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Screen printed contacts formation by rapid thermal annealing in multicrystalline silicon solar cells

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Abstract

The aim of the present work is to optimized the annealing parameter in both front and back screen printed contacts realization on p-type multicrystalline silicon and with phosphorus diffused. The RTA treatments were carried out at various temperatures from 600 to 850℃ and annealing time ranging from 3 min to 5 min in air, O_2 and N_2 ambiance. The contacts parameters are obtained according to Transmission Line Model measurements. A good RTA cycle is obtained with a temperature plateau of 700℃ - 750℃ and annealing ambiance of air. Several processing parameters required for good cell efficiency are discussed with an emphasis placed on the critical role of the glass frit in the aluminum paste. A anamolus behaviour of Aluminum n-doping on p-type Si wafer, contact at high temperature have also been studied.

1. Introduction

Screen printing contacts for both mono and multy-crystalline is a well know industrial applied metallisation technique. [1,2] Silver-Aluminum/Aluminum paste is commonly used for back contact while silver paste is normally used to form ohmic contact in the front of closely spaced metal grid lines of an optimized grid pattern of front surface. After printing and drying of the pastes, contact firing is necessary in order to obtain the desired electrical properties of the contacts, Infrared (IR) heated conveyor belt furnaces is usually used for firing of screen printed paste in an industrial scale solar cell manufacturing unit.

Rapid thermal Annealing(RTA) for firing of screen printed contact is an alternative promising approach compared to IR heated conveyor belt furnace process. This RTA process can cut down the process time a s well as the thermal budget [3], another advantage of the RTA is every single process step can be designed highly flexible with regard to thermal cycle and gas atmosphere.

The capability of fire screen printed contact by RTA is shown in number of papers [4,5]. In the most of industrial multicrystalline mc silicon solar cells fabrication process sequence, both surface of the mc-Si is usually n^+ diffused. So in order to achieve good contact behavior of the back surface of the mc-Si solar cells, on the selection of Aluminum paste firing temperature and ambient are a vital parameters.

The aim of this present paper is to optimized the RTA process parameters of bare p-type mc-Si/aluminum contacts and Al/n-doping p type contact. The contacts parameters are also measured using transmission line model(TLM) measurement technique. Surface morphology using SEM analysis of different contacts at different RTA process temperature have been also studied in this paper.

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2. Experimental

The TLM pattern were fabricated on p-type 1-5 ohm/cm, 270 ㎛ mc-si(Baysix)wafer. The set of samples analyzed in the present work corresponds to the following fabrication procedure: after acid etching , some polish samples were kept for direct TLM pattering and other samples both surface were diffused at 850℃ using $POCl_3$ sources and then TLM pattern was patterning on every diffused wafers. The TLM patterns were set up by screen printing method with Aluminum screen printing paste. The dry was carried out by dry air for 20 min at 120℃. Finally, the RTA treatments were carried out at various temperatures ranging from 600 to 850℃ and annealing time ranging from 3 to 5 min in N_2, O_2 and air ambiance. After the heating up as of 600-800℃, the sample was loaded. The temperature kept for 3-5min. The cooling rate is 23℃/sec.

The performance of ohmic contact to semiconductors can be quantitatively studied by measuring the ohmic contact, this parameter can be determined by a method based on the Transmission Line Model(TLM) [6]. Since TLM pattern were realized on each sample : Each pattern consisted of six identical contacts, (Fig 1) each

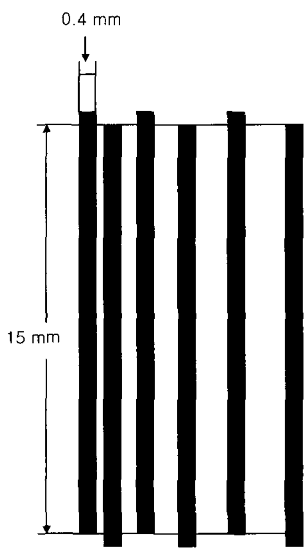

Fig. 1. Al pattern for resistivity calculation by TML method.

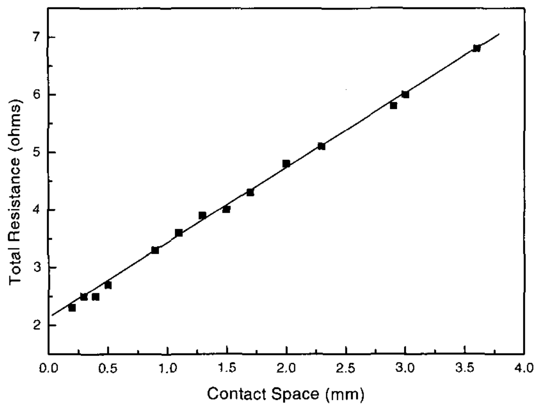

Fig. 2. Typical plot of total resistance versus contact spacing for the determination of contacts parameters.

pair of contacts being separated by a variable distance, namely 0.2, 0.3, 0.4, 0.5 and 0.6 mm respectively. The total resistance Rt between any two contacts is obtained from the I-V characteristic given by a four probe technique. Different experimental R_t values are plotted versus different separation distance and fitted by a linear regression compulation : We obtain a straight line which the slope yields R_{sh}, the sheet resistance of the semiconductor layer outside the contact region. R_t=0 for $I_o=2L_T\ R_{sk}/R_{sh}$ which gives L_T assuming that $R_{sh} \approx R_{sk}$. Then equation $\rho_c=R_{sk}\ L_T^2$ gives contact resistivity, R_c being declared from the R_t-contact separation curve (Fig 2).

3. Discussion

Fig. 3 give the variation of contact resistivity of Al/mc-Si with different RTA process temperature in N_2, O_2 and Atmosphere ambiance. In the case, it has been found that increase of contact resistivity is more predominant with the increase of RTA process temperature in N_2 ambiance. Actually N_2 ambiance at time of RTA treatment may reduce the reaction rate of glass frit with Aluminum. The glass frit has effects on ohmic contact formation though the following process : upon heating, the glass frit melt and flows over silicon surface. Upon cooling, the silicon that has been taken

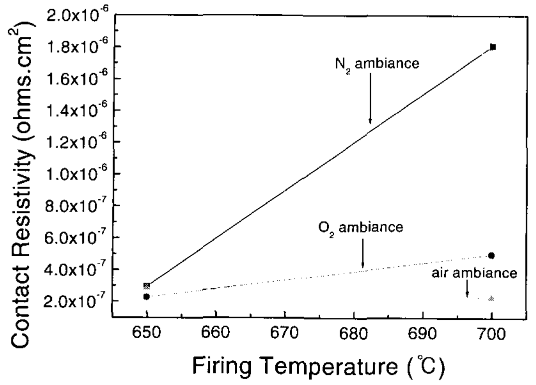

Fig. 3. Contact resistivity versus firing temperature for N_2, O_2, air ambiance.

into the liquid state recrystallizes epitaxially.

This recrystallized silicon layer, under the contacts, partly determines the final solar cell parameters. The etching of the silicon surface by the frit is function of crystal orientation, firing temperature and the percentage and type of glass frit [7]. So the reduction of reaction rate of Aluminum with glass frit in N_2 ambiance may be the cause of bad contact formation of Aluminum past with bare mc-Si and n-doping mc-Si, which reflects the increase of contact resistivity.

From Fig. 3, we have noticed that there were also little increase of contact resistivity of Al past/p-type mc-Si contacts with the increase of temperature RTA process in O_2 ambience. During firing, the aluminum in the past melts and alloys with silicon, while a portion of aluminum is heavily oxidized. The p-type layer containing high concentrated aluminum below the aluminum silicon alloyed layer is proceed by the diffusion of aluminum atoms from molten aluminum-silicon layer in the silicon of the heating step, and liquid phase epitaxial growth of primary silicon during the cooling step. In these steps, the thickness of the paste decrease the alloyed layer becomes discontinuous.

The discontinuity due to the heavy oxidation for a portion of aluminum may cause high sheet resistivity of the p-type layer. This is the cause of increase of contact resistivity of both the cases for RTA process in O_2 ambience.

Decrease of contact resistivity(Fig. 3) with increases with RTA process temperature in atmosphere ambiance has been also noticed. This may be due to this reasons : The presence of little amount of N_2 in atmosphere helps the reduction of oxidation rate of some portion of the past, which in turn help to decrease the sheet resistivity value of p-type layer and thereby decrease of contact resistivity value with increase of RTA process temperature in atmospheric ambience.

The surface morphology of different contacts at different RTA process temperature in atmospheric ambiance have been analyzed with help of SEM photographs as shown from Fig. 4 to Fig. 11. We have noticed from the SEM photographs that more and more glass frit were melt due to increase of RTA process temperature and flows over silicon surface(decrease of globule size on the surface) and aluminum-silicone alloyed layer is proced by the diffusion of aluminum atoms from molten aluminum-silicone layer into the silicone at the heating step, more and more aluminum form p-type layer on p-type mc-Si surface.

Figure 12 and Fig. 13 show the variation of contact resistivity of p-type mc-Si/Al and Al/n-doping, p-type mc-Si with different RTA processing temperature in atmospheric ambiance. From both the figures, we have noticed that the contact resistivity value for both cases decreases with increase of temperature up to 750℃ for Al/p-type Si and 700℃ for Al/n-doping/p-type Si wafer ; It is obvious due to the increase of temperature more and more glass frit melts and flows over silicon surface(which explain detail previously at the time of SEM studied) and improve the contact behavior. A sudden increase of contact resistivity value after 750 for Al/p-type Si and 700℃ for Al/n-doping/p-type Si wafer have also noticed in both contact cases. This is may be due to discontinuity of alloy layer due to the heavy oxidation for a portion of aluminum may cause high sheet resistivity of p-layer, and thereby high contact resistivity value which explain earlier in details. In Fig. 13, we have also noticed. That the contact resistivity value of Al/n-doping p-type mc-Si contact again decrease if

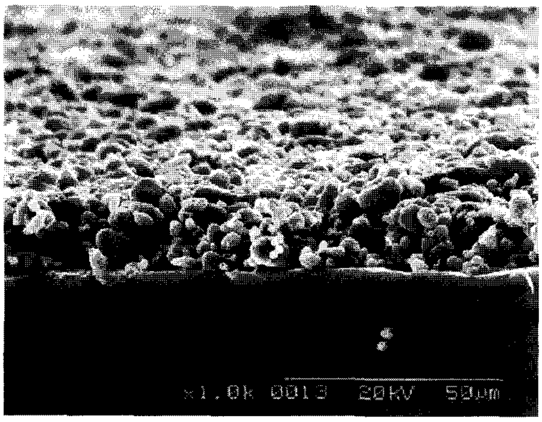

Fig. 4. SEM of Al/p-type mc-Si wafer at firing temperature 600℃ in air ambiance.

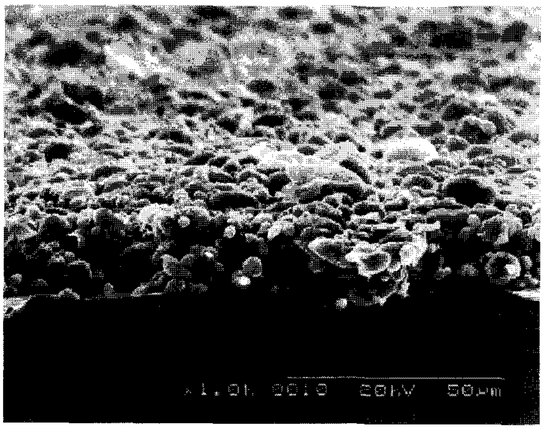

Fig. 5. SEM of Al/p-type mc-Si wafer at firing temperature 700℃ in air ambiance.

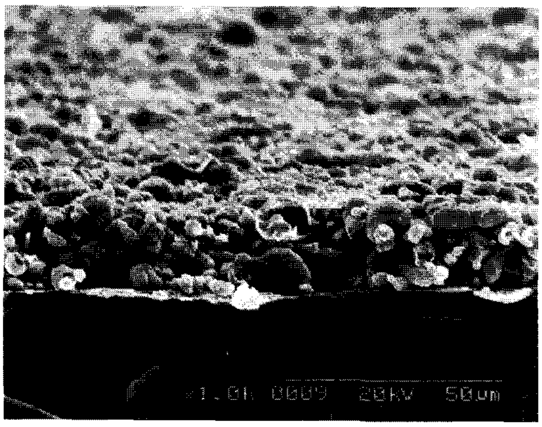

Fig. 6. SEM of Al/p-type mc-Si wafer at firing temperature 750℃ in air ambiance.

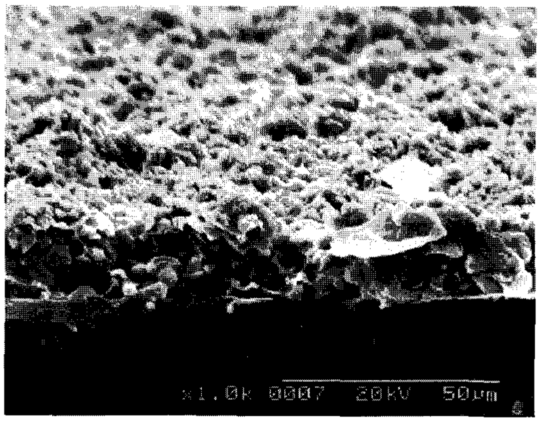

Fig. 7. SEM of Al/p-type mc-Si wafer at firing temperature 850℃ in air ambiance.

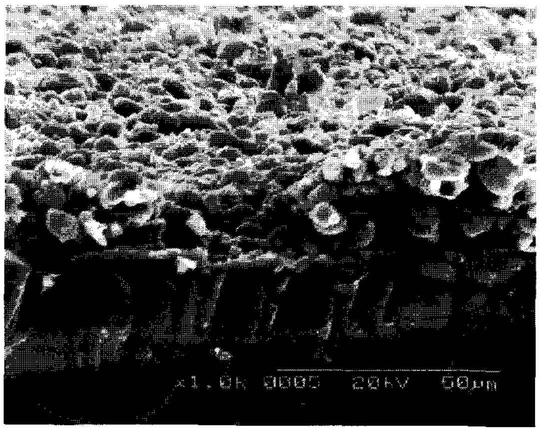

Fig. 8. SEM of Al/n-doping/p-type mc-Si wafer at firing temperature 600℃ in air ambiance.

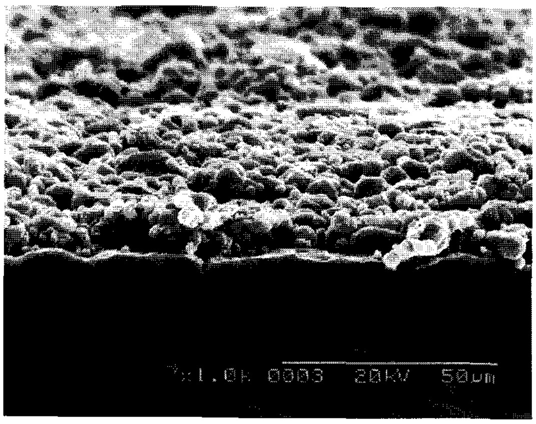

Fig. 9. SEM of Al/n-doping/p-type mc-Si wafer at firing temperature 700℃ in air ambiance.

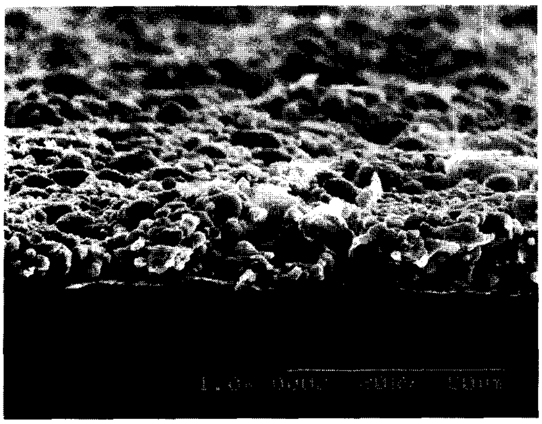

Fig. 10. SEM of Al/n-doping/p-type mc-Si wafer at firing temperature 750℃ in air ambiance.

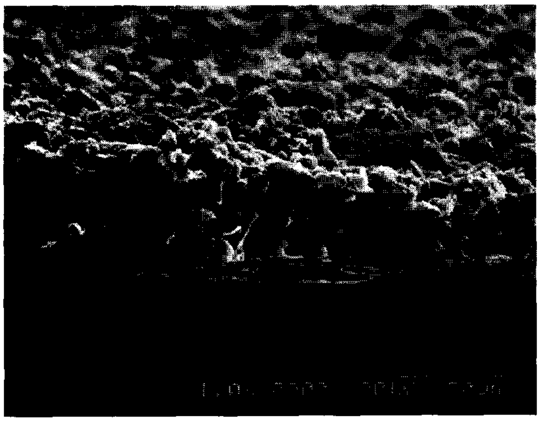

Fig. 11. SEM of Al/n-doping/p-type mc-Si wafer at firing temperature 850℃ in air ambiance.

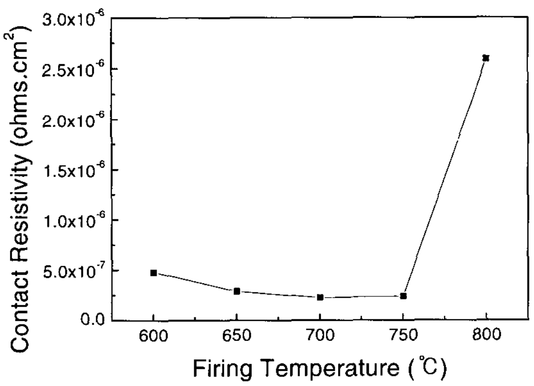

Fig. 12. Contact resistivity versus firing temperature Al/p-type Si wafer.

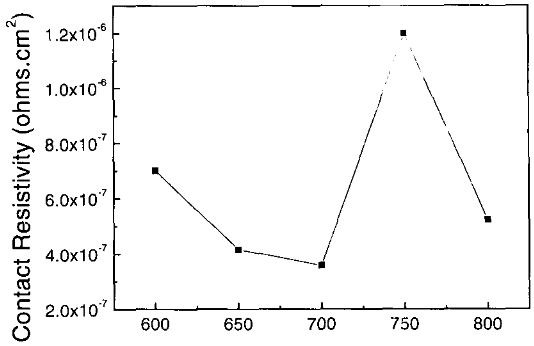

Fig. 13. Contact resistivity versus firing temperature Al/n-doping/p-type Si wafer.

RTA process temperature exceeded 800℃. This may be due to this high temperature opposite polarity n^+ silicon diffused in the aluminum layer, for this some aluminum goes inside silicon inform of spike improves the contact behavior the some low value and also may increase the thickness of Aluminum BSF layers of surface.

4. Conclusion

The aim of the present work is to optimize the RTA parameters in back screen printed contacts realization on p-type multicrystalline silicon phosphorous diffused. The contacts parameters are obtained according to Transmission Line Model measurements. A good RTA cycle is obtained with a temperature plateau of 700℃ -750℃. Some important processing parameters was described when implementing the screen printing technology on multicrystalline silicon substrates. The composition of the Al paste is critical for good cell performance. A mechanism explaining the role of the glass frit has been proposed.

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