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Description	

Application of Crystalline Silicon Surface Oxidation to Silicon Heterojunction Solar Cells

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ABSTRACT

We study the effect of ultra-thin oxide (SiO_x) layers inserted at the interface 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.

Keywords:

Heterojunction solar cell, Ultra-thin SiO_x layer, Cat-CVD, Passivation, Epitaxial growth

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].

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 $\sim 2 \Omega\text{cm}$, and a bulk lifetime (τ_b) of >10 ms. We first cleaved c-Si wafers into 2 cm \times 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 seconds 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 second, 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 formed by screen printing and successive annealing at 200 °C.

The deposition condition of the a-Si films is summarized in Table I. 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/cm²) illumination.

3 RESULTS AND DISCUSSION

3.1 Prevention of epitaxial growth

Figure 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 H₂O₂ and 30 wt% for HNO₃ 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 H₂O₂ and HNO₃ 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 H₂O₂ concentration of as low as 0.5 wt% in H₂O₂, while the effective suppression of epitaxial growth is realized only at much higher HNO₃ 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 epitaxial growth. In the case of high oxidant solution concentration, under which epitaxial growth is sufficiently suppressed, it is thus possible to deposit a-Si passivation layers at higher temperatures. This would lead to the utilization of a-Si films with better film quality.

We also confirm the prevention of the epitaxial growth by forming ultra-thin SiO_x layers on c-Si by TEM observation. Figures 2(a) and (b) show the cross-sectional TEM images of a-Si/c-Si and a-Si/SiO_x/c-Si structures. Note that these TEM images were observed in the SHJ structures, and deposited Si exists in the region of 8-9 nm from c-Si interface. In the case of the sample without oxidation, epitaxially-grown c-Si is definitely seen at some places. On the other hand, the epitaxial growth is almost completely prevented in the sample with H₂O₂ oxidation. This result clearly demonstrates the benefit of the SiO_x layer insertion to obtain high quality a-Si/c-Si interfaces.

3.2 Oxidant concentration dependence of minority carrier lifetime

Figure 3 shows τ_{eff} of i-a-Si/c-Si/i-a-Si structures with c-Si oxidized in H₂O₂ or HNO₃ with up to 10 wt% oxidant concentrations. i-a-Si films on the structures were deposited at 160 °C. The samples without SiO_x layers show low τ_{eff} of less than 50 μs .

According to the results shown in Figure 1, the epitaxial growth of defective c-Si occurs, and the a-Si/c-Si interface quality is thus deteriorated. On the contrary, τ_{eff} is improved in the samples with SiO_x layers. This result indicates that the formation of ultra-thin SiO_x layers on c-Si surfaces is effective in improving the quality of a-Si/c-Si heterojunction interfaces. The H_2O_2 -oxidized samples show the maximum τ_{eff} of 600 μs at an oxidant concentration of 3-5 wt%. H_2O_2 with a concentration of more than 5 wt% may induce surface damage due to excessive oxidation and resulting reduction in τ_{eff} . Compared to the H_2O_2 -oxidized samples, the dependence of τ_{eff} on HNO_3 concentration is not clear. Furthermore, the maximum τ_{eff} of H_2O_2 -oxidized samples is much higher than those of HNO_3 -oxidized samples. These may be not only due to the degree of epitaxial growth but also due to the difference of the quality of SiO_x layers themselves.

3.3 J-V characteristics

The relationship between the oxidant concentration and V_{OC} or fill factor (FF) of the SHJ solar cells with ultra-thin SiO_x layers formed in H_2O_2 or HNO_3 are shown in Figure 4. The SHJ cells with ultra-thin SiO_x layers show better V_{OC} compared to the cells without oxidation. V_{OC} is nearly independent of oxidant concentration at more than 0.5 wt% in both oxidant solutions. This result is unlikely the i-a-Si passivation experiments, in which clear dependence of τ_{eff} on oxidant concentration is seen. This may be due to the difference of sample structure. In the SHJ cells, n- and p-a-Si films are additionally deposited, and these doped a-Si films may affect the quality of a-Si/c-Si interfaces. Focusing on the absolute values of V_{OC} , the SHJ cell with SiO_x layers formed by H_2O_2 has higher V_{OC} than that with HNO_3 -oxidized layers. This fact is consistent with

previous results demonstrating more suppressed epitaxial growth and higher τ_{eff} shown in Figures 1-3.

On the other hand, FF shows a different tendency against oxidant concentration depending on oxidant solutions. The SHJ cells with H_2O_2 treatment has lower FF than the cell without oxidation treatment, and FF decreases to ~ 0.4 with increasing H_2O_2 concentration. The SHJ cells with HNO_3 treatment have a constant FF regardless of the oxidant concentration. FF is generally affected by series or shunt resistances. The SHJ solar cells fabricated in this study have sufficiently large shunt resistance, which was confirmed through pseudo FF (pFF) obtained by Suns- V_{OC} measurement. A possible impact on the FF is thus series resistance. In the SHJ cells with H_2O_2 treatment, SiO_x layers themselves may act as series resistance since FF decreases with increase in oxidant concentration. In particular, increase in the thickness and density of SiO_x layers by high concentration treatment can be a significant impact on series resistance and FF. On the contrary, the FF of the SHJ cells with HNO_3 oxidation has no dependence on oxidant concentration. This may be because the thickness of SiO_x layer formed by HNO_3 treatment does not increase significantly even higher HNO_3 concentration [21].

The previous results show that H_2O_2 treatment leads to better a-Si/c-Si interface quality and cell performance. Figure 5 and Table II show J-V characteristics of SHJ solar cells with and without H_2O_2 treatment. Note that the deposition conditions of a-Si films were slightly changed to obtain better solar cell performance, which are shown in parentheses in Table I. We can clearly see the impact of SiO_x layer insertion on τ_{eff} and V_{OC} . In particular, implied V_{OC} reaches 0.714 V, which is much larger than the implied V_{OC} of the sample without H_2O_2 treatment of 0.591 V. It should be noted that V_{OC} obtained by J-V measurement is smaller than implied V_{OC} for both SHJ cells. This may

be due to plasma damage onto a-Si/c-Si interfaces during ITO sputtering [22]. Although the FFs of J-V curves are insufficient at present due to relatively high series resistance, this can be partly improved by optimizing the sheet resistance of ITO and the thickness of a-Si layers.

3.4 ATR-FTIR measurement of oxidized Si (100)

In order to understand the different tendency of passivation quality and cell characteristics depending on the type of oxidant solution, we have attempted to evaluate the characteristics of ultra-thin SiO_x film using ATR-FTIR measurement. Figure 6 shows the FTIR spectra of Si (100) samples treated in (a) H_2O_2 and (b) HNO_3 . One can see two characteristic peaks at 2110 cm^{-1} and 2141 cm^{-1} , corresponding to SiH_2 and SiH_3 stretching vibration band, respectively [23,24], for the samples with oxidation in low concentration oxidant. These peaks derive from hydrogen-terminated Si surfaces formed by HF dipping. With increasing H_2O_2 concentration, SiH_2 and SiH_3 vibration bands disappear, while the intensity of a peak at 2243 cm^{-1} increases. This peak originates from SiO_3H bonds which can be created if all the back bond Si atoms are replaced to O by oxidation [25]. The emergence of the SiO_3H peak is a clear evidence of the oxidation of Si. On the other hand, In spite of reduction in SiH_2 and SiH_3 peaks, a SiO_3H peak does not appear after HNO_3 oxidation even at high HNO_3 concentration. This suggests that oxygen atoms in HNO_3 solution hardly react with the back bond Si atoms. SiO_3H is a dominant structure on a Si (100) surface oxidized in H_2O_2 [26]. When the back bonds are oxidized, strain due to the interfacial volume expansion occurs [27]. This may behave as an electrical resistance, which could explain the decrease in FF of SHJ cells with increase in H_2O_2 concentration. In the case of HNO_3 -oxidized samples,

according to Gondek *et al.*, compared with the oxidation of H-terminated Si surfaces by H₂O₂, HNO₃-oxidized samples show higher SiOH species (3000-3600 cm⁻¹) than H₂O₂ oxidized samples [28], although it was not clearly observed in this measurement. This indicates more adsorption of H₂O on HNO₃-treated c-Si surfaces [29]. Oxidation by HNO₃ is generally performed at higher HNO₃ concentrations and at high temperatures [20,21]. Oxidation in HNO₃ at room temperature performed in this study may be insufficient for effective Si surface oxidation. We should also discuss the suppression of epitaxial growth by HNO₃ treatment even without the formation of SiO_x layers. As mentioned above, a number of OH bonds are adhered on a Si surface after HNO₃ treatment. This might contribute to the suppression of epitaxial growth to some extent, which is less effective for the prevention of epitaxial growth than the case of H₂O₂ oxidation. The difference in the passivation quality may thus be related to the presence of SiO₃H bonds.

4. CONCLUSION

The formation of ultra-thin SiO_x layers by dipping in oxidant solution is applied to SHJ solar cell process. The introduction of ultra-thin SiO_x layers between a-Si/c-Si interfaces results in improvement in τ_{eff} and V_{OC} due to the prevention of the epitaxial growth. τ_{eff} significantly improves when we apply H₂O₂ treatment with a concentration of 3-5 wt%. A SHJ solar cell with 4 wt% H₂O₂ treatments shows V_{OC} and implied V_{OC} up to 0.683 V and 0.714 V, respectively. The results obtained have clearly demonstrated the effectiveness of ultra-thin SiO_x layers formed by H₂O₂ dipping for improvement in the performance of SHJ solar cells.

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FIGURE CAPTIONS

Figure 1 Thickness of a-Si films as a function of substrate temperature during film deposition on c-Si treated in (a) H₂O₂ and (b) HNO₃ at various concentrations.

Figure 2 Cross-sectional TEM images of (a) a-Si/c-Si and (b) a-Si/SiO_x/c-Si stacked structures.

Figure 3 τ_{eff} of c-Si wafers passivated with i-a-Si films as a function of oxidant concentration.

Figure 4 Oxidant concentration dependence of V_{OC} and FF of SHJ solar cells treated using (a) H₂O₂ or (b) HNO₃.

Figure 5 J-V characteristics of the SHJ solar cells without and with ultra-thin SiO_x layers on c-Si formed by dipping in 4.0 wt% H₂O₂.

Figure 6 ATR-FTIR spectra of Si (100) surfaces oxidized for 30 seconds at room temperature in (a) H₂O₂ or (b) HNO₃ solutions with various concentrations.

Table I Process conditions for a-Si deposition.

	Gas flow rate /sccm					P_{gas}/Pa
	$T_s/^\circ\text{C}$	SiH_4	H_2	PH_3	B_2H_6	
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

Table II Characteristics of the SHJ solar cells without and with ultra-thin SiO_x layers on c-Si formed by dipping in 4.0 wt% H₂O₂.

	a-Si/c-Si/a-Si	a-Si/SiO _x /c-Si/SiO _x /a-Si
τ_{eff} (μs)	72.6	1480
Imp. V _{OC} (V)	0.591	0.714
J _{sc} (mA/cm ²)	31.1	30.5
Cell V _{OC} (V)	0.568	0.683
FF	0.723	0.668
Efficiency (%)	12.8	13.9











