Microcrystalline SiGe Absorber Layers in Thin-Film Silicon Solar Cells


Abstract

We report on physical properties of microcrystalline silicon-germanium (μc-SiGe:H) absorber layers for the use as a bottom structure in silicon based multijunction thin-film solar cells. Due to incorporation of Ge the absorption of the film is enhanced compared to pure μc-Si:H films. This provides the opportunity to significantly reduce the absorber layer thickness. The experiments were carried out in a 13.56MHz PECVD reactor using germane, silane and hydrogen as process gases. Single layers were characterized for their optical and electrical properties. Results from single and multijunction solar cells using a μc-SiGe:H absorbers will be shown. In tandem solar cells a reduction of about 60% of the absorber layer thickness could be reached by using SiGe alloys compared to pristine silicon tandem cells.

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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 multijunction devices like tandem or triple junction solar cells. In a tandem configuration based on the micromorph technology (amorphous silicon and microcrystalline silicon) the stabilized efficiencies exceed 12% [1]. Recently, Kim et al. published a new record for silicon based thin-film solar cells. The solar cell exhibits a stabilized efficiency of 13.4% and is based on triple junction technology consisting of amorphous and microcrystalline silicon absorber layers [2]. One drawback of the technology is the relatively large bottom cell absorber thicknesses. In tandem configuration the absorber layer thickness is in the range of 1.3-1.7μm; in triple junction configuration the bottom cell absorber layer has to be increased to about 2.5μm due to the poor absorption of the material [3]. This in fact has the disadvantage of long tact times in production and thus high production costs. One solution to overcome this problem is to optimize light trapping by using high scattering transparent conductive oxide front contacts and novel back scattering structures. On the other hand it is also possible to increase the deposition rate. An alternative and attractive way is to decrease the absorber layer thicknesses. However, in best case all of the above mentioned points have to be optimized. One way to decrease the film thickness is to increase the absorption coefficient of the materials. Matsui introduced the usage of hydrogenated microcrystalline silicon/germanium alloys (μc-SiGe:H) which might be favorable due to higher absorption of incident light [4, 5].

In this contribution we report on the development of μc-SiGe:H absorber layers for the usage as ultrathin bottom absorbers in silicon based multijunction solar cells. It has been reported by several authors, that a Ge concentration in the film larger than 20% leads to a high defect formation and thus the Ge variation is limited in this contribution to maximum about 22% [4, 5]. The experiments were compared to samples and solar cells without Ge in the films.

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2. Experimental

Microcrystalline silicon and silicon-germanium films were prepared using plasma enhanced chemical vapor deposition (PECVD) working at 13.56MHz which is implemented in a VonArdenne PECVD/PVD cluster tool. For solar cell preparation the precursor gases, SiH₄, GeH₄, H₂, PH₃ and B₂H₆ were used. The substrate temperature during the absorber layer deposition was 200°C, the pressure was 9mbar and the power density 0.14 W/cm². The
SiH₄ flow was fixed to 5sccm, whereas the GeH₄ flow was varied between 0.2 and 0.5sccm. Single layers were deposited on glass substrates, solar cell structures on sputtered and HCl-etched ZnO:Al substrates on glass with structure height of about 80-100nm. The germanium gas-phase concentration GC is defined as:

\[
GC = \frac{[\text{GeH}_4]}{[\text{SiH}_4]+[\text{GeH}_4]}
\]  

(1)

Whereas X is the germanium concentration in the resulting SiGe film given in at.% measured by energy dispersive X-ray spectroscopy. The absorption coefficient was determined using a Varian UV-VIS spectrometer. Raman measurements were performed by using a Bruker Senterra system with an excitation wavelength of 488nm. To determine the Ge concentration in the films energy dispersive X-ray spectroscopy (EDX by Oxford) was used which is implemented in a Zeiss scanning electron microscopy system. Solar cell efficiencies were measured by a 2-lamp system from WACOM and the external quantum efficiency by a system from RERA.

3. Results and discussion

Fig. 1 shows the absorption coefficient as a function of the incident photon energy for samples with different Ge concentrations, X, in the films. The dashed lines represent the pristine materials (∅c-Ge:H and ∅c-Si:H). The absorption coefficient of Ge is about 2 magnitudes higher than of Si at 1.5 eV. It can be seen clearly, that the

![Fig.2: Raman spectra of ∅c-SiGe:H absorbers with different Ge concentrations X.](image-url)
absorption coefficient in the interesting energy region is increasing when $X$ is increased starting from pristine μc-Si:H films as expected. The E04 band gap value decreases from 2.15eV for $X=0\%$ to 1.88eV for $X=17\%$. The incorporation of germanium in the film has also influence on the lattice parameters. In Fig. 2 Raman spectra are shown for the same samples as in Fig. 1. The microcrystalline growth, indicated by the LO-TO phonon line of crystalline silicon located around 520cm$^{-1}$ dominates the spectrum for $X = 0$ which is broadened by a resonance located around 505cm$^{-1}$ and the α-Si:H resonance at around 480cm$^{-1}$. With increasing germanium content in the film the LO-TO phonon resonance shifts to smaller wave numbers. Additionally, a new resonance emerges when $X$
increases located at around 400 cm\(^{-1}\) which is a symmetrical SiGe resonance. The shift of the Si LO-TO phonon mode is shown in more detail in Fig. 3. As already mentioned the LO-TO phonon mode shifts from about 521 cm\(^{-1}\) to about 507 cm\(^{-1}\) when X is increased from 0% to 17% (Fig. 3, black triangles). This can be attributed to internal stress due to the incorporation of Ge in the silicon network. This is accompanied by a reduction of the Raman crystallinity from values larger than 88% to about 86% (in the range of 0<X<13 at.% - not shown here). The Raman crystallinity was calculated by only using the resonance of the silicon lattice after Droz et al [6]. The SiGe or Ge resonances were not taken into account for the calculation of the Raman crystallinity. It should be noted that the Raman crystallinity for the use in tandem solar cells should be in the range of 50-60% [7]. The approximately linear decrease of the LO-TO phonon resonance with increasing Ge concentration can be used to estimate the Ge content in the microcrystalline SiGe film from the gas phase concentration. Alonso et al. [8] proposed a linear dependency as

\[ \omega_{Si-Si} = 520 - 70X \]
In this equation $\omega_{\text{Si-Si}}$ denotes the LO-TO resonance and X the Ge-content; 520 is the value of the silicon LO-TO resonance. Equation 2 was evaluated for X and the Peak position for different germane gas-phase concentration was used as input parameter. These values are plotted in Fig. 4 for different germane gas-phase concentrations. For comparison values for X determined by EDX are also shown in the same figure. It can be seen in Fig. 4 that the evaluation of $\omega_{\text{Si-Si}}$ is a fast and useful method for the estimation of the Ge concentration in the film.

The microcrystalline absorber layers were implemented in single junction solar cells consisting of TCO/$\mu$-Si(p):H/$\mu$-SiGe(i):H/a-Si(n):H/Ag. Fig. 5 summarizes the EQE data for the solar cells with different Ge concentrations. As expected from the absorption measurements in Fig. 1 the EQE in the red part of the spectrum increases with increasing X. This also affects the estimated short circuit current which increases from 20.7 mA/cm² to values larger than 22 mA/cm². This result shows that, to gain the same short circuit current, the film thickness of the absorber by using SiGe alloys can be reduced compared to $\mu$-c-Si:H absorbers. Fig. 6 shows $V_{OC}$ and efficiency of the same solar cell series but with extended range of X. The open circuit voltage, $V_{OC}$, stays nearly constant with increasing X for X < 18%. When the Ge concentration increases to values larger 18% the $V_{OC}$ drops down to about 350mV for X=22%. The relatively low values for $V_{OC}$ (best $\mu$-c-Si:H single cells achieved show values of $V_{OC}$ up to 550mV) can be explained by the high Raman crystallinity of the films (about 80%). The efficiency increases from about 5% to 5.5% at about X=12-16% due to enhanced short circuit current and then drops down to 3% when X increases to values larger 20%. This decrease in $V_{OC}$ and efficiency can be attributed to enhanced defect creation in the absorber due to the incorporation of Ge in the Si-network and has been also seen by other authors [9].

The $\mu$-c-SiGe:H solar cells were implemented in a-Si:H/$\mu$-c-SiGe:H tandem solar cells and were compared to conventional a-Si:H/$\mu$-c-Si:H solar cells. The aim of this evaluation is to show the possibility to reduce the bottom cell absorber by using SiGe alloys, significantly. Fig. 7 shows the EQE for three different tandem solar cells with the same short circuit current of about 11.7mA/cm². The thickness of the a-Si:H top-cell was held constant at 330nm. The Ge concentration for the $\mu$-c-SiGe:H solar cells was adjusted to about 12 at.% The thickness of the pristine $\mu$-c-Si:H bottom cell absorber was 1.3µm. The Raman crystallinity of the bottom absorbers was about 80%. As shown in the figure by incorporating the $\mu$-c-SiGe:H absorbers the film thickness could be reduced up to 60% exhibiting the same bottom cell current (violet EQE curve – 0.52µm). This is a remarkable result since the tact
time of solar module production can be reduced significantly. A further reduction of the film thickness is possible
due to an optimization of the Raman crystallinity of the film. An overall increase of the efficiency can be achieved
by an optimized back contact and large band gap p- and n-doped layers. In the next step this concept will be
implemented into triple junction solar cells.

4. Summary

In summary, the usage of thin microcrystalline silicon-germanium absorbers in thin-film silicon solar cells has
been described. Due to incorporation of Ge in the Si-network the absorption coefficient increases. This is
accompanied by a shift of the LO-TO Raman resonance towards smaller wave numbers. From the shift of the
Raman resonance with increasing Germane concentration in the gas phase the Germanium concentration in the
resulting film was estimated which stays in good agreement with EDX measurements. The incorporation of Ge
causes an increase of the EQE in the red part of the spectrum and thus to an increased current while the absorber
layer thickness stays constant. Optimized single μc-SiGe:H solar cells were obtained by a Ge concentration of
about 12-16 at.%. Applying these findings in a-Si:H/μc-SiGe:H tandem solar cells show that the absorber thickness
could be reduced by up to 60% compared to a-Si:H/μc-Si:H solar cells. This result shows that the deposition tact
time in thin-film silicon solar cell production can be reduced significantly. This will be even more significant for
bottom cells in triple junction concepts.

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