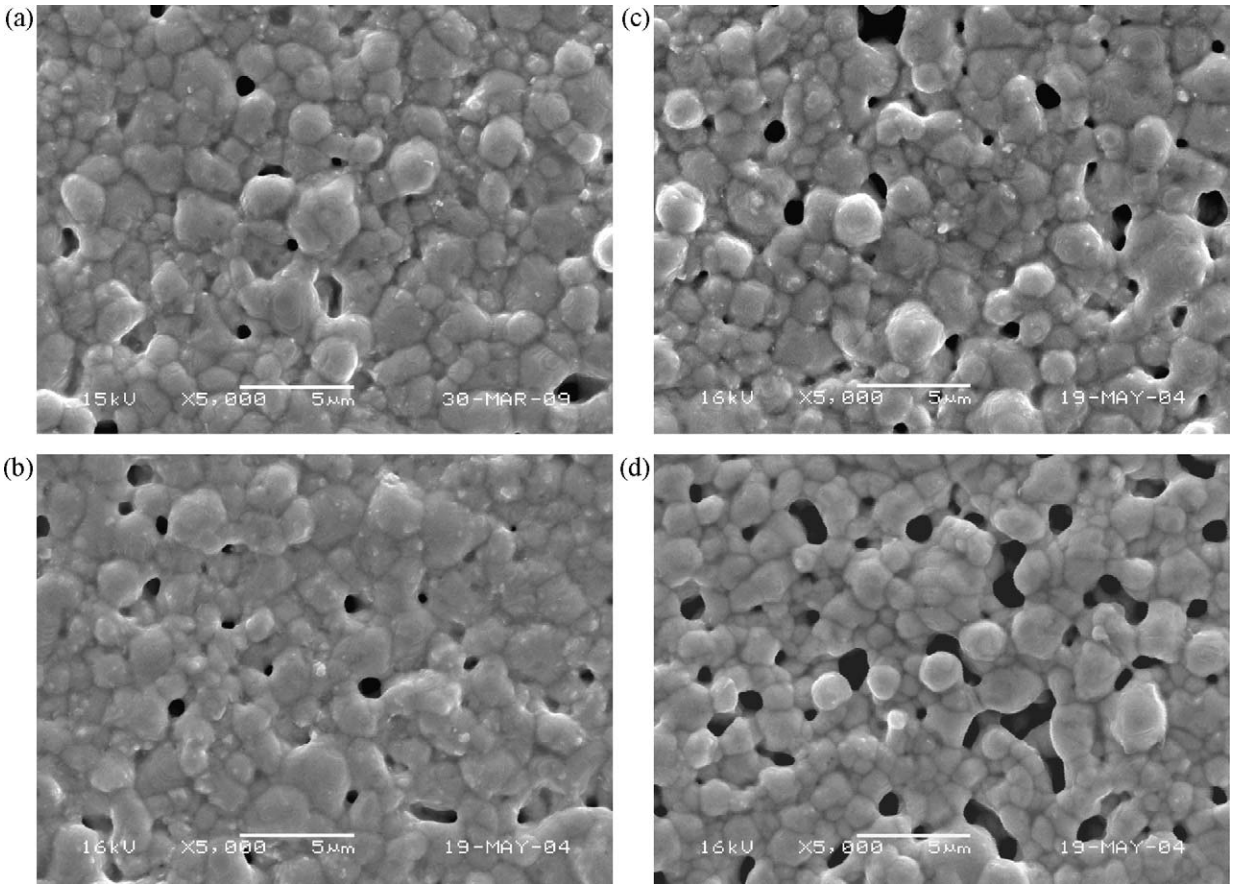

Fig. 5. SEM images of the surfaces of the silver-conducting films fired at 500 °C: (a) Air, (b) Ar, (c) N_2, and (d) 20% H_2/Ar.

99%), tetraethyl orthosilicate (TEOS, Aldrich, 98%), $Al(NO_3)_3{\cdot}9H_2O$ (Junsei, 98%), $ZrO(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98%) and $(NH_4)_2HPO_4$ (Junsei, 99%) to distilled water with a small amount of nitric acid. The concentration of silver nitrate was fixed at 0.5 M. The glass content was fixed at 3 wt.% of Ag component.

Silver electrodes were fabricated by firing of a printed layer formed by a screen-printing method using silver paste containing a silver-glass composite powder and a resin binder. The silver-glass composite powders prepared by spray pyrolysis at various gas environments were mixed with an organic vehicle that consisted of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). Silver paste was screen printed onto a Si wafer substrate. The printed Si wafer substrate was dried at 120 °C for 30 min. The printed Si wafer was fired by two steps, at first temperature of 400 °C for 30 min at a heating rate of 5 °C min^{-1} and in the second temperatures between 500 and 800 °C for 10 min at a heating rate of 5 °C min^{-1}.

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

3. Results and discussion

The morphologies of the composite powders prepared by spray pyrolysis under various gas environments are shown in Fig. 1. The composite powders had bimodal size distributions of nanometer and submicron sizes. AgO and Ag_2O phases are formed inside the hot wall reactor by decomposition of $AgNO_3$ in the preparation of Ag powders by spray pyrolysis. The silver

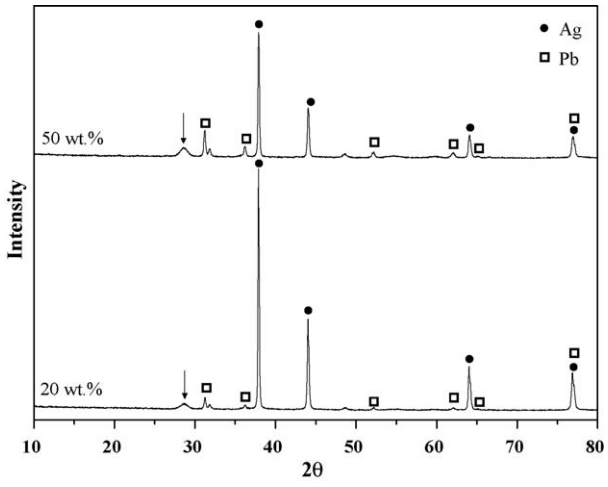

Fig. 6. XRD patterns of the composite powders with 20 and 50% glass contents of Ag component.

oxide intermediates are volatile at high temperatures. Reduction of intermediate product into Ag metal occurred slowly inside the hot wall reactor due to the high flow rate of the carrier gas. Therefore, evaporation of some of silver component occurred inside the hot wall reactor when the air, N_2 and Ar were used as the carrier gas. Therefore, nano-sized powders were formed from the evaporated vapors by nucleation and growth mechanisms. On the other hand, reduction of the intermediate product into Ag metal occurred immediately when the 20% H_2/Ar reducing gas was used as the carrier gas. Therefore, the number of nano-sized powders decreased when the reducing gas was used as the carrier gas. Figs. 2 and 3 show the TEM image and EDS spectrum of the nano-sized powders formed from the evaporated vapors when the air was used as the carrier gas. Cu and C peaks in the EDS spectrum originated from carbon-coated cupper TEM grid. Therefore, pure Ag powders with nanometer size were formed from the evaporated vapors. The nano-sized Ag powder had single crystal structure as shown by high resolution TEM image.

Fig. 4 shows the XRD patterns of the composite powders prepared at various gas environments. The composite powders had pure Ag crystal structures irrespective of the gas environment. The mean crystallite sizes of the composite powders were changed from 44 to 55 nm according to the gas environment in the preparation process. The composite powders prepared under 20% H_2/Ar atmosphere had the lowest mean crystallite size.

Fig. 5 shows the SEM images of the surfaces of the silver-conducting films formed from the composite powders prepared from the various gas environments at a firing temperature of 500 °C. Melting of the composite powders occurred irrespective of the gas environment in the preparation of the composite powders. The silver-conducting films formed from the composite powders obtained in air, Ar and N_2 atmospheres had similar grain size of several microns. On the other hand, the silver-conducting film formed from the composite powders obtained in 20% H_2/Ar atmosphere had fine grain size. The gas environment affected the formation of glass phase in the composite powders. The composite powders with high glass contents were prepared by spray pyrolysis using carrier gas of 20% H_2/Ar to show the formation of glass material in the reducing atmosphere. Fig. 6 shows the XRD patterns of the composite powders with 20 and 50 wt.% glass contents of Ag component. The composite powders with high glass contents had broad peaks at around 28° as shown by arrows in the XRD patterns, which is the experimental evidence of the amorphous crystalline structure. The peaks of Pb metal are observed in the XRD patterns. Reduction of some Pb component consisting of glass material occurred at reducing preparation condition. However, the crystalline peaks of components consisting of glass material except Pb component are not observed from the XRD patterns. Therefore, Pb-based glass material was well formed in the preparation of the Ag-glass composite powders by spray pyrolysis in the reducing atmosphere.

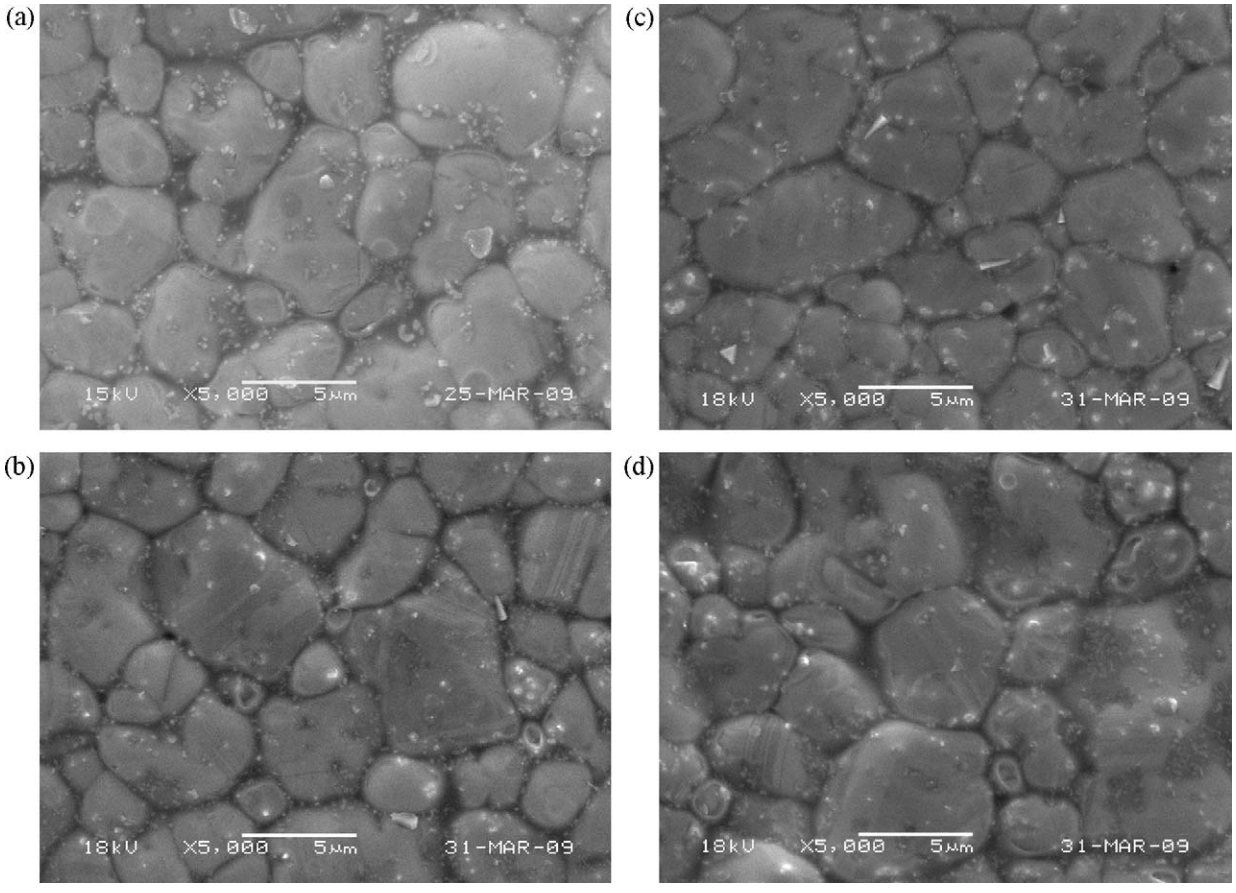

Fig. 7. SEM images of the surfaces of the silver-conducting films fired at 700 °C: (a) Air, (b) Ar, (c) N_2, and (d) 20% H_2/Ar.

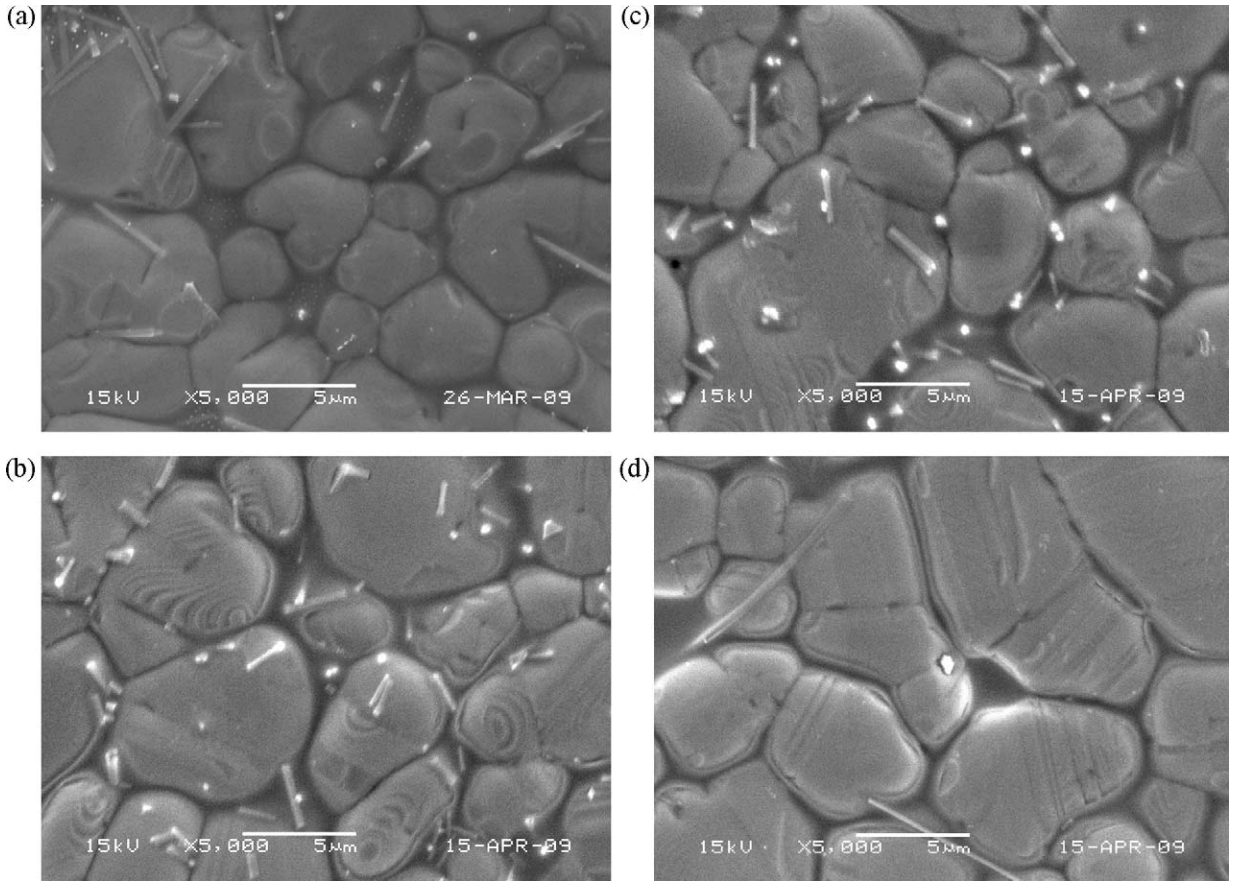

Fig. 8. SEM images of the surfaces of the silver-conducting films fired at 800 °C: (a) Air, (b) Ar, (c) N_2, and (d) 20% H_2/Ar.

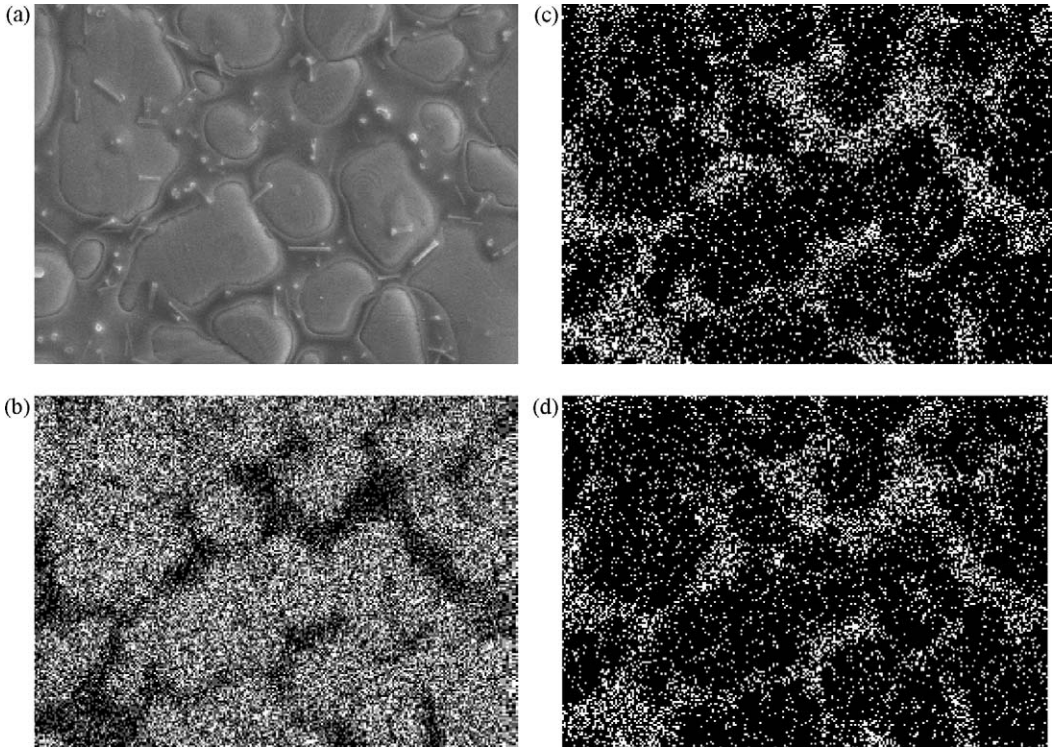

Fig. 9. Results of dot mapping of the silver-conducting films obtained from the composite powders prepared under H_2/Ar atmosphere: (a) SEM image, (b) Ag, (c) Pb, and (d) Si.

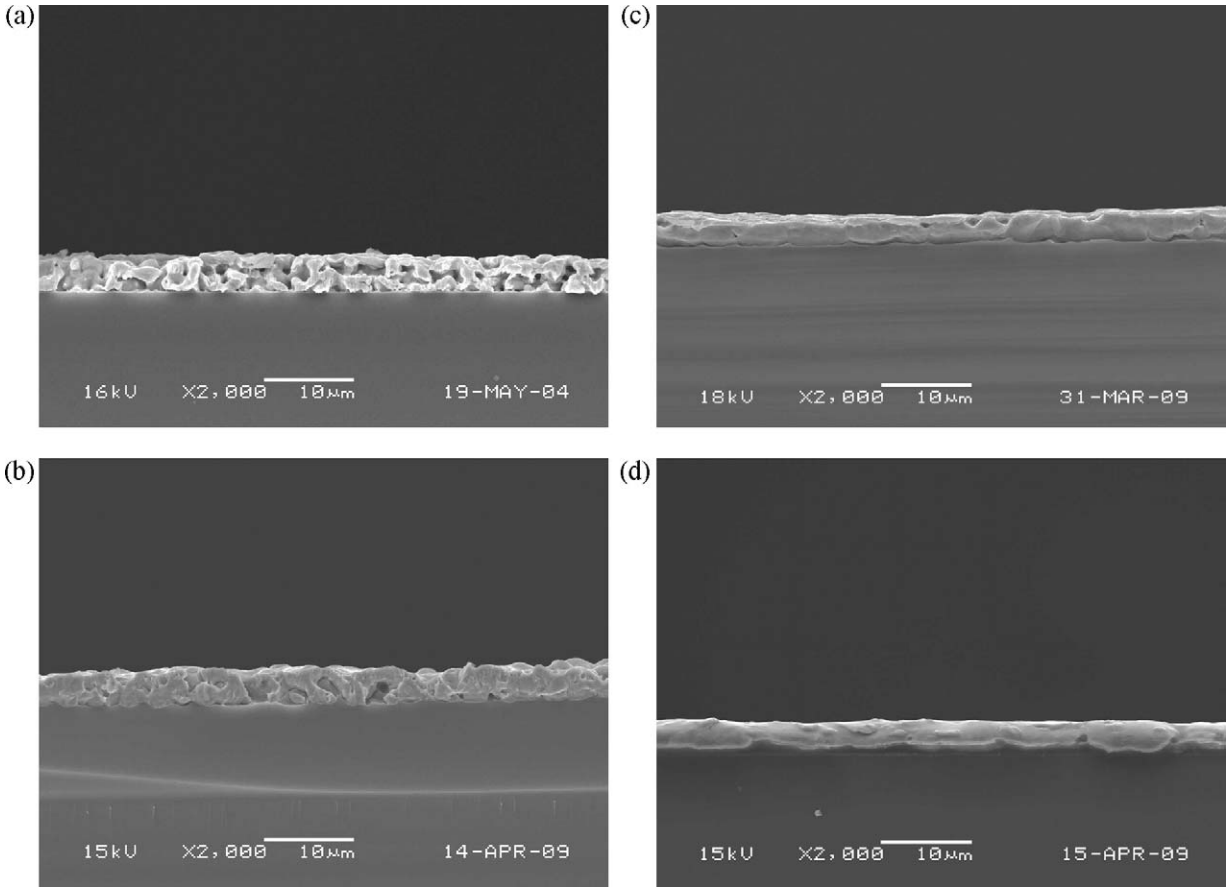

Fig. 10. SEM images of the cross-sections of the silver-conducting films obtained from the composite powders prepared under H_2/Ar atmosphere: (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

Figs. 7 and 8 show the SEM images of the surfaces of the silver-conducting films formed from the composite powders at firing temperatures of 700 and 800 °C. The silver-conducting films had dense structures without pores irrespective of the gas environment in the preparation of the composite powders. Grain growth of Ag and segregation of Ag and glass material occurred irrespective of the gas environment in the preparation of the composite powders. Needle-like crystals formed by crystallization of some glass material are observed from the SEM images as shown in Fig. 8. Fig. 9 shows the result of dot mapping of the silver-conducting film formed from the composite powders prepared by spray pyrolysis using carrier gas of 20% H_2/Ar. Glass materials are segregated between micron-sized silver grains at a high-firing temperature of 800 °C.

Fig. 10 shows the SEM images of the cross-sections of the silver-conducting films obtained from the composite powders prepared by spray pyrolysis using carrier gas of 20% H_2/Ar. The conducting film fired at 500 °C had porous structure. However, densities of the conducting films increased with increasing firing temperature. The conducting film fired at 800 °C had dense structure without pores. The conducting films had good adhesion properties to the substrate irrespective of the firing temperatures.

Fig. 11 shows the sheet resistances of the silver-conducting films formed from the composite powders prepared by spray pyrolysis in various gas environments. The firing temperature of the films was 700 °C. The sheet resistances of the films were slightly changed from 5.1 to 6.0 mΩ/sq according to the gas environment in the preparation of the composite powders. The conducting film formed from the composite powders prepared under 20% H_2/Ar atmosphere had the lowest sheet resistance.

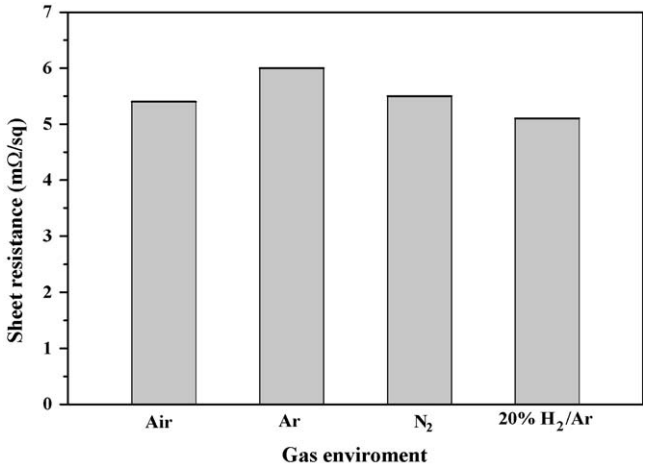

Fig. 11. Sheet resistances of the silver-conducting films fired at 700 °C.

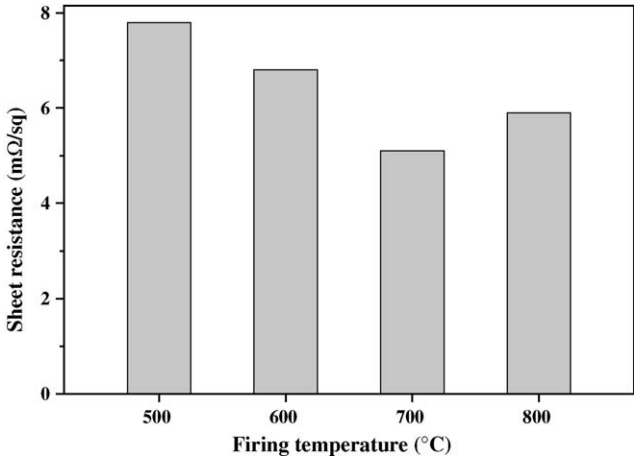

Fig. 12. Sheet resistances of the silver-conducting films fired at various temperatures.

Fig. 12 shows the sheet resistances of the silver-conducting films formed from the composite powders prepared under 20% H_2/Ar atmosphere at various firing temperatures. The silver-conducting films had low sheet resistances of 7.8, 6.8, 5.1 and 5.9 mΩ/sq at firing temperatures of 500, 600, 700 and 800 °C, respectively. The crystallization of the glass material at a high temperature of 800 °C increased the sheet resistance of the silver-conducting film.

4. Conclusions

Ag powders coated with Pb-based glass material were prepared by spray pyrolysis under various gas environments. The composite powders prepared under reducing atmosphere had narrow size distribution because volatilization of silver oxide intermediate inside the hot wall reactor was minimized by fast reduction to Ag metal. The Ag-glass composite powders prepared by spray pyrolysis had good sintering characteristics at firing temperatures between 500 and 800 °C. Therefore, silver-conducting film formed from the composite powders had dense structures and low sheet resistances.

References

[1] S.B. Rane, P.K. Khanna, T. Seth, G.J. Phatak, D.P. Amalnerkar, B.K. Das, Firing and processing effects on microstructure of fritted silver thick film electrode materials for solar cells, Mater. Chem. Phys. 82 (2003) 237–245.
[2] Y. Zhang, Y. Yang, J. Zheng, W. Hua, G. Chen, Thermal properties of glass frit and effects on Si solar cells, Mater. Chem. Phys. 114 (2009) 319–322.
[3] M.M. Hilali, S. Sridharan, C. Khadilkar, A. Shaikh, A. Rohatig, S. Kim, Effect of glass frit chemistry on the physical and electrical properties of thick-film Ag contacts for silicon solar cells, J. Electron. Mater. 35 (11) (2006) 2041–2047.
[4] K.J. Park, D.S. Seo, J.K. Lee, Conductivity of silver paste prepared from nanoparticles, Colloid Surf. A 313–314 (2008) 351–354.
[5] S.H. Park, D.S. Seo, J.K. Lee, Preparation of Pb-free silver paste containing nanoparticles, Colloid Surf. A 313–314 (2008) 197–201.
[6] P.F. Becher, W.L. Newell, Fracture energy of a glass-bonded thick-film. conductor: effect of firing conditions, J. Mater. Sci. 12 (1977) 90–96.
[7] T.T. Hitch, Adhesion, phase morphology and bond- ability of reactively-bonded and frit bonded gold and silver thick-film conductors, J. Electron. Mater. 3 (1974) 553–577.
[8] H.Y. Koo, S.K. Hong, S.H. Ju, I.S. Seo, Y.C. Kang, PbO–B_2O_3–SiO_2 glass powders with spherical shape prepared by spray pyrolysis, J. Non-Cryst. Solids 352 (2006) 3270–3274.
[9] H.Y. Koo, S.K. Hong, S.H. Ju, D.Y. Kim, Y.C. Kang, Effect of preparation temperature on the characteristics of PbO–B_2O_3–SiO_2 glass powders with spherical shape, J. Alloys Compd. 428 (2006) 344–349.
[10] S.K. Hong, H.Y. Koo, D.S. Jung, Y.C. Kang, Transparencies of dielectric layers formed from size-controlled Bi-based glass powders obtained by spray pyrolysis, Appl. Phys. A Mater. Sci. Process. 85 (2006) 63–68.
[11] S.K. Hong, H.Y. Koo, D.S. Jung, I.S. Suh, Y.C. Kang, Preparation of Bi_2O_3–B_2O_3–ZnO–BaO–SiO_2 glass powders with spherical shape by spray pyrolysis, J. Alloys Compd. 437 (2007) 215–219.