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Electroless silver plating on Pb-based glass frits by a one-step activation method without stannum and palladium

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Abstract

In this paper, a new activation method—taking ethylene glycol as reducing agent for the formation of metallic silver (Ag^0) from silver ions (Ag^+)—has been introduced to form silver nuclei on Pb-based glass frits for silver paste. Electroless silver plating on glass frits is successfully realized by adding the activated glass frits into two kinds of electroless plating baths. The result shows that the silver particles with an average grain size around 100 nm are well distributed on the glass frits. Compared with the traditional electroless plating method, this process avoids the interference of chloride ions which may cause AgC1 precipitation as well as the tin ions which are harmful to human health. Furthermore, roughening treatment is not involved in the activation, so composition change will not happen to glass frits and front silver paste in the follow-up process.

Keywords: Electroless silver plating; Glass frits; Activation; Ethylene glycol; Solar energy materials

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1. Introduction

Silver paste for solar cell consists of three parts: silver powder, glass frit and organic carrier. Although glass frit holds the minimum weight percentage in the pastes (1–5 wt%), it plays an important role in Ag/Si metal–semiconductor contact formation by etching through the antireflection coating and ensuring a stable mechanical contact [1]. During the process of sintering, the following processes will happen as the temperature increases: metallic lead precipitates are formed when heating up glass frit containing PbO on silicon [2], for an oxidation–reduction reaction that has taken place between silicon and PbO in the glass frit [3]. Then, glass frits begin to melt and cover on the surface of silver particles at the temperature of around 450 °C, and in the temperature range between 600 °C and 700 °C, silver powder is wrapped by melted glass and dissolved into lead precipitates [4]. During the cooling process, silver crystallites are found to grow into the silicon surface from the glass containing dissolved silver [2]. The silver particles far from the Si surface can also be gathered mutually. The transfer process of silver through the glass to grow into the silicon seems to be the key process in electrical contact formation [3]. Therefore, it is expected that the glass frits coated with nano-silver material can play an assistant role in accelerating the dissolution and the transfer of silver, therefore the silver electrode by sintering can form a good contact with silicon.

Various methods have been explored to prepare metal-coated materials, such as sputtering [5], sol–gel [6], spin coating [7], dip coating [8], chemical vapor deposition (CVD) [9] and electroless plating [10], etc., among which electroless plating appears to be the most facile and effective way due to its low cost, good controllability and uniform coatings.

The conventional electroless silver plating involves three steps: pretreatment, activation and plating [11]. The activation is the key to the subsequent successful electroless metal deposition.

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The traditional activation process includes a two-step method, using sensitization solution of $SnCl_2$ and activation solution of $PdCl_2$, and a one-step method, using a colloidal mixture of $SnCl_2$ and $PdCl_2$ [12]. However, these methods have a few drawbacks, such as the chemical composition change of glass frits in the pretreatment process, and the hazard of highly toxic tin. Moreover, Cl^- involved in sensitization and activation solutions will attach to tin activation layer. It cannot be washed away completely and will adversely affect photoelectric conversion efficiency.

In the present work, we have developed a short process plating method for preparing glass frits coated with Ag material. This method involves the deposition of primary crystal nucleus and the reduction of silver nitrate with formaldehyde.

2. Experimental procedure

Glass frits with an average diameter of 1.73 μm were obtained via ball-mailing. All the other chemical reagents were of analytic grade and used without further purification.

5 g glass frits and a certain amount of $AgNO_3$ were dispersed into 25 mL ethylene glycol, reacting for 24 h at the room temperature with mechanical agitation until dark brown precipitation (nano-Ag@glass frits) appeared, and then the supernatant was removed. The product was washed for several times with deionized water and alcohol by centrifugation at 3000 rpm and dried at 60 °C for 4 h.

3 g activated glass frits was placed directly into the reducing solution constituted by formaldehyde ($5.5\ mL\ L^{-1}$), alcohol ($500\ mL\ L^{-1}$). Then the solution of $AgNO_3$ ($0.1\ mol\ L^{-1}$), ammonia (25 wt%, $100\ mL\ L^{-1}$) was added slowly, and the pH value was adjusted to 13.4 by NaOH. The plating process was carried out at room temperature with ultrasonic vibration for 5 min.

Silver electrodes were fabricated by firing of a printed layer formed by a screen-printing method using silver paste containing Ag/glass frits, silver powder and organic carrier. For the preparation of paste, organic vehicle (a mixture of terpineol, tributyl citrate, xylene, ethyl cellulose and castor oil), the Ag/glass frits (or glass frits), additive were mixed with silver powder, keeping the ratio of silver (including silver powder and silver particles on glass frits)/organic vehicle/glass frit/additive to 79.5/17/3/0.5 (wt%) respectively. The solid materials and organic vehicle were carefully mixed in a mixer so that all the solid materials could adequately get wet and dispersed in the vehicle. Then the paste was grinded by three roll milling for four times to make it completely homogeneous. The printed Si wafer was dried in air at 220–280 °C for 4 min and put into a belt-line furnace (six zone) for 1 min with peak firing temperature about 800 °C.

3. Characterization

The structure and the size of Ag particles were identified by the measurement of X-ray diffraction (XRD, D/Max2500) by using Cu K_α radiation. The morphologies of glass frits, nano-Ag@glass frits, Ag/glass frits and silver electrodes were directly observed with environmental scanning electron microscope (ESEM, Quanta-200), while the EDS analysis was performed to reveal the surface chemical constituents of Ag/glass frits. The photo-voltaic parameters of finished cells were tested by a solar cell testing system (DLSK-FXJ7). The content of Ag in Ag/glass frits was determined with atomic absorption spectrophotometer (HG-9602).

4. Results and discussion

Fig. 1 shows the image of glass frits acquired by ball-mailing. It can be seen from Fig. 1 that most parts of glass frits have flat surfaces and sharp edge angles. Analyzed by laser particle size analyzer, glass frits have an average particle size of 1.73 μm and a maximum of 4.33 μm [13].

Fig. 2 shows the ESEM micrographs of nano-Ag@glass frits and Ag/glass frits. As shown in Fig. 2a, silver clusters have formed on the surfaces of glass frits. The activation mechanism has been investigated. $AgNO_3$ can be gradually reduced to silver particle by ethylene glycol and glass frits added into this solution can provide heterogeneous nucleation centers for silver. As the time goes on, effective catalytic sites are formed. Evenly-distributed silver clusters attached to the surfaces of glass frits will provide effective catalytic sites for electroless silver plating. It can be seen from Fig. 2b that monodisperse glass frits with homogeneous, discontinuous silver coating are obtained. This phenomenon can be explained from the following perspectives. Firstly, the distribution of effective catalytic sites is even and dense, which can much more efficiently catalyze the redox reaction of Ag^+ in the electroless plating process. Secondly, ultrasonic agitation and mechanical stirring are used to release hydrogen bubbles so that glass frits can disperse in electroless plating solutions homogeneously.

In Fig. 3, curves 1, 2, and 3 are the XRD patterns of glass frits, nano-Ag@glass frits and Ag/glass frits respectively. On curve 3, there are four characteristic peaks at $2\theta = 38.3°$, 44.5°, 64.6° and 77.6°, which are attributed to Ag (111), (200), (220) and (311)

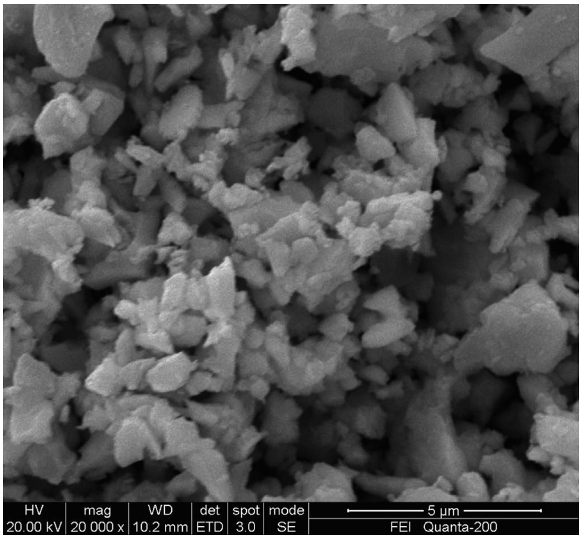


Fig. 1. ESEM image of the glass frits.

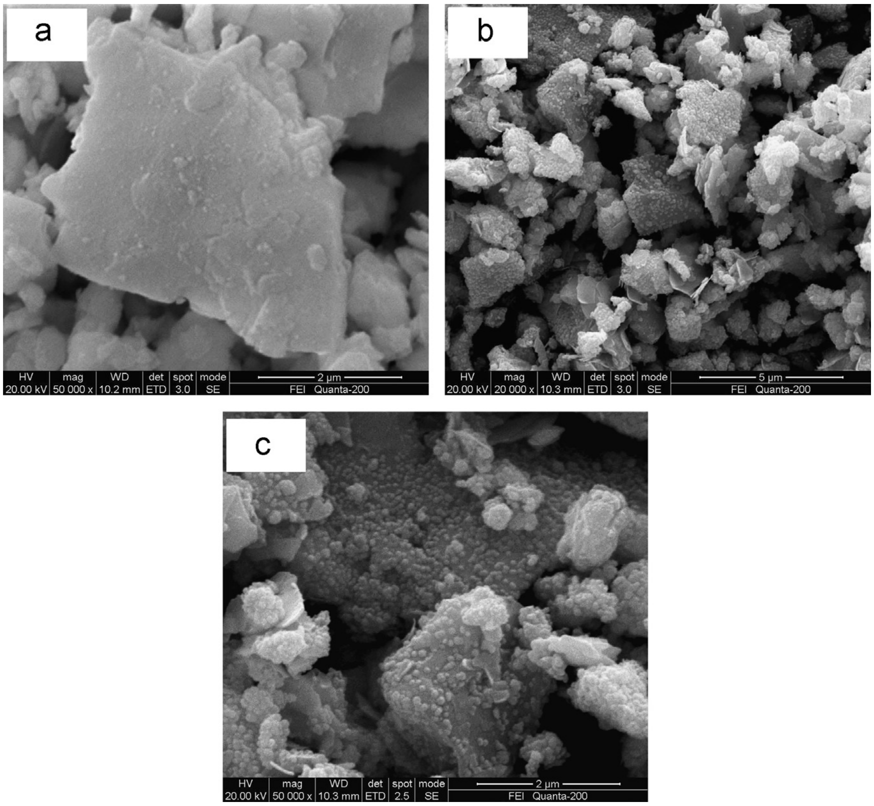


Fig. 2. ESEM images of nano-Ag@glass frits (a), Ag/glass frits (b) and its detailed view (c).

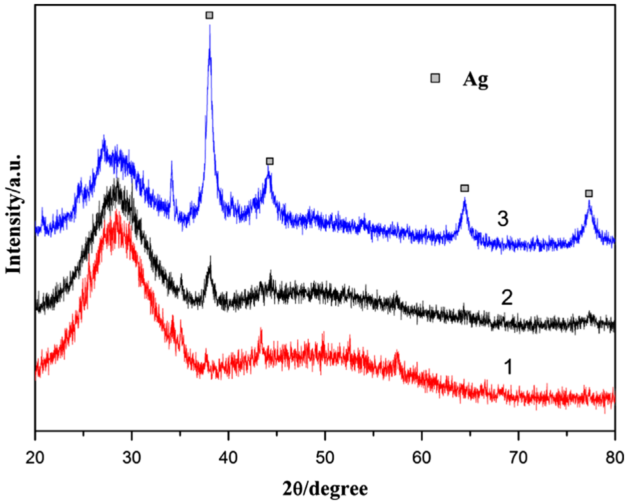


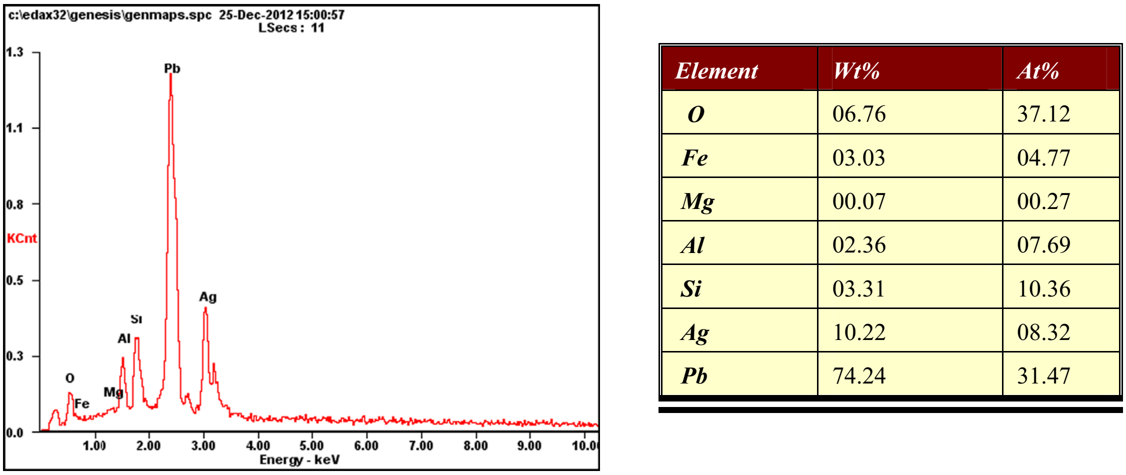
Fig. 3. XRD pattern of glass frits (1), nano-Ag@glass frits (2) and Ag/glass frits (3).

(JCPDS: 65-2871), indicating that the pure Ag particle's structure is cubic. The average grain size of Ag particles, calculated by Scherrer formula, is about 100 nm. However, there is no obvious peak on curve 2 for the crystallinity of silver particles deposited in step one is low, so the diffraction peaks are very weak and cannot be recognized easily Fig. 4.

The main components of glass frit are PbO, SiO_2 and Al_2O_3, with a small amount of iron oxides and magnesium oxides. Fig. 5 shows the surface component of glass frits after electroless plating. Pb, Si, Al and O peaks in the EDS spectrum originate from glass frits. Therefore, Pure Ag particles with nanometers size are formed from electroless plating. Since the content of silver is not very high, the Ag peak is less intensive.

Fig. 5 shows the ESEM images of the surfaces and cross-sections of the silver electrodes. In Fig. 5b and d the silver electrodes are formed from the silver paste containing Ag/glass frits, while the silver electrodes in Fig. 5a and c prepared from the paste without Ag/glass frits. Both the silver electrodes have a porous structure. However, The silver-conducting films obtained from the silver paste containing Ag/glass frits have dense structures with fewer pores. It is believed that nano-silver particles on glass frits play an assistant role in sintering of Ag powder particles.

Table 1 shows the electrical performance of the silicon solar cells obtained from silver pastes containing glass frits or Ag/glass frits. The series resistor is an important parameter for Eff improvement in industrial Si solar cells. And the average series resistor (R_s) is slightly changed from 0.092 Ω to 0.091 Ω by using Ag/glass frits. Moreover, the average photoelectric conversion efficiency (η) is improved from 15.726% to 15.875%. It can be concluded that the electrical performance of cells is enhanced with the application of Ag/glass frits.



Element	Wt%	At%
O	06.76	37.12
Fe	03.03	04.77
Mg	00.07	00.27
Al	02.36	07.69
Si	03.31	10.36
Ag	10.22	08.32
Pb	74.24	31.47

Fig. 4. EDS spectrum of glass frits after electroless plating (Wt%—mass fraction (%); At%—atomic fraction (%)).

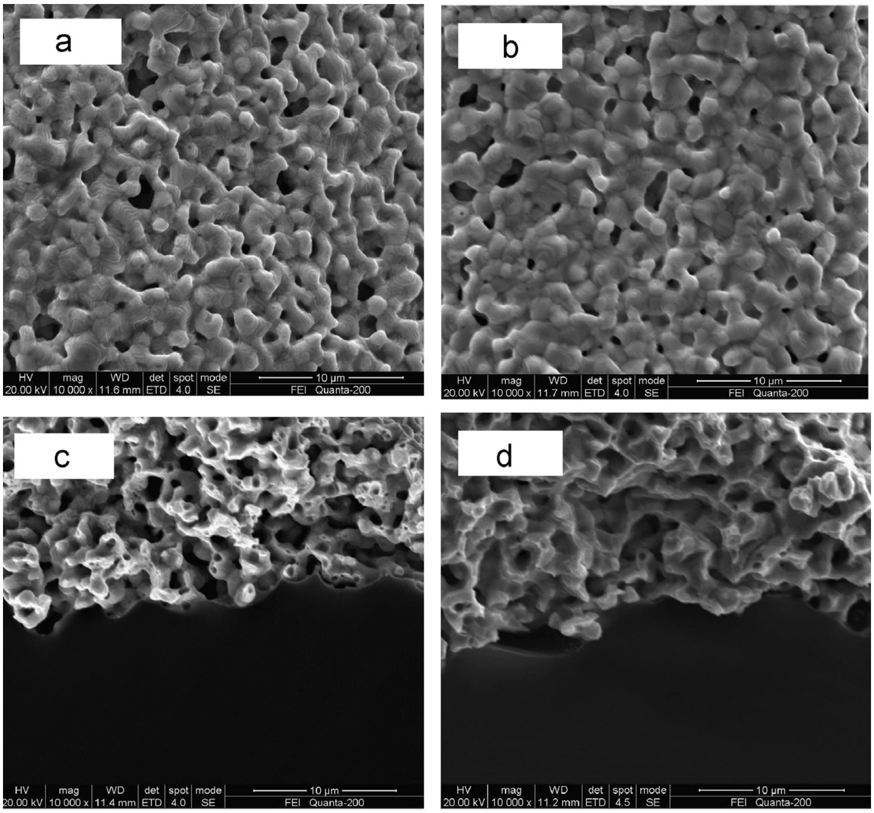


Fig. 5. ESEM images of the surfaces and cross-sections of the silver-conducting films.

Table 1
Electrical performance of the solar cell.

Paste formulation	Open circuit voltage (V_{oc}) (V)	Shot circuit current (I_{sc}) (A)	Maximum output voltage (V_{pm}) (V)	Maximum output current (I_{pm}) (A)	Series resistor (R_s) (Ω)	Photoelectric conversion efficiency (η) (%)
Glass frits	0.618	2.111	0.488	1.962	0.092	15.726
Ag/glass frits	0.619	2.126	0.489	1.976	0.091	15.875

5. The determination of silver content in Ag/glass frits

In the activation process, the mass ratio of glass frits to silver nitrate is about 100–1. The majority of silver ions will be reduced and deposit on glass frits. A small part of reduced silver ions will deposit on the inner surface of the beaker or be separated as free silver particle. As a result, the silver content of nano-Ag@glass frits cannot be measured precisely. Therefore, we ignore the silver content of nano-Ag@glass frits temporarily and treat the weight of nano-Ag@glass frits (M_0) as the weight of glass frits (M_a). And M_0 approximately equals to M_a.

After being coated with the silver particles, Ag/glass frits become heavier and will gradually deposit in a short time. Remove the supernatant after Ag/glass frits completely precipitate to the bottom of the beaker. Wash the product for several times with deionized water and alcohol, and dry it at 60 °C. Then, weigh the Ag/glass frits with the beaker (M_1) and remove the Ag/glass frits and again weigh the beaker (M_2). Therefore, Ag/glass frits' weight (M_b) could be calculated:

$$M_b = M_1 - M_2 \tag{1}$$

where M_b is the weight of Ag/glass frits, M_1 is the weight of the beaker and Ag/glass frits, and M_2 is the weight of the beaker. And the content of silver particles in Ag/glass frits is obtained:

$$M = M_b - M_a \approx M_b - M_0 \tag{2}$$

where M is the content of silver particles in Ag/glass frits, M_a is the weight of glass frits, and M_0 is the weight of nano-Ag@glass frits.

When the pH value of the ammonia–silver solution is 13.4 and the loading capacity in plating is 30 g L^{-1}, the quality ratio of silver particles in Ag/glass frits is calculated by this method. And the weight percentage of silver particles is about 9.02%, which provided a result almost similar to that of the atomic absorption spectrometry (9.13%).

6. Conclusion

In this paper, a novel and facile surface activation for electroless silver plating on glass frits is put forward. This activation process needs no pretreatment and can avoid the interference of chloride ions and tin ions. Moreover, evenly-distributed silver coatings with the particle size around 100 nm can be obtained, and the optimal ratio of Ag/glass frits in the silver paste can also be determined. Consequently, this one-step, low cost, environment-friendly surface activation method has the potential to be applied in large-scale industry production.

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