Effects of cooling rate on the structural Al-p$^+$ layer for n-type silicon solar cell

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Abstract. In this paper, we have made a simple Al-p+ layer on n-type silicon wafers with a commercially available aluminum paste, screen-printing and traditional annealing furnace. The influences of firing cooling rate on the structure and thickness of Al-Si recrystalline layer are discussed. By changing the cooling rate and peak temperature, we find the general relationship between cooling rate and the structure of p+-layer. Relatively complete and uniform structure was obtained by slowing down cooling rate between peak temperature and 550˚C. The result of the present work implies that a moderate thick pn junction can be formed by lower cooling rate using peak temperature range from 830˚C to 880˚C.

Introduction

At present, many researches have reported that n-type crystalline silicon wafers are more suitable for ground application as solar cells and the efficiency is increased greatly [1-9]. As one of the approaches to creating pn junction, Al-p$^+$ rear emitter alloyed from screen-printed pastes have caused wild concern because its production process is well established for the BSF formation in conventional p-type cell production lines resulting in high productivity and low cost. And compared to boron diffusion, the aluminum firing process is less heating and costs less time which could decrease the crystallographic defects in n-type silicon bulks [10,11]. Furthermore, for laboratory solar cells with Al rear emitter, the performances of n-type solar cells has improved to more than 20% with many mature techniques such as screen-printing, FSF, passivation and so on [8,12-14]. However, it is not easy to control the Al-p$^+$ layer's quality with traditional firing furnace [10,15]. The cooling rate during firing process is an important factor for the structure of p$^+$-layer which is significant for conversion efficiency of n-type solar cells. Overly rapid cooling rate would bring more defects and impurities in recrystalline layer. This condition could grow a polycrystalline p$^+$-layer or severely not form a pn junction. It is valuable to pay attention to research a suitable cooling rate during firing process for manufacturing a good quality pn junction.

In this study, the effect of cooling rate during firing is investigated to find out its influence on the structure of p+-layer by changing cooling rate(Rc) in range of 1˚C/min to 100˚C/min under different firing temperature. We present cross-sections of samples to observe the change of Al-p+ layer and simply analyze the structure trend of p+ layer along with the changing cooling rate.

Experiment

The crystalline Si wafers in experiments were n-type ,0.5-3.5Ω·cm and 200 μm thick. Every group had 5 samples for each experiment. Fig. 1 shows the applied experiment process in a flow chart.

The samples were prepared with cleaning of chemical solution. After removal of the native oxide in 5% HF for 5 minutes, the complete wafers were subjected with screen-printing .The aluminum paste amount was more than 6.41mg/cm2. Then wafers were cut into about 30×30 mm² area samples by laser scribing after drying. The detail firing process with different cooling rates and peak temperatures can be explained by the curve plot of firing process in Fig. 2.

First, the whole heat treatment was in N2 ambient minimizing samples being oxidized. When the temperture of furnace was up to 300˚C at t2, the samples were preheating for 15 minutes at furnace

mouth then put them in the middle of furnace at t3.After rising to 660˚C at t4(Al melting temperature), the heating rate is slowed down until reaching the firing peak temperature(Tpeak) then keeping the Tpeak for 5 minutes. The next step (t5-t6) represented the most critical process in which the cooling rate(Rc) was changed from Tpeak to 550˚C (lower than Al-Si eutectic temperature 577˚C) in the rate range from 1˚C/min to 100˚C/min and then samples were cooled in nature.

Finishing heat treatment, samples were treated by moving paste residuals and Al-Si eutectic layer with a HCl and NaOH solution before a short HF dip. Finally, we tested samples by Conduction Type Tester, confocal Laser Scanning Microscopy (CLSM) and X-ray diffraction (XRD).

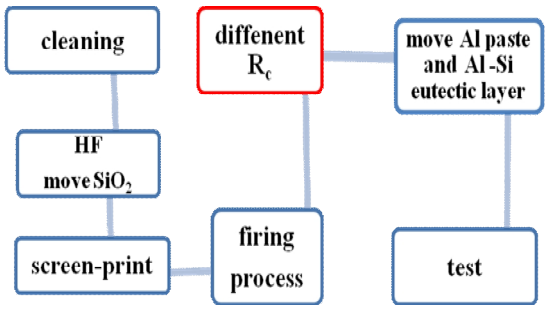


Fig. 1 Flow diagram of experiments

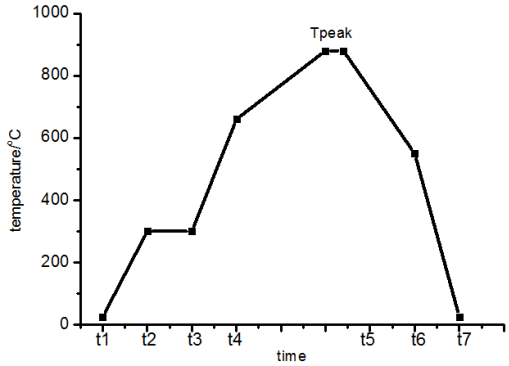


Fig. 2 Temperature curve plot of firing

Result and discussion

Conduction type of Al-p$^+$ layer

Table 1 shows the samples' conduction types after cleaning their surfaces. We can clearly see that the conduction types are almost p- type at a low cooling rate and the n- type appears when cooling rate is higher than 50˚C/min.

When cooling rate is 1˚C/min, more aluminum atoms are incorporated into the Si lattice. This means that recrystallized p+-layer contains more aluminum atoms before saturation in Si surface. There is enough time for aluminum atoms to obtain more power moving in p+-layer homogeneously so conduction types of sample's surface are p- type. There is not enough time for aluminum atoms to reaching their right place in Si lattice when cooling rate is higher than 50˚C/min at a lower peak temperature. Below 800˚C with a higher cooling rate, the concentration of dissolved Al is less in recrystallized layer and p+-layer can not be formed that's why the surfaces are n-type [16].

Table 1 The conduction type of Al-p$^+$ layer

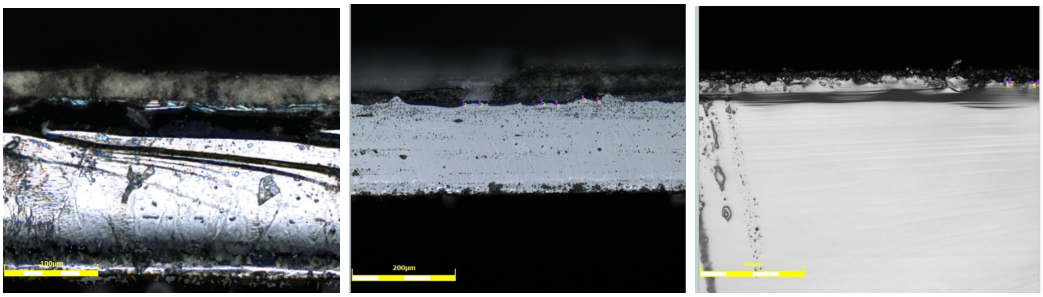
T_{peak}(˚C) / R_c (˚C/min)	**680**	**780**	**800**	**830**	**850**	**880**
1	N	Little P	P	P	P	P
50	N	N	Dot P	P	P	P
100	N	N	N	P	P	P

When temperature is too low like 680˚C, the samples' conduction types are all n- type by considering the glass cement in Al paste. Glass cement can't reach its softening point and prevents Al paste from contacting Si surface even with a long cooling time. High firing temperature makes glass cement with good mobility and also leads to a deeper p+-layer no matter how fast their cooling rate is which result in all p-type of samples' surface after cleaning in alloying temperature higher than 830˚C.

Thickness of Al-p$^+$ layer(X_j)

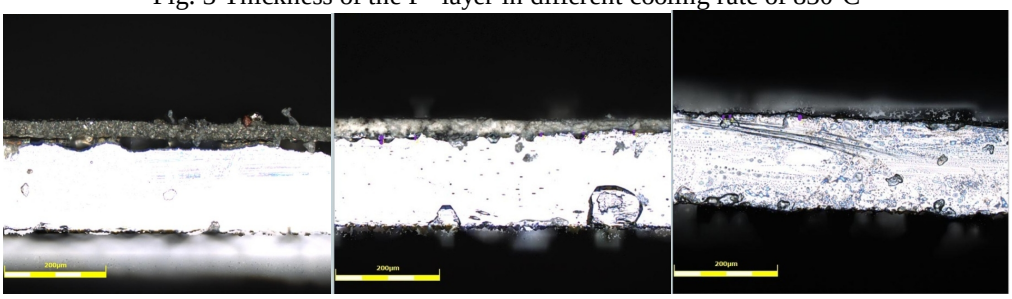
Fig. 3-Fig. 5 show the CLSM images of p+-layer in different cooling rates (Rc) under different peak temperature (T_{peak}). Comparing three images in identical peak temperature, we can clearly observe that

the thickness of p+-layer with slow cooling rate is thicker and more uniform. The thickest Al-p+ layer can only achieved by the slow cooling with high peak temperature. On the other side, the fast cooling with low peak temperature results in the thinnest and discontinuous p+-layer. In Fig. 3(a), Fig. 4(a) and Fig. 5(a), we can see that alloy layer exhibits more smooth and uniform properties thanks to the long cooling duration. It is believed that low cooling rate makes the contact between Al particles in paste and Si surface more sufficient.



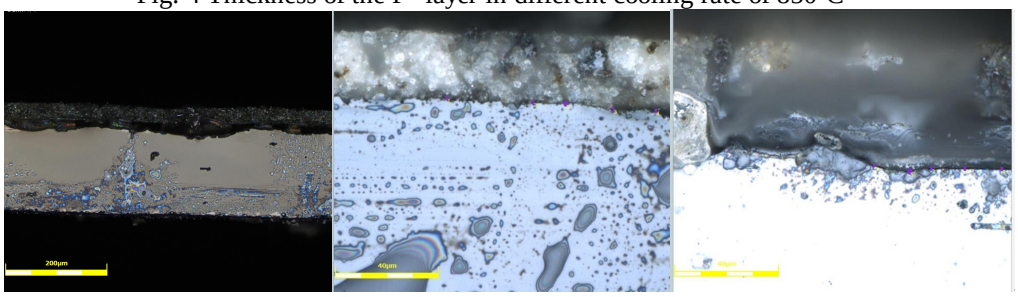
(a) 1˚C/min (b) 50˚C/min (c) 100˚C/min

Fig. 3 Thickness of the P^+-layer in different cooling rate of 830˚C



(a) 1˚C/min (b) 50˚C/min (c) 100˚C/min

Fig. 4 Thickness of the P^+-layer in different cooling rate of 850˚C



(a) 1˚C/min (b) 50˚C/min (c) 100˚C/min

Fig. 5 Thickness of the P^+-layer in different cooling rate of 880˚C

Effect of Rc on Xj are shown in Fig.6. The thickness of p+-layer (Xj) is plotted as a function of Rc in firing process. It demonstrates that the thickness of p+-layer decreases with the increasing of Rc under the same Tpeak. At 830˚C, the thickness decreases approximately 5μm when cooling rate increases from 1˚C/min to 100˚C/min.Moreover, the thickness of Xj decreases about 9μm between 1˚C/min and 100˚C/min at Tpeak=880˚C. But it is only decreased 4μm between 1˚C/min and 100˚C/min at 850˚C. In other words, although Xj reduces greatly in the 880˚C firing condition, we can't come to a conclusion that the thickness of p+-layer will decrease more and more fast between 1˚C/min and 100˚C/min with an increasing Tpeak. However, it is proved that the rate of Xj decreasing below 50˚C/min is much more flat than over 50˚C/min.

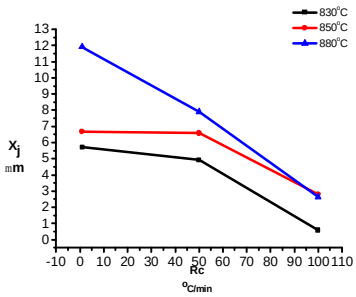
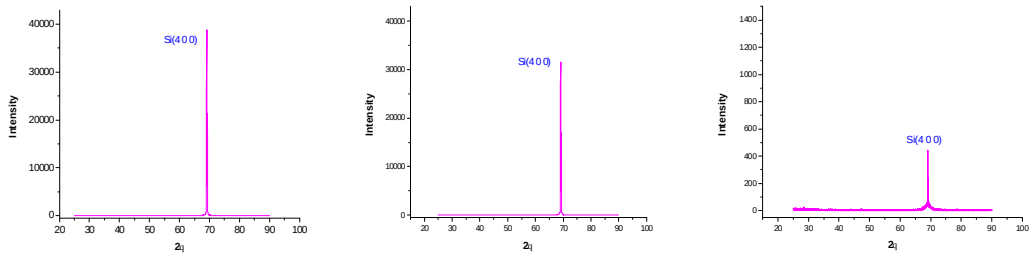


Fig. 6 Effect of R_c on X_j under the three friring conditions

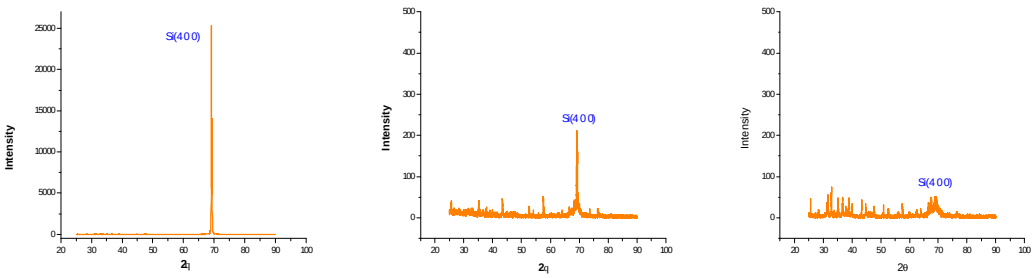
Structure of Al-p$^+$ layer

Fig. 7 and Fig.8 are x-ray diffraction spectrum of samples. In Fig. 7(a) and Fig. 8(a), it is shown that with the low cooling rate, there is only one main peak in two diffraction spectrograms and the maximum value of 880˚C in Fig 8(a) has dropped more compared with 850˚C. The main peak strength of diffraction spectrogram reduces when cooling rate is 50˚C/min and some faint impure peaks appear in Fig. 7(b). We can also observe one main peak in Fig. 7(c), but the value declines greatly and more strengthened miscellaneous peaks appear. There is hardly noticeable peak in Fig. 8(b) , (c) and almost impure peaks with different values.



(a) 1˚C/min (b) 50 ˚C/min (c) 100˚C/min

Fig. 7 The x-ray diffraction spectrograms of different cooling rates` samples at 850˚C



(a) 1˚C/min (b) 50 ˚C/min (c) 100˚C/min

Fig. 8 The x-ray diffraction spectrograms of different cooling rates` samples at 880˚C

The one main peak in spectrogram under low cooling rate is indicating that sample's surface with Al-p+ layer is a monocrystalline layer growing as a epitaxial layer along with the original Si lattice orientation (100). During long cooling with high peak firing temperature, the diffusion processes is slow enough to transport aluminum atoms to Si lattice to build a complete and thick p+-layer. The doping concentration of Al in p+-layer increases for higher Tpeak [15]. On the contrary, the amount of Si of 880˚C in p+-layer is less than 850˚C, that's why the maximum value of 880˚C in Fig 8(a) is lower than 850˚C. When cooling rate is higher than 50˚C/min, it is too fast for recrystalline layer to grow along with one lattice direction so impure peaks appear demonstrating that p+-layer have a polycrystalline or eutectic structure. Fast cooling duration can make p+-layer inhomogeneous or destroy its whole structure. Severely, pn junction can't be formed [17]. In other side, the slow cooling process is good for the quality and mechanical property of pn junction.

Conclusion

In this study, we have investigated the effect of cooling rate on p+-layer between firing peak temperature and 550˚C in order to find out its impact on structure and depth of pn junction. By the same screen-printing of Al paste and annealing furnace, slowing down the cooling duration is easy to get a thicker p+-layer in common with increasing Tpeak. However, higher peak temperature will bring more defects and impurities. Long cooling process have advantages in low temperature firing. To obtain a good quality pn junction, it is demonstrated that peak temperature should be higher than 830˚C and the cooling rate should be lower in which a uniform and thick p+-layer can be acquired while the sample with high cooling rate shows a thin and intermittent p+-layer.

With the 1˚C/min cooling rate, recrystalline layer is conformal and have a complete structure. Considering commercial efficiency, the cooling rate should be in the range of 1˚C/min to 50˚C/min.

In the next research, we should focus on optimizing the Al-alloying process especially refining cooling rate. Making the theoretical analysis have more reference value by using more testing instruments for n-type silicon solar cell with Al- p+ emitter.

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