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On the effects of hydrogenation of thin film polycrystalline silicon: A key factor to improve heterojunction solar cells



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ABSTRACT

The hydrogen plasma passivation of thin film polycrystalline silicon (pc-Si) was investigated in conjunction with plasma texturing process to make efficient heterojunction solar cells. The pc-Si layers were first treated using direct and remote hydrogen plasma technologies. The heterojunction solar cells were then fabricated by subsequent deposition of i/n^+ a-Si:H. Hydrogenation at high temperature (610 °C) results in enhanced dissolution and diffusion of hydrogen in pc-Si by a factor of about 3 and 4, respectively, in comparison with those at low temperature (420 °C). The hydrogen atoms in the pc-Si layer mainly bond to the silicon dangling bonds and form complexes with dopant atoms. In addition, platelets defects are generated by the hydrogen plasma in the sub-surface region of pc-Si hydrogenated at 420 °C and cause higher saturation current in the space charge region whilst they form in the region deeper than 1 μm at 610 °C. Removal of the platelets using SF₆/N₂O plasma post-texturing after low-temperature hydrogenation not only enhances the short circuit current but also improves the open circuit voltage and the fill factor simultaneously. Combining plasma pre-texturing with high-temperature hydrogenation, the best 2 μm-thick pc-Si heterojunction solar cell reaches an efficiency of 8.54%.

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1. Introduction

The mainstream of the current photovoltaic technology is based on silicon wafer solar cells [1]. Thin film polycrystalline silicon (pc-Si) has attracted a lot of attention in the field of photovoltaics in recent years due to its capability in reducing the material usage and eliminating the costly and polluting wafer production process [2–4]. Inline manufacturing from crystalline Si to modules and high energy conversion efficiency potentially comparable to wafer-based solar cells are projected by this technology. The produced electric power per gram of silicon can increase by 100 times by using pc-Si [5]. A key challenge for this technology is to obtain a pc-Si layer with sufficient material quality to provide high open-circuit voltage (V_{OC}). Many methods have been applied to prepare high quality pc-Si layers such as chemical vapor deposition (CVD) [6], solid-phase crystallization (SPC) [7], aluminum induced crystallization (AIC) [8], laser crystallization (LC) [9] and e-beam crystallization [10]. Regrettably, all these materials encounter some inherent material limitations,

including the large grain boundary areas and high density of intragrain defects in pc-Si, which act effectively as recombination centers. Therefore, the highest demonstrated pc-Si solar cell efficiency is still below 10.5% so far with V_{OC} of only 492 mV [11].

To improve the efficiency of thin film pc-Si solar cells the aforementioned recombination has to be inhibited to the greatest possible extent. Many works have focused on hydrogen plasma treatment of pc-Si layer, commonly referred to as ‘hydrogenation’ [12–15]. This technique has been proven efficient in passivating the silicon dangling bonds at the grain boundaries and at the intragrain defects [16,17]. Another promising technique is to use heterojunction by depositing amorphous silicon (a-Si:H) emitter on pc-Si, which further reduces the recombination at the junction and leads to higher V_{OC} [18]. In addition, light trapping structure is essentially important for enhancing the cell performance since the light absorption in such thin silicon layer is very weak. Due to the thickness limitation texturing process for wafers cannot be applied to pc-Si directly.

The hydrogen atom has a small radius and can easily migrate into the silicon from the gas phase. It exists in several states in silicon: (1) bound to a dangling Si bond at a defect site, such as grain boundaries or trapped at an impurity atom; (2) molecular hydrogen (H₂) occupying the tetrahedral interstitial (T_d) site;

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(3) atomic hydrogen occupying the so-called M site [19]. The hydrogen atom bonded to Si at the defect sites saturating a dangling bond has the lowest potential energy [20], which is the mechanism behind the hydrogen passivation for pc-Si. It was found that the density of states introduced by the dangling bonds in the pc-Si decreased by more than one order of magnitude after hydrogen passivation [16,17]. On the other hand, plasma hydrogen reacts with crystalline silicon resulting in formation of new defects. For instance, hydrogen plasma introduces surface bombardment by the ions (i.e. surface damage), which causes degradation in V_{OC} of the pc-Si solar cell [21,22]. It is also well known for silicon that hydrogenation induces a specific type of defect named hydrogen platelet in sub-surface regions [23]. They are in fact microcracks between two adjacent planes of Si atoms stabilised by hydrogen and are filled with hydrogen molecules formed via the coalescence of H atoms. These defects are electrically active and introduce gap states probably by the lattice strain [24]. From the device point of view, these defects should be harmful and will increase the Shockley–Read–Hall (RSH) recombination. However, so far no existing literature has been able to discern the effect of hydrogenation-induced platelets on the solar cell level.

In this paper, we applied different types of hydrogen plasma on pc-Si prepared by AIC process. The relation between the hydrogenation of pc-Si and the solar cell performance was studied. The formation of hydrogenation-induced platelets in pc-Si was studied using Raman spectroscopy and transmission electron microscopy (TEM) measurements. By using a heterojunction amorphous silicon (a-Si) emitter, we observed the direct influence of the hydrogen platelet defects on the pc-Si solar cell parameters. At the same time, we demonstrate an approach to remove these defects using SF_6/N_2O plasma texturing [25]. This approach also forms effective light trapping structure on the pc-Si surface at the same time. Through these studies, we show that the simultaneous improvement for both the V_{OC} and the short circuit current (J_{SC}) can be realised with optimised combination of hydrogenation and plasma texturing.

2. Experimental section

2.1. Fabrication of thin film polycrystalline Si

Thin pc-Si seed layers were made via the aluminum-induced crystallization process [8]. First, bilayers of 200 nm thick Al and 230 nm thick a-Si were deposited on flowable oxide (FO_{x-25}) smoothed alumina substrates by electron beam evaporation. After the deposition, the samples were annealed under nitrogen ambient at 500 °C for 4 h. During this annealing, the a-Si crystallises into pc-Si and both layers exchange their places. The Al layer was etched away selectively using phosphoric acid afterwards. Epitaxial layers were deposited on the AIC seed layers by thermal atmosphere pressure CVD (ASM Epsilon 2000) at 1130 °C. Double layers of boron-doped p^+ and p silicon were grown with doping densities of $5 \times 10^{18} \text{ cm}^{-3}$ for the p^+ layer and 3×10^{16} – $1 \times 10^{17} \text{ cm}^{-3}$ for the p layer. The p layer thickness is 2–3 μm and the p^+ thickness was fixed to 0.5 μm .

2.2. Hydrogen plasma treatment and surface texturing

The pc-Si layers were passivated using two different plasma technologies: direct plasma hydrogenation (denoted as DPH) and remote plasma hydrogenation (denoted as RPH). In the first case, a direct plasma enhanced CVD system (Oxford Plasma Technologies Plasmalab 100) with an RF-source (13.56 MHz) was used. The samples received 30 min of hydrogen plasma exposure at 420 °C. The plasma power used was 20 W, corresponding to a power

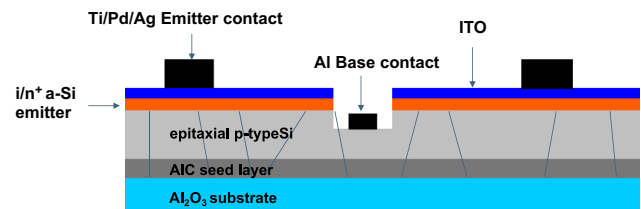


Fig. 1. Thin film pc-Si solar cell structure [8]. The surface texturing is not shown.

density of 0.06 W cm^{-2} . Then they were cooled down in the system for 30 min while keeping the plasma ignited. In the other case, a research tool with an inductively coupled remote plasma source from Advanced Energy was used. The samples received hydrogen plasma exposure from the remote source for 8 min at 610 °C and then for a further 20 min during cool-down. The plasma power used for the treatment was 3300 W, but the power density is not applicable in this remote system.

For light trapping the pc-Si layers were dry-textured in a prototype reactor from Secon using micro-wave antennas as the power source and a mixture of SF_6 and N_2O as etch gases at room temperature [25] (denoted as ‘tex’ for simplification). Typically, around 1 μm of pc-Si was removed from the surface.

2.3. Fabrication of solar cell

After the hydrogenation and/or texturing, a stack of intrinsic and doped amorphous silicon layers ($i/n^+ \text{ a-Si:H}$) were deposited in the Plasmalab 100 system to form p – n junction. The resulting heterojunction layer was around 16 nm thick with 8 nm for each layer. Then 75 nm of indium tin oxide (ITO) layer was sputtered onto the a-Si to serve as the transparent front contact and the anti-reflection coating. Interdigitated metal fingers were formed by photolithography and wet chemical etching in combination with metal evaporation. Details of the processing can be found in Ref. [8]. Fig. 1 shows schematically the cross section of the finished cells. All the solar cells were measured under 1000 W m^{-2} AM 1.5 Global spectrum using WACOM2 solar simulator. Some of them were also measured using the Sinton Suns- V_{OC} system.

3. Results and discussion

3.1. Direct and remote hydrogenation

To study the impact of hydrogenation on the performance of thin film pc-Si solar cells, solar cells were prepared without and with direct or remote plasma hydrogenation (denoted as DPH and RPH, respectively). The average electrical parameters of the cells are shown in Table 1. The average efficiency of the non-hydrogenated cells (3.7%) was significantly lower than those of the hydrogenated cells (>5%). The open circuit voltage V_{OC} and the short circuit current J_{SC} are much lower for non-hydrogenated cells, which indicates a lower material quality without hydrogen passivation. Furthermore, the fill factor (FF) of the non-hydrogenated cells is also lower, due to the higher series resistance (R_s). This is reflected in the current–voltage (I – V) curve of the representative cell shown in Fig. 2a. It has been proved that hydrogenation can decrease the concentration of defects, suppress the band bending at grain boundaries and increase the Hall mobility of majority carriers [26]. Standard two-diode model fits to Suns- V_{OC} data were performed to extract the saturation current density J_{01} and J_{02} for each diode. Generally, J_{01} is related to recombination in the bulk of the pc-Si with $n=1$ and J_{02} related to recombination at grain boundaries and in the space charge region (SCR) with $n=2$. On the other hand, the local ideality factor n at

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