Application of crystalline silicon surface oxidation to silicon heterojunction solar cells

CrossMark

Takafumi Oikawa [a], Keisuke Ohdaira [a, b, *], Koichi Higashimine [a, b], Hideki Matsumura [a, b]

[a] Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
[b] CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

A B S T R A C T

We study the effect of ultra-thin oxide (SiO_x) layers inserted at the interfaces of silicon heterojunction (SHJ) solar cells on their open-circuit voltage (V_{OC}). The SiO_x layers can be easily formed by dipping c-Si into oxidant such as hydrogen peroxide (H_2O_2) and nitric acid (HNO_3). We confirm the prevention of the undesirable epitaxial growth of Si layers during the deposition of a-Si films by the insertion of the ultra-thin SiO_x layers. The formation of the SiO_x layers by H_2O_2 leads to better effective minority carrier lifetime (τ_{eff}) and V_{OC} than the case of using HNO_3. c-Si with the ultra-thin SiO_x layers formed by H_2O_2 dipping, prior to deposition of a-Si passivation layers, can have high implied V_{OC} of up to ~0.714 V.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The demand of solar cells has been growing in the last decade, and for more spread of photovoltaics, further improvement in the conversion efficiency is required [1]. Since crystalline silicon (c-Si) wafer-based solar cells are the most popular structures in the photovoltaic market at present, the enhancement of their conversion efficiency is of great importance [1]. Of a variety of Si wafer-based solar cells, Si heterojunction (SHJ) solar cells have recently received much attention [2–6]. The SHJ solar cell is composed of a c-Si wafer and hydrogenated amorphous Si (a-Si) films, and has a plenty of advantages such as high conversion efficiency accompanied by high open-circuit voltage (V_{OC}) and low manufacturing temperatures. Intrinsic a-Si (i-a-Si) films are utilized for the passivation of crystalline Si (c-Si) surfaces owing to the effect of abundant hydrogen in the a-Si films. The best reported V_{OC} is 0.750 V with an efficiency of 24.7% for a conventional SHJ structure [2] and 0.740 V with an efficiency of 25.6% for a heterojunction back-contact (HBC) structure [3]. The SHJ solar cells have thus been expected to be in the mainstream of next-generation c-Si solar cells.

For high-efficiency SHJ solar cells, i-a-Si passivation layers

realizing sufficiently low surface recombination velocity is essential. The i-a-Si passivation films are generally formed by plasma-enhanced chemical vapor deposition (PECVD), in which the suppression of plasma damage onto c-Si surfaces is often problematic. In contrast, catalytic CVD (Cat-CVD), often also referred to as hot-wire CVD, can form i-a-Si passivation films without plasma damage since its gas decomposition mechanism is not based on plasma process but through catalytic cracking on a heated catalyzing wire [7,8]. Cat-CVD is thus expected to be superior for the fabrication of SHJ solar cells. It should be noted that the passivation property of a-Si/c-Si interfaces is governed not only by the quality of i-a-Si itself and a degree of damage onto c-Si during deposition but also by the presence or the absence of the epitaxial growth of Si [9,10]. Silane (SiH_4) molecules are decomposed to one Si and four H atoms on a heated catalyzed wire in Cat-CVD [11–16], and due to the existence of bare Si radicals, the epitaxial growth of Si is more likely to occur in Cat-CVD [17]. The development of a method to prevent the Si epitaxial growth is thus required particularly for the application of Cat-CVD to the formation of a-Si passivation films. One of the possible approaches is to vanish the periodicity of c-Si lattice on the surface by forming an amorphous thin film on the c-Si. The formation of ultra-thin Si oxide (SiO_x) layers is a promising candidate for such a thin film since it can be easily formed by the oxidation of a c-Si surface and does not prevent carrier transport if it is sufficiently thin [18–21].

* Corresponding author. Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan.
E-mail address: ohdaira@jaist.ac.jp (K. Ohdaira).

In this study, we have attempted to form ultra-thin SiO_x layers on c-Si surfaces for preventing the epitaxial growth during the Cat-CVD of a-Si films by dipping c-Si wafers into hydrogen peroxide (H_2O_2) or nitric acid (HNO_3). We have also applied the c-Si surface oxidation to the fabrication of SHJ solar cells to confirm the effect of oxidation process against solar cell performance.

2. Experimental details

We used double-side-polished floating-zone (FZ) n-type c-Si wafers which have (100) orientation, a thickness of 290 μm, a resistivity of ~2 Ωcm, and a bulk lifetime (τ_b) of >10 ms. We first cleaved c-Si wafers into 2 cm × 2 cm-sized pieces, and native oxide layers on the Si wafers were removed in a 5% HF solution diluted with deionized water. The wafers were then immediately dipped in 0.5–10 wt% H_2O_2 or HNO_3 for 30 s at room temperature to form the ultra-thin SiO_x layers on c-Si surfaces. We used H_2O_2 and HNO_3 solutions with impurity range in parts per million. It should be noted that longer dipping in the oxidants does not lead to any different results, which is probably because of low treatment temperature and resulting saturation of oxidation. The thickness of the ultra-thin SiO_x layers evaluated by ellipsometry was 0.8–1.0 nm. Some of the ultra-thin SiO_x layers formed were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. We prepared i-a-Si/c-Si/i-a-Si and i-a-Si/SiO_x/c-Si/SiO_x/i-a-Si structures to confirm the effect of epitaxial growth and passivation quality. In these experiments, a-Si layers were deposited in a Cat-CVD system with changing substrate temperatures. Deposition pressure and SiH_4 flow rate were fixed at 1.0 Pa and 10 sccm, respectively. Deposition duration was also fixed at 30 s, which resulted in the a-Si thickness of 8–9 nm. We used a tungsten wire as catalyzer heated at 1800 °C for all the experiments. After the deposition of a-Si films, the samples were annealed at 200 °C for 30 min in air in order to improve the quality of a-Si/c-Si and a-Si/SiO_x/c-Si interfaces. The emergence of epitaxial growth was evaluated by spectroscopic ellipsometry and cross-sectional transmission electron microscopy (TEM). The quality of the a-Si/c-Si interfaces was characterized from the effective minority carrier lifetime (τ_{eff}) measured by the microwave photoconductivity decay (μ-PCD) method.

For SHJ solar cell fabrication, n-a-Si/i-a-Si films were deposited on one side of c-Si after the formation of ultra-thin SiO_x layers and p-a-Si/i-a-Si films were then deposited on the other side. We used PH_3 and B_2H_6 gases diluted with helium to 2.25% to form the doped a-Si layers. 80-nm-thick indium tin oxide (ITO) films were sputtered on the both sides of the samples at a substrate temperature of 100 °C. We then formed comb-shaped Ag electrodes by screen printing and successive annealing at 200 °C. The deposition condition of the a-Si films is summarized in Table 1. Note that the values in the parentheses represent those used for SHJ solar cell fabrication. We also prepared solar cells without the oxidation of c-Si surfaces for comparison. We measured τ_{eff} and implied V_{OC} by μ-PCD and quasi-steady-state photoconductivity (QSSPC), respectively, before the formation of ITO films and Ag electrodes. We characterized the solar cell performance by current density–voltage (J–V) measurement under 1-sun (AM1.5, 100 mW/cm^2) illumination.
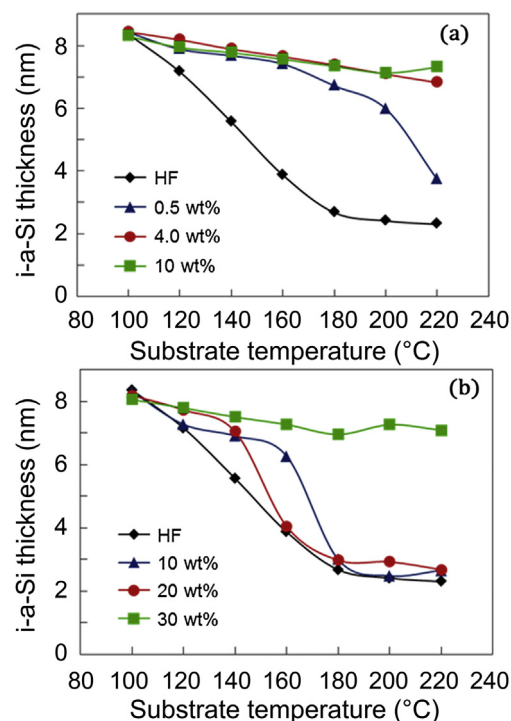
3. Results and discussion

3.1. Prevention of epitaxial growth

Fig. 1 shows the thickness of i-a-Si films on c-Si wafers with and without oxidation under various oxidant concentrations up to 10 wt% for H_2O_2 and 30 wt% for HNO_3 as a function of substrate temperature during the deposition of i-a-Si films. The thickness of i-a-Si films on c-Si without ultra-thin SiO_x layers decreases significantly with increase in substrate temperatures. This is probably because deposited Si layers are epitaxially grown in some parts, and such epitaxially grown c-Si layers with same optical properties as c-Si wafers cannot be distinguished by spectroscopic ellipsometry. Reduction in a-Si film thickness thus indicates the emergence of epitaxial growth. On the contrary, reduction in i-a-Si film thickness is less significant in the case of the samples with oxidation. This tendency is more remarkable for the structures treated in higher oxidant concentration. These results clearly indicate that the ultra-thin SiO_x layers formed on c-Si can effectively prevent the epitaxial growth.

The results above indicate that the epitaxial growth can be suppressed both by H_2O_2 and HNO_3 treatment. One can also see in Fig. 1 that epitaxial growth is adequately prevented at a deposition temperature of around 180 °C even at a H_2O_2 concentration of as low as 0.5 wt% in H_2O_2, while the effective suppression of epitaxial growth is realized only at much higher HNO_3 concentration of about 30 wt%. The reason for this difference may originate from different oxidation mechanism depending on oxidant, which will be discussed in Section 3.4.

According to these results, we have clearly confirmed the effectiveness of inserting thin SiO_x layers for the prevention of

Table 1
Process conditions for a-Si deposition.

	Gas flow rate/sccm					
	T_s/°C	SiH_4	H_2	PH_3	B_2H_6	P_{gas}/Pa
i-a-Si	160	10	—	—	—	1
n-a-Si	250	20 (10)	50 (—)	4.4	—	2
p-a-Si	250	10	50	—	8 (16)	2

Fig. 1. Thickness of a-Si films as a function of substrate temperature during film deposition on c-Si treated in (a) H_2O_2 and (b) HNO_3 at various concentrations.