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Glass frit effect on solar cells performance

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***Abstract*— The aim of this study is to prepare glass frits with different compositions used in conductive pastes for solar cells metallization. The relationship between the metallic contacts they generated was investigated. The screen printed silver (Ag) thick film contacts are widely used for the front side metallization of crystalline silicon (Si) solar cells. The Ag thick film pastes primarily consist of three constituents, active metal powders (Ag), glass frit and organic vehicle. The particular attention is given to the glass frit which is a mixture of metal oxides guarantying the formation Ag/Si contacts.**

Four lead-boron-silicate glass frits with different percentages of PbO and B_2O_3, termed as F1, F2, F2, and F4, were prepared through traditional melt-quenching method and characterized with the help of several experimental techniques.

The phase structure of the prepared glass frits was characterized using X-ray Diffraction (XRD). The morphological characteristics were investigated by Scanning Electron Microscopy (SEM). The particles size was determined using a laser-diffraction granulometer. Powders XRD analysis indicated that the glass frits are amorphous in nature. The SEM study showed unshaped particles with partial agglomeration. The results of laser granulometry characterization of the synthesized frits with different compositions have an average value around of 1.4 µm.

It was confirmed that the glass frits play a critical role on performance of prepared solar cells as demonstrated by efficiencies (Eff) of 6.5, 6, 5.3 and 5.2% corresponding to F1, F2, F3 and F4, respectively.

***Keywords*— Glass frit, Synthesis, characterization, conductive paste, solar cell.**

I. INTRODUCTION

Crystalline silicon solar cells have attracted significant attention in the past decades as a promising renewable energy source due to their high photoelectric conversion efficiency and reliable mass production [1-4]. However, it is necessary to reduce the fabrication cost for its large scale application in the world. The most effective way of reducing the cost is to increase the photoelectric conversion efficiency of solar cells.

The optimization of the front metallization contact of crystalline silicon solar cells is a hot research topic due to its potential to improve overall performance of silicon solar cells. Currently, silver conductive thick films are applied widely used as front side metallization of crystalline or polycrystalline silicon solar cells [5].

The Ag thick film pastes primarily consist of three constituents: (1) active metal powder with appropriate particles size and shape (Ag powders), as a conductive phase for its superior conductivity, higher chemical stability and lower price among the noble metals; (2) glass frit (usually lead–boron–silicate glass), as a binder phase to enable binding of the metal film to the Si substrate and promote sintering of metal powders during firing; and (3) organic phase (usually ethylcellulose-terpiniol), as a disperser to impart the desired rheological properties to the pastes [6, 7].

The glass frit in conductive pastes plays a critical role in the screen-printed metallization process for industrial silicon solar cells [8]. For screen-printed contact formation, the glass frit is obviously a crucial factor for good-quality Ag-Si ohmic contacts as it is necessary to punch through the antireflection coating (ARC) and because it plays a very important role in the contact formation mechanism [9].

As the binder phase, the glass frit not only sticks to the substrate during high-temperature firing but also dissolves the metal powders, and even affects the metal powder sintering kinetics. Therefore, the glass frit in Ag thick-film pastes is the main factor that determines the Si surface etching, contact resistance, and ultimately the overall Ag grid surface performances.

II. EXPERIMENTAL

The glass frit powders were obtained by traditional melting method. Reagent grade chemicals PbO, B_2O_3, SiO_2 and Al_2O_3 were used as starting materials. The weight percentage of SiO_2 and Al_2O_3 were fixed at 3.5% and 1.5% respectively, while remaining was adjusted by mixture of PbO and B_2O_3. The compositions of glass frits are presented in table I. The mixture of the oxides was heated at 1100°C for 30 min in an

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aluminum crucible after milling them in an agate mortar for 40 min. For each composition, we quickly pour the content of the crucible in deionized water at room temperature. After granulation, we proceed to the grinding of the glass frit using a semiautomatic grinder. Finally, we washed, sieved and then dried the glass frit powder at 70°C overnight.

Four different pastes were formulated. All the pastes contained the same Ag powder, and the same organic vehicle, but with the different prepared glass frits. For each paste, the ratio of Ag powder particles/glass frit/organic vehicle was fixed at 76/4/20 wt%; and the mixing of the three parts was carefully homogenized in a home-made three roll mill.

Pastes were screen-printed on to single-crystalline Silicon wafer. The printed Si-wafer was dried at 200°C for 5 min and fired at temperature of 700°C for 3 min.

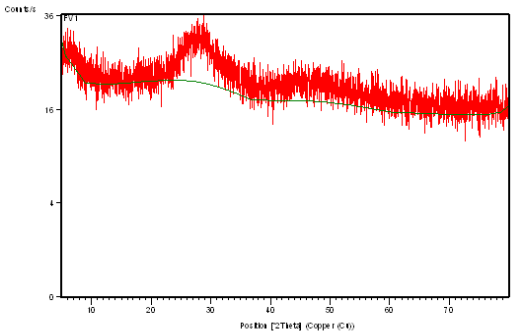
The crystal structures of the prepared glass frits were investigated by X-Ray Diffraction (XRD), their morphological characteristics were determined by scanning electron microscopy (SEM), the average diameter of particles were determined by Laser Granulometer. Finished cells were characterized by I(V) analysis at standard operating condition of AM 1.5 (1000Wm^{-2}) irradiance, open circuit voltage (Voc), fill factor (FF) and efficiency (Eff) were determined by this test.

TABLE I
COMPOSITION OF GLASS FRITS

Reference	PbO (%)	B_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)	PbO / B_2O_3 ratio
F1	75	20	3.5	1.5	3.75
F2	70	25	3.5	1.5	2.8
F3	65	30	3.5	1.5	2.16
F4	60	35	3.5	1.5	1.71

III. Results and Discussion

Powder X-ray diffraction pattern (Fig.1) shows that the glass frits exhibit no line characteristic of a crystalline phase; this confirms the presence of a single amorphous phase.



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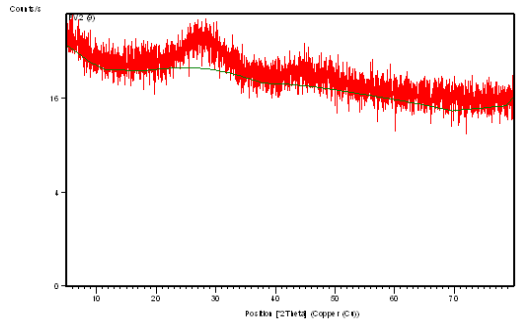

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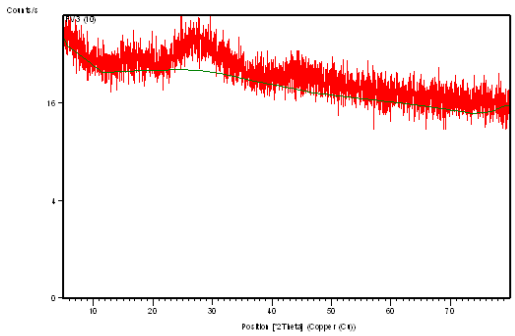

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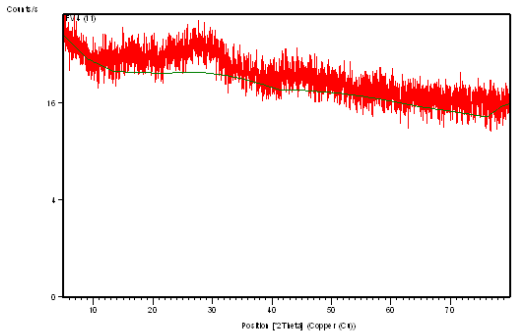

(d)

Fig. 1 XRD patterns of glass frits powders: (a) F1, (b) F2, (c) F3, (d) F4

The morphologies of glass frits prepared are shown in Fig 2. The photos show grain more or less rounded and an abundance of fine particles.

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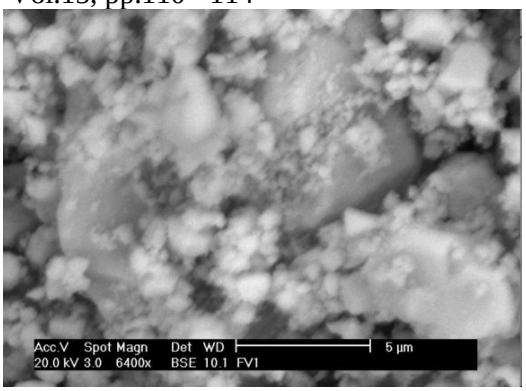

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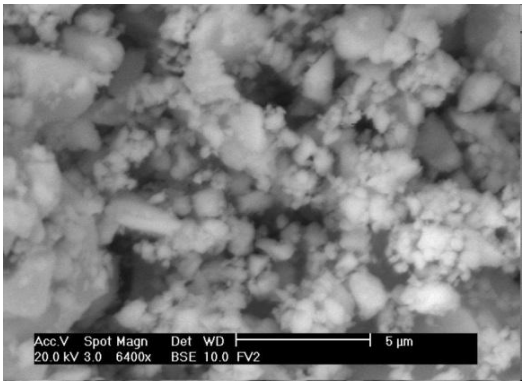

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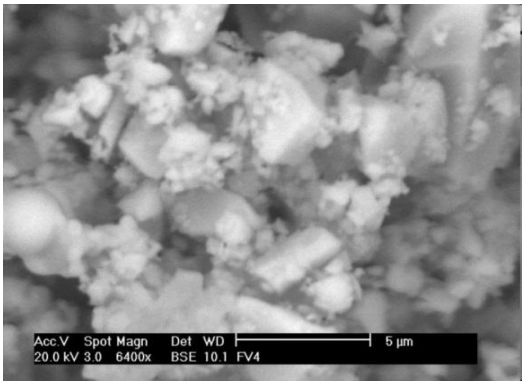

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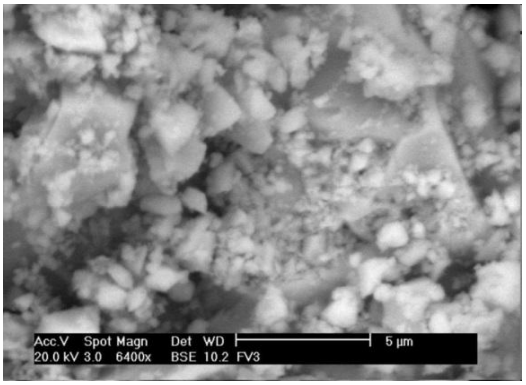

(d)

Fig. 2 SEM images of (a) F1, (b) F2, (c) F3, (d) F4

The values of the average particle diameters of glass frit are grouped in table II.

TABLE II

AVERAGE PARTICLE DIAMETER OF GLASS FRITS

GLASS FRIT	F1	F2	F3	F4
DIAMETER [µM]	1.3	1.4	1.3	1.3

The results obtained show that the diameters of the glass frit grains are similar, which confirm that the particle size distribution of the glass frit powder is not influenced by their composition.

The fill factor (FF), open voltage (V_{oc}), and efficiency (Eff) of cells as a function of type of glass frit as shown in table III. It is seen from figure 3 that cells using F1 with the higher PbO/B_2O_3 ratio possesses the highest FF, V_{oc}, and Eff. Therefore, glass with the proper PbO/B_2O_3 ratio is the key factor for optimizing performances of cells.

As showed by our results, glass frit plays the most important role during Ag/Si metal/semiconductor contact formation. During sintering, the glass frits wet and etch the SiNx coating into silicon. As a result, metallic liquid lead is produced due to a redox reaction between lead oxide and silicon. The liquid lead in turn comes into contacting with silver to form a liquid silver-lead eutectic which is prone to dissolve Si at temperature around 700°C. On cooling down, Ag tends to separate from Pb according to the phase diagram, thus re-crystallizes on the Si emitter surface [10-13]. Therefore, the complete corrosion of SiNx coating is necessary to form perfect Ag/Si ohmic contact.

TABLE III

PERFORMANCE OF SOLAR CELLS

Reference	**V_{oc} (mv)**	**FF (%)**	**Eff (%)**
F1	578	52.0	6.5
F2	578	47.2	6.0
F3	576	43.0	5.3
F4	576	44.0	5.2

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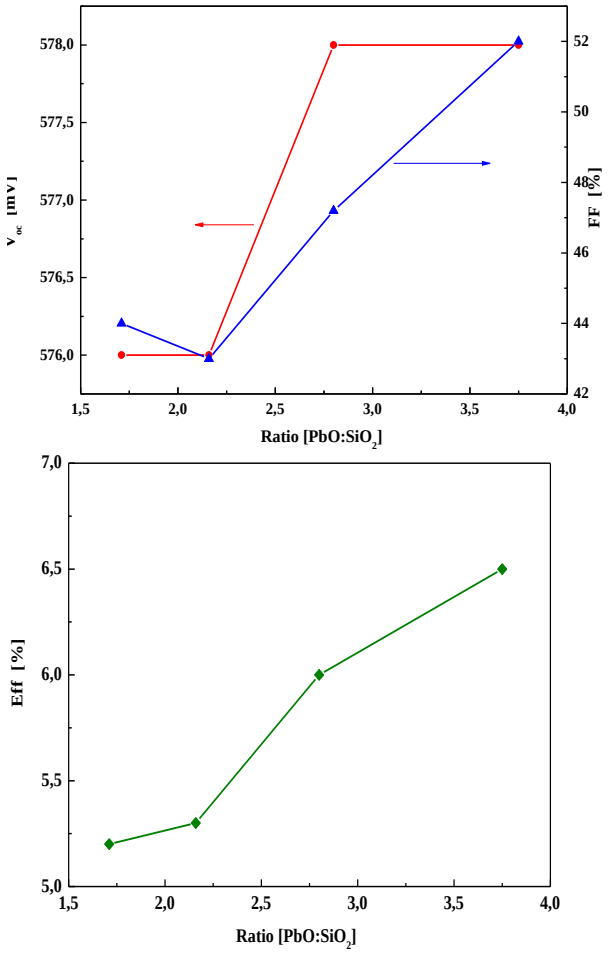

Fig 3. Effect of glass frits on Voc, FF and Eff.

IV. Conclusion

In this study, four glass frits were prepared by mixture of oxides: PbO, B_2O_3, Si_2O_3 and Al_2O_3 with different PbO/B_2O_3 ratios. These glass frits are used in the preparation of silver pastes used in the screen printed front contact metallization in crystalline silicon solar cells. Their characteristics were investigated. The fabricated solar cells containing the as-prepared glass frits were characterized by I(V). It was found that the solar cell, metallized with the conductive paste which was prepared with the glass frit containing higher PbO/B_2O_3 ratio, gave higher FF and Eff than the others.

ACKNOWLEDGMENTS

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