# Impact of Process Steps on the Performance of Heterojunction Solar Cells



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## 1 Introduction

Solar cells based on n-type crystalline silicon wafers with a passivated by hydrogenated intrinsic amorphous silicon surface and doped amorphous silicon (SHJ) layers have a number of advantages over cells made using conventional PERC technology [1]. These are a small number of process steps, a low thermal budget, and the possibility of reducing the thickness of the wafers. The most unique feature of this type of solar cells, which determines their high efficiency, is the layer of intrinsic amorphous hydrogenated silicon (a-Si:H). During the growth of the layer on the surface of the silicon wafer, the number of defects decreases, which leads to a decrease in recombination at the silicon-amorphous silicon interface (the so-called passivation). To obtain an efficient solar cell, it is important to get a a-Si:H layer that creates efficient passivation and efficient carrier transport, and to maintain these properties when exposed to subsequent technological steps. To create effective passivation and charge transfer, various techniques are used, such as the use of combined compositions with amorphous hydrogenated silicon oxide (a-SiOx:H) [2, 3], amorphous hydrogenated silicon carbide (a-SiCx:H) [4], high-temperature treatments [5], porous layers of intrinsic silicon, bilayers with different density [6], bilayers [7], and additional hydrogen plasma treatments [8]. Overlaying doped layers affects surface passivation, too [7]. The choice of PECVD process parameters: gas pressure, RF power, and dilution with hydrogen are associated with minimizing defects in the form of dangling bonds and preventing the formation of silicon epitaxial growth [9]. High ordered layer of intrinsic hydrogenated amorphous silicon with lower void density is beneficial to the solar cell parameters [10-12], but parameters of the layer deposition are such that any fluctuation can lead to epitaxial

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growth. Such reasons as interaction with holders and vacuum cups, incorrect timing after final HF dip until amorphous silicon deposition and overheating lead to the disappearance of silicon-hydrogen bonds on the wafer surface and create a starting point for epitaxial growth. The deposition of amorphous silicon bilayers, where the first layer is thin and characterized by a low density, and the second layer with a correspondingly high density, makes it possible to obtain high cell efficiency [13], but requires very careful surface preparation before deposition [14] and appropriate handling. Exposure to radiation during the sputtering of a transparent conductive oxide, mechanical stress during screen-printing of conductive pastes, laser radiation when opening contact windows in a mask for copper plating can damage the layers of amorphous silicon. Subsequent annealing increases the minority carrier lifetime, but the properties of the amorphous silicon layer will differ from the original ones. Therefore, it is necessary to carefully take into account the impact of process steps on the layers of amorphous silicon and noncontact nondestructive measurement methods to create high-efficiency solar cells [15, 16].

This work is devoted to the investigation of impact of process steps, such as a hydrogen plasma treatment, transparent conductive oxide sputtering and subsequent annealing, laser openings of contact window on the properties of a-Si:H layers and solar cells performance. We investigated impact on the level of surface recombination, the lifetime of minority charge carriers, layer microstructure, and solar cell parameters.

#### 2 Experiment

For the manufacture of solar cells, n-type silicon wafers doped with phosphorus,  $156.75 \times 156.75$  mm in size,  $160 \mu$ m thick, with (100) orientation, with a resistivity of 1–5 Ohm cm were used.

For material characterization, layers of intrinsic amorphous silicon were deposited on both sides of polished c-Si wafer, in orientation (111), thickness of 560 microns.

After the process of removing the damaged layer by a KOH solution and texturing by KOH-based solution to obtain pyramids of 4–5  $\mu$ m in size, the wafers were treated in solutions of H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>2</sub>O<sub>2</sub> and dipped in diluted HF to strip off the silicon oxide. To determine the parameters of PECVD process during hydrogen plasma treatment, a series of intrinsic hydrogenated amorphous silicon layers were deposited. Deposition was conducted in an Applied Materials Precision 5000. The P5000 is equipped with parallel plate type reactor RF-PECVD (13.56 MHz excitation frequency). In this work, we used relatively high deposition rate of amorphous silicon, above 1.6 nm/s, and high hydrogen dilution. As a result of meeting two conditions such as a high deposition rate simultaneously with a high degree of dilution with hydrogen, a high-density electronic quality layer is generated, while the epitaxial growth of this layer is prevented. We set the ratio of silane to hydrogen as 1 to 5 at a pressure of 3.2 Torr and an RF discharge power of 250 mW/cm<sup>2</sup>. Processing with hydrogen plasma is a rather multifactorial process and the choice of the correct parameters is difficult. We were based on the idea of obtaining a relatively small number of ions with sufficient energy for implantation in the near-surface region. In this way, the etching rate can be reduced, which is critically important given the small thickness of the amorphous silicon layer and the relief of the textured surface. The power density and process pressure of hydrogen plasma treatment were chosen as the determining parameters and varied from 40 to 180 mW/ cm<sup>2</sup> and from 2 to 3.2 Torr, respectively. The effective lifetime of minority carriers was chosen as an indicator and characterized by the QSSPC method using a Sinton WCT-120 flash tester. The resulting dependencies are shown in Fig. 1a. The best set of parameters is defined as a pressure of 2 Torr and an energy of 80 mW/cm<sup>2</sup>.

Based on the assumption that amorphous silicon bilayers lead to better parameters of the intrinsic amorphous silicon layer [13], at the next stage, the thickness of the first layer was determined, after which this layer was subjected to hydrogen plasma treatment. The processing sequence is as follows—deposition of the first layer, starting with a thickness of 2 nm, then treatment with hydrogen plasma for 60 s, then deposition of the second layer until a total layer thickness of approximately 10 nm is obtained. As shown in Fig. 1b, at a small thickness of the amorphous layer, degradation occurs due to hydrogen plasma treatment, apparently caused by etching of amorphous silicon to a crystalline surface and subsequent epitaxial growth. At layer thicknesses of more than 4 nm, the layer parameters improve, the best lifetime is achieved in the range of 5–6 nm.

The following series of samples were fabricated with intrinsic and doped amorphous silicon layers using textured and polished substrates, one series with hydrogen plasma treatment, the other without treatment. The layers deposited in this process had a thickness of 10 nm for intrinsic silicon layers, for doped with boron—5 nm, for doped with phosphorus—15 nm. A Bruker IFS66 spectrometer was used to perform Fourier transform infrared spectroscopy of SI-H bonds microstructure of amorphous silicon layers on polished wafers. The same layers were deposited on both sides of the wafer to get decent signal-to-noise ratio.



**Fig. 1** (a) Dependence of minority carrier lifetime at injection level of  $e15 \text{ cm}^{-3}$  on the RF power in chamber for different pressure levels (2, 2.6, 3.2 Torr). (b) Lifetime in dependence of the first layer thickness



Fig. 2 Laser openings with different fluence: (a) 0.8, (b) 0.9, (c) 1 J/cm<sup>2</sup>

Then, two groups were formed, for one group, 75 nm thick ITO layers were deposited by magnetron sputtering of a target consisting of 90% In and 10% Sn, and for the other group, 40 nm layers were deposited. MRC943 was used for sputtering. Layers of a selective seed layer of different thicknesses were formed on substrates with an ITO layer 40 nm thick, and then a layer of silicon nitride 40 nm thick was deposited. Further, these samples were used to open contact windows with ultrashort laser radiation pulses and to study the protective properties of the seed layer and the nature of damage to the amorphous silicon layer. To open the contact windows in the silicon nitride layer, we used an Avesta Theta 6 laser with a wavelength of 1033 nm, a power up to 6 W, a pulse duration of 270 fs TEM00, with a frequency of up to 100 kHz, and a Raylase scanning system, spot size 10 micron. The opening of the contact windows was performed with different fluence ranging from 0.5 to 2 J/cm<sup>2</sup> with a step of 0.1 J/cm<sup>2</sup> (Fig. 2a-c). For characterization, a fixed system with a microscope objective was used, which makes it possible to obtain a focused spot size of about 5 µm at the single pulse mode. For completing solar cells, copper plated contact grid was formed. I-V characteristics of fabricated cells were evaluated using a solar simulator under standard test condition (AM 1.5, 1000 W/m<sup>2</sup>, 25 °C).

## **3** Results and Discussion

The etching rate of the amorphous silicon by hydrogen plasma is relatively higher than the etching rate of the areas of epitaxial growth. Thus, the area of the epitaxial growth regions increases after etching with hydrogen plasma, which negatively affects the subsequent growth of the amorphous silicon layer. As result, the quality of passivation deteriorates. Reduce in the etching rate with decreasing power and pressure is beneficial. Since the etching rate can exceed 1 nm/min, the process time is limited by the thickness of the amorphous layer. The choice of the treatment parameters with hydrogen plasma should be based on the following assumptions about the energy and concentration of hydrogen, as follows:

- 1. Avoid the appearance of a large number of low-energy hydrogen atoms providing etching.
- 2. It is preferable to obtain a small number of hydrogen atoms with a high enough energy so that they can penetrate into the near-surface region and then diffuse into the volume at the maximum allowable temperature.

Since the process of hydrogen plasma treatment for amorphization and hydrogenation of the layer is limited by the simultaneous etching process and etching rate can exceed 1 nm/min, especially of the edges and tips of the pyramids, it is necessary to search for compromise processing parameters. Si-H bonds incorporated in amorphous silicon in different manners. Si-H<sub>2</sub> bonds form nano-sized voids, while Si-H bonds are isolated. The FTIR spectra of intrinsic amorphous silicon layer and intrinsic amorphous silicon layers with intermediate hydrogen plasma treatment are shown in Fig. 3a. Gaussian-distributed absorption peak centered at wave numbers of 2000 cm<sup>-1</sup> represents Si-H bonds (low-stretching mode) and peak at 2100 cm<sup>-1</sup> represents Si-H<sub>2</sub> (high-stretching mode). Absorption by high-stretching mode increases noticeably after hydrogen plasma treatment. This means that the density of nanovoids in the amorphous silicon layer increased and this effect had a positive influence on the surface passivation. It is worth to note that hydrogen dilution prevents creation of Si-H<sub>2</sub> bonds during the applied process of deposition of ordered



**Fig. 3** (a) FTIR spectra of amorphous silicon with (+) and without hydrogen plasma treatment, fitted with Gaussian distributed peaks of absorption of Si-H<sub>2</sub> at wavenumber 2100 cm<sup>-1</sup> and Si-H at wavenumber 2000 cm<sup>-1</sup>. (b) FTIR spectra of amorphous silicon before and after sputtering of transparent conductive oxide and sintering, fitted with Gaussian distributed peaks of absorption of Si-H<sub>2</sub> at wavenumber 2100 and Si-H at 2000 cm<sup>-2</sup>

intrinsic amorphous silicon. Layer with lower void density is preferable as a carrier transport channel. Since a layer of disordered intrinsic hydrogenated silicon with a high density of  $Si-H_2$  bonds is not an effective carrier transport channel, its thickness is determined by the need to find a balance between the level of passivation and series resistance.

The change in the ratio of the number of Si-H and Si-H<sup>2</sup> bonds allows us to conclude that damage after ITO sputtering has a complex nature. Surface is damaged with high-energy argon ions, volume of the layer is damaged by UV radiation. Subsequent annealing leads to a redistribution of hydrogen in the layers of amorphous silicon (Fig. 3b). While the level of Si-H<sub>2</sub> bonds decreases insignificantly, the level of Si-H decreases largely, while Voc increases, which indicates a crystallization process without an increase in defectiveness, while maintaining the structure of nanovoids with boundaries passivated by hydrogen.

The opening of a contact window in a thin dielectric layer is possible by partial removal of the underlying layer. When exposed to a femtosecond laser pulse, because of multiphoton absorption, the ionization of the dielectric layer and the underlying metal layer occurs, after which energy is transferred to the lattice. Destruction of the lattice and evaporation occurs. The mechanism of removal of the dielectric film from the surface seems to be mainly associated with the removal of the evaporating metal by the flow. The nuclei of the process are local point defects, in which there is a high concentration of energy and the formation of an outflowing jet of evaporated metal begins.

An analysis of SEM images allows us to establish that for a textured surface of silicon wafer, the tips and, with a further increase in the energy density, the edges of the pyramids act as the starting points for the ablation process due to a faster increase in temperature and the formation of an outflowing jet. The very process of removal of the dielectric layer is determined by a combination of two mechanisms—the ablation itself and the explosive destruction of the dielectric layer by an evaporating metal flow. The SEM image (Fig. 2c) shows that the flow of the evaporated metal deformed the edges of the dielectric coating around the crater contour.

Damage to the layer of amorphous silicon occurs when the thickness of the seed layer is insufficient. It has been experimentally established for this type of structure, when using silver, that the layer thickness should exceed 400 nm.

At the same time, as the fluence increases, the size of the damaged area does not grow linearly (Fig. 4), which apparently indicates that the damage occurs in places where energy is concentrated—at the tops of the pyramids and on their edges. In these places, the energy level exceeds the energy level on the plane by a factor of 2; therefore, an increase in energy to a lesser extent does not lead to a proportional increase of the damaged area.

Thus, by changing the surface geometry, one can significantly change the level of admissible fluence.



Fig. 4 Damage area in dependence of the fluence

### 4 Conclusion

The conducted research has the following results:

- Hydrogen plasma treatment makes it possible to amorphize and hydrogenate an amorphous silicon layer, thereby increasing the number of dihydride bonds and forming a layer structure with nanovoids.
- A layer of amorphous silicon with a large number of dihydride bonds is more stable to the effects of temperature and radiation during the manufacture of a solar cell than a layer with monohydride bonds.
- The optimal conditions for obtaining a stable, repeatable process of hydrogen plasma treatment of amorphous silicon layer are established.
- The process of removing the dielectric layer from the metal seed layer is determined largely by the geometry of the textured surface.

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