

THE SILVER AND METAL OXIDE COMPOSITE FOR HIGH PERFORMANCE OF FRONT SILVER ELECTRODE WHICH APPLIED BULK SILICON SOLAR CELL

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Keywords: *Silver-metal oxide composite, silver paste, High Emitter*

1 Introduction

Solar energy is one of the good solutions for energy and environmental problems because fossil fuel and nuclear power generation cause serious environmental pollution. Photovoltaic (PV) technology and converting efficiency is remarkably progress. Various types of solar cells with high efficiency and low fabrication cost have been developed such as CdTe, Amorphous Si, and CIGS solar cell etc. Although, bulk Silicon based solar cell is still having best converting efficiency [1]. Front Ag paste is the most important materials for High efficiency of the solar cell because front Ag determine omic contact with emitter layer and collect electrons. Recent technology trend of the solar cell is decreasing the emitter doping concentration because lightly doped emitter can lead to lower emitter saturation current density (J_{oc}) and higher blue response with good surface passivation. However, lightly doped emitter has shallow emitter thickness and narrow thermal budget to preventing junction leakage because silver has fast diffusivity even at lower temperature. Regularly, depth of heavy doped emitter which is $45\Omega/\text{sq}$ emitter resistance has junction depth of $0.495\ \mu\text{m}$. In case of $100\ \Omega/\text{sq}$ emitter, Junction depth is shallower than $45\ \Omega/\text{sq}$ emitter which is $277\ \mu\text{m}$. Junction leakage reduces the open-circuit voltage (V_{oc}) and fill factor (FF) of the solar cell [2]. To solve this problem, high emitter resistance cells usually manufactured by selective emitter Process. It has selectively deep emitter thickness beneath silver electrode. A lot of selective emitter techniques have been established such as two step diffusion with oxide layer, doping

(phosphorous) paste and laser scribing [3][4]. However, these methods need additional process and chemical wastes. In this study, focus on another approach about high emitter without additional process. We synthesized core-shell type of silver and metal composite with spray pyrolysis using thermal atomizer. Generally, diffusivity of metal oxide is lower than metal. Therefore metal oxide shell prohibits excessive diffusion or migration of Ag to prevent junction leakage.

2 Experimental Method

2.1 Synthesize Ag and metal oxide composite.

400 ppm of AlNO_3 was mixed into the aqueous solution of AgNO_3 and well dispersing. Spray pyrolysis process using thermal atomizer at $920\ ^\circ\text{C}$ in air condition and rapid cooling. This composite material manufactured using thermal spray pyrolysis atomizing furnace at Kornatech Co. Ltd.

2.2 Manufacturing front silver paste

Silver paste is composed of four different materials such as silver powder, glass frit, organic vehicle and inorganic additives. The Ag- Al_2O_3 composite was 84 wt%. The contents of glass frit (SJ22, LG Innotek. Co. Ltd) was 3.5 wt%. Organic vehicle was ethyl cellulose polymer solution and include tiny amount of dispersing agent. The total organic was 12.5 wt%. Silver paste manufactured following general paste process such as weighing, planetary mixing, 3-roll-milling with four pass, and filtering with 325 meshes.

2.3 Fabrication Bulk-Si Solar Cell

Different Ag pastes were screen printed on the single-crystal Si-wafer ($156\ \text{mm} \times 156\ \text{mm}$) which has SiNx layer for antireflection and laser edge

isolation processed. The printing pattern has 2 bus bars and 56 fingers with 80 μm pattern opening. The screen type was ST290 combi with 15 μm emulsion thickness (GNT-i Co. Ltd). The printing speed was 230 mm/s and pressure was 80 N with a semi automatic screen printer (X5-ST5, ASYS Solar Co. Ltd). Next, the wafers dried at 300 $^{\circ}\text{C}$ within a minute and fired in IR lamp-heated belt furnace (CF-7210, Despatch Co. Ltd). The firing actual peak temperature was about 770 $^{\circ}\text{C}$ and firing time was about 30 seconds.

2.4 Evaluation Solar Cell performances

First, we evaluated converting efficiency of solar cells using solar simulator (Triple A grade of WACOM simulator) under AM1.5 light source. Next, evaluate junction leakage current using Core Scan method (Core Scan, Mechatronics Co. Ltd.). The Core Scan method uses the fact that series resistance sources can be detected by potential differences that occur over these resistances while current is flowing in the device. It is very effective method to visually realize the junction leakages and there uniformity. In this step, we realized that which paste is the better performance in bulk-Si solar cell.

3. Result and Discussion

At first, we analyzed the crystal structure of composite material using X-Ray diffraction (XRD). Fig. 1 compares the XRD diffraction patterns of the composite material and general silver powder which manufactured from wet reduction process. We realized that the crystallinity of the composite material is bigger than general Ag powder. In case of composite material, there are not Al_2O_3 peaks and any peak shifts. It needs other analyze to define about a tiny amount of Al_2O_3 . Therefore, we analyzed the composite using inductively coupled plasma (ICP). As a result the composite consists of 300 ppm of Al with more than 95 % silver. Next, we use transmission electron microscope (TEM). Fig. 2 is the TEM image of the composite materials. We confirmed the core-shell type of composite and core Ag powder uniformly coated by amorphous alumina with about 10nm of thickness. In spray pyrolysis process with high temperature, Ag and Al crystallize together from mixture aqueous solution of AgNO_3 and 400 ppm of AlNO_3 . Small amount of Al exist not only inside but also surface of agglomerated Ag

crystal. In rapid cooling process, the Al atoms start to diffusion form inside of agglomerated crystals to surface for oxidation because Al_2O_3 is more stable state than Al. As a result, amorphous Al_2O_3 formed surface of Ag powder uniformly. Even, silver powder coated by oxide layer, the conductivity is not a big problem. Because, Ag powders can contact each other by broken oxide shell during the firing and maintain conductivity. Because extension of Ag powders are about two and half times bigger than extension of Al_2O_3 . CTE of Ag is $19.2 \times 10^{-6}/^{\circ}\text{C}$ and Al_2O_3 is $8.0 \times 10^{-6}/^{\circ}\text{C}$. Therefore, Al_2O_3 shell is broken by unbearable extension of Ag during the firing process. Moreover, electrical current transport could occur by tunneling through the fired oxide layer. This is a very familiar phenomenon in solar cell technology. In the metallization process, Glass frit melt and etch or react with SiN_x antireflection layer and Ag particles begin to sinter and dissolve in the glass frit. Upon cooling, the excess Si in the glass frit epitaxial crystallizes and some of the dissolved Ag in the frit precipitates as Ag crystallites [5]. The Ag crystallites are surrounded by a quasi-continuous layer of modified glass. Electrical current transport occurs by via tunneling through the fired glass layer between the Ag bulk and the underlying Si emitter [6]. The important fact is that the oxide shell formed nano scale thickness for via tunneling of electron for high conductivity. The oxide coated layer has another advantage to apply Ag paste. Generally, the atomized powder has rough surface and it is increase paste viscosity. However, the composite material has smooth surface morphology by amorphous oxide layer. It is good for rheology property of the paste. Each Ag pastes manufactured using the Ag-oxide composite and pure atomized Ag powder without mixture to clearly define the influence by each powder and analyzed rheology property using Rheometer (AR-G2, TA instrument). As a result, the Ag paste which applied the composite materials has lower viscosity such as Figure 3. It is very useful property for screen printing. Solar cell finger width continually decreases to increasing light absorption area. It is link to improve I_{sc} property and archive high efficiency. Therefore, Ag paste challenged excellent printability with high aspect ratio and fine line finger pattern. Currently 80 μm of the finger pattern opening on the screen mesh is the general

specification but already started the research for 60 um pattern printing.

Finally, Ag paste which applied composite materials printed on the SiNx coated monocrystal wafer and fabricate solar cells to evaluate cell performance. As a result the composite materials were increase the cell efficiency about 0.4 % such as Table 1. It is show that the most of characteristic was improved such as V_{oc} , FF, and shunt resistance (R_{sh}) except series resistance (R_s).

V_{oc} is mainly affected by band gap by the back surface layer (P+ layer) and junction leakage. In this paper, using same back aluminum paste (BAL-202, LG Innotek Co, Ltd) and printed same amount as 1.5g. It means that Junction leakage of Ag pastes only effect to V_{oc} property. R_{sh} is also sensitively affected by junction leakage. Therefore, increase the V_{oc} and R_{sh} property mean that the Ag- Al_2O_3 composite materials help to preventing junction leakage in solar cell. We additional analyzed junction leakage with Core Scan method to verify clearly. Figure 4 compare core scan data of solar cell which applied pure Ag and Ag- Al_2O_3 composite paste. If have junction leakage, the core scan data should have high R_s value which expresses close to red color. Figure 4(b) which is applied Ag- Al_2O_3 composite materials has low R_s value and superior uniformity compare than 4(a) which applied pure atomized Ag powder. It means Al_2O_3 oxide layer could effectively prohibit the excessive Ag penetration and maintain junction. So the probability of junction leakage is remarkably decreased. In the table 1, R_s property was only decreased. However, the gap was very small and not affected to cell efficiency. It means that electrical current transport was not disturbed by oxide shell after firing.

4. Conclusion

We realized the effective method to preventing junction leakage as using silver and metal oxide composite materials. In this paper, we synthesized Ag- Al_2O_3 composite materials and apply to front Ag paste for solar cell. The amorphous oxide layer is effectively preventing excessive Ag penetration and maintain optimum junction. Even, Ag coated by alumina, the composite could be applied conductive electrode. The nano scale of oxide layer could be broken after firing process and electrical current tunneling. The core-shell structure of composite was

verified from TEM analysis. The composite has another advantage. The oxide shells change the morphology smoothly. It is suitable fine line printing. As a result, we confirmed the silver and metal oxide composite improves about 0.4 % of converting efficiency and good and uniformly omic contact with emitter layer with minimized junction leakage.

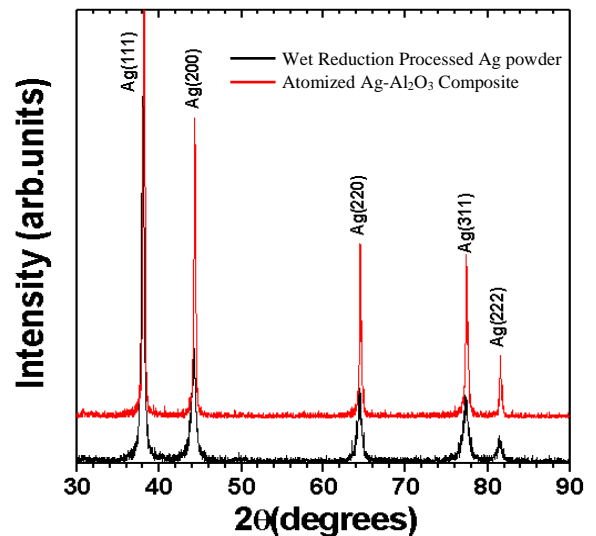


Fig 1. XRD diffraction patterns of silver powder synthesized by atomized and wet reduction method

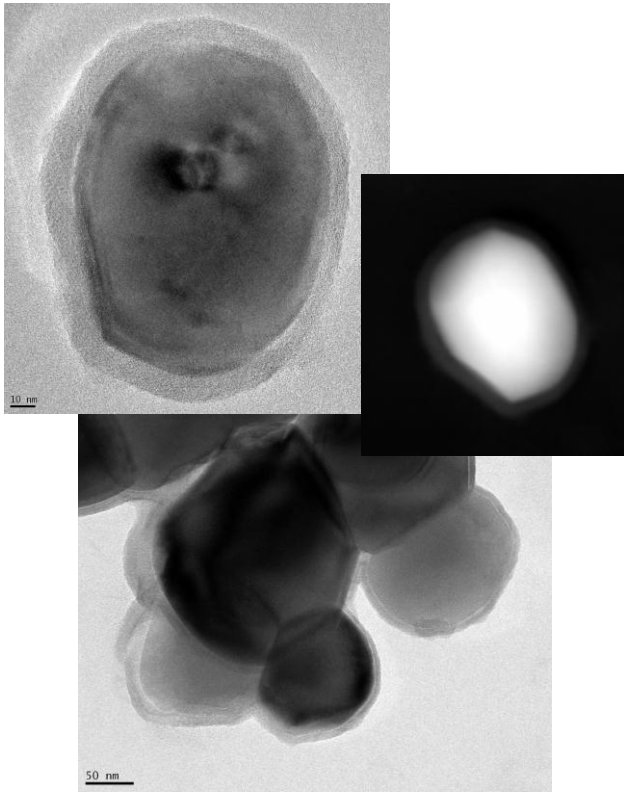


Fig 2. TEM image of core-shell type of Ag-Al₂O₃ composite materials

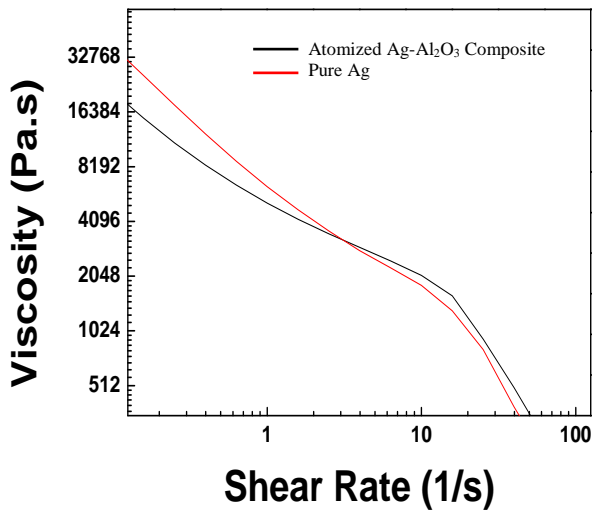


Fig 3. Rheology data about viscosity flow curve of Ag paste

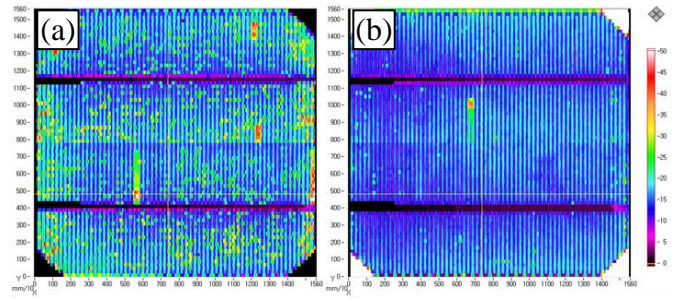


Fig 4. Core Scan data of solar cell (a) The solar cell which applied Ag paste using pure Ag (b) The solar cell which applied Ag paste using Ag-Al₂O₃ Composite materials.

	Applied only pure Ag powder	Applied 30wt% of Ag-Al ₂ O ₃ composite
Isc [A]	8.54	8.55
Voc [V]	0.622	0.636
F.F.	0.764	0.769
Eff [%]	17.04	17.43
Rsh [Ω]	30.7	40.6
Rs [Ω]	0.0068	0.0070

Table 1. Average property of Solar Cell performance

5. References

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