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Study on the Performance of Aluminum Thick Film Contacts for Silicon Solar Cells

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Abstract. Aluminum rear contacts of silicon solar cells are made commonly by screen-printing aluminum paste and sintering process. Aluminum thick film contacts have a direct effect on photoelectric properties of solar cells, like open circuit voltage (V_{oc}), short circuit current (I_{sc}), conversion efficiency (η), etc. The principle of Al-back surface field (BSF) has been studied in this paper. With thermal gravimetric analysis and differential scanning calorimetry (TGA-DSC) method, the chemical reactions between aluminum thick film and silicon substrate during heat treatment have been investigated. The microstructure of aluminum thick film contacts were analysed by SEM. The electrical properties of Al-BSF are improved by adding a proper amount of nano silicon to the aluminum paste.

Introduction

Polycrystalline silicon solar cells and monocrystalline silicon solar cells are the mainstream products of photovoltaic cells at present, which account for more than 85% of the total cells. C- silicon solar cells have several merits such as high efficiency, good working stability and easy for industrial production, etc. The BSF of silicon solar cells is produced commonly by vacuum sputtering Al film or screen-printing Al thick film. Vacuum sputtering technology is mainly used for research in the lab and unsuitable for industrial production because of the high cost. In screen-printing process, the Al thick film is printed on the back side of solar cells and the Al-BSF is formed after drying and sintering. Al thick film has two functions of the BSF and rear electrodes, which has a direct effect on the performances of solar cells such as Voc, Isc and η [1]. So the composition of Al paste will directly affect the electrical properties of Al thick film contacts. Al thick film contacts also have some other problems [2]. First, Al thick film are printed on almost the whole back side surface of cells, and the thickness of Al contacts is more than 20μm and the thickness of silicon wafer is about 200μm, as the large difference of the expansion coefficient between Al thick film and silicon wafer, cells will have a certain degree of warping after sintering. Second, as the high activity of Al powder in the Al pastes, Al powder can easily over-react with silicon during sintering, the aluminum protuberances or thorns on the back side surface would occur probably. In addition, the adhesion of Al thick film will affect the stability and lifetime of solar modules [3]. In this paper, the analysis of Al-BSF principle, the chemical reactions of Al-BSF formation were studied. The effects of nano silicon addition to Al paste on the performances of cells were also investigated.

Composition of Al paste and Al-BSF principles

Al paste comprises: Al powder, glass frit, organic vehicle, inorganic additives and organic modifiers, etc. Al powder is the main composition of Al paste, the weight ration is 70- 80%. Glass frit is melted during sintering and acts as an inorganic binder in the thick film. Inorganic powders are dispersed uniformly in organic vehicles. Organic and inorganic additives are crucial to the performances of Al paste.

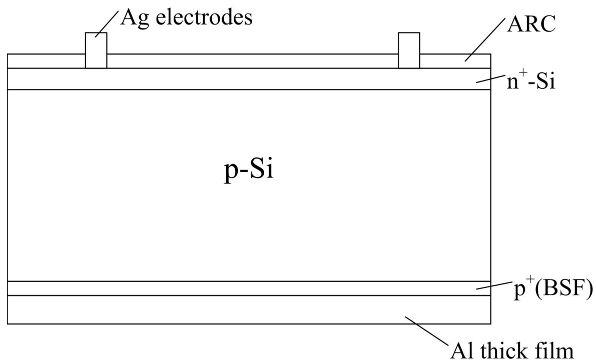

Fig. 1 Structural schematic diagram of silicon solar cells.

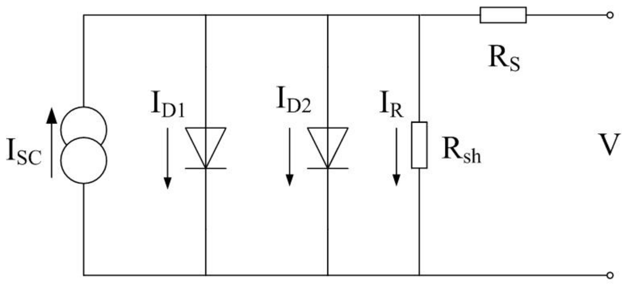

Fig. 2 Equivalent circuit of silicon solar cell.

Al thick film is formed on the back side of solar cells by screen-printing process, the thickness is about 20-30μm. Al thick film reacts with silicon substrate to form Al-Si alloy during annealing. The alloy layer is an acceptor heavy doping layer, which is about 5-8μm thick [4]. The structure of a solar cell is shown in Figure 1.

Silicon solar cell can be expressed by the equivalent circuit shown in Figure 2. I_{D1} is the dark saturation current related to recombination at neutralism region of p-type and n-type. I_{D2} is the dark saturation current related to recombination at depletion region. Shunt resistor R_{sh} and series resistor R_s are parasitic resistances of cells. The I-V characteristics of cells can be expressed as [5]:

$$I = I_{SC0} - I_{D1}[e^{q(V+IR_s)KT} - 1] - I_{D2}[e^{q(V+IR_s)/2KT} - 1] - \frac{(V+IR_s)}{R_{sh}} \tag{1}$$

In the ideal condition, R_{sh} is ∞ and R_s is zero, I_{D2} contribution is small. (1) can be simplified to:

$$I = I_{SC0} - I_{D1}(e^{qV/KT} - 1) \tag{2}$$

when I = 0:

$$V_{OC} = \frac{KT}{q}\ln\frac{I_{SC0} + I_{D1}}{I_{D1}} \approx \frac{KT}{q}\ln\frac{I_{SC0}}{I_{D1}} \tag{3}$$

The above equation indicates: the decrease of I_{D1} will result in the increase of V_{oc}. I_{D1} is mainly effected by the back surface recombination velocity S_{BSF}:

$$I_{D1,n} = qA\frac{n_i^2}{N_A}\cdot\frac{D_n}{w_p - x_p}\cdot\frac{S_{BSF}}{S_{BSF} + D_n/(w_p - x_p)} \tag{4}$$

when there is no Al-BSF, S_{BSF} will be ∞. Al-BSF serves to decrease S_{BSF}, the smaller the S_{BSF}, the less the I_{D1} and the more the V_{oc}.

Experimental

Al pastes were prepared by mixing a certain weight percentage of Al powder, glass frit, organic vehicle and a certain amount of additions. The thermogravimetric and difference thermal integrated analysis of Al paste were given using TGA-DSC tester. The chemical reactions of Al paste during heat treatment were analyzed under heating rate of 10°C/min, the range of temperature was 25-800°C and the ambient was pure air during heating. The Al paste was printed on the back side of cells passivated with SiN_x film by using 280 mesh stainless steel screen. After being dried under 150°C /5min, the chemical reactions between Al thick film and silicon wafers were studied by TGA-DSC method. The Al pastes were modified by adding nano silicon powder to the pastes, the amount of additions was in the range of 0-1.0wt%. Silicon solar cells were made by using modified Al pastes, the size of cells was 1/4 of 5-inch mono-crystalline silicon wafer. The photoelectric properties of solar cells were characterized by solar simulator (Model GSCT-B). The four point probes resistivity measurement system (Model RTS-8) was used to measure the sheet resistance of Al thick film. The microstructure of Al thick film was studied by SEM.

Results and Discussions

Chemical reactions of Al paste during the process of heat treatment. The TGA-DSC curve of Al paste is shown in Figure 3, which indicates that the solvents of paste evaporate at a low temperature (<270°C) and the weight loss is 21.43%. At higher temperatures (270-500°C), the weight loss is about 1.62%, mainly due to the decomposition of resins. There is an obvious weight increase started from 568°C, the weight increase is 2.31%. And corresponding to DSC curve, there is an obvious exothermic peak at 614.05°C. The exothermic peak is due to the oxidation reaction of Al powder in paste [6]:

$$Al+O_2 \rightarrow Al_2O_3. \tag{5}$$

The weight is still slowly increased as temperature rises, which indicates the oxidation reaction of Al powder is still in progress.

One endothermic peak appears in the DSC curve of sample at 660.58°C. This indicates that Al powder is melted at 660.58°C and the liquid phase appears, which consistent with the melting point of metallic aluminum 660°C.

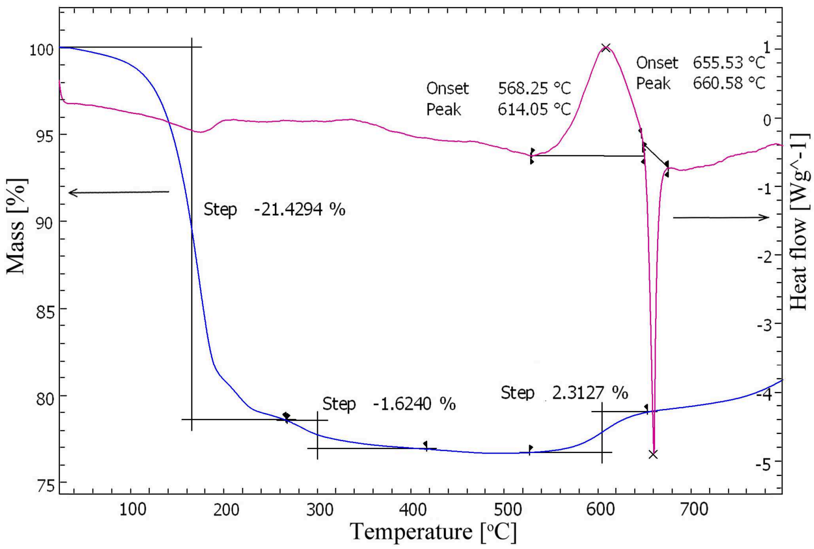

Fig. 3 TGA-DSC curve of Al paste.

Chemical reactions between Al thick film and silicon wafer. The TGA-DSC curve of Al thick film and silicon wafer is shown in Figure 4. The Al thick film was firstly dried at 150°C /min and then the difference thermal analysis was carried out. The TGA curve of Figure 4 shows that the weight of Al thick film gradually decreases as temperature increases when temperature is below 500°C, the weight loss is 0.48%. This is mainly due to the evaporation of the solvents of high flash point in Al thick film and the decomposition of resins. There are two exothermic peaks appear in the DSC curve of sample at 578.9°C and 594.95°C respectively, and obvious weight increase appears in the TGA curve. There is a weight increase of more than 0.36% corresponding to TGA curve, which indicates the oxidation reactions proceed all the way. This illustrates that the oxidation reactions occur in Al thick film and the degree of oxidation increases as the temperature rises. One endothermic peak appears in the DSC curve of sample at 584.92°C, which is just above to the eutectic temperature of

Al-Si 577°C, this is mainly due to the occurrence of mutual solution of Aluminum and silicon. The integrated thermal analysis shows that the oxidation reactions of Al thick film continue at high temperatures and the Al-Si liquid phase appears during the oxidation reactions.

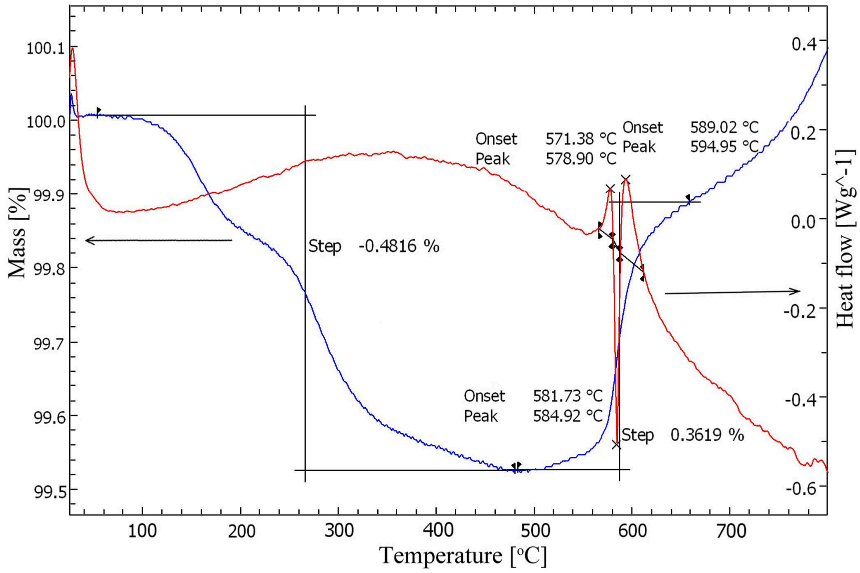

Fig. 4 TGA-DSC curve of Al thick film.

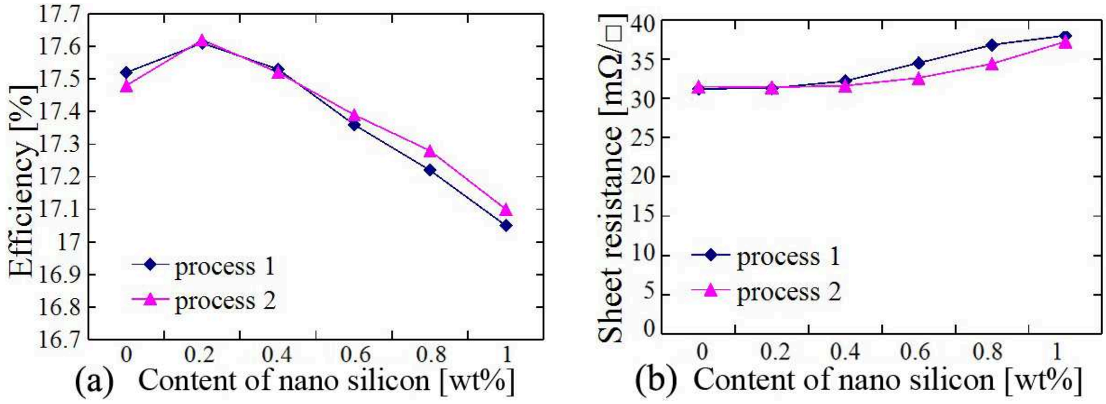

Fig. 5 Relationship between the properties of thick film and the content of nano silicon.

Experiment of adding nano silicon powder to Al pastes. The weight percentage of nano silicon was: 0.2%, 0.4%, 0.6%, 0.8% and 1.0%. Two sintering processes were adopted respectively:

Process 1, the temperatures of infrared sintering furnace were: 300°C, 320°C, 330°C, 450°C, 520°C, 580°C, 690°C, 780°C, 890°C, and the conveyor speed was 5.5 m/min.

Process 2, the temperatures of heating region 8 and heating region 9 were 800°C and 910°C respectively, with other temperature regions the same as the process 1.

The relationship between efficiency and the content of nano silicon is shown in Figure 5a. The relationship between the sheet resistance of Al thick film and the nano silicon content is shown in Figure 5b.

The experimental results indicate that in the normal sintering process (process 1), the cell efficiency will be improved by adding 0.2-0.4wt% nano silicon powder, the maximum improvement is about 0.09%. The cell efficiency fell slightly when the addition is more than 0.4wt%. When the sintering temperatures increased (the process 2), the cell efficiency and the sheet resistance of the samples with nano silicon powder changed less compared with sample without nano silicon powder. With the observation of the Al film appearance, when the sintering temperatures increase (the process 2), several aluminum protuberances appear on the thick film surface of the sample without adding nano silicon. The cross-sectional structure of the cell with aluminum protuberance is shown in Figure

6, which indicates that adding certain amount of nano silicon powder to Al pastes can improve the heat-resisting property of Al thick film.

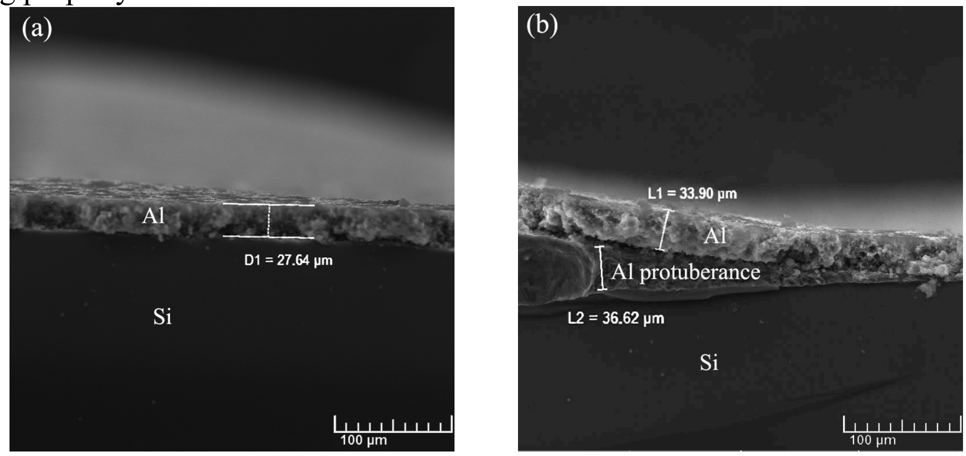

Fig. 6 Cross-section SEM photographs of Al thick film: (a) normal Al film, (b) Al film with aluminum protuberances.

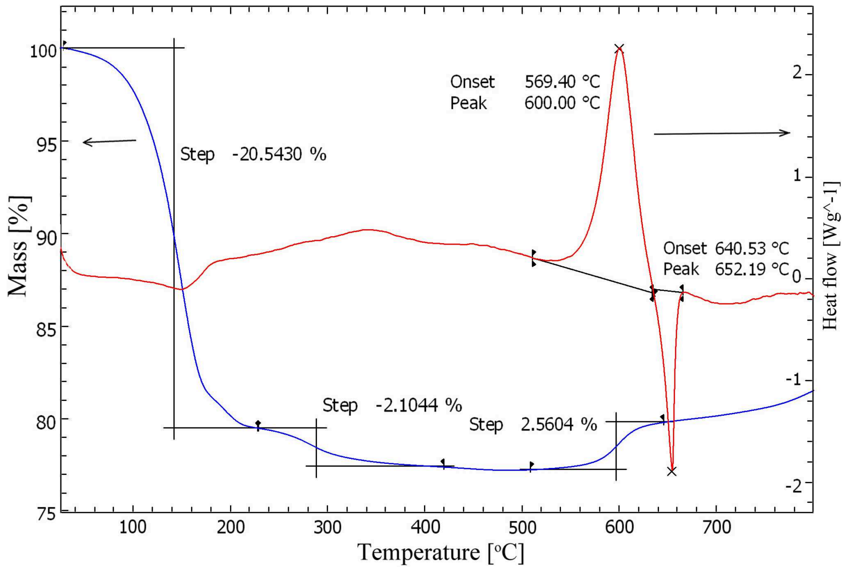

Fig. 7 TGA-DSC curve of the Al paste added 1.0wt% nano silicon powder.

The Al paste and the Al thick film added 1.0wt% nano silicon powder were studied by integrated thermal analysis. The DTA curve of Al paste with 1.0wt% silicon power is shown in Figure 7:

The thermal analysis indicates that the oxidation reactions appear at 600°C, the weight increase is 2.56%, and Al powder is melted into liquid phase at 652.19°C. The oxidation temperature and the melting temperature of this sample are lowered 14°C and 8°C respectively, compared with the sample without adding nano silicon (see Fig. 3), in which the oxidation reaction appears at 614°C, Al powder is melted into liquid phase at 660°C, the weight increase is 2.31%. The decreases in oxidation temperature and melting temperature are mainly because the reactivity of Al pastes are improved by the higher activity of nano silicon powder added.

The Al paste added 1.0wt% nano silicon powder was printed on silicon wafer and dried to form Al thick film. The TGA-DSC curve of Al thick film is shown in Figure 8.

The thermal analysis indicates that the oxidation reactions appear in Al thick film at high temperatures and there is an endothermic reaction, which produces liquid phase in the process of oxidation reactions, these phenomena are similar to the sample without adding nano silicon powder (see Fig. 4). The oxidation temperature of sample is 578.56°C and the temperature of endothermic peak is 585.81°C, compared with the sample without adding nano silicon, the endothermic peak is increased 0.89°C. This indicates that the addition of nano silicon will increase the liquid phase formation temperature to some extent, which increases the heat treatment temperature of Al-BSF. The main reason for heat-resistant property is improved by adding nano silicon powder is that the diffusion rate between Al and Si wafer is decreased by adding a certain amount of nano silicon powder to Al paste. The addition of a proper amount of nano silicon causes the formation of Al-Si alloy, which enhances the efficiency of cells. The addition of an excessive nano silicon powder leads to the poorer conductivity of Al film and thus causes the low efficiency of cells.

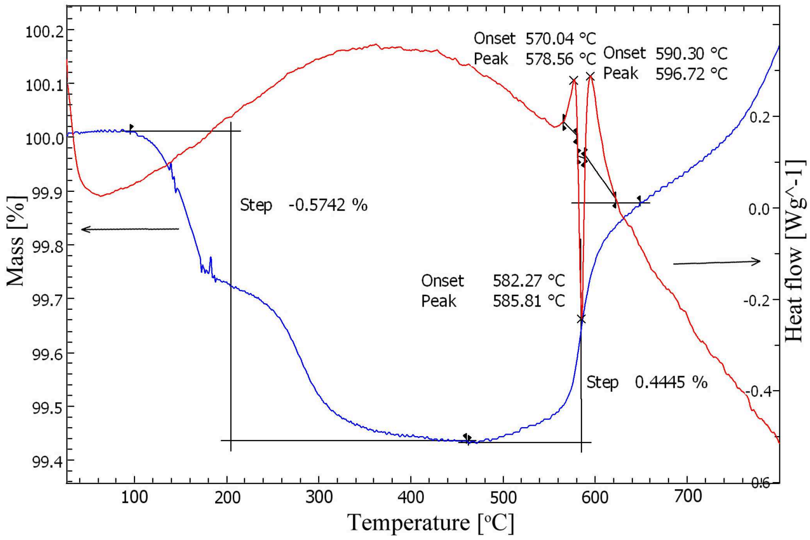

Fig. 8 TGA-DSC curve of Al thick film added 1.0wt% nano silicon powder.

Conclusions

The integrated thermal analysis of Al pastes indicates that the normal Al paste starts to oxidize at 614.05°C and liquid phase occurs at 660°C. The paste weight increase caused by oxidation is 2.31% at 500-650°C.

During heat treatment of Al thick film, the oxidation proceeds all the way above 500°C. The DSC curve has two exothermic peaks of 578.9°C and 594.95°C, and a endothermic peak at 584.92°C, which is just above to the eutectic temperature of Al-Si 577°C.

The addition of a proper amount of nano silicon powder (0.2-0.4wt%) to Al pastes improves the cell efficiency at a maximum of 0.09% and enhances the sintering-resistant property of Al thick film.

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