EPJ Photovoltaics **6**, 65301 (2015)
www.epj-pv.org
DOI: 10.1051/epjpv/2015002

Effects of process parameters on μc-Si$_{1-\mathrm{x}}$Ge$_{\mathrm{x}}$:H solar cells performance and material properties

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Received: 16 October 2014 / Received in final form: 9 January 2015 / Accepted: 21 January 2015

Abstract On our way to develop a very thin and highly efficient triple-junction thin-film solar cell in a-Si:H/μc-Si:H/μc-SiGe:H configuration and μc-SiGe:H single cell samples were prepared and characterized using an industrial relevant 13.56 MHz 0.5 nm/s process on an industrial like 30×30 cm^2 PECVD tool. To attain a better understanding of the μc-SiGe:H absorber we varied process pressure, germane flow, dilution and silane flow while looking at the electrical and material properties. By realizing a total absorber thickness less than 2 μm for high efficiency cell concepts in triple technology, our intention is to develop an industrial relevant process with attractive fabrication times by benefiting from the enhanced absorption of μc-SiGe:H compared to μc-Si:H.

1 Introduction

Beside low production costs and the usage of abundant raw materials, silicon based thin-film solar cells have the advantage to be built up as multi junction devices like tandem or triple junction solar cells. Comparing silicon solar cells based on wafer technology and thin film silicon solar cells, the advantages of the thin film variant are low energy payback time, better temperature coefficient, large area fabrication and mechanical stability. Therefore developing cheap thin film silicon solar cells with high efficiencies plays a key role.

Typical absorber thicknesses of a-Si:H single junction solar cells are 300–400 nm having very low production costs. However, amorphous silicon degrades under illumination (Steabler-Wronski effect, light-induced degradation (LID)) limiting the efficiency of single junction solar cells. To circumvent this effect, a-Si:H is used in tandem configurations as top cell paired with μc-Si:H as bottom cell i-layer material that does not degrade. Typical absorber thicknesses for tandem cell configurations are 200–250 nm for a-Si:H top cells and 900–1200 nm for μc-Si:H bottom cells.

For a-Si:H/μc-Si:H tandem cell configurations, stabilized efficiencies exceeding 12% were already demonstrated [1]. Recently, Kim et al. published a new efficiency record for silicon based thin-film solar cells which exhibits a stabilized efficiency of 13.4% and is based on the triple junction technology consisting of amorphous and microcrystalline silicon absorber layers [2].

Because of the poor absorption of μc-Si [3], the bottom absorber of triple junction solar cells has to be deposited very thick (>2500 nm) resulting in quite cost intensive industrial application due to corresponding long layer deposition times. There are different approaches to reduce the thickness of the absorber layer. Optimizing light trapping due to scattering structures at the front contact and thereby increasing the path length of light through the device is one of such options. Using novel back reflectors at the back interface is another. A different approach is to substitute conventional doped layers with more transparent oxygenated doped layers where more light reaches the absorber layer and increases the cell current densities enabling a reduced layer thickness. Another approach is to increase the absorption coefficient of the absorber material by alloying silicon with germanium. Matsui et al. introduced the usage of microcrystalline silicon germanium alloys (μc-SiGe:H) with increased absorption coefficient compared to μc-Si:H [4, 5].

This contribution addresses the development of μc-SiGe:H absorbers and their application as bottom absorber in triple junction configuration. It is part of a triennial research project based in the Photovoltaic Innovation Alliance established by the BMU (German Federal Ministry for the Environment) and BMBF (German Federal Ministry of Education and Research), that started in July 2011. Partners of Next Energy in that joint research project are the solar module manufacturer

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Inventux Solar GmbH, Hüttinger Elektronik GmbH & Co. KG, a manufacturer of generators for plasma deposition processes, and the Competence Centre Thin-Film and Nanotechnology for Photovoltaics Berlin (PvcomB). In this paper, we will present a comprehensive study of the effects process parameters of the intrinsic layer in a single μc-SiGe:H cell have on the material properties in terms of germanium content and crystallinity while also looking at the device performance. Finally we will compare our triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells with the triple solar cell type in a-Si:H/μc-Si:H/μc-SiGe:H configuration.

2 Experimental

All μc-Si:H and μc-SiGe:H bottom absorber and μc-SiGe:H single junction solar cells were deposited in pin sequence in a PECVD reactor from Leybold Optics at NEXT ENERGY for 30×30 cm^2 substrate size at substrate temperatures below 250 °C. The solar cells were deposited using a 13.56 MHz plasma excitation frequency at narrow electrode gap under high pressure. The intrinsic μc-Si:H and μc-SiGe:H layers were deposited under high power conditions with deposition rates above 0.5 nm/s.

10×10 cm^2 ZnO:Al coated glass served as substrate for the single junction cells. Ag back contact pads prepared by electron beam evaporation define test cell areas of 1 cm^2. For triple junction solar cells we applied a combination of a 80 nm thick ZnO:Al layer and an Ag layer as back reflector. ZnO:Al layers were prepared by magnetron sputtering.

After deposition all solar cells were annealed for 30 min at 160 °C, followed by IV-measurements. To keep the defined cell area at 1 cm^2 for the triple-junction cells, excess ZnO:Al was removed by etching with HCl.

Raman spectroscopy was performed on single μc-SiGe:H cells. The wavelength of the used laser light was 633 nm. IV-curves of solar cells under illumination (AM 1.5, 100 mW/cm^2, 25 °C) were measured under a continuous light (DC) sun simulator of class A (WACOM). For determining the external quantum efficiency (EQE) of μc-SiGe:H solar cells, monochromatic probe beams using RERA System equipment with wavelength from 300 to 1100 nm were used.

As presented in previous contributions [6,7], we developed a high-quality process for a μc-SiGe:H i-layers on a 15×15 cm^2 PECVD reactor and transferred this process to a small scale industrial PECVD tool which can deposit on 30×30 cm^2 substrates at higher tact times. To benchmark the obtained μc-SiGe:H i-layer quality on the 30×30 cm^2 PECVD tool, μc-SiGe:H single junction cells with an absorber thickness of 1.2 μm were deposited. As substrate rough ZnO substrates from Solayer were used. The p-layer consisted of 50 nm μc-Si:H doped with diborane. The n-layer consisted of 40 nm a-Si:H doped with phosphine. The cell area of 1 cm × 1 cm was determined by evaporating silver pads. The germanium content in μc-SiGe:H layer was determined by measuring the raman crystallinity and using the correlation of the shift of the 520 cm^{-1} LO-TO phonon resonance to smaller wave numbers to the germanium content in the layer as suggested by Alonso and Winer [8] using equation (1) below:

$$\omega_{\mathrm{Si-Si}} = 520 - 70x.$$

This was found to stay in good accordance to EDX measurements of μc-SiGe:H films [9]. The optimal germanium content in μc-SiGe:H i-layers was found to be 10% because incorporating more germanium leads to the formation of acceptor like states induced by germanium dangling bond defects that decrease the solar cell performance [10].

To gain a better understanding of the relation between the process parameters and the performance of the μc-SiGe:H absorber, different process parameters were varied and the impact on IV cell performance, germanium content and crystallinity was evaluated. The ultimate goal is to reach μc-SiGe:H absorber performances that are comparable to μc-Si:H absorbers in terms of fill factor and V_{oc} but excel in terms of generated current density.

3 Results and discussion

3.1 Germane flow variation

In the first study the germane flow of the μc-SiGe:H absorber was varied from 1.0 sccm to 1.6 sccm in steps of 0.1 sccm while all other parameters were kept constant. As seen in Figure 1, the increased flow of germane leads to an increased germanium content in the absorber by a factor of 6.3%/sccm. This steep increase can be attributed to the high gas utilization because of the lower dissociation energy of germane molecules compared to silane molecules. At the same time the crystallinity decreases from 80% to 71%. When increasing the germane flow the increased germanium contend introduces stress into the lattice and thereby reduces the crystallinity. Looking to the V_{oc} values of the cells in Figure 1, one can see a decrease in V_{oc} for a germanium flow up to 1.2 sccm. The crystallinity stays nearly constant in this range, but the germanium content increases. As alloying of μc-Si:H with germanium narrows the band gap and increases the carrier recombination rate it may be responsible for the change in V_{oc} [4].

The very steep change in crystallinity in the variation between $1.2 <$ germane flow < 1.4 sccm could account for the increase in V_{oc} values. A shift to a more amorphous phase and thus higher band gap over-compensates the effect of V_{oc} loss due to higher germanium content. At high and low germane flows the reverse happens: Raman-crystallinity stays constant, germanium content increases and the V_{oc} values drop. Since state of the art μc-Si:H single junction cells exhibit V_{oc} values of 500 mV or more, V_{oc} values for the μc-SiGe:H absorbers have to optimized with other process parameter variations in order to build efficient triple junction cells.

3.2 Silane flow variation

Increasing the silane flow from 21.5 sccm to 25.5 sccm (while keeping all other parameters constant) reduces

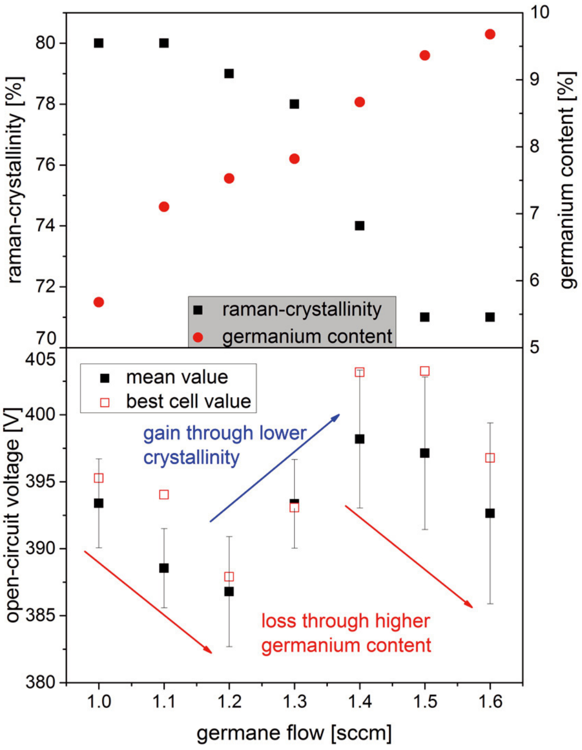

Fig. 1. Raman crystallinity, germanium content and V_{oc} values in relation to the germane flow of single μc-SiGe:H cells. Best cell values were taken from the best cells in terms of efficiency (true for all figures).

the raman crystallinity from 80% to 62% due to a larger amorphous volume fraction in the absorber. Comparing Figures 1 and 2 it should be remarked that changing the germane flow had a similar effect on the crystallinity but changing the silane flow did not have the same effect on the germanium content of the layer. The reason for the almost constant germanium content despite changes in crystallinity might be found in the low dissociation energy of germane. Splitting two hydrogen atoms from silane takes twice the energy compared to splitting two hydrogen atoms from germane [11]. Because of the high energy plasma used in microcrystalline depositions all available germane is dissociated and deposited. Changing the relation between hydrogen and silane in the plasma alters the crystallinity while still incorporating all germanium.

The linear decrease in crystallinity depicted in Figure 2 leads to a linear increase in V_{oc} values. The higher amorphous volume fraction shifts the band gap to higher energies without the additional influence of a great variation in germanium content.

Similar to the fill factor values of the germane flow variation (not shown) the fill factor values do not change with increasing silane flow (Fig. 3) and remain around 52%. The low value can be explained by the presence of germanium dangling bonds that act as acceptor like states. Since the presented values were deposited with a not optimized p-layer part of the low values can also be attributed to a reduced interface quality and insufficient internal field.

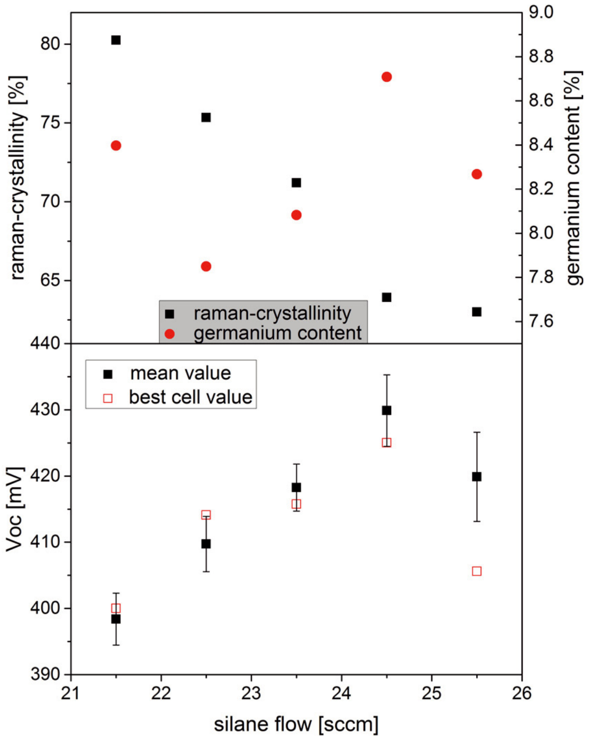

Fig. 2. Raman crystallinity, germanium content and V_{oc} values in relation to the silane flow of single junction μc-SiGe:H cells.

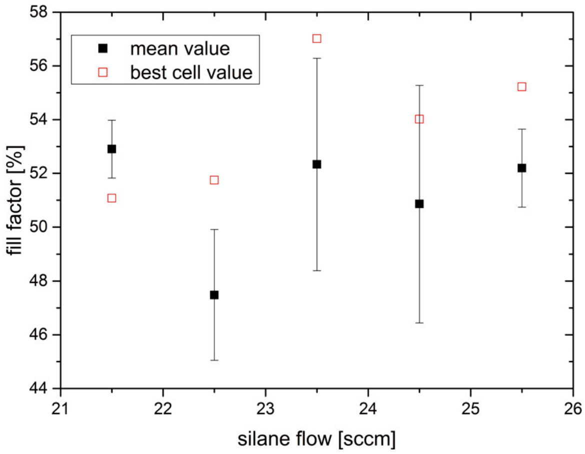

Fig. 3. Fill factor values in relation to the silane flow of single μc-SiGe:H cells.

3.3 Pressure variation

In addition to the germane and silane flow, the process pressure is a key parameter in μc-SiGe:H depositions.

As can be seen in Figure 4, the pressure was varied from 8.5 to 11 mbar. The germanium content is almost constant and varies only slightly between 8.3% and 8.7%. As the pressure increases, the crystallinity declines from 77% to 61%.

Comparing Figures 2 and 4 one can see that increasing the silane flow shows the same effect on crystallinity and germanium content as increasing the pressure: crystallinity decreases but germanium content stays constant.

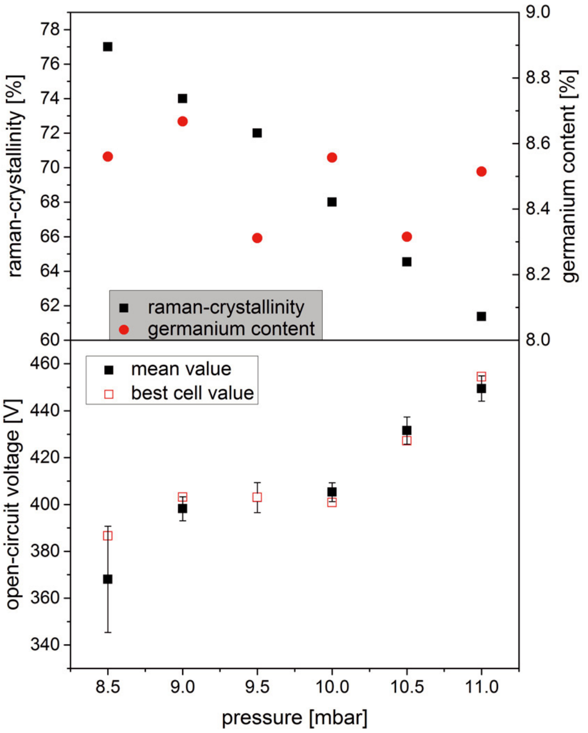

Fig. 4. Raman crystallinity, germanium content and V_{oc} values of single μc-SiGe:H cells in relation to the intrinsic layer process pressure.

The reduction of crystallinity has an enhancing effect on the open circuit voltage.

Because bad material quality will influence the shunt and series resistance, fill factor values are a good gage to estimate the material quality. Figure 5 shows a linear increase of fill factor values with increasing process pressure. Similar to the silane flow variation this parameter does not change the germanium content in the absorber. Comparing Figures 3 and 5, one can see that changes in the crystallinity due to process pressure variations are crucial to good fill factor values while a change in crystallinity through variation in the silane flow has no impact. The increased pressure leads to compact material and thereby reduces defect density of germanium dangling bonds [12].

3.4 Triple junction cells

To show the total cell thickness reduction potential in triple solar cells by the application of μc-SiGe:H bottom cells, we fabricated an a-Si:H/μc-Si:H/μc-Si:H triple-junction cell with a total cell thickness of 4.4 μm. As shown in Figure 6, the V_{OC} performance of the stacked cell is good with a value of 1.8 V resulting in a cell efficiency of 11.0%. Bringing such a device into industrial production is not very feasible, because production costs attributed to 4.4 μm total cell thickness and the corresponding deposition time would be very cost intensive.

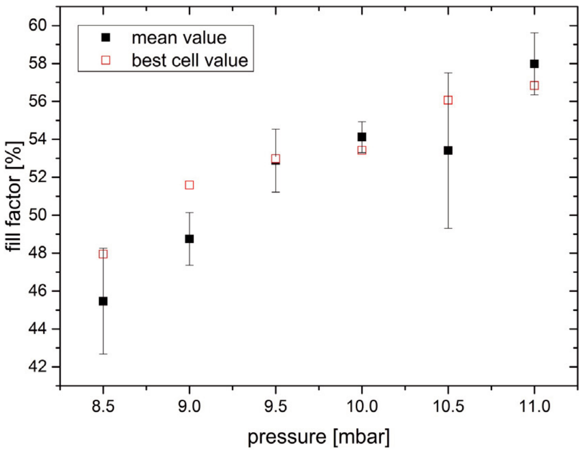

Fig. 5. Dependency of fill factor values on the increase of process pressure.

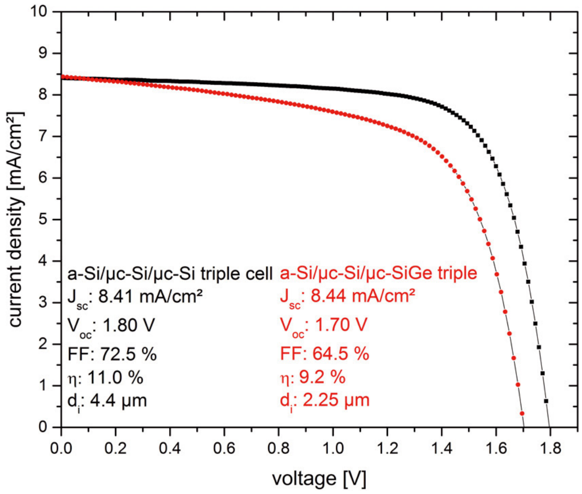

Fig. 6. Comparison of IV-curves of a triple-junction solar cellc in an a-Si:H/μc-Si:H/μc-Si:H and a-Si:H/μc-Si:H/μc-SiGe:H configuration.

Figure 6 also shows the IV-curve under illumination of an a-Si:H/μc-Si:H/μc-SiGe:H triple-junction solar cell with a reduced total cell thickness by a factor of 2 compared to the a-Si:H/μc-Si:H/μc-Si:H reference solar cell. Though the fill factor is only at 64.5%, the remarkable fact is that we managed to produce the same short-circuit current density with 58% of the absorber thickness.

Since the deposition of those triple junction cells were done before we did the extensive material study, we were able to use the knowledge to reduce the difference in V_{oc} values to 60 mV. The next goal will be to achieve fill factor values that are comparable to the μc-Si:H counterpart. By reducing the deposition time of the triple junction technology it should enable the industry to bring triple junction cells with efficiencies greater 14% to the market.

4 Conclusions

The presented work shows the current status of the BMU joined research project SiliziumDS12plus concerning the development of a-Si:H/μc-Si:H/μc-SiGe:H triple-junction solar cells. First we gave a comprehensive overview of the impact of different process parameters on the electrical performance, germanium content and crystallinity of single μc-SiGe:H cells. Since this two phase, two component material is very difficult to fabricate at high qualities, this paper gives the opportunity to gain insight into the parameters needed to reach a good deposition regime. The material quality of the μc-SiGe:H absorber has to be increased further in order to rise the triple cell fill factor above 70%. By using the knowledge gained, we were able to reduce the V_{oc} difference between μc-Si:H and μc-SiGe:H absorbers to 60 mV. A remarkable result is that the same short-circuit current density can be achieved with a 44% thinner triple-junction cell compared to an a-Si/μc-Si/μc-Si reference triple-junction cell by using μc-SiGe:H bottom cells.

The authors would like to thank the BMU for financial support for our work on a-Si:H/μc-Si:H/μc-SiGe:H triple-junction solar cells within the project SiliziumDS-12plus under contract number FKZ0325317. Help from the PV group at NEXT-ENERGY is gratefully acknowledged.

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Cite this article as: Nies Reininghaus, Martin Kellermann, Karsten von Maydell, Carsten Agert, Effects of process parameters on μc-$\mathrm{Si}_{1-\mathrm{X}}\mathrm{Ge}_{\mathrm{X}}$:H solar cells performance and material properties, EPJ Photovoltaics **6**, 65301 (2015).