

Electronic Supporting Information

Novel Ag-doped glass frit for high-efficiency crystalline silicon solar cells

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Experimental Section

Preparation of Ag-doped glass frit

All chemical reagents were of analytic grade and used without further purification. Firstly, 0.16 g/0.32 g/0.48 g/0.64 g/0.80 g AgNO₃ (Aladdin, 99.99%) was dissolved into 10 mL deionized water (Ag wt% =2%, 4%, 6%, 8% and 10%), 2.26 g PbO, 2.54 g TeO₂ and 0.20 g Bi₂O₃ (Aladdin, 99.99%) powders were mixed in an agate mortar and added in AgNO₃ aqueous solution. To mix thoroughly various metal oxides with AgNO₃, the suspension was stirred vigorously for 20 minutes at 70 °C until water was completely dried. Following drying treatment, mixed solid was transferred to alumina crucible and heated in a furnace at 1000 °C for 20 minutes to melt the mixture. In order to form glass frit, melt-mixed blends were water-quenched to room temperature by melt-quenching technology. Then product was collected and ball-milled with a planetary mill for 10 h at 400 rpm to obtain glass frit. Finally glass frit was cleaned using ethanol for 3 times and dried in 60 °C vacuum drying oven.

Preparation of Ag paste

Ag paste was composed of three parts, namely, Ag powder, organic phase and glass frit. Ag powder (Kajet, Shanghai, 99.9%) were used as conducting phase. The average particle size of the spherical silver powder was 1-2 μm (Figure S7). The organic phase was a mixed solution prepared by dissolving 8 wt% ethyl cellulose (Aladdin, 99.8%), 4.5 wt% polyamide wax and some additives in the 85 wt% terpineol (Alfa Aesar, 98%). At first, Ag powder and as-prepared glass frit were mixed with the ratio of 97:3 wt%. Then, organic phase was added in the above mixture to further mix for 20 min by a planetary mixer. The ratio of the mixture and organic vehicle was 86:14 wt%. Finally, Ag paste was completed by further mixing and grinding with a three-roll grinder.

Fabrication of c-Si solar cells

In order to make the consistency of experiments, we chose the commercial semi-finished c-Si solar cells with SiN_x layer and PN junction. During fabrication of front contact electrode, to strictly control parameters of silver grid lines such as line width (LW), line height (LH), aspect ratio (LH/LW) and line spacing (LS), we adopted 3D printing technology. A self-designed 3D printing equipment was used to complete printing of front contact electrode. In this work, grid lines of all c-Si solar cells were designed and printed according to parameters in parenthesis (LW is 90 μm, LH is 80 μm and LS is 1.6 mm). Then the c-Si solar cells with printed silver grids were dried at 180 °C for 20 min

to evaporate organic phase. Finally they were put in a seven-stage furnace to sinter. Seven peak temperatures of seven stages furnace was 960, 860, 760, 660, 560, 450 and 300 °C respectively. Detail sintering curve was shown in Figure S8.

Characterizations

The X-ray diffraction (XRD) patterns of glass frits were measured by a Bruker D8 Advance diffractometer using Cu-K α radiation at room temperature, from 10° to 90° (The scan speed is 1° min⁻¹). XPS measurements were carried out in a Thermo Scientific K-Alpha system, equipped with an Al X-ray source (K α , 1486.6 eV). Glass transition temperature (T_g) and liquefaction temperature ($T_{l,peak}$) of glass frit were studied by TGA/DSC 3+ - Thermogravimetric Analyzer (Heating rate is 10K/min). The surface and cross-sectional views of c-Si solar cells and SEM images of glass frit were characterized by Zeiss SUPRA-55 scanning electron microscope (SEM). While the composition and distribution of chemical elements were observed by energy X-ray spectroscopy (EDX, Oxford X-Max 20, 20 kV). Photocurrent density–voltage characteristics of solar cells were measured under AM 1.5 illumination by ABET sun 3000 solar simulator. And the light power of simulator was calibrated to one sun light intensity by using a NREL-calibrated Si cell (Oriell 91150).

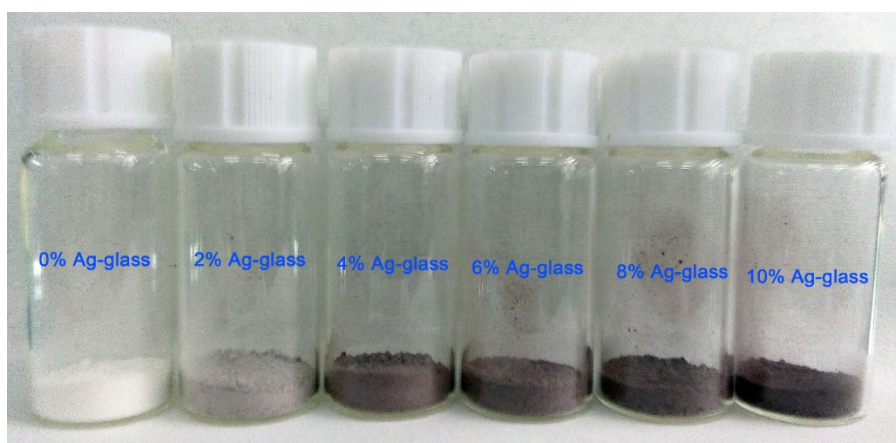


Figure S1 Six kinds of glass frits with different Ag doping contents (0 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt% and 10 wt%).

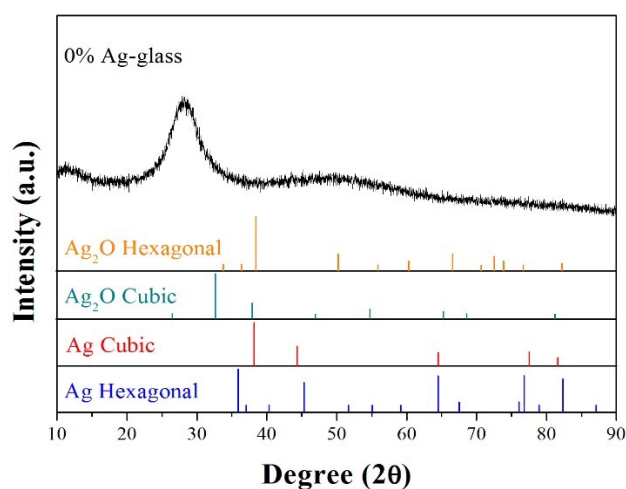


Figure S2 The XRD patterns of undoped glass frit (0 wt% Ag), cubic Ag (PDF#04-0783), hexagonal

Ag (PDF#41-1402), cubic Ag_2O (PDF#41-1104) and hexagonal Ag_2O (PDF#19-1155).

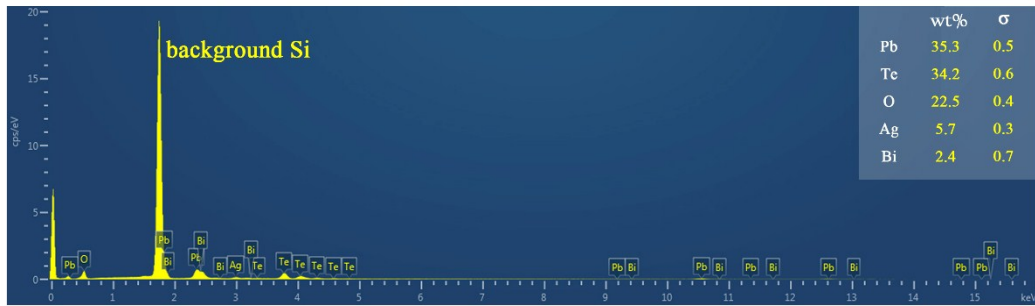


Figure S3 EDX spectra and analysis of element content of Ag (6 wt%) doped glass frit.

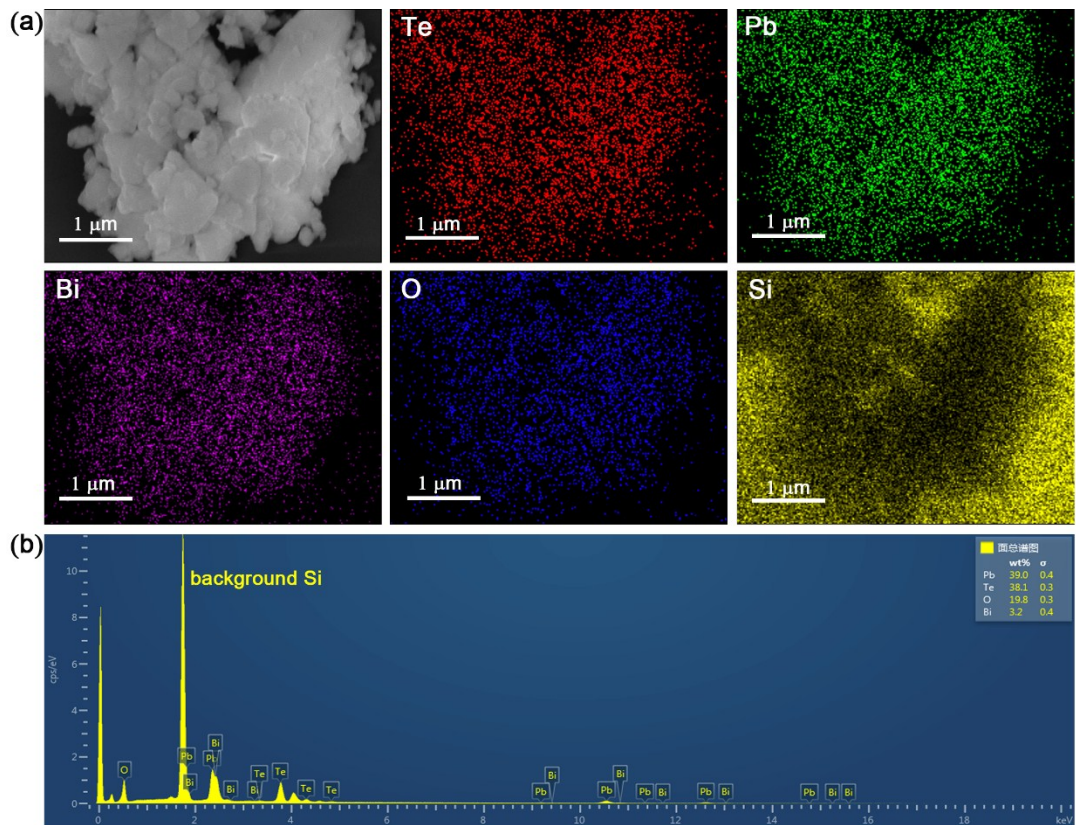


Figure S4 (a) SEM image of undoped glass frit (0 wt% Ag) and corresponding elementary mapping of Pb, Te, Bi, O and Si. (b) EDX spectra and analysis of element content of undoped glass frit (0 wt% Ag).

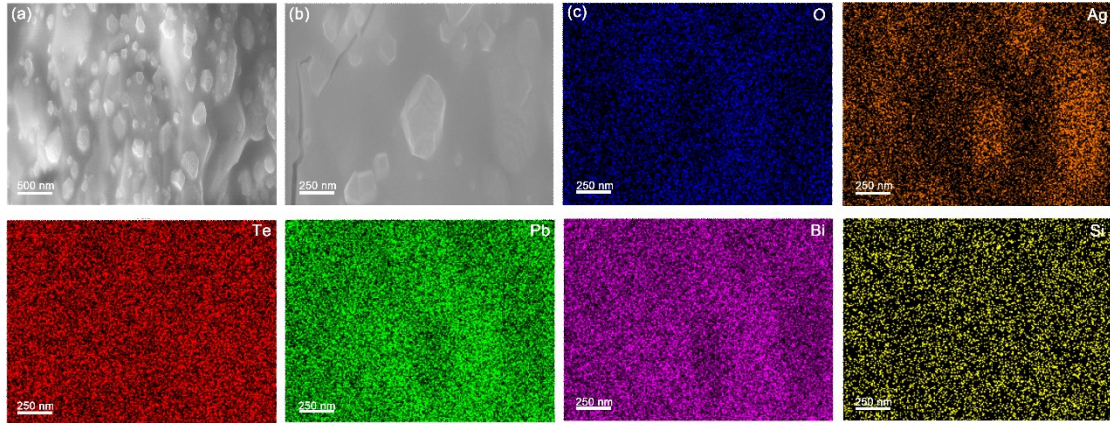


Figure S5 (a) Low magnification SEM image of c-Si wafers with SiN_x layer coated with a thin 6% Ag-glass layer after annealing at 400 °C for 100 s, (b) High magnification SEM image and (c) corresponding elementary mapping of O, Ag, Te, Pb, Bi and Si.

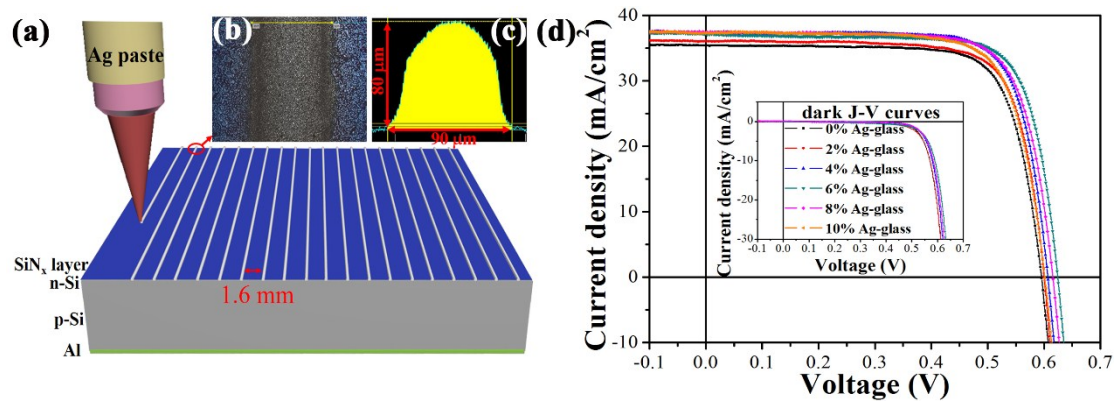


Figure S6 (a) The 3D model that Ag gridlines were printed by a 3D printing machine, (b) laser confocal scanning microscopic image of Ag gridlines, (c) cross section view and parameters of gridlines. (d) current density-voltage (J-V) curves of solar cells with six kinds of glass frits under AM 1.5 illumination, the inset shows corresponding dark density-voltage (J-V) curves.

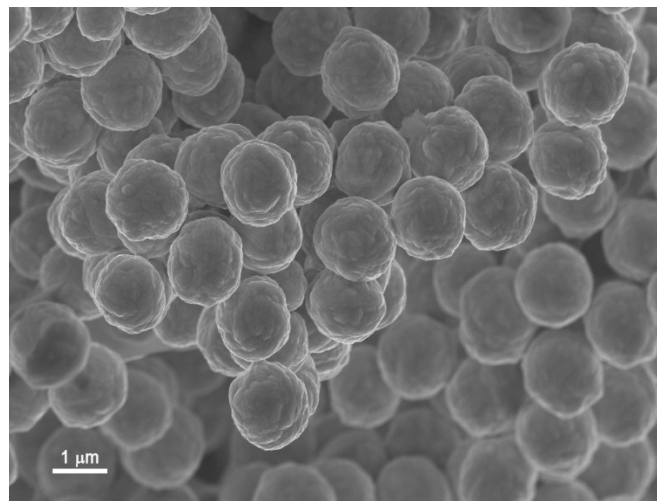


Figure S7 SEM image of silver particles used in Ag paste.

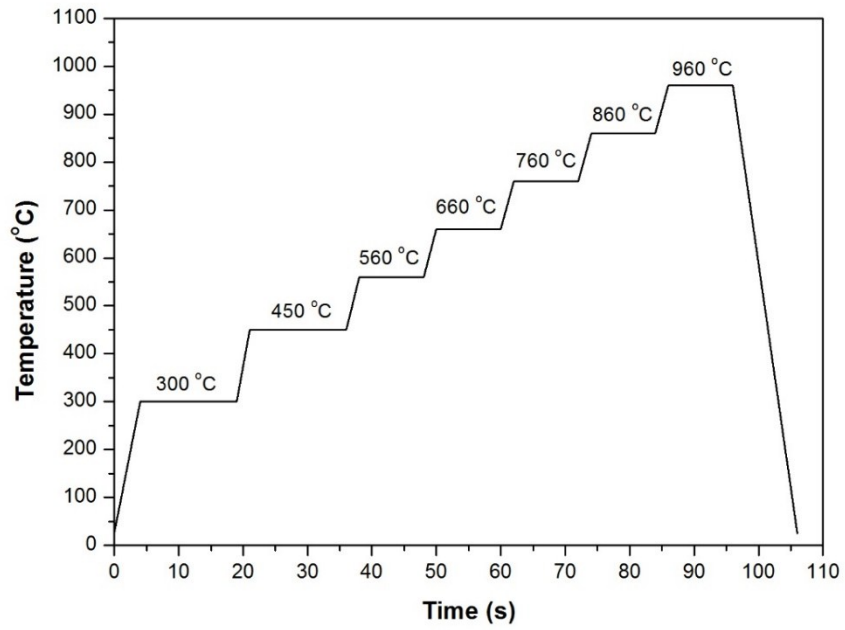


Figure S8 The sintering curve of c-Si solar cells.

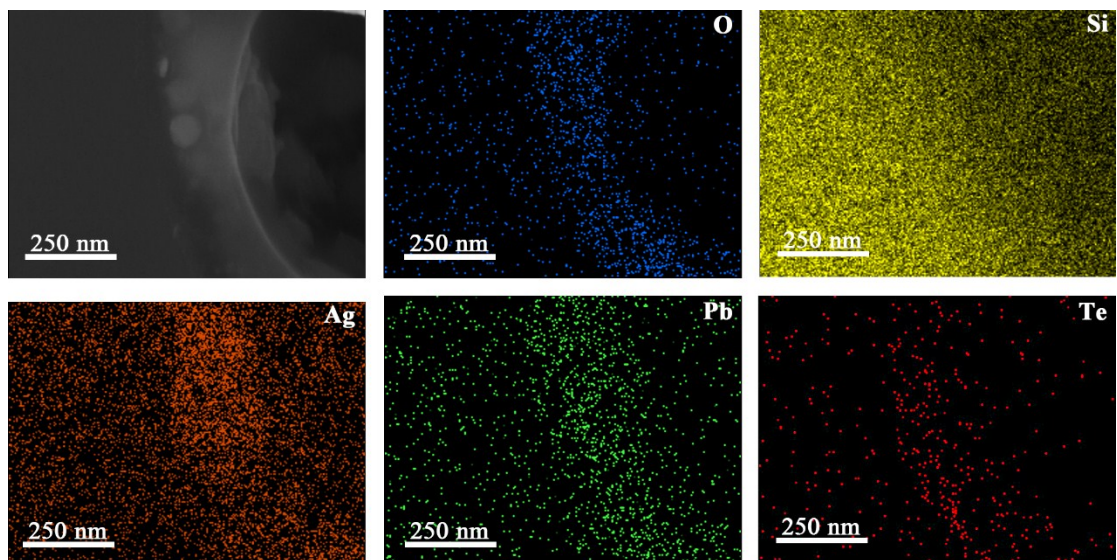


Figure S9 The cross section view SEM micrograph of solar cell with 4% Ag-glass frits and corresponding EDX images.