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Effect of MW-ECR Plasma Hydrogenation on Polysilicon Films Based Solar Cells

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Abstract

Here we have investigated the hydrogenation process of thin film polycrystalline n^+pp^+ silicon cells using MW-ECR plasma in a standard PECVD system. Influence of various process parameters such as MW-ECR power, hydrogenation temperature and hydrogen flow on the sheet resistance of the n^+ emitter region and on the open-circuit voltage of the structure were investigated. The n^+- type emitter regions were obtained by phosphorous diffusion using a spin-on dopant P507 or P509 solutions from Filmtronics. For both levels of emitter doping, the open-circuit voltage of poly-Si mesa cells increases with increasing the MW-ECR plasma power from 180-220 mV without hydrogenation up to 368 mV with plasma hydrogenation at 650 W. The sheet resistances of the n^+ emitter region measured by the four-point probe technique show an increase upon hydrogenation and quantitatively depend on the initial doping level. In a further study hydrogenated and non-hydrogenated samples were annealed under a forming or neutral gas. Post-hydrogenation in FGA reveals an increase of V_{oc} that can reach 20-80 mV depending on annealing temperature.

Polycrystalline silicon, Plasma, Hydrogenation, passivation, out-diffusion

1. Introduction

The ability to improve the performance of solar cells based on fine-grained polycrystalline silicon (poly-Si) layers deposited by thermal CVD by means of hydrogen passivation has received more attention in recent years [1, 2]. There are several ways of introducing hydrogen in a material. The easiest way is to anneal a piece of semiconductor in a H_2 atmosphere. However, this technique does not seem to be efficient, because H_2 molecules are not usually found as moving species in solids [3]. Common techniques are ion implantation, mostly direct plasma exposure and remote-plasma exposure involving an electron cyclotron resonance (ECR) system [4, 5]. These techniques can passivate defects at grain boundaries, but they cause plasma damage to materials at the same time [5-7]. Thus, different plasma conditions have been optimized [5]. Electron cyclotron resonance plasma has been used widely and industrially for CVD and for etching in semiconductor processes. It has some excellent

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features, such as low pressure plasma generation and high ionization efficiency. Ditizio et al. [8] examined hydrogen passivation of grain boundaries in thin film poly-Si transistors by comparing a microwave involving an electron cyclotron resonance (MW-ECR) plasma and a RF plasma. Their results showed that the MW-ECR plasma was the most effective in passivating the electrically active defects due to large quantity of passivating species and low damage effects.

In this work, we examined the MW-ECR plasma hydrogenation of thin film polycrystalline n^+pp^+ silicon cells. Different operating parameters were varied such as the doping level of the emitter region, MW–ECR power and annealing temperature either under forming gas or nitrogen atmosphere. The main objectives are an efficient defects passivation of poly-Si and slight emitter damaging. The passivation effectiveness is witnessed through the open-circuit voltage of mesa structures on n^+pp^+ poly-Si films, while the etching process is monitored via optical interferometric microscope and sheet resistance of the n^+ emitter region.

2. Experimental

A schematic of the MW-ECR plasma system (Roth-Rau) used for such experiments has been shown elsewhere [5]. The hydrogenation experiments were carried out by changing the MW-ECR plasma power, operating at 2.45 GHz, and maintaining the treatment time constant for 60 min at the substrate temperature of 400°C. The gas pressure of plasma was 0.6 Pa at hydrogen flux of 30 sccm. In order to avoid out-diffusion of hydrogen during the cool-down phase, the plasma was maintained around 10 min until the substrate reached 280 °C.

The poly-Si films were formed onto thermally oxidized Si wafers and had the similar structure characteristics reported in [9, 10]. The layers consisted of stack of 0.5 µm of p^+ (5×10^{19} cm^{-3}) - 3.5 µm of p (3×10^{16} cm^{-3}) layers. The n^+- type emitter regions were obtained by phosphorous diffusion at a temperature of 850 or 900°C in a tube furnace for 60 min. The phosphorus sources are spin-on dopant solutions (noted P509 and P507) from Filmtronics. After the diffusion process, the samples were subjected to a 10% HF solution to remove the residual dopant oxide. An average sheet resistance of the n^+ emitter region of 30 Ω/□ was measured by the four-point probe technique. As for the solar cell structure, we used the side-contacted mesa. Access to the base and BSF was made by reactive ion etching (RIE), where a gas SF_6 etches the n^+p with a rate of 1.6 µm/min, thus forming a mesa cell. Note that this study is related to the n^+pp^+ mesa structures without metallic evaporated contacts and without antireflection coating. The samples were then loaded in a Roth-Rau reactor for MW-ECR hydrogen treatment. The passivation effect was monitored mainly through the open-circuit voltage measured on mesa-type cells. Finally, some samples were subject to thermal annealing under forming gas (10% H_2 and 90% N_2) or under nitrogen ambient.

3. Results and discussions

3.1 Effect of MW-ECR plasma hydrogenation

The MW-ECR plasma hydrogenation technique was used for the purpose of an efficient defects passivation of poly-Si and reduction of surface damage of the emitters. The measured V_{oc} of the as-deposited silicon film were 180 ± 10 (mV) for P509 and 220 ± 10 (mV) for P507 based emitters mesa-structure. Figure 1 plots the measured open-circuit voltage versus MW-ECR plasma power of the n^+pp^+ mesa-structures. After 1 hour of MW-ECR plasma hydrogenation at 400°C, a significant and continuous increase of V_{oc} is observed for both levels of emitter doping. For a MW power of 650 W, V_{oc} reached 368 mV. This enhancement in V_{oc} is due to the passivation of defects states at the grain boundaries and suppression of the band bending, which act as barriers for majority carriers and recombination sites for minority carriers. This result is in good concordance with those reported in [8, 11, 12]. According to Youn et al. [13], the electrons, in MW-ECR plasma under low pressure, act as the agents that absorb the microwave energy; the ionization of hydrogen species will occur by a collision with the energetic electrons, resulting in the formation of H^+_3 ions and H^+ ions. Since H^+ ions have a much smaller recombination rate in comparison with H_3^+ ions, they become a dominant fraction in the hydrogen plasma [14]. With increase in microwave power, more and more H_2 molecules could be excited, dissociated and ionized, leading to an increase in both hydrogen ions and electron densities. The incident ions impinging the sample surface in contact with plasma is usually caused by the divergent magnetic field and the sheath potential originating from the differences in ion and electron velocities. The increased availability of atomic hydrogen ions reaching the sample surface with increasing microwave power and its higher mobility in silicon give rise to an increased passivation at lower pressure. Based on

hydrogen diffusion coefficient data [15], the penetration depth of hydrogen H^- in the n-silicon layer and H^+ and H° in the p-silicon layer can be estimated to be 68.4 µm, 74.6 and 130 µm, respectively. This means that the solubility of hydrogen in silicon is reached under the selected conditions of MW-ECR plasma hydrogenation. However, because of the type of the charges, n^+-type region in the structure used for the V_{oc} measurements could hinder the diffusion of the hydrogen atoms through the whole sample and therefore could reduce the passivation effectiveness of defects. Another road that may be influence the hydrogen diffusion in polysilicon is the presence of oxygen. It has been often suggested that the high electrical activity of grain boundaries in polysilicon deposited at high temperature is linked to decoration by oxygen atoms [16, 17]. The origin of the oxygen is probably from the bulk and/or from the surface or other defects [17]. In this case H will diffuse slowly because the presence of oxygen lowers the propensity for generation of vacancies [18, 19].

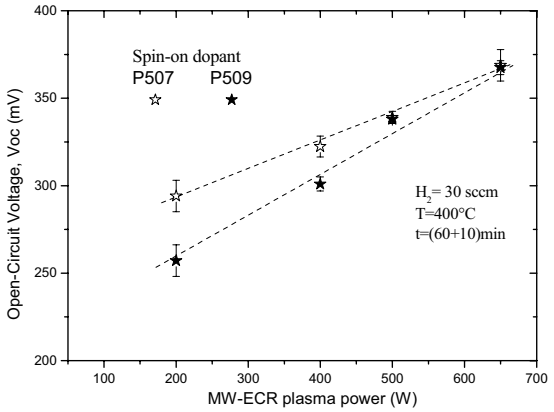

Figure 1. Influence of MW-ECR plasma power on open-circuit voltage measured on the n^+pp^+ mesa cells. The hydrogenation conditions are indicated.

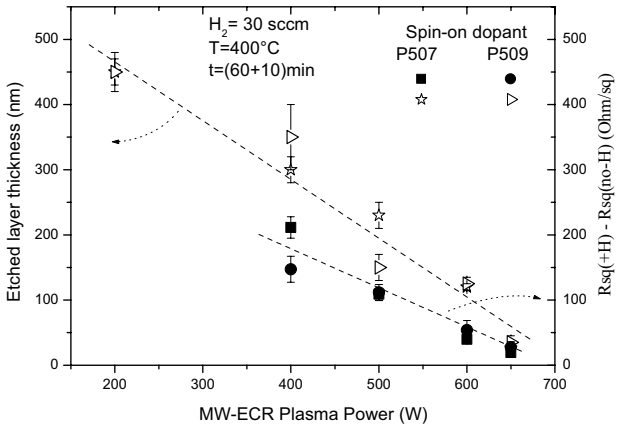

Figure 2. Etched layer thickness and the difference in emitter sheet resistance without and with hydrogenation versus MW-ECR plasma power as a function of the plasma power

Measurements of the emitter sheet resistance of the n^+pp^+ structures by the four-point probe technique showed an increase by a factor of 1.5 to 7 after MW-ECR plasma hydrogenation. Before hydrogenation, a sheet resistance value of 30 Ω/□ was measured for both emitters. In figure 2, the difference in emitter sheet resistance before and

after hydrogenation decreases when the MW-ECR plasma power increase. A slight increase is observed at 650 W for both levels of emitter doping. The enhancement of the sheet resistance can be correlated to the etching of the emitter region. To evaluate accurately the etched layer thickness due to the hydrogenation we have applied the plasma process on n^+pp^+ structure. Part of the sample was covered by a piece of silicon which play a role of mask while the other is exposed to the plasma. The step due to etching was measured by optical interferometry. The data are plotted in figure 2. First, a strong linear decrease relationship is observed between the etched silicon thickness and the MW-ECR plasma power. Second, a good correlation is observed between the increase of the difference in sheet resistance values without and with hydrogenation and the etched silicon thickness. We can see for example that an increase of sheet resistance by 20 and 110 Ω/□ after hydrogenation corresponds to an etching of about 25-35 nm and 300-350 nm emitter thickness measured by interferometry microscope at 650 and 400 W, respectively. However, for 200 W and for both levels of emitter doping, the total thickness of the emitter was almost completely etched and the four-point probe technique was not valid to give a correct measure of the emitter sheet resistance.

3.2 Post-hydrogenation under forming gas annealing (FGA)

In order to gain better understanding of effects of forming gas annealing on open-circuit voltage of fine grained silicon solar cells, thermal annealing under forming gas (10% H_2 + 90% N_2) were carried out on samples already hydrogenated by MW-ECR plasma. These samples will be referred later as MW+FG. The temperatures of accumulative annealing process were varied from 100 to 800°C during 30 min in a furnace tube at atmospheric pressure. The data are plotted in Fig. 3. After post-hydrogenation treatment in FG at moderate temperatures (e.g. 200-350°C), it can be seen a strong improvement in Voc for samples pre-hydrogenated before by MW-ECR plasma at 500 W and 300 W. Indeed, an increase of 40 and 80 mV was recorded on the 500 W and 300 W treated samples, respectively. For the 300 W case, the open circuit voltage reaches a value of 350 mV at 350°C. This observed increase in Voc is much more moderated for the samples pre-hydrogenated by MW-ECR plasma at 650 W and post-thermal treated in FGA at temperatures below 350°C. For high annealing temperatures (> 350°C) Voc drops abruptly to low values, followed by a slight increase starting at 500°C. A nearly total recovery of the open circuit voltage to the non-hydrogenated value is observed at 800°C.

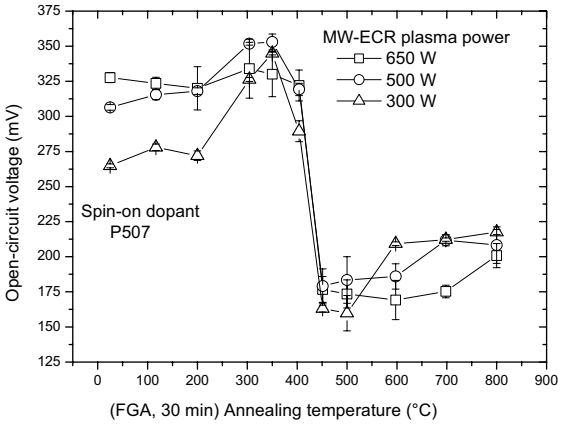

Figure 3. Open-circuit voltage versus forming gas annealing temperature of MW-ECR plasma hydrogenated n^+pp^+ poly-Si mesa structures. The FG annealing time is 30 min.

The observed increase in open-circuit voltage in the temperature range 200-350°C can be due either to the structure change at the grain boundaries, to thermal activation of residual hydrogen in the samples or to diffusion of hydrogen from the FG ambient into the n^+pp^+ mesa structures leading to an additional passivation of defects. To clarify which of these processes is responsible for the observed behavior, mesa-cell structures n^+pp^+ were simply thermally annealed at 100 to 800°C in nitrogen atmosphere (NA) or in forming gas (FG) during 30 min. The

resulting Voc values are compared to those measured on hydrogen plasma and thermal annealed structures. The results are given in figure 4 for NA and FGA post-treatments respectively.

As can be seen in Fig. 4, the thermal annealing of the n^+pp^+ structures at T < 350°C under pure nitrogen did not result in an improvement in Voc while a little increase is observed for the pre-hydrogenated MW plasma samples. However, at higher annealing temperatures a continuous decrease in V_{oc} is observed for the latest samples whereas a slight increase ($\Delta V_{oc} \sim 10$ mV) is detected for non pre-hydrogenated samples. On the other hand, figure 4 shows an increase in V_{oc} of about 25 after a process of FGA on samples not subjected to a hydrogenation plasma treatment. It is therefore clear that the observed increase of open-circuit voltage (Fig. 3) is due to the passivation of defects by hydrogen diffusion from the ambient of forming gas into the n^+pp^+ mesa structures. Passivated defects become more and earlier reactivated in hydrogen atmosphere. Indeed, the decrease of V_{oc} occurs at 450°C under thermal annealing in N_2 compared to 400°C under FGA atmosphere for samples pre-hydrogenated by MW-ECR plasma.

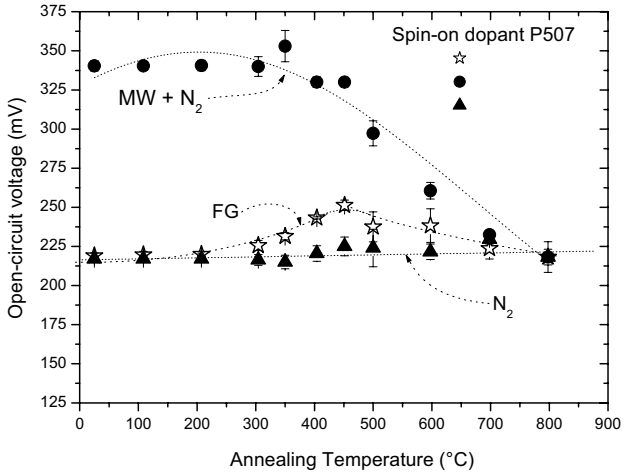

Figure. 4. Open-circuit voltage vs annealing temperature under forming gas or pure nitrogen of hydrogenated and non-hydrogenated n^+pp^+ poly-Si mesa structures. The annealing time is 30 min.

Several researchers [20, 21] have reported that the performance of some low-cost silicon solar cells improves upon annealing in forming gas atmosphere and that hydrogen is responsible for the improvement. As the thermal annealing under neutral gas does not produce the same effect, this is consistent with former statements.. Furthermore, Sapori et al. [19] have showed that the amount of hydrogen diffusing into the silicon bulk increases with increasing surface damage, which is responsible for the dissociation of molecular hydrogen and surface solubility. Thus, the increase in the open-circuit voltage observed in our study is due to the passivation of defects induced by hydrogen atoms diffusing into the bulk of material via surface damage caused during MW-ECR plasma hydrogenation process. It was also reported that excessive hydrogenation induces defects formation such as Si-H_2 inside the grains rather than at grain boundaries and the dissociation of such Si-H_2 defects was observed at annealing temperature of 450°C [22]. This ensures that the observed abrupt decreasing of V_{oc} for samples post-hydrogenated in FGA can be assigned to the formation of Si-H_2 defects. In addition, the increase of annealing temperature leads to the out-diffusion of hydrogen. Thus, a density of defects became larger than those before hydrogenation and subsequent thermal annealing was probably sufficient to cure a part of damage.

4. Conclusion

We have investigated the effect of MW-ECR plasma hydrogenation on the electronic properties of n^+pp^+ mesa structure solar cells made on fine-grained polysilicon films. We have shown a large improvement of the open-circuit voltage and a slight damage of the emitter surface using the MW-ECR plasma power at 650 W. However, the

passivation and etching effects depend quantitatively on the emitter initial doping level. Post-hydrogenation in FGA reveals an increase of Voc which can reach 20-80 mV and is more effective when the surface is more damaged.

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