Preparation of silver-coated glass frit and its application in silicon solar cells

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A simple electroless plating process was employed to prepare silver-coated glass frits for solar cells. The surface of the glass frits was modified with polyvinyl-pyrrolidone (PVP) before the electroless plating process. Infrared (IR) spectroscopy, field emission scanning electron microscopy (FESEM), and x-ray diffraction (XRD) were used to characterize the PVP modified glass frits and investigate the mechanism of the modification process. It was found that the PVP molecules adsorbed on the glass frit surface and reduced the silver ions to the silver nanoparticles. Through epitaxial growth, these nanoparticles were uniformly deposited onto the surface of the glass frit. Silicon solar cells with this novel silver coating exhibited a photoelectric conversion efficiency increase of 0.33%. Compared with the electroless plating processes, this method provides a simple route to prepare silver-coated glass frits without introducing impurity ions.

Keywords: electroless plating, silver nanoparticle, glass frit, solar cell

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1. Introduction

Among the renewable energy technologies, photovoltaics (PV) provide some of the most efficient, lowest cost, safest, and cleanest energy sources. Commercial PV technologies span a wide range, including silicon solar cells, dye-sensitized solar cells, thin film solar cells, and organic solar cells. Among all the commercial PV devices, crystalline silicon solar cells dominate the global PV market, with more than 90% of the market share.[1] Silicon solar cells provide the highest commercial photoelectric conversion efficiency, 15%–18.5%,[2] compared to 12% in the best dye-sensitized solar cells,[3] 12.6% in thin film solar cells,[4] and 8.3% in organic solar cells.[5] However, the progress in crystalline silicon solar cell development has slowed down in recent years, with only a 0.6% relative efficiency improvement each year, presumably due to the limitations of material properties and module technologies. Further improvements in PV module efficiency require novel module technologies. One of the important processing technologies used in silicon solar modules is the fabrication of metal electrodes by sintering a printed layer of silver paste. A typical silver paste consists of three parts: silver powder, glass frit, and organic carrier. Even though the glass frit represents a very small fraction of the total silver paste (1–5 wt.%),[6] it is critical for the formation of effective front contacts, and subsequently the performance of the resulting solar cell. Glass frits serve various functions, including dissolving the metal powder, etching the antireflective coating, and providing adhesion to silicon.[7] They also significantly influence the sintering kinetics of the metal powders. Schubert *et al.*[8] reported that the formation of a silver contact with a glass frit consists of four steps. First, liquid phase PbO is formed when the annealing temperature is increased to the softening point of Pb-based glass frits. The PbO liquid then etches through the SiN_x antireflective coating, enabling contact with the silicon wafer. Meanwhile, the silver powder dissolving in the Pb liquid diffuses towards the silicon wafer. Lastly, during the process of cooling, the silver particles precipitate from the Pb liquid and recrystallize on the surface of the silicon wafer to form inverted pyramidal pits. According to this mechanism, improving the dissolution of Ag in the glass frit can boost the efficiency of the resulting solar cell by forming a better electrical contact between the metal and the silicon wafer. A silver nanoparticle coating on the glass frit can increase the dissolution of Ag in the melt glass frits by increasing the contact area between the glass frit and the Ag powder and shortening the diffusion path of the electrons.[9]

In the recent years, several methods, including sputtering,[10,11] electrochemical deposition,[12,13] electroless plating,[14,15] and chemical vapor deposition,[16,17] have been developed to deposit silver on non-metallic materials. Among them, electroless plating is the most preferred and widely used technique due to its cost-effectiveness and ease. The conventional electroless plating, however, has a few drawbacks. First, it requires pre-treatments such as sensitization and activation, where $SnCl_2$ and $PdCl_2$, both highly toxic, are commonly used as the activators.[18] Second, the Cl^- impurities are hard to completely remove. The Cl residues change the composition of the glass frits and adversely affect the formation of a dense and conductive network.[19] These drawbacks may limit the power conversion efficiency of the silicon solar modules.

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There are several other approaches to activate the substrates for electroless plating. Li *et al.*[20] modified the glass frits by mixing them with a gum Arabic solution and then immersing the modified glass frits in an electroless silver-plating bath to form a layer of silver seed to activate the glass frits. Schaefer *et al.*[21] used a PVP/Ag precursor solution to modify the glass substrate to form a pure Ag nanoparticle seed layer to activate the glass substrate. In this work, we develop a simple, low-cost, single-step activation method to produce uniform silver-coated glass frits at room temperature. Polyvinylpyrrolidone (PVP) is used to modify the glass frits instead of $SnCl_2$ and $PdCl_2$. PVP adsorbed on the glass frit causes the reduction of silver ions to silver nanoparticles, which then serve as seeds to form a silver coating. The silicon solar cells prepared using the silver paste containing PVP-treated glass frits exhibited enhanced PV performance.

2. Experimental details

2.1. Synthesis of silver-coated glass frits

A mixture of 5 g glass frits and 50 mL 0.1 M PVP solution (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was stirred at room temperature for 1 h. To remove the PVP residue, the pretreated glass frits were centrifuged and washed with deionized water. The modified glass frits were added to a silver-plating bath containing 50 mL 0.1 M $[Ag(NH_3)_2]OH$ solution and stirred for 0.5 h. Then, 50 mL 0.1 M ascorbic acid was introduced to the bath solution and agitated at room temperature for 0.5 h. The pH value of the reactant mixture was adjusted to 12 with 0.1 M $NH_3{\cdot}H_2O$ after agitation. Silver-coated glass frits were formed when the reactant mixture turned black. Finally, the frits were washed with deionized water and alcohol and dried in an oven at 60 °C. These specimens were labeled as G1. The control samples of silver-coated glass frits without the PVP treatment were labeled as G2.

2.2. Preparation of silver pastes

Silver-coated glass frits, silver powder, and an organic vehicle (Table 1 shows the composition of the organic vehicle) were mixed at a weight ratio of 4:86:10 and ground 4 times in a three-roll mixer. The as-prepared silver pastes were screen-printed on the front side of polycrystalline silicon wafers containing a silicon nitride antireflective coating and back silver and aluminum contacts. The printed silicon wafers were dried in air at 220–280 °C for 3 min and sintered in a belt line furnace for 1 min at a peak firing temperature of 850 °C. The resulting pastes containing G1, G2, and pure glass frits were labeled as P1, P2, and P, respectively.

Table 1. Composition of the organic vehicle.

Composition	Butyl carbitol acetate ester	Tributyl	Butylcarbi	Ethyl	Terpineol	Castor oil
Weight /%	5	7	70	6	9	3

2.3. Characterization

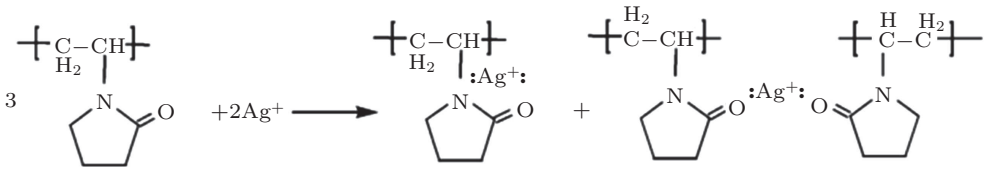
The morphologies of the glass frits and the silver-coated glass frits were characterized with a scanning electron microscope (SEM, MIRA3, TESCAN) equipped with an energy dispersive x-ray analysis detector (EDAX). The Fourier transform infrared (FTIR) spectra of the samples were measured by an FTIR spectrometer (Nicolet 6700). The electrical performance of the solar cells prepared using the silver pastes was tested using a solar simulator and testing system (DLSX-FXJ7, Beijing Delicacy Laser Optoelectronics Co. Ltd).

3. Results and discussion

3.1. Modification mechanism of PVP

PVP acts as both a capping agent and a reducing agent in the synthesis of the silver nanoparticles. When it is mixed with $AgNO_3$, PVP reacts with Ag^+ to form complex compounds of (PVP–Ag^+), which are then reduced to form silver nanoparticles by the –OH groups of PVP.[22] Figure 1 shows the FTIR spectra of PVP, glass frits, and glass frits modified with PVP. The characteristic vibrational peaks of PVP at 1645 cm^{-1}, 1496 cm^{-1}, 1424 cm^{-1}, and 1288 cm^{-1} are observed in the spectrum of the PVP-modified glass frits. The peak at 1645 cm^{-1} is the resonance peak of C=O, the peaks at 1495 cm^{-1} and 1440 cm^{-1} are the resonance peaks of C–H_2, the peak at 1288 cm^{-1} is the resonance peak of C–N, and the peaks at 1440 cm^{-1} and 1288 cm^{-1} are characteristic peaks of PVP. Furthermore, the peak of C=O is shifted from 1655 cm^{-1} to 1645 cm^{-1} when PVP is mixed with the glass frit, indicating that the C=O function groups of PVP are adsorbed on the surfaces of the glass. The oxygen atom of C=O can donate a pair of electrons to the metal oxide surface of the glass frits; the observed shift may therefore result from the chemisorption of C=O to the glass surface.

Figure 2 shows the SEM images of pure and silver-coated glass frits. The pure Pb-based glass frits were prepared with a traditional melting process.[23] The glass frits were ground by ball-milling and the particle size of the frits was about 2 μm (Fig. 2(a)). Figures 2(b) and 2(c) show the morphology of G1. After electroless plating, the silver nanoparticles are well-distributed on the surfaces of the glass frits. The nanoparticles are quasi-spherical in shape and have a mean particle size of 53 nm. In the process of electroless plating, PVP plays a crucial role in the formation of the silver coating. The Ag^+ ions are captured by the PVP molecules adsorbed on the surface of the glass frits through O–Ag and N–Ag bonds, as shown in the following:[24]



These PVP molecules act as heterogeneous nucleation and catalysis centers. Since the ligand of C–N and C=O in PVP contributes more electron density to the s–p orbital of the silver ions than H_2O, the Ag^+–PVP complex compounds are more easily reduced to silver nanoparticles than Ag^+–H_2O in solution.[25] The Ag nanoparticles form the seeds of the silver coating. Figure 2(d) shows the morphology of G2, the control sample without PVP treatment. There are fewer Ag particles on the surface of the glass frits, and the diameter of these particles is about 250 nm, much larger than that in G1. Because the glass frits were not pre-treated with PVP, Ag^+ ions had more difficulty adsorbing to the surface and therefore produced fewer nucleation and catalysis sites.

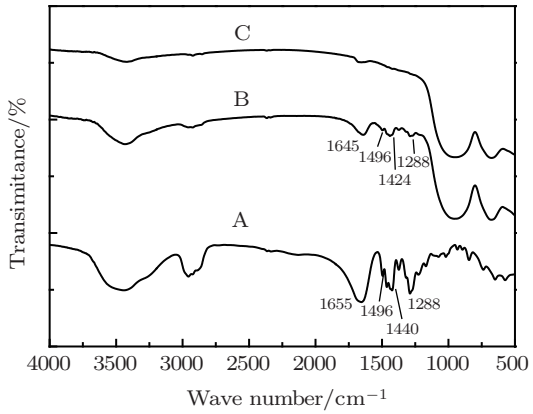


Fig. 1. FTIR spectra of PVP (A), glass frits modified with PVP (B), and glass frits (C).

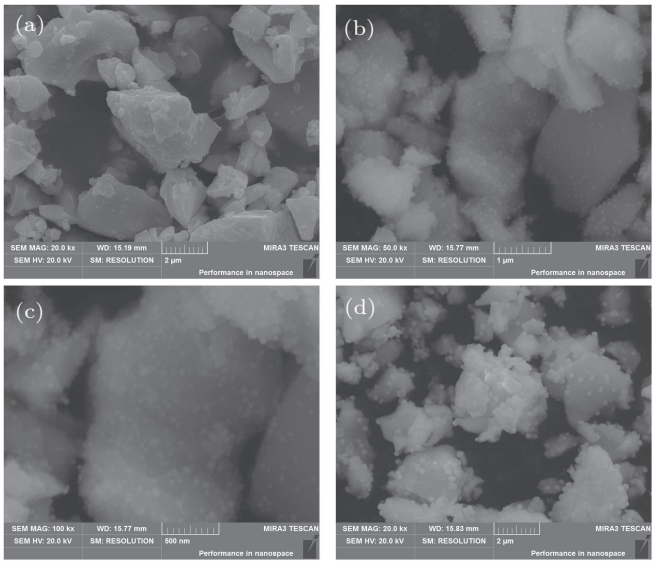


Fig. 2. SEM morphological images of (a) glass frits, (b), (c) PVP treated silver-coated glass frits (G1), and (d) control sample (G2).

3.2. Compositional analysis

The glass frits in the silver paste greatly affect the formation of the front contacts. An appropriate composition is necessary for good contact formation; even small compositional variations can prevent the formation of an Ohmic contact and thus reduce the performance of the solar cell. Figure 3 shows the EDAX spectra of pure glass frits, G1, and G2. The glass frits are mainly composed of SiO_2, TeO_2, PbO, and a small amount of ZnO and MgO. After Ag-coating, the weight percentage of Ag is 17.89 wt.% in G1 and 10.34 wt.% in G2. The weight percentage of Ag in G1 increases by 7.67 wt.% compared with that in the literature.[26]

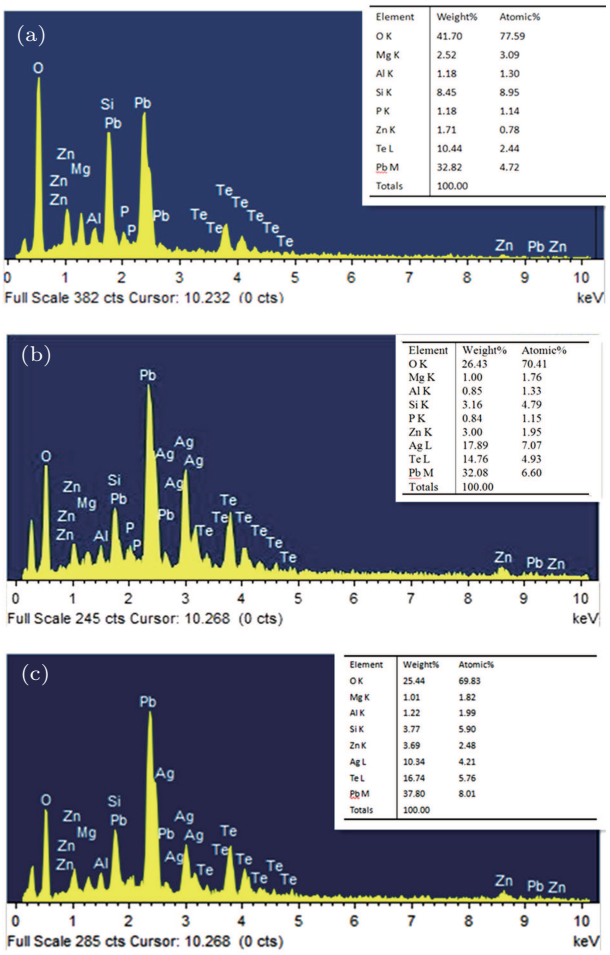


Fig. 3. (color online) EDS analysis of (a) glass frits, (b) PVP treated silver-coated glass frits (G1), and (c) control sample (G2).

3.3. Phase analysis

To obtain the phase properties of the samples, XRD measurement was performed. Figure 4 shows the XRD patterns of the pure and the silver-coated glass frits. The glass frits show

a broad peak at 28° corresponding to amorphous glass. The PVP-modified sample (G1) exhibits the characteristic peaks of crystalline silver (cubic) at $2\theta = 38°$, which agrees with the literature (JCPDS No. 04-0783).[27] The average grain size of the silver nanoparticles, calculated using Scherrer's equation,[28] is 6 nm. The particle size of the silver nanoparticles is larger than the grain size, indicating that the nanoparticles are polycrystalline.

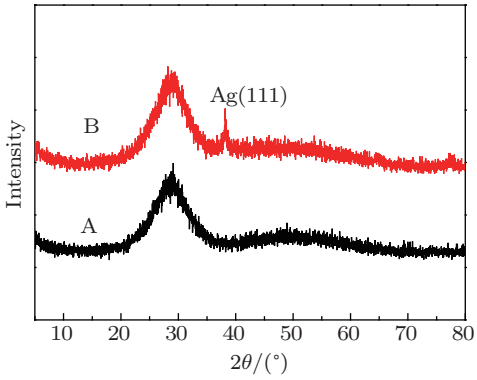


Fig. 4. (color online) XRD patterns of pure glass frits (A) and the PVP-modified silver-coated glass frits (B).

3.4. Performance of solar cells

Table 2 and figure 5 show the performance of the solar cells prepared using P, P1, and P2 silver pastes. Devices using P1 and P2 exhibit higher power conversion efficiencies (η) and fill factors (FF), as well as lower series resistances (R_s) than those using P. Series resistance R_s is one of the most important factors in solar cell power loss. For P, P1, and P2 devices, the series resistances are 0.083 Ω, 0.078 Ω, and 0.080 Ω, respectively, and the efficiencies are 16.820%, 17.150%, and 16.973%. The factors contributing to the series resistance include the substrate resistance, the gate line resistance, the lateral resistance of the silicon, and the contact resistance. Among them, the contact resistance is especially critical.[29] Figures 6(a)–6(c) show the SEM top images of the silver electrodes. All the silver electrodes have a porous structure, but sample P has the largest number of pores while sample P1 has the least. We attribute this phenomenon to an enhanced wettability of Ag on the glass frits, promoting densification of the film, due to the Ag nanoparticle coating.

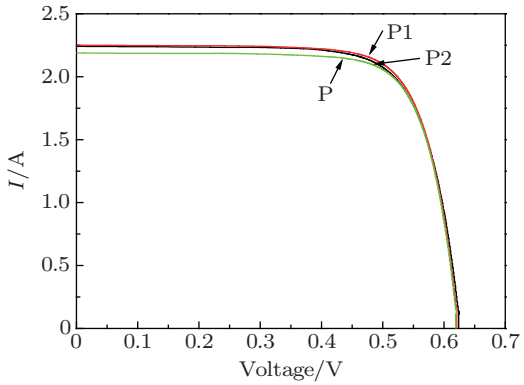


Fig. 5. (color online) Current–voltage (I–V) curves of the fabricated silicon solar cells using pastes P, P1, and P2.

Table 2. Performance of solar cells using pastes P, P1, and P2.

	R_s/Ω	V_{oc}/V	I_{sc}/A	FF	E_{ff} /%
P	0.083	0.621	2.177	0.757	16.820
P1	0.078	0.625	2.201	0.759	17.150
P2	0.080	0.620	2.193	0.760	16.973

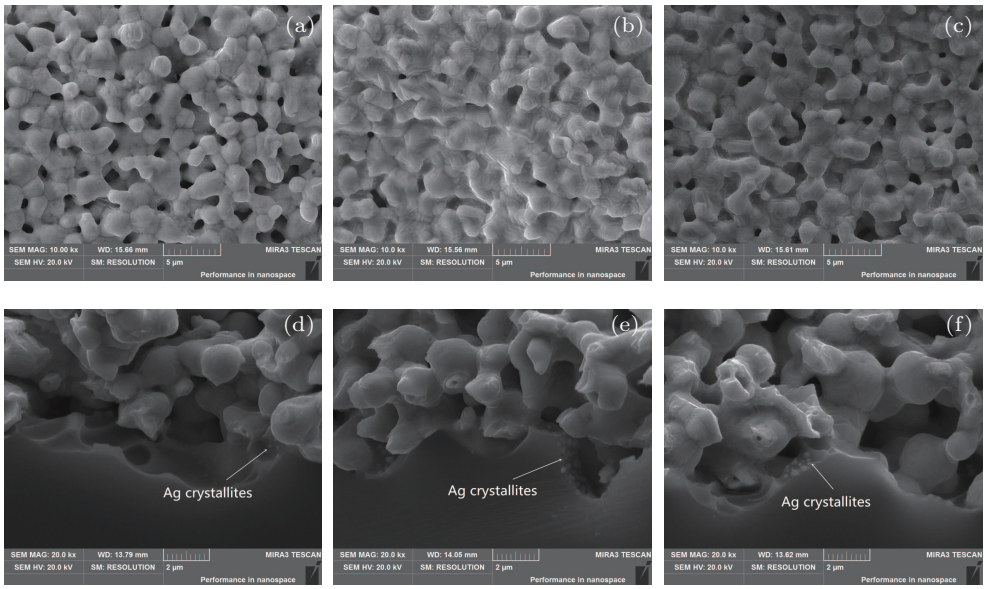


Fig. 6. SEM top images of (a)–(c) the surface and (d)–(f) the cross-section of the silver electrodes based on (a), (d) the glass frit (P), (b), (e) PVP-modified silver-coated glass frits (P1), and (c), (f) controlled silver-coated glass frits (P2).

Figures 6(d)–6(f) show the cross-sectional SEM images of the silver electrodes with Ag crystallites deposited on the Si surface. The P1 and P pastes contain the highest and the lowest numbers of Ag nanoparticles. This may be due to the increase in the contact area and the shortened diffusion distance between the Ag particles and the glass frits after silver plating, Ag can then diffuse into the melt glass frit more easily in the firing process, and more Ag crystallites can deposit on the Si surface in the cooling process. The concentration of Ag in the melt glass frit will affect the size of Ag crystallites growing in epitaxial relation with Si. When the content of Ag in the melt glass frits is too low, Ag crystallites cannot grow on the Si wafer, causing a poor Ohmic contact. Conversely, if the content of Ag in the melt glass frits is too high, Ag crystallite growth will continue for too long and the Ag crystallites will overgrow, causing junction shunting.[30] Table 2 and figure 5 show that the devices using P1 and P2 exhibit lower series resistances than those using P, this is because the Ag crystallites on the Si wafer provide a good Ohmic contact between the silver electrodes and the Si wafer. It indicates that the Ag content of G1 is appropriate for silicon solar cell production.

4. Conclusion

We developed a simple and low-cost method to deposit silver nanoparticle coating on the surface of glass frits for silicon solar cell electrode applications. Compared with the conventional electroless plating, which can introduce impurities and lower the compactness of the conductive network, this method provides a Pb-free activation route to prepare the glass frits. Additionally, PVP can be used as a surface modifier and a dispersant in electroless plating, leading to a uniform silver coating. A dense and conductive network can be formed using the silver-paste-containing silver-coated Pb-glass frits, leading to an improvement in the power conversion efficiency of the resulting silicon solar cells.

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