Towards wafer quality crystalline silicon thin-film solar cells on glass

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ABSTRACT

In this paper we present our latest progress in fabricating high quality crystalline silicon thin film solar cells on glass. Large silicon grains are directly formed via electron-beam induced liquid phase crystallization (LPC) from a nanocrystalline precursor film. The LPC process is carried out on an amorphous SiO_2 layer, and both a high quality self-passivating interface and excellent electronic bulk properties are obtained. Solar cells with stable efficiencies of 11.5% and open-circuit voltages well above 600 mV with a maximum value of 656 mV are presented. So far, such high V_{OC} values have only been achieved on wafer-based silicon solar cells.

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1. Introduction

Silicon is an abundant, non-toxic and well-known material which has evolved to be the dominating raw material for photovoltaic devices. This is reflected by a world wide market share of solar cells based on multi- or monocrystalline silicon wafers exceeding 80% [1]. With efficiencies in production approaching the laboratory world record, a further reduction of electricity generation costs can only be achieved by reduction of silicon costs for instance by reduced material consumption. The high energy demand for the production of silicon wafers gave rise to several other solar cell technologies aiming at cost reduction. One approach is to use much thinner silicon wafers. Efficiencies up to 20.1% have been reached for absorber thicknesses in the range of 40 μm [2–4] and 13.7% on a nano-textured absorber of only 10 μm thickness on a commercial SOI wafer [5]. Although the efficiencies are undoubtly on an impressively high level, these approaches benefit from superior material quality of the monocrystalline silicon wafers which comes along with the high energy demand of the production processes, namely: Czochralski [2,5] or even float-zone in the case of Ref. [3]. In order to mitigate this problem, many other approaches rely on the preparation of thin-films of semiconductor material directly on glass. The most efficient thin-film technologies to date are based on chalcogenides. Efficiencies of up to 20.3% on cell level (CIGS [6]) have been reached. Current silicon based thin-film solar cells have comparatively low module efficiencies in the range of 8–10%. The highest efficiency for a silicon

thin-film solar cell (13.4% [7]) has been reached with a rather complex device of three either amorphous or microcrystalline sub-cells stacked to a triple-junction solar cell. The highest single junction silicon thin-film solar cell efficiencies are 10.1% for amorphous hydrogenated silicon (*a*-Si:H) [8], and 10.7% for microcrystalline silicon [9]. For both, the device consists of a *pin* structure, to benefit from field enhanced current collection at the expense of an intrinsically lower fill-factor. For devices with a classical *pn*-junction the highest efficiency is 10.4% [10]. It has been reached on a minimodule based on polycrystalline silicon (poly-Si), crystallized using the solid phase crystallization (SPC) approach.

Only recently, the liquid phase crystallization (LPC) of amorphous or nanocrystalline silicon thin-films directly on a glass substrate has received increased attention again for photovoltaics. By using a line source such as an electron-beam [11] or a laser [12] moving across the substrate the entire silicon precursor film is molten and subsequently recrystallizes to form large grained polycrystalline material. In the scanning direction the grains grow to a size of centimeters, and to millimeters in the orthogonal direction as can be seen in Fig. 1. Based on these large grained silicon thin-films, solar cells with initial efficiencies of up to 11.7% (10.4% stable, laser) [12] and 7.8% stable, electron-beam [13] have been reported, the latter suffering mainly from missing light trapping. Although already on a high level when compared to SPC, open-circuit voltages so far have been limited below 600 mV for solar cell devices based on both laser crystallized (LC) (585 mV [14]) and electron-beam crystallized (EBC) (582 mV [15]) absorbers.

From wafer-based solar cells it is known that n-doped silicon is less prone to e.g. metallurgical impurities compared to p-doped [16], and does not suffer from light induced degradation due to the

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B–O complex [17]. Also for the Si/SiO_2 interface, n-type silicon is superior to p-type, leading to lower recombination velocities [18].

In this paper we report on the development of liquid phase crystallized silicon absorber materials for thin-film solar cells on glass focusing on an adequate choice of n-type doping level for the absorber. Although the solar cells are currently far from being optimized, the open-circuit voltages, quantum efficiency measurements and accompanying device modeling clearly reveal the extraordinarily high quality of this new silicon on insulator technology.

2. Methods

2.1. Absorber preparation

As substrates, 5 cm × 5 cm Corning Eagle XG™ glass samples were used. The samples were cleaned with a standard alkaline cleaning solution (Mucasol®). After cleaning, the glass is coated with a triple stack of 250 nm SiO_x, 80 nm SiN_x and 20 nm SiO_x (ONO) by reactive RF-magnetron sputtering, acting as a diffusion barrier and an anti reflection coating (ARC). Afterwards, the silicon absorber was deposited by high rate electron beam evaporation [19] with a rate of 500–600 nm min^{-1} up to the desired thickness of 11 μm. The substrate temperature was kept at 600 °C. On top of the nanocrystalline and nominally intrinsic silicon a thin layer of

n-doped hydrogenated amorphous silicon (a-Si:H(n)) was deposited using plasma enhanced chemical vapor deposition (PECVD). Subsequently, the samples were annealed for one hour at 600 °C in a tube furnace to drive out the hydrogen. For a stable liquid phase crystallization process using a line shaped electron beam, an additional 200 nm SiO_2 capping layer was sputtered as described in [13]. During crystallization, the substrate was moved underneath the line using a constant scanning speed of 6 mm s^{-1} and an electron energy density of 1 J mm^{-2}. To reduce stress in the glass induced by the crystallization the samples were annealed in a rapid thermal annealing furnace for 1 min at 950 °C. After annealing, the capping layer was removed in hydrofluoric acid (5% in H_2O). To remove defects generated during the crystallization process the samples were treated with an $HF/HNO_3/H_3PO_4$ based silicon etchant for 60 s removing the first 300–500 nm of the poly-Si absorber. The samples were then exposed to a hydrogen plasma for 15 min at 600 °C at a pressure of 1 mBar to passivate dangling-bonds, mainly at the Si/SiO_2 interface [13]. The hydrogen plasma process is described in detail in [20]. After passivation, the samples were etched again for 60 s in the etching solution mentioned above to remove plasma induced surface defects. Subsequently, the samples were cleaned with a standard RCA cleaning procedure to ensure good a-Si:H/c-Si interface quality.

2.2. Device fabrication

Two different types of solar cell devices were prepared for this study. A back contacted silicon heterojunction (BC-SHJ) solar cell, aiming at high efficiency and a test structure aiming at a very simple and fast preparation process. Both devices are depicted schematically in Fig. 2.

The test structure features an emitter area of 8 mm × 8 mm, the absorber contact is placed outside this area (cf. Fig. 2b). It accepts an inherently lower fill-factor for the sake of simplicity and processing speed. However, the two major characteristic parameters open-circuit voltage (V_{OC}) and generated photocurrent density (j_{Ph}) can be easily extracted from the jV-characteristic – the latter under reverse bias, if required.

The BC-SHJ solar cell is based on the FrontERA device, first presented in [15], and features a cell area of 6 mm × 10 mm. FrontERA has been initially designed for p-type silicon absorbers and makes use of the formation of aluminium absorber contacts through an a-Si:H layer [21]. For n-type silicon, a Ti/Pd/Ag stack
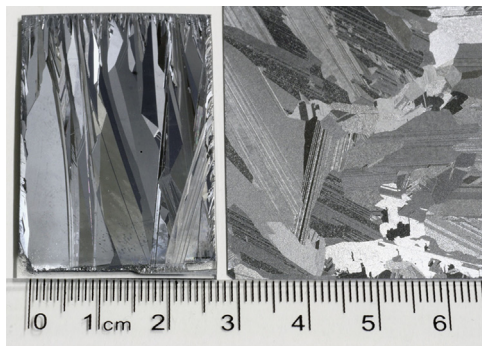
Fig. 1. Photograph of a 40 μm electron-beam crystallized silicon absorber on glass, treated with an alkaline etchant to enhance visibility of the grains (left) and a KOH damage etched multicrystalline silicon wafer (right).
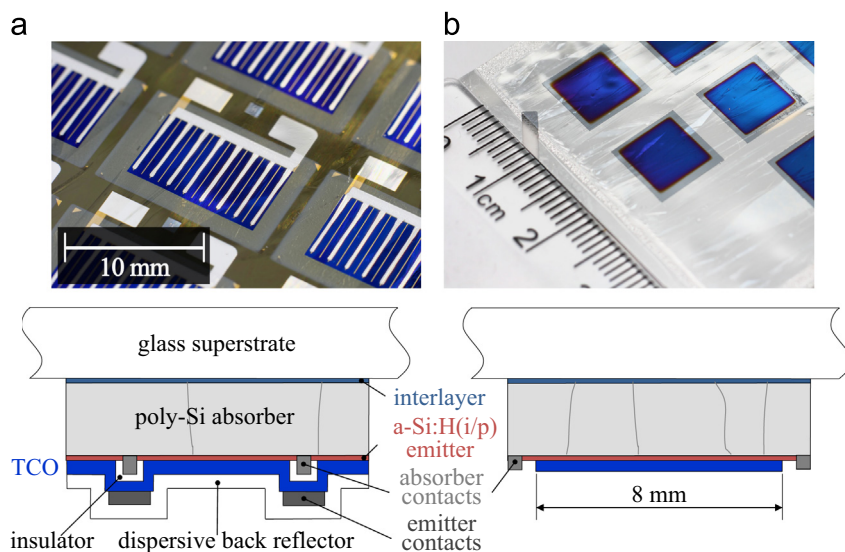
Fig. 2. Photographs as well as schematic cross sections of the two devices discussed in this paper. (a) Back contacted silicon heterojunction solar cell (photograph is without back reflector) and (b) test structure.