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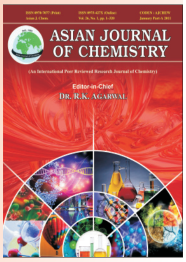

Electrical Contact Mechanism of Front Electrode Using Bi-Based Glass Frit in Si-Solar Cell†

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The front electrode of a solar cell must form an ohmic contact through the etching of the antireflection coating layer of a Si-wafer and glass frit helps the formation of an ohmic contact in the materials of the front electrode of a solar cell. Some studies have reported on the sintering mechanism of glass frit at the front electrode of a solar cell, but this has not been clearly investigated through experiment. Therefore, this study investigated the sintering mechanism of glass frit by the fabrication of Ag pastes to be applied to the front electrode of a solar cell by using glass frit commercially available in the electronic material field as well as by seeking glass frit conditions that allow efficient etching of the antireflection coating. The study found that Bi-based glass frit cause significant changes in contact resistance with variation of the etching degree of the SiN_x layer in relation to the composition and amounts added. When the B composition's added amount was 2.5 vol % among the Bi-based glass frit, it allowed sufficient etching of the SiN_x layer. On the contrary, when the added amount was over or below, surface resistance increased.

Keywords: Front electrode, Ag paste, Si-wafer, Sintering.

INTRODUCTION

Among new and renewable energy sources, photovoltaic power generation, which uses sunlight as its energy source, is known to be sustainable with zero carbon emission. Solar cells, using solar energy, are based mainly on silicon and have the greatest commercial availability today[1].

A solar cell is a semiconductor device that converts solar energy into electric energy directly and it has the same basic structure as a diode. The silver paste is often used for the front electrode. Silver metal contained in the Ag paste comes in an ohmic contact with the emitter, or the *n*-type semiconductor, through the antireflection coating during the heat treatment process to form an electrode[2]. The Ag paste used in the front electrode of a solar cell is composed mainly of Ag powders, glass frit, an organic vehicle and additives. Among these, the Ag paste melts during the heat treatment process and helps form the ohmic contact by etching the antireflection coating of the Si-wafer and enabling contact between the Ag paste and the *n*-type semiconductor[3].

Already, several reports on the mechanism to form a front electrode of a Si-solar cell have been published.

Cheek *et al.*[4] reported that the contact mechanism is caused by electric conduction due to direct contact among Ag grains separated from Ag crystals and from the front electrode, whereas Ballif *et al.*[5] claimed that conduction occurs between electrodes and semiconductors due to a tunneling phenomenon resulting from passage through a thin glass layer. Moreover, Nakajima *et al.*[6] argued for electric conduction by a tunneling phenomenon through discontinuous metal granules at the glass layer. Meanwhile, Hilali *et al.*[7,8] suggested that a tunneling phenomenon occurs at the glass layer by Ag crystals as glass frit with low T_g and T_s melts during heat treatment with widespread etching over the antireflection coating layer and then Ag penetrates underneath the glass layer and is crystallized during the cooling process. However, among these claims, no clear mechanism which can provide a full explanation has been identified.

Therefore in this study, various Ag pastes were created by changing the composition and amounts of glass frit added, whose properties are similar to those of glass frit used in electronic materials and samples were made to evaluate the resistance between an Ag electrode and a semiconductor using the Ag pastes. Moreover, based on observation of the interface

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between the Si-wafer antireflection coating and the front electrode, the study aimed to propose a sintering mechanism for the front electrode of a solar cell.

EXPERIMENTAL

Among commercially available glass frit in the electronic material field, five kinds of glass frit, whose low T_g and T_s were suitable for front electrode pastes of a solar cell, were selected and made into Ag pastes. The properties and composition of the five kinds of glass frit are presented in Table-1.

To make the Ag pastes, α-terpineol (99.5 %, Daejung chemical and metals Co. Ltd., Korea) and diethylene glycol monobutyl ether acetate (98.0 %, Junsei chemical Co. Ltd., Japan) at 20 vol % as solvents, BYK-111 (BYK-chemie, Germany) at 2 vo l% as a dispersing agent and ethyl cellulose (Acros Organics, USA) at 24 vol % as a binder were weighed and then dissolved in an oven at 100 ºC. To 30 g of Ag powder (Heesung Metal Ltd., Korea) mixed, each glass frit was added and the amount was varied from 0.5 to 25 vol %. Preliminary mixing was carried out using a conditioning vacuum mixer (ARV-200, THINKY, Japan) and a 3-roll mill.

The resulting Ag pastes were used for screen printing shown in Fig. 1. Each of the Ag pastes made with various vol % of added glass frit was used for printing, which resulted in samples of various compositions and kinds. Heat treatment was carried out 760-800 ºC to be maintained for 0.5 h and then cooled down in the furnace.

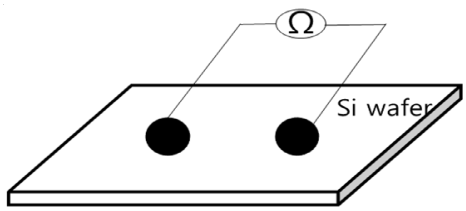

Fig. 1. Schematic diagram of sample to measure resistance between front electrode and SiN_x-coated Si-solar cell

The resistance between the two Ag electrodes on the heat-treated silicon wafer was measured by using a digital multimeter (Asahi, Japan). The interface between the Ag paste and the silicon wafer was cut off by using a focused ion beam (HELIOS600, FIB Korea, Korea) and the cross section was examined by using scanning electron microscopy (HELIOS600, FIB Korea, Korea), while its property distribution was analyzed by EDAX (EDAX Inc., Corp., Korea) line scanning.

RESULTS AND DISCUSSION

Fig. 2 shows changes in resistance in relation to the amounts of glass frits A and B. Glass frits A and B are both Bi-based and A has lower T_g than B, while their density is similar, as are their glass properties. Fig. 2 (a) had high resistance below 5 vol % and its lowest resistance was measured at 5 vol %. Fig. 2(b) shows changes in the resistance of glass frit B. It displayed the lowest resistance value at 2.5 vol %. However, an increase of as much as 10^3 in resistance could be found when the amount added was less than 2.5 vol %. Overall, the result of differences in composition rather than of T_g of the glass frit.

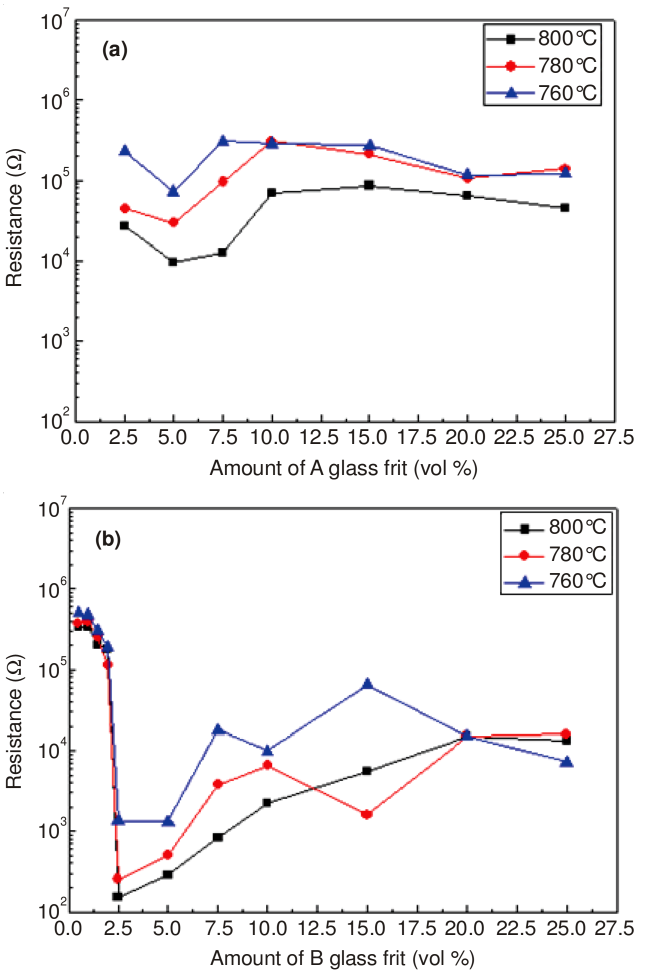

Fig. 2. Resistance of front electrode paste with the amounts of glass frit; (a) glass frit A and (b) glass frit B

TABLE-1
PROPERTIES AND COMPOSITION OF COMMERCIAL GLASS FRIT

		A glass	B glass	C glass	D glass	E glass
Manufacturer		Particlogy Co., Ltd. (Korea)	SSC Co., Ltd. (Korea)	SSC Co. Ltd. (Korea)	NEG Co. Ltd. (Japan)	Particlogy Co. Ltd. (Korea)
Product name		PSC1002	EG	EY	GA-1	PSC1001
Properties	T_g (ºC)	388	454	458	453	417
	CTE (10^{-7}/ºC)	103	77	–	61.9	97
	T_s (ºC)	441	510	461	588	542
	Density (g/cm^3)	5.52	5.9	5.7	4.03	6.69
Composition (wt %)	Main	Bi_2O_3, ZnO, B_2O_3, SiO_2	Bi_2O_3, ZnO, B_2O_3, SiO_2	Bi_2O_3, ZnO, SiO_2	B_2O_3, SiO_2	PbO_2, SiO_2
	Additive	Na_2O, PbO_2, CaO,Al_2O_3	–	B_2O_3, Al_2O_3	–	Al_2O_3, P_2O_5, ZrO_2

Fig. 3(a-b) show several large pores and no glass properties but only Si were detected from the contact interface with the Si-wafer. This is because the SiN_x layer etched and then move toward the Ag electrode. Meanwhile, the Ag crystals and the *n*-type semiconductor layer were put into contact with each other. Fig. 3(c) and (d) show few pores and no glass layer can be confirmed.

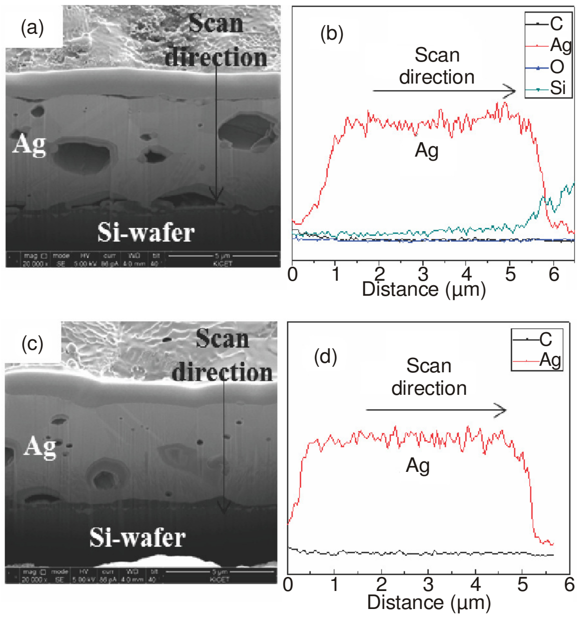

Fig. 3. Cross section images and the composition profile of contact interface between front electrode and the SiN_x-coated Si-wafer with the amounts and kinds of glass frit; (a) and (b) B glass 2.5 vol % and (c) and (d) B glass 2.0 vol %

Based on these results, Fig. 4 presents schematic diagrams of the reaction process when the glass frit-added Ag pastes and the Si-wafer are sintered. Fig. 4 (a) indicates that among glass frit reacting with the SiN_x layer or the glass composition, the glass properties that are not involved in the etching of the SiN_x layer are thinly distributed underneath the Ag electrode, thereby raising the resistance. Fig. 4(b) shows how the SiN_x layer is etched, how the Si ions are diffused within the Ag electrode either on the SiN_x layer or on the Si layer and how the Ag metal fills in the place where the SiN_x layer used to be to form an ideal ohmic contact with the *n*-type semiconductor layer. Meanwhile, Fig. 4(c) shows a case where reaction was not sufficiently induced because an insufficient amount of glass frit was added, which led to incomplete etching of the SiN_x layer.

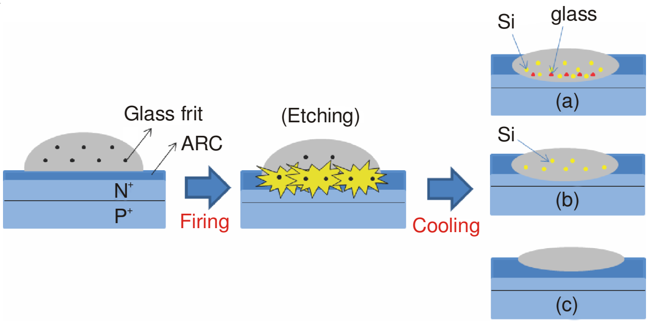

Fig. 4. Schematic diagram of contact mechanism between front electrode and the SiNx-coated Si-wafer with the amounts and kinds of glass frit; (a) A glass 2.5 vol %, (b) B glass 2.5 vol % and (c) B glass 2.0 vol %

Conclusion

When the Bi-based B glass frit was used, the SiN_x layer was properly etched during low temperature heat treatment below 800 ºC when the amount added was 2.5 vol %. When the amount added was less than this, the antireflection coating was not sufficiently etched, leading to a sharp increase in resistance. On the contrary, if an excessive amount of glass frit was added, the SiN_x layer was etched, but an excessive amount of glass remained between the solar cell front electrode and the Si-wafer, thereby increasing the interfacial resistance. The study suggests a contact mechanism between the front electrode of the solar cell and the *n*-type semiconductor layer.

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