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Amorphous silicon passivation of surfaces promoting epitaxy

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Abstract

A two-step approach to passivate crystalline silicon (c-Si) with hydrogenated amorphous silicon (a-Si:H) for amorphous/crystalline silicon (a-Si:H/c-Si) heterojunction solar cells is discussed: The combination of low temperature a-Si:H deposition of 7 nm (i)a-Si:H and hydrogen plasma post deposition treatments (HPT) is shown to yield charge carrier lifetimes of 8 ms on c-Si<100>, i.e. a crystal surface which can be difficult to passivate because it promotes epitaxial growth. It is shown that the passivation improvement upon HPT stems from diffusion of hydrogen atoms to the heterointerface and subsequent dangling bond passivation. Upon HPT, the a-Si:H hydrogen density increases, leading to a valence band offset increase at the heterojunction. However, the film disorder is not increased. Thus, HPTs allow for a-Si:H band gap and a-Si:H/c-Si band offset engineering. Furthermore a HPT enables the application of a-Si:H/c-Si-heterojunction solar cells concepts on surfaces that promote epitaxy, like Si<100> and (nano)structured surfaces.

Keywords: amorphous silicon passivation; hydrogen plasma; silicon-heterojunction solar cell; crystalline silicon

1. Introduction

Wafer based amorphous-crystalline silicon-heterojunction solar cells (a-Si:H/c-Si-HJ-SC) receive growing interest due to steadily growing record efficiencies exceeding 24 % [1]. The main advantage of this approach is the potentially high open circuit voltage (V_{OC}), which can be reached due to excellent interface-passivation with intrinsic amorphous silicon. Unintentional epitaxial growth during deposition of the passivation layer is known to deteriorate the passivation quality [2]. The prevention of unintentional epitaxial growth can be challenging for <100>-oriented silicon surfaces [3], or random pyramid textures [4].
In recent years a-Si:H/c-Si-HJ have been applied in back-contact back-junction configuration [5]. For this concept it can be technology beneficial to form the heterojunction on a Si<100> surface. Furthermore

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the implementation of nanostructured absorbers with unspecified crystalline orientations [6] in amorphous-crystalline silicon-heterojunction concepts may be a promising concept for future research. Therefore it is necessary to reliably passivate different crystalline surface phases.
An early alternative to the direct deposition of hydrogen rich amorphous silicon for solar cell application was the deposition of hydrogen free amorphous silicon combined with a HPT to hydrogenate the layer [7]. This was successfully adapted to a-Si:H passivation [8] and back-surface field layers [9] of a-Si:H/c-Si-solar cells on Si<111>-surfaces. Here we present a two-step approach combining the deposition of a non-optimal but epitaxy-free a-Si:H passivation layer with a HPT and apply this to Si<100>.

2. Experimental details

In this study we use 280 μm thick <100>-oriented 1 - 5 Ωcm phosphorus-doped high quality float zone silicon wafers as substrate material. Prior to deposition the wafers were cleaned following the RCA procedure and dipped in diluted hydrofluoric acid (2 min, 1 %) to strip off the native silicon oxide. Plasma-enhanced chemical vapor deposition (PECVD) was used for a-Si:H(i) deposition. The layers were deposited at 0.5 mbar process pressure, 170°C substrate temperature, 20 mW/cm^2 power density, a silane gas flow of 10 sccm and an excitation frequency of 13.56 MHz, as specified previously [10]. The previously presented HPT process [11] was performed at 1 mbar process pressure, 60 mW/cm^2 power density, a hydrogen gas flow of 20 sccm, an excitation frequency of 13.56 MHz or 60 MHz and 170 or 195°C substrate temperature. For determination of the a-Si:H band gaps spectral ellipsometry was conducted using a Sentech SE850 (wavelength range 350-2500 nm) and a Tauc-Lorentz model[12] was fitted to the data. A Sinton Consulting WCT-100 photoconductance decay (PCD) setup was used to determine minority carrier lifetimes (τ) of symmetrically treated samples [13]. Near-ultraviolet PES (NUVPES) measurements were conducted, in the constant-final-state-yield mode (CFSYS) [14], to characterize the valence band tail, reflecting the bond angle disorder in the a-Si:H layers. The samples have been vacuum transferred from the deposition to the CFSYS analysis chamber. The a-Si:H(i) parameters were obtained fitting a model density of states to the data[15].
Deuterium (D) in-diffusion experiments were conducted to analyze hydrogen (H) in-diffusion into the passivation layer during the hydrogen/deuterium plasma treatment. Therefore, c-Si wafers were a-Si:H(i) coated on one side, exposed to a deuterium plasma at different substrate temperatures from 110 to 170°C and coated with an a-Si:H(i) capping layer at a substrate temperature of 90°C to prevent oxidation of the deuterated layer and to provide a sacrifical layer for the early sputtering phase of the SIMS measurement. Secondary-Ion-Mass-Spectroscopy measurements were conducted at RTG Mikroanalyse GmbH with a Cameca IMS-4f using Argon ions at a kinetic energy of 6.5 keV.

3. Results and Discussion

3.1. Impact of the hydrogen plasma treatment

For understanding the influence of the HPT different treatment times have been applied to symmetrical passivated samples, a-Si:H layers on wafers and passivation layers that were included on the emitter side of solar cells. In Fig. 1a the influence of HPT on minority carrier lifetimes in symmetrically passivated wafers is displayed. The displayed values are averages of two to four samples. The minority carrier lifetime increases exponentially with the treatment time and saturates after about three to four minutes. In Fig. 1b the influence of the HPT on the band gap of a-Si:H(i) layers is displayed. The band gap follows the trend of the minority carrier lifetime. The band gap also saturates after about four minutes of HPT. Both can be explained with an increased hydrogen density in the layer. As hydrogen in a-Si:H chemically passivates the crystalline silicon surface and the band gap of a-Si:H(i) increases with the density of bonded hydrogen

in the layer. To verify this trend solar cells whose passivation layers on the emitter side have been treated for different times with a HPT step have been processed. This is shown in Fig1c. The V_{OC} is significantly increased and saturates already after about 45 s of hydrogen plasma.

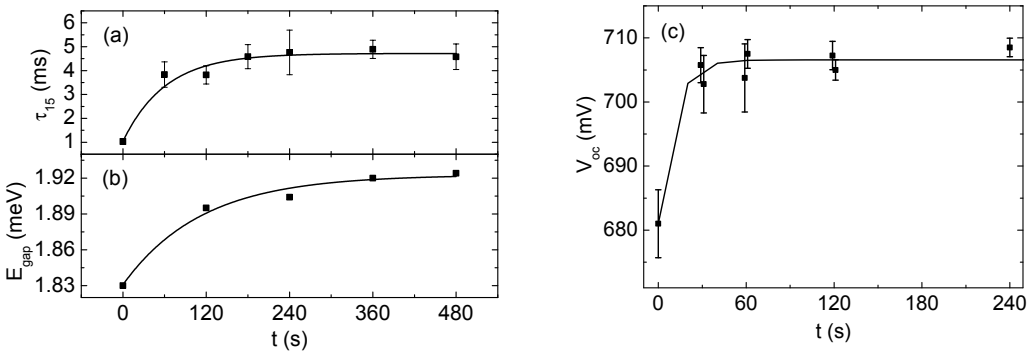

Fig. 1. (a) Charge carrier lifetime of symmetrically passivated a-Si:H(i)/c-Si(n)/a-Si:H(i)-structures in dependence of the HPT and (b) band gap of the amorphous silicon passivation layers in dependence of the HPT time. (c) open circuit voltage of solar cells in dependence of the HPT time of the passivation layers between n-typ wafer and p-type a-Si:H(p) emitter.

3.2. Variation of the substrate temperature during the hydrogen plasma treatment

To better understand the lifetime improvement upon HPT the substrate temperature during the process has been varied. The dependence of the minority carrier lifetime in symmetrically passivated a-Si:H(i)/c-Si(n)/a-Si:H(i)-samples on the substrate temperature during the process is shown in Fig. 2. In the range from 40°C to 150°C the charge carrier lifetime depends exponentially on the substrate temperature. The red circle data points show that for all samples processed below 150°C the lifetime increases upon an additional thermal annealing step at 200°C. This thermal annealing step equilibrates lateral hydrogen concentration gradients within the layer and projects the defect density of the amorphous silicon bulk on the a-Si:H/c-Si-interface [10]. The distinct temperature dependence and the reaction to thermal annealing lead to the assumption that the diffusion of hydrogen from the plasma to the interface is the reason for the lifetime improvement upon HPT.

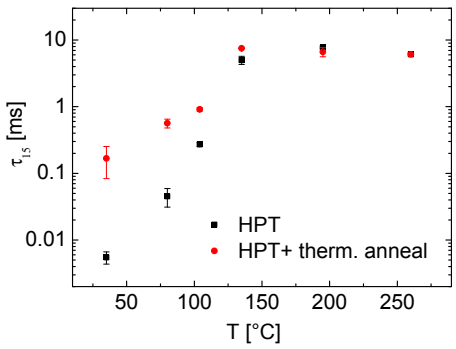

Fig. 2. Charge carrier lifetime of symmetrically passivated a-Si:H(i)/c-Si(n)/a-Si:H(i)-structures in dependence of the substrate temperature during the HPT. Black squares mark values directly after HPT and red circles are lifetime values after an additional thermal annealing step (200°C, 20min).

3.3. Deuterium diffusion profiles

Deuterium in-diffusion experiments and SIMS profiling were conducted to verify the diffusion of hydrogen from the plasma to the interface as source of the lifetime improvement. Fig. 3 shows deuterium, hydrogen and oxygen profiles taken from samples that were treated with a deuterium plasma step at four different substrate temperatures. The peaks in the oxygen profiles enable to identify the position of the a-Si:H/c-Si-interface and the interface to the capping layer. All samples show distinct peaks in the deuterium and hydrogen concentation close to the a-Si:H/c-Si-interface. This is typical for atomically sharp and good passivated a-Si:H/c-Si-interfaces [16, 17]. It is recognizable that the deuterium density in the samples increases with increasing substrate temperature during the deuterium plasma treatment (Fig. 2c), while the hydrogen density is decreased in the a-Si:DH layer and at the a-Si:H/c-Si-interface. Since the deuterium density at the a-Si:H/c-Si-interface and the minority carrier lifetime both increase with increasing minority carrier lifetime, it can be assumed that the reason for the lifetime increase upon HPT is the diffusion of hydrogen to the interface leading to dangling bond saturation.

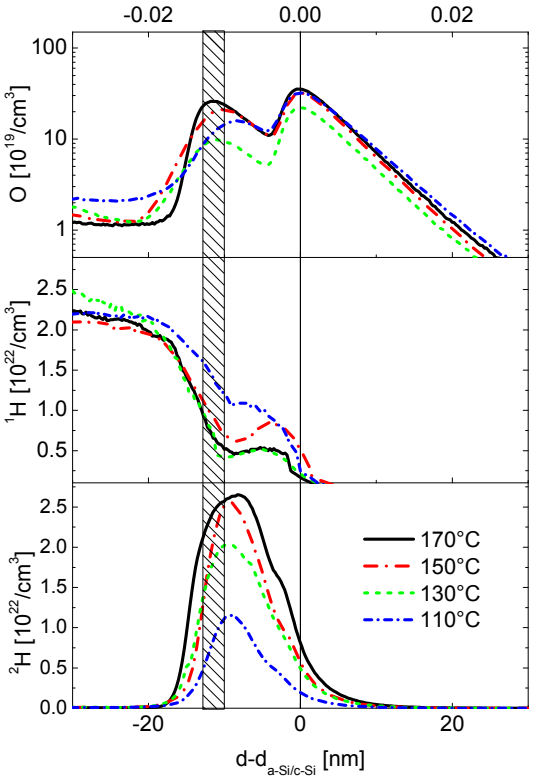

Fig. 3. (a) oxygen, (b) hydrogen and (c) deuterium profiles of four samples treated with a deuterium plasma at different temperatures. The single line marks the a-Si:H/c-Si-interface and the shaded box the interface between the deuterated layer and a deuterium free capping layer. Part of this data was published previously [11].

3.4. Electronic states

The hydrogen concentration in a-Si:H is commonly expected to be related to the amount of disorder in the layers and the valence band offset at the heterojunction [18]. Therefore the increase of the hydrogen density in the layers should lead to an increase in disorder and an increase of the valence band offset. In

Fig. 4 the measured density of occupied states in the valence bands of a typical as deposited and a hydrogen plasma treated sample is shown. It is discernible that the valence band is shifted about 130 meV away from the Fermi-level after the HPT, but the slope of the band tails is unaffected. The valence band tail slope is quantified by the Urbach-energy, which is a measure for the amount of strain in the amorphous network. The Urbach energy increases during the HPT from about 65 meV to 70 meV after the treatment, which is within error margin. The constant or insignificantly increased Urbach energy thus indicates that the HPT of amorphous silicon is not forcing a significant increase of structural disorder in the layers. Although the band gab is increased by a shift in the valence band. This is an important difference to PECV deposition of a-Si:H. For PECVD it was found that altering the deposition conditions of a-Si:H to increase the hydrogen content of the layers, leads to an increase of disorder in said layers [18]. Therefore HPT allows for tailoring the band offsets at the a-Si:H/c-Si-HJ and decreasing the defect density at the interface without deteriorating the electronic quality of the a-Si:H passivation layer.

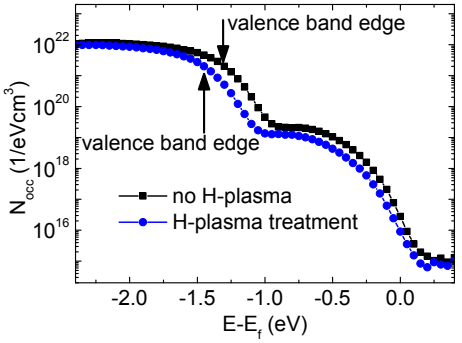

Fig. 4. Density of occupied states of the valence band of amorphous silicon for a sample treated with a hydrogen plasma and an untreated samples.

3.5. Solar cell results

Hydrogen plasma treated a-Si:H layers were incorporated into solar cell test structures. Planar Si<100>-wafers were used in order to investigate a surface that is prone to epitaxial growth. Thus, the absence of a light trapping structure limits the short circuit current of the devices. The solar cells parameters are listed in Table 1. It is evident that the HPT leads to a significant improvement in V_{OC}, without the higher band offset abating the fill factor. In fact the fill factor is slightly increased. Mainly due to better passivation in the low injection region.

Table 1. Solar cells parameters for devices fabricated on planar Si<100>-wafers incorporating standard and hydrogen plasma treated a-Si:H(i) passivation layers.

Cell type	V_{OC} (mV)	J_{SC} (mA)	FF (%)	η (%)
Without hydrogen plasma treatment	680	28.7	71.6	13.9
With hydrogen plasma treatment	714	30.6	74.6	16.4

4. Conclusions

The combination of free a-Si:H deposition and HPT is a possibility to expand the usage of a-Si:H/c-Si-heterojunctions to Si<100> and possibly nanostructured polycrystalline surfaces. If the deposited a-Si:H

is free of unitentional epitaxial growth zones the lifetimes reachable on this surface can compete with state of the art values for Si<111> reaching up to 8 ms corresponding to an implied V_{OC} of 737 mV. The reason for the lifetime increase upon HPT is the diffusion of hydrogen from the plasma to the interface and the saturation of dangling bonds. Furthermore HPT offers possibilities regarding band offset engineering since it offers a possibility to influence the hydrogen concentration and band gap of a-Si:H without significant influence on the electronic disorder in the layer.

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