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Impact of microcrystalline silicon carbide growth using hot-wire chemical vapor deposition on crystalline silicon surface passivation

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ABSTRACT

Highly crystalline microcrystalline silicon carbide (μ c-SiC:H) with excellent optoelectronic material properties is a promising candidate as highly transparent doped layer in silicon heterojunction (SHJ) solar cells. These high quality materials are usually produced using hot wire chemical vapor deposition under aggressive growth conditions giving rise to the removal of the underlying passivation layer and thus the deterioration of the crystalline silicon (c-Si) surface passivation. In this work, we introduced the n-type μ c-SiC:H/n-type μ c-SiO_x:H/intrinsic a-SiO_x:H stack as a front layer configuration for p-type SHJ solar cells with the μ c-SiO_x:H layer acting as an etchresistant layer against the reactive deposition conditions during the μ c-SiC:H growth. We observed that the unfavorable expansion of micro-voids at the c-Si interface due to the in-diffusion of hydrogen atoms through the layer stack might be responsible for the deterioration of surface passivation. Excellent lifetime values were achieved under deposition conditions which are needed to grow high quality μ c-SiC:H layers for SHJ solar cells. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

Highly crystalline microcrystalline silicon carbide (μ c-SiC:H) as a wide optical gap material has attracted considerable interest of the photovoltaic community. The material consists of a wide range of material properties [1,2]. Its crystallinity gives rise to both the high transparency and the high electrical conductivity [3]. Doped μ c-SiC:H thin films have been implemented into silicon thin-film solar cells as wide gap window layer due to their outstanding optical properties combined with a sufficiently high electrical conductivity [1]. Implementation of doped μ c-SiC:H as emitter material in silicon heterojunction (SHJ) solar cells has also been reported [4].

These high quality materials are usually produced using hot wire chemical vapor deposition (HWCVD) under aggressive growth conditions giving rise to the removal of the underlying passivation layer and thus the deterioration of the crystalline silicon (c-Si) surface passivation [5]. In this work, we introduce the n-type μ c-SiC:H/n-type μ c-SiO_x:H/intrinsic a-SiO_x:H stack as a promising front layer configuration for p-type SHJ solar cells with the n-type microcrystalline silicon oxide (μ c-SiO_x:H<n>) layer acting as an etch-resistant layer against the reactive deposition conditions during the n-type μ c-SiC:H(μ c-SiC:H<n>) growth. Moreover, we investigate the hydrogen effusion and diffusion processes during the HWCVD that result in the deterioration of surface passivation. Even more, we show that excellent effective

* Corresponding author. *E-mail address:* m.pomaksa@fz-juelich.de (M. Pomaska). minority charge carrier lifetime values can be achieved under deposition conditions for high quality μ c-SiC:H layers.

2. Experimental details

The μ c-SiC:H<n> was deposited in a HWCVD vacuum chamber with three curled rhenium filaments and monomethylsilane (SiH₃CH₃, MMS) diluted in hydrogen (H₂) with a concentration of 0.3%. Although no doping gas was used, the films exhibit n-type doping character, which we referred as unintentional n-type doping [1]. The pressure was kept at 75 Pa, the heater temperature (T_H) was 250 °C, unless mentioned elsewise, and the filament temperature (T_F) was varied between 1400 °C and 2100 °C. All intrinsic amorphous silicon oxide (a-SiO_x:H<i>) and n-type microcrystalline silicon oxide (μ c-SiO_x:H<n>) layers were deposited by Plasma enhanced chemical vapor deposition (PECVD), as reported by K. Ding et al. [6], with an oxygen concentration of 5% and 22–25%, respectively. We used double side polished p-type float zone c-Si wafers with (100) orientation, 1–5 Ω cm specific resistivity, and 280 µm wafer thickness.

We measured the effective minority charge carrier lifetime (τ_{eff}) of μ c-SiC:H<n>/ μ c-SiO_x:H<n>/a-SiO_x:H<i>/c-Si/a-SiO_x:H<i>/ μ c-SiO_x:H<n> samples using a Sinton Instruments WCT-120 Photoconductance Lifetime Tester [7]. The τ_{eff} is defined as

$$\tau_{eff} = \frac{\Delta n}{G - \frac{d\Delta n}{dt}} \tag{1}$$





with Δn as the minority carrier density and *G* as the photogeneration rate. The τ_{eff} was determined at $\Delta n = 10^{15} \text{ cm}^{-3}$.

The dark conductivity (σ_d) was measured at room temperature in atmosphere. The optical absorption coefficient was evaluated from transmission and reflection measurements using a PerkinElmer Lambda 950 UV/VIS Spectrometer. The excitation energy at an absorption coefficient of 10^4 cm⁻¹ is defined as the optical band gap of the material (E_{04}). Scanning electron microscopy (SEM) images were taken with a FEI Helios NanoLab 600i, whereas the samples were prepared using Focused Ion Beam (FIB).

3. Results

The $\tau_{\rm eff}$ samples with intrinsic amorphous silicon or intrinsic amorphous silicon oxide (a-SiO_x:H<i>) passivation layer showed that the $\tau_{\rm eff}$ is strongly decreased from >1 ms to <10 µs during the deposition of µc-SiC:H<n> on top of the passivation layer using HWCVD. The deterioration of the passivation is likely due to the hydrogen radical induced etch-off of the amorphous passivation layers as reported by several groups [3,8,9]. A promising approach to prevent the etch-off of the passivation layer is the introduction of an etch-resistant layer before the growth of the µc-SiC:H<n> layer. At the same time, the etch-resistant layer may not negatively affect the optical and electronic performance of the final device.

By measuring the thickness of a μ c-SiO_x:H<n> layer (d_{μ c-SiO_x:H}) on a Corning glass substrate before and after the μ c-SiC:H<n> deposition, we found out that d_{μ c-SiO_x:H} remained almost unchanged during the HWCVD process, which indicates an etch-resistance of the μ c-SiO_x:H<n> material against the reactive HWCVD process conditions. In addition, the μ c-SiO_x:H<n> offers a high optical transparency (E₀₄ = 2.0–2.8 eV) and a high electrical conductivity (σ d = 10⁻⁵–10⁰ S/cm) [10]. Thus, μ c-SiO_x:H<n> fulfills all the requirements of the etchresistant layer between the amorphous passivation layer and the μ c-SiC:H<n> layer. The SHJ front layer stack that we decided to work on in the following is μ c-SiC:H<n>/ μ c-SiO_x:H<n>/a-SiO_x:H<i>/c-Si (Fig. 1). The rear layer stack was always c-Si/a-SiO_x:H<i>/ μ c-SiO_x:H<n>(not shown).

In Fig. 2, τ_{eff} is plotted versus the µc-SiC:H<n> deposition time (t_{dep}) for different deposition conditions and different d_{µc-SiOX:H}. In Fig. 2(a) the T_F was varied between T_F = 1400–1950 °C. Two regimes are distinguishable: For $T_F \le 1800$ °C the τ_{eff} remained constant around $\tau_{eff} \approx 1.0$ ms or increased up to $\tau_{eff} \approx 2.0$ ms after $t_{dep} = 40$ min, whereas for T_F ≥ 1850 °C the τ_{eff} decreased within $t_{dep} = 5$ min from $\tau_{eff} \approx 1.0$ ms to $\tau_{eff} \le 10$ µs and remained at $\tau_{eff} \le 10$ µs after $t_{dep} = 40$ min. This sharp transition at T_F = 1800–1850 °C was reproduced in another series (not shown).

Fig. 2(b) shows the τ_{eff} of samples with variant $d_{\mu c-SiOx:H}$ of 0, 8 nm, and 16 nm. For all three samples the $\mu c-SiC:H < n >$ depositions were performed at $T_F = 1800$ °C. The sample with $d_{\mu c-SiOx:H} = 16$ nm remained



Fig. 1. Front layer configuration for a SHJ solar cell with a flat p-type silicon wafer of orientation (100), an a-SiO_x:H<i>, a μ c-SiOx:H<n>, a μ c-SiC:H<n>, and an ITO layer, and the silver contacts and the corresponding layer thicknesses.



Fig. 2. Effective lifetime (τ_{eff}) versus the HWCVD deposition time (t_{dep}). For every process a μ c-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-SiO_x:H<n>/a-S

constant at $\tau_{eff}\approx 1.0$ after $t_{dep}=40$ min. For samples with $d_{\mu c-SiOX:H}=0$ nm and 8 nm, a strong decrease from $\tau_{eff}\approx 1.0$ ms to $\tau_{eff}\approx 10\,\mu s$ was observed after $t_{dep} \ge 5$ min.

In Fig. 2(c) the τ_{eff} of the following three special cases are presented: i) At $T_F=1800~^\circ\text{C}$ and $T_H=350~^\circ\text{C}$ instead of 250 $^\circ\text{C}$, the τ_{eff} remained ≈ 1.0 ms after $t_{dep}=40$ min. ii) Using Argon instead of hydrogen and MMS at a $T_F=2100~^\circ\text{C}$, the τ_{eff} decreased from 0.7 ms to 0.3 ms after $t_{dep}=40$ min. iii) Using no gas at all at $T_F=2100~^\circ\text{C}$, the τ_{eff} increased from 1.5 ms to 1.7 ms.

Fig. 3 shows a SEM image of the sample with the μ c-SiC:H<n> layer deposited at T_F = 1950 °C (Fig. 2(a)). A top view and a cross section view are presented. In the top view a "rippled" and a flat zone are distinguishable. The cross section view reveals microscopic bubbles that size approximately 1.3 μ m in width and 0.2 μ m in height. No "ripples" and no bubbles were found with the SEM for the sample with the μ c-SiC:H<n> layer deposited at T_F = 1400 °C that did not show a decrease in $\tau_{\rm eff}$ (Fig. 2(a)).

Fig. 4 presents σ_d versus E_{04} of the $\mu c\text{-SiC:H}\mbox{-}n>$ material using HWCVD. The σ_d ranges between 10^{-12} and 10^{-1} S/cm and the E_{04} between 2.2 and 3.5 eV. The $\mu c\text{-SiC:H}\mbox{-}n>$ samples deposited at $T_F=1800\ ^\circ C$ and $T_H=250\ ^\circ C$ are highlighted in green, whereas the shaded area represents the optoelectronic regimes, $\sigma_d=10^{-7}\mbox{-}10^{-4}$ S/cm and $E_{04}=2.9\mbox{-}3.2$ eV, for these deposition conditions.

4. Discussion

The investigation of the τ_{eff} under different µc-SiC:H<n> deposition conditions and with different $d_{\mu c-SiOx:H}$ shows that it is possible to maintain a high τ_{eff} with µc-SiO_x:H on top of the a-SiO_x:H passivation layer, if: i) $T_F \le 1800$ °C, and ii) $d_{\mu c-SiOx:H} \ge 16$ nm. Otherwise, the τ_{eff} was strongly decreased within 5 min.

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