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Defect passivation in chemical vapour deposited fine-grained polycrystalline silicon by plasma hydrogenation

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Abstract

This study investigates defect passivation in fine-grained polycrystalline silicon layers by means of hydrogenation. The polycrystalline silicon layers are deposited on oxidized Si wafers using high-temperature chemical vapour deposition. The hydrogenation treatment is performed in a direct plasma enhanced chemical vapour deposition system. The samples are characterized by resistivity vs. temperature measurements of p-type layers and by quasi-steady state open-circuit voltage measurements of p-n diodes made in the material. The results show a large increase of the measured open-circuit voltage by the hydrogenation treatment, with the open-circuit voltage of the samples at a light intensity of 1 Sun rising from 180 mV without hydrogenation to values up to 380 mV. This corresponds to a defect concentration decrease by a factor of three.

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1. Introduction

Thin film polycrystalline silicon solar cells are considered to be one of the most promising alternatives to bulk silicon solar cells. By using thin films, the material cost, which accounts for half of the total cost in standard silicon solar modules, will decrease significantly. Chemical vapour deposition (CVD) at temperatures above 1000 °C offers the opportunity of combining high growth rates (>1 µm/min) with the use of cheap ceramic substrates. Attempts to make thin-film solar cells in fine-grained polycrystalline silicon layers deposited by thermal CVD have so far led to moderate energy conversion efficiencies, well below those achieved in plasma enhanced chemical vapour deposition (PECVD) microcrystalline silicon [1]. A likely reason for this is the low amount of mono-atomic hydrogen atoms incorporated at these high temperatures and the small grain size ($\sim 0.5 \,\mu m$) of the layers. In this fine-grained polycrystalline material, the minority and majority carrier transport properties are

dominated by the grain boundaries and the grain size. In order to obtain good quality films for solar cell use, hydrogen needs to be introduced in a separate subsequent step, usually by exposure to a hydrogen plasma, or else the grain size has to be enhanced. The effect of applying aluminum-induced crystallization of amorphous silicon to achieve a larger grain size is presented in a companion article [2], while this paper investigates hydrogen passivation.

Plasma hydrogenation has been applied for a long time for crystalline silicon solar cells. It was first proposed for the improvement of multicrystalline silicon [3,4], although nowadays hydrogenation through firing of a PECVD silicon nitride is considered a better solution. However, for very defect-rich materials, a separate plasma hydrogenation appears to be crucial [5,6]. Fine-grained polycrystalline silicon, with an even higher defect concentration, reacts even more favorably to such a treatment [7,8].

In this paper, we investigate the plasma hydrogenation process in fine-grained polycrystalline silicon material, varying important process parameters and studying the passivation effect both on resistivity and diode properties.

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2. Experimental method

Fine-grained polycrystalline silicon layers were deposited on an oxidized Si wafer in a single-wafer CVD reactor at 1130 °C using trichlorosilane as precursor gas. The layers were 5 µm thick, were doped with boron, and showed an average grain size of about 0.5 µm. The samples meant for resistivity measurements were uniformly p-type doped with a concentration of 10^{17} cm⁻³. The other samples consisted of a stack of 2 μ m of p⁺ $(5 \times 10^{19} \text{ cm}^{-3})$ -3 µm p (10¹⁷ cm⁻³) layers. The p⁺ p-type layers then underwent a phosphorous diffusion from a solid source at 860 °C to create an n^+ -type emitter. After a standard RCA clean, all samples were hydrogenated by means of a H plasma in a direct PECVD system operating at 13.56 MHz. During each hydrogenation run, samples of both types were treated. The diodes were afterwards characterized by four-point probe measurement and by quasi-steady state open-circuit voltage measurements $(Suns-V_{oc})$ [9], without previous metallization [10]. On the p-type layers, four parallel 2 µm thick aluminum strips were evaporated, which were then annealed at 300 °C for 30 min to ensure an ohmic contact. These samples were then measured using a four-point probe resistivity vs. temperature (ρ vs. T) technique [11].

3. Results and discussion

In this paper, different hydrogenation parameters are varied (e.g., temperature, pressure, and time).

The open-circuit voltage (V_{oc}) of the device expresses the quality of the polycrystalline layers by:

$$V_{\rm oc} = \frac{nkT}{q} * \ln\left(\frac{I_{\rm l}}{I_{\rm s}} + 1\right) \tag{1}$$

with *n* the ideality factor, *k* is the Boltzmann constant, *q* is the electronic charge, *T* is the absolute temperature, I_1 is the light generated current, and I_s is the saturation current. The $V_{\rm oc}$ is normally taken from the I-V curve of a solar cell. Since solar cell processing needs a lot of steps, a quasisteady state setup can speed up the investigation of different samples significantly. In this setup, a reference cell measures the varying illumination ("Suns") while simultaneously an oscilloscope measures the $V_{\rm oc}$ of the device. By plotting the Suns vs. $V_{\rm oc}$ curve, the $V_{\rm oc}$ can be determined at 1 Sun (1000 W/m²).

Measurement of the resistivity vs. the temperature of p-type polycrystalline layers allows us to see the height of the potential barrier at the GB. The resistivity of the p-type polycrystalline layer generally shows a clear Arrhenius behavior, with the activation energy about equal to the potential barrier height $\varphi_{\rm b}$. For a given potential barrier height $\varphi_{\rm b}$ (see Fig. 1) and doping level



Fig. 1. Influence of the grain boundaries on the energy band model with $\varphi_{\rm b}$ as the potential barrier height at the GB for grains of size $L_{\rm g}$ (taken from Ref. [11]).

N, the carrier trapping model of GB predicts a trap density equal to:

$$N_t = \sqrt{\frac{8\varepsilon_{\rm s}N\varphi_{\rm b}}{q}} \tag{2}$$

where $N_{\rm t}$ is the trap density $[\rm cm^{-2}]$, $\varepsilon_{\rm s}$ is the permittivity of Si, N is the active doping concentration, q is the electronic charge, and $\varphi_{\rm b}$ is the potential energy barrier height [11].

3.1. Influence of the hydrogenation time

The influence of the hydrogenation time at a sample temperature of 380 °C and at a pressure of 1 Torr was investigated and is shown in Table 1. The data are extracted from Suns– $V_{\rm oc}$ and resistivity vs. *T* measurements. The hydrogenation time, the slope of the log (ρ) vs. 1000/*T* curve, the potential barrier height $\varphi_{\rm b}$, the resistivity ρ , and the $V_{\rm oc}$ at 1 Sun are presented. The results are discussed below.

In Fig. 2, two Suns– V_{oc} curves are shown, one for a hydrogenated sample (sample D) and one for an unhydrogenated sample (sample A). It is clear that the V_{oc} improves significantly by the hydrogenation, mainly due to a reduction of the saturation current density I_s . The open circuit voltage increases from 179 mV before hydrogenation to values around 360 mV already after only 10 min of hydrogenation. The influence of longer hydrogenation is not really obvious since the Suns– V_{oc} values saturate already after 10'. The ideality factor n at 1 Sun can be predicted from the slope of the curves and is about 1.5 for both the hydrogenated and the unhydrogenated samples. This indicates that the V_{oc} at this light intensity is still affected by recombination at the GB in both the space charge regions and the quasi-neutral regions.

Before hydrogenation, the resistivity at room temperature was 51 Ω cm (see Table 1). After 10 min of hydrogenation this reduces to 1.20 Ω cm. This very big decrease of the

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