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Keywords

Low temperature, Epitaxy; PECVD; Si thin film; Solar cell

Abstract

We report on heterojunction solar cells whose thin intrinsic crystalline absorber layer has been obtained by plasma enhanced chemical vapor deposition at 165°C on highly doped p-type (100) crystalline silicon substrates. We have studied the effect of the epitaxial intrinsic layer thickness in the range from 1 to 2.4 µm. This absorber is responsible for photo-generated current whereas highly doped wafer behave like electric contact, as confirmed by external quantum efficiency measurements and simulations. A best conversion efficiency of 7% is obtained for a 2.4 µm thick cell with an area of 4 cm^2, without any light trapping features. Moreover, the achievement of a fill factor as high as 78.6% is a proof that excellent quality of the epitaxial layers can be produced at such low temperatures.

1. Introduction

The photovoltaic industry has been growing with astonishing rates over the past years, but expansion plans of silicon feedstock manufacturers were not synchronized with those of solar cell manufacturers; this was responsible for a large silicon feedstock shortage until 2010. Research on epitaxial growth for thin film crystalline silicon solar cells has gained in importance[1–3] due to the cost of crystalline silicon and lessons learned from this feedstock shortage. Even though various approaches have been studied, they all involve high temperature processes, in excess of 600°C, which limits the range of suitable substrates and often require post-hydrogenation to passivate defects in the crystalline silicon layer. On the other hand, epitaxial growth by plasma enhanced chemical vapor deposition at ~200°C is a common feature encountered by research groups working on heterojunction solar cells. Indeed, growing a-Si:H on (100) crystalline wafers often results on a crystalline growth over some thickness, which may lead to poor surface passivation and is deleterious to the efficiency of heterojunctions solar cells[4–6]. Nevertheless, we have shown that if the interface between the epitaxial layer (epi-layer) and the a-Si:H emitter is sharp enough, then high efficiency cells can be produced[7]. Pursuing this approach, we have studied the growth of thick epitaxial layers and have found that the epitaxial growth can be sustained up to a thickness of 3 µm at such low-temperature conditions. Moreover, by using an SiF_4 plasma etching step on the wafer substrate before deposition, we have found that it is possible to produce a crystalline silicon layer having a porous interface with the crystalline silicon wafer, which allows to easily detach the epitaxial film from the substrate[8,9]. In this way it is possible to produce thin and flexible crystalline silicon wafers that could be used for electronic devices, in a similar way to the

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"smart-cut" process[10]. Last but not least, we have also shown that it is possible to grow doped epi-layers and produce in this way efficient p-n junction solar cells[11]. Even though the macroscopic structural properties of the epi-layers are consistent with crystalline silicon, as deduced from Raman spectroscopy, spectroscopic ellipsometry, and transmission electron microscopy measurements, these techniques do not provide information on the electronic properties of such layers. Indeed, for such low growth temperature, one could expect the crystalline layers to have a high density of electronic defects. We have thus used these epi-layers as the absorber in heterojunction solar cells, as a mean to evaluate their electronic quality.

2. Experiments

Heavily boron-doped, (100)-oriented, Si wafers with a resistivity of 0.02-0.05 Ω.cm and a thickness of 525 µm were used as a substrate for the epitaxial growth, and as the electrical contact of the solar cell. We removed the native oxide from the c-Si by a 30 seconds dip in a 5%-diluted hydrofluoric acid solution[12] just before loading them into a standard (13.56 MHz) capacitively coupled RF-PECVD reactor[13]. Non-intentionally doped epitaxial Si layers of various thicknesses (0.9 µm, 1.7 µm and 2.4 µm) were deposited from the dissociation of a silane-hydrogen mixture and completed with the deposition of a standard (n+) a-Si:H emitter in the same PECVD reactor, without breaking vacuum. The substrate temperature was kept at 165°C throughout the deposition process. The area of the cells (2×2 cm^2 for the largest ones) was defined by sputtering ITO through a shadow mask and evaporating Al grid contacts. Note that all the interfaces are flat and that there is no light trapping scheme. The structure of the devices is shown in Fig. 1. The undoped epitaxial layer was deposited by the dissociation of 6% silane in hydrogen gas mixture under a total pressure of 2000 mTorr and an RF power density of 60 $mW.cm^{-2}$, resulting in a deposition rate of 1.5 $Å.s^{-1}$ (electrode spacing 17 mm). The n-type a-Si:H layer was deposited from the dissociation of 0.4% PH_3 in silane under a total pressure of 100 mTorr and an RF power of 6 $mW.cm^{-2}$ resulting in a deposition rate of 0.5 $Å.s^{-1}$ (electrode spacing 28 mm). UV-visible spectroscopic ellipsometry (Jobin Yvon - MWR) measurements within the 1.5-5 eV photon energy range were used to check the thickness and crystallinity of the epi-layers. Quantum efficiency and I-V measurements under AM1.5 illumination were carried out to determine the solar cell parameters. In addition, the experimental results were checked against PC1D[14] simulations of the cell structure.

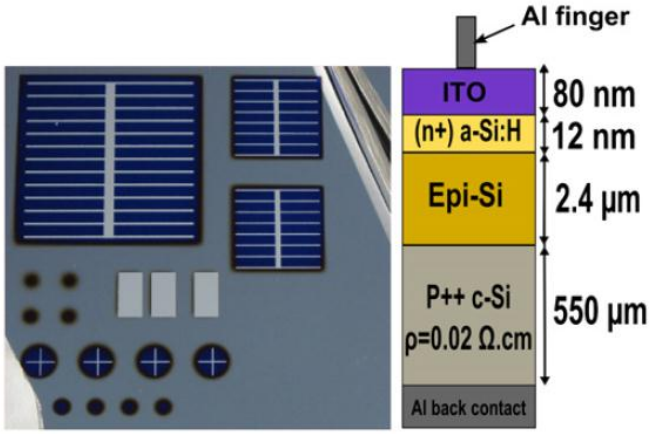

Figure 1. Top-view picture of our sample: 2×2 cm2 cell on 5×5 cm2 substrate (left). Schematic lateral view of our solar cell structure (right).

3. Results and discussion

Fig. 2 shows the imaginary part of the pseudo-dielectric functions of : i) monocrystalline silicon (black line), ii) an undoped epi-Si layer grown by PECVD after HF cleaning (open squares) and iii) the full silicon stack consisting of an undoped epi-Si layer coated with a (n+) a-Si:H emitter (open circles). The dielectric function corresponding to the full layer stack was fitted to an optical model using the dispersion curve of monocrystalline silicon for the epi-layer, as obtained by Aspnes[15], a Tauc-Lorentz dispersion formula for the amorphous silicon layer[16], as well as layers combining these materials with a void fraction using the Bruggeman effective approximation theory[17].

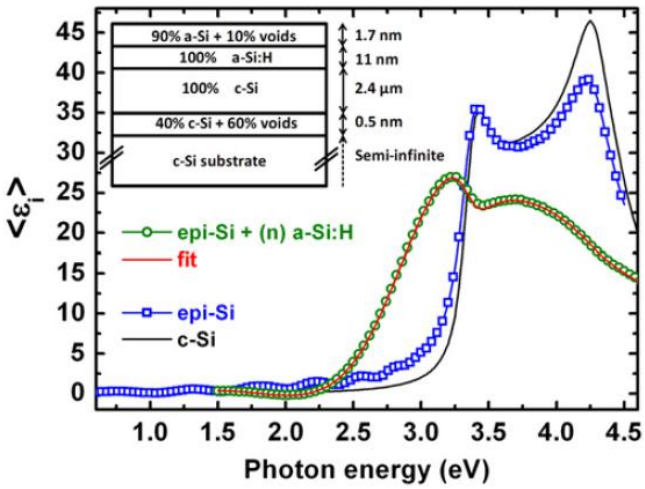

Figure 3. Ellipsometric spectra of a monocrystalline wafer (black line), an epitaxial layer (blue squares) and a solar cell made of an epitaxial layer with an amorphous emitter on top (green circles). The red line is a fit of our data to the model shown in the inset.

The model we used is shown in the inset of Fig. 2 with the fitting result represented by the red line. As one can see in this figure, the Im(ε) spectrum of a thick epi-layer deposited on the HF cleaned wafer is almost the same as that of the bare wafer, suggesting that the deposited film has the same structural composition and quality as the c-Si wafer.

At high energy, photons are more sensitive to surface as their penetration depth is very small; the slightly lower amplitude of Im(ε) at 4.2 eV for the epi-Si can be accounted by the roughness of the films and the presence of a thin surface oxide layer[18,19]. And the oscillations observed at low photon energies (< 3 eV) can be accounted by a very thin interface layer between the film and the wafer, allowing us to determine precisely the thickness of the epitaxial film. The spectrum of the i-n stack (green circles) is dominated by that of 11 nm a-Si:H emitter which buries the characteristic c-Si signature. The fit of the layer stack, represented by the red line in Fig. 2, perfectly reproduces the experimental spectrum (open circles) and reveals that the 2.4 µm thick epitaxial layer is 100% crystalline, without any porous interface layer between the c-Si wafer and the epi-Si layer. The a-Si:H emitter can be accurately described as a 100% amorphous silicon layer of 11 nm having a roughness of 1.7 nm. The characterization of the epitaxial layer in terms of defects and doping profile has not been carried out yet since we have so far focused on the fabrication of photovoltaic cells to check the material electronic properties. Regarding the growth process at such low temperature, there is still a lot to be understood as well. It has been shown previously in our laboratory that in some process conditions, crystalline Si nanoparticles are generated in the gas phase[20]. These nanocrystals play an important role in the deposition and can be incorporated to the film resulting in polymorphous or microcrystalline silicon materials on glass substrates[21,22]. Those specific process conditions applied onto (100) c-Si substrates lead to an epitaxial growth[7].

Figure 3 shows the current-voltage characteristics of three heterojunction solar cells for which we only varied the thickness of the intrinsic absorber layer. As expected, the short circuit current of the solar cells increases from 15 mA.cm^{-2} for the 0.9 µm cell to 16.6 mA.cm^{-2} for the 2.4 µm cell. However, the most striking feature is the high values of the FF achieved for these devices, which compare favourably with these of heterojunction solar cells

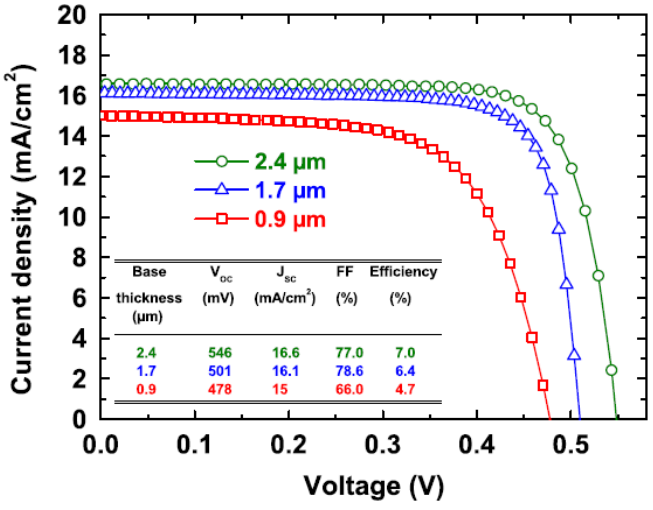

Figure 2. Current-voltage characteristics of solar cells having three different thicknesses.

produced on c-Si wafers in our laboratory[7].

Fill factor, as it's sensitive to recombination and parasitic resistances, is a key parameter in thin film solar cells : good FF indicates good transport properties in the intrinsic layer, and consequently good epitaxy. Interestingly, the thicker cells exhibit higher V_{OC} and FF suggesting that the quality of the intrinsic absorber layer improves with thickness. Indeed, one would normally expect epitaxy break down as thickness increases, which is not the case for this thickness range. Two main reasons can explain this behaviour: i) The thicker the intrinsic epitaxial layer, the less the device is penalized by the p++ c-Si wafer epi-layer interface. ii) Specific growth mechanism at such low temperatures may account for to this improvement. Note that the efficiency of these solar cells compares very favourably with that of similar devices produced by HWCVD at 700°C[3]. Our best cell reaches an efficiency of 7% with a FF of 77%, a V_{OC} of 546 mV and a J_{SC} of 16.6 mA.cm^{-2}. The high values of fill factor show the viability of using epitaxial growth by PECVD at 165°C for the production of thin c-Si films. In order to check that the photocurrent is really generated by the intrinsic epi-layer and that the highly doped p-type c-Si wafer does not contribute to J_{SC}, we performed quantum efficiency measurements and PC1D modelling of the solar cells, and results are shown on the same plot (see fig.4). The external quantum efficiency (EQE) measured on the cells having an intrinsic absorber layer thickness of 1.7 and 2.4 µm are shown in Figure 4 (respectively blue open circles and green open squares). As expected, the spectral response is low in the infrared part of the spectrum due to the thin c-Si layer and thus confirming that the c-Si substrate does not contribute to the photocurrent.

The influence of the emitter/base thickness has been investigated with PC1D using the p-i-n layer stack shown in Fig. 1. Material parameters used for modelling this c-Si/a-Si heterojunction are the result of an optimisation made by Lien and Wuu[23]. We have used the experimentally measured front

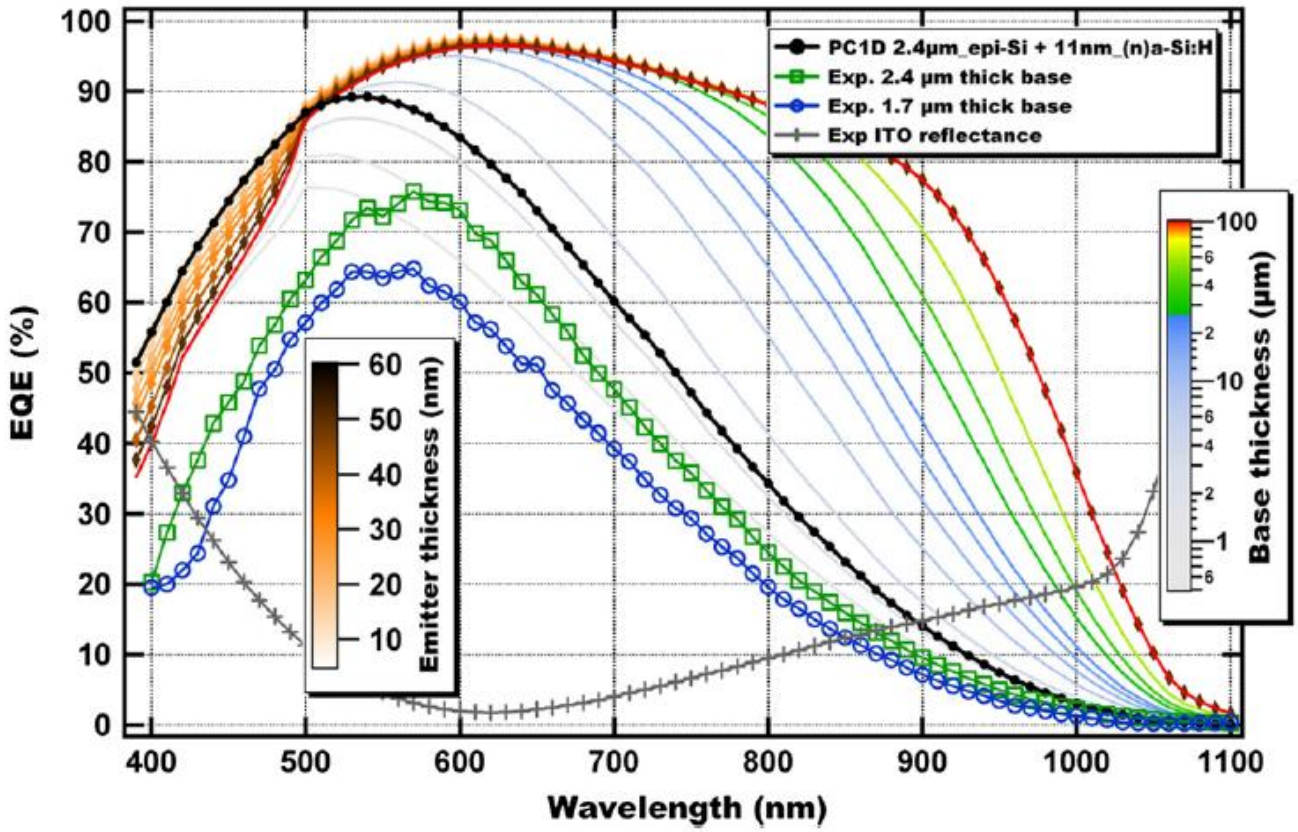

Figure 4. External quantum efficiencies obtained by PC1D simulations varying the emitter (5 to 60 nm) and the base (0.5 to 100 µm) thickness for the structure describe in Fig.1. Experimental EQE of our 1.7 µm and 2.4 µm cells is represented by the blue and green open symbols respectively.

reflectance of ITO (grey crosses on Fig. 4) in the simulation, and the diffusion length in the epi-Si layer was set to 300 µm, which is probably higher than the actual value in our epi-Si layer. However, the diffusion length as very little influence on cell performances as long as it exceeds three times the absorber thickness. The results of the device simulation for different emitter and base thicknesses are shown in Fig. 4. The graph is composed of two groups of curves: i) those corresponding to devices having a thick emitter (60 nm) and variable base thickness (right part) and ii) those corresponding to devices having a thick base (100 µm) and a variable emitter thickness (left part). Since carriers generated in the emitter by the short wavelength photons are subject to surface and bulk emitter recombination, the short wavelength EQE is particularly sensitive to surface passivation and emitter thickness. The simulated device with same structural parameters as the 2.4 µm p-i-n solar cell, is represented by black circles. At 800 nm, simulation predicts 35% EQE which is not far from that of the fabricated device: 25%. In the blue region of the spectrum, two main reasons can explain the discrepancy between model and experimental data: i) The ITO anti-reflective coating of our device absorbs a non-negligible fraction of the incident light. The simulation doesn't take into account those losses. ii) The growth of the amorphous emitter on the epitaxial layer may produce a rough interface and thus higher defect density with respect to the growth on a crystalline silicon wafer. Anyway, the simulated device reaches almost 22 $mA.cm^{-2}$ with a Voc of 530 mV and 9% efficiency. Thus, a good understanding of the front surface recombination combined with a better anti-reflection coating can lead to better current collection. Further studies are needed; nevertheless these results validate the relevance of low temperature PECVD assisted epitaxial growth for the production of ultrathin crystalline silicon solar cells.

4. Conclusions

As a conclusion, we have demonstrated a new approach to produce quality ultrathin crystalline silicon films at 165°C. Furthermore, these epitaxial layers have been used as the absorber in heterojunction solar cells resulting in FF values as high as 78.6 and an efficiency of 7% for a 2.4 µm absorber. Better current collection can be achieved: the device efficiency is so far limited by the short circuit current, in agreement with PC1D modelling of the solar cells. Quantum efficiency measurements and simulations reveal that there is still room for improvement, and that particular care is needed to reduce the front surface recombination affecting the blue response of the solar cells.

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