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Description	

Suppression of the epitaxial growth of Si films in Si heterojunction solar cells by the formation of ultra-thin oxide layers

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Abstract

The epitaxial growth of silicon (Si) films during the catalytic chemical vapor deposition (Cat-CVD) of intrinsic amorphous Si (i-a-Si) passivation films on crystalline Si (c-Si) wafers is suppressed by the oxidation of c-Si surfaces simply by dipping the c-Si wafers in hydrogen peroxide (H_2O_2). This oxidation treatment is also effective for (111)-oriented c-Si surfaces particularly at high a-Si deposition temperatures. The suppression of the epitaxial growth leads to the better effective minority carrier lifetime (τ_{eff}) of c-Si wafers passivated with Cat-CVD i-a-Si films. SHJ solar cells show remarkably high open-circuit voltage (V_{oc}) exceeding 0.7 V. These results clearly show the effectiveness of the insertion of SiO_x layers on the improvement in Cat-CVD a-Si/c-Si interfaces.

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1. Introduction

Silicon heterojunction (SHJ) solar cells have been expected to be one of the most promising next-generation solar cell structures because of its high open-circuit voltage (V_{oc}) and resulting superior performance at high operation temperatures [1-7]. The high V_{oc} of the SHJ solar cells originates from high-quality hydrogenated amorphous silicon (a-Si)/crystalline Si (c-Si) interfaces owing to the high passivation ability of a-Si films. Needless to say, the deposition of a-Si films on c-Si wafers must be carefully performed to realize sufficiently low surface recombination velocity (SRV). Plasma-enhanced chemical vapor deposition (PECVD), most widely utilized technique for a-Si deposition, generally requires special care to suppress plasma damage during a-Si deposition onto c-Si surfaces [8,9]. Catalytic CVD (Cat-CVD), often also referred to as hot-wire CVD, can form a-Si films by decomposing source gases on a heating metal wire through catalytic reaction, and hence, can realize the plasma-damage-less deposition of a-Si films [10]. Cat-CVD can thus provide high-quality passivation films on c-Si surfaces, and we have so far actually demonstrated the formation of Cat-CVD high-quality passivation films with low SRV [11-18].

The formation of epitaxial layers during the deposition of a-Si films is another phenomenon which should be avoided for the realization of high-quality passivation films because a large number of defects are included inside them [19]. The epitaxial layers tend to be formed more easily by Cat-CVD than by PECVD [20]. One possible reason of this may be the difference of gas decomposition mechanism. Many kinds of radicals, such as SiH_3 , SiH_2 , and SiH , are formed through the collision of electrons with silane (SiH_4) molecules in PECVD [21]. On the other hand, SiH_4 radicals are decomposed to $\text{Si} + 4\text{H}$ atoms in Cat-CVD [22], and the bare Si radicals may trigger the

formation of low-quality epitaxial layers on c-Si. Hence, the suppression of the epitaxial growth is particularly important for the deposition of a-Si passivation films by Cat-CVD. One way to prevent the epitaxial growth is to erase the periodicity of Si crystal on the surface by the formation of a very thin different material. Thin Si oxide (SiO_x) is the most promising candidate for such a material because it can be formed simply by the oxidation of c-Si surfaces. Our approach is to form ultra-thin oxide layers by dipping in liquid oxidant [11]. We have already confirmed that the epitaxial growth on Si(100) can be suppressed by the formation of SiO_x layers by dipping in hydrogen peroxide (H_2O_2) [11]. The effect of the formation of SiO_x layers, however, may affect differently on different surface orientations. In particular, the effect on Si(111) is more important since it appears on the facet of pyramid textures formed by alkali etching. In this study, we have attempted to clarify the effect of the oxidation of c-Si wafers by H_2O_2 on the suppression of epitaxial growth and resulting improvement in the passivation quality of Cat-CVD a-Si films.

2. Experimental procedures

We used (100) and (111)-orientated double-side-polished floating-zone n-type c-Si wafers. The wafers had a resistivity of $\sim 2 \text{ } \Omega\text{cm}$, thickness of $290 \text{ } \mu\text{m}$, and a bulk lifetime of $>10 \text{ ms}$. We first cut the c-Si wafers into $2 \times 2 \text{ cm}^2$ -sized square-shaped pieces, and removed native oxide layers on the Si wafers in a 5% HF solution. We then immediately dipped the c-Si wafers in 4 wt% H_2O_2 for 30 s at room temperature for the formation of the ultra-thin SiO_x layers on their surfaces. The analysis of the ultra-thin SiO_x films by spectroscopic ellipsometry (SE) revealed their thickness to be 0.8-1.0 nm. We deposited 8-9 nm-thick hydrogenated intrinsic a-Si (i-a-Si) films at various substrate

temperatures on both sides of the c-Si wafers with and without the ultra-thin SiO_x layers to investigate the effect of SiO_x formation on epitaxial growth and passivation quality. We employed a deposition pressure and a SiH₄ flow rate of 1.0 Pa and 10 sccm, respectively, for the deposition of i-a-Si films. A tungsten wire heated at 1800 °C was used as a catalyzer for the decomposition of SiH₄ gas molecules. The c-Si wafers coated with the i-a-Si passivation films were then annealed at 200 °C for 30 min in air for the improvement in the quality of i-a-Si/c-Si interfaces. If the epitaxial growth takes place on the c-Si, the epitaxially-grown layers have the same optical property as c-Si, and cannot thus be optically distinguished. Hence, we used SE as a method to evaluate a degree of epitaxial growth. We also visualized Cat-CVD a-Si/c-Si interfaces by cross-sectional transmission electron microscopy (TEM). The passivation ability of Cat-CVD i-a-Si films was characterized through the effective minority carrier lifetime (τ_{eff}) of the c-Si wafers with i-a-Si films measured by the microwave photoconductivity decay (μ -PCD) method. It should be noted that the ultra-thin SiO_x layers formed by dipping in H₂O₂ do not have any passivation ability. Figure 1 shows the τ_{eff} of c-Si wafers with only ultra-thin SiO_x films (without i-a-Si passivation films) as a function of H₂O₂ concentration during oxidation process. τ_{eff} values are significantly low and rather decreases by the introduction of oxidation process. The formation of ultra-thin SiO_x films is thus only for the suppression of the epitaxial growth.

For the fabrication of SHJ solar cells, we deposited n-type a-Si (n-a-Si)/i-a-Si films on one side of the c-Si wafers and then p-type a-Si (p-a-Si)/i-a-Si films on the other side. PH₃ and B₂H₆ gases diluted with helium to 2.25% were used to deposit the doped a-Si films. We then formed 80-nm-thick indium tin oxide (ITO) films on the both sides of the c-Si wafers by sputtered at a substrate temperature of 100 °C, followed by the formation

of comb-shaped Ag electrodes by screen printing and successive annealing in air at 200 °C. The SHJ solar cells without the oxidation of c-Si surfaces were also fabricated for comparison. The area of the SHJ cells was 2.25 cm². The detailed deposition conditions of the a-Si films have been summarized elsewhere [11]. The current density-voltage (*J-V*) characteristics of the SHJ solar cells fabricated were measured under 1-sun (AM1.5, 100 mW/cm²) illumination. We also characterized the SHJ solar cells by internal quantum efficiency (IQE).

3. Results and discussion

Figure 2 show the SE-measured thickness of Cat-CVD i-a-Si films deposited on (100)- and (111)-oriented c-Si wafers as a function of substrate temperature during i-a-Si deposition. The SE-measured thickness of i-a-Si films on (100)-oriented c-Si wafers without the ultra-thin SiO_x formation decreases significantly with increase in the substrate temperature. This indicates the emergence of epitaxial growth during a-Si deposition. The (100)-oriented c-Si wafers with the ultra-thin SiO_x layers do not show such a serious reduction in the SE-measured i-a-Si thickness, indicating the suppression of the epitaxial growth by the introduction of the ultra-thin SiO_x layers. This fact has been reported in our previous literature [11]. On the contrary, (111)-oriented c-Si wafers do not show the serious reduction of SE-measured i-a-Si film thickness even without the formation of SiO_x layers particularly at low substrate temperatures. This result may correspond to the general nature of Si(111) surfaces with more tolerance for the epitaxial growth [19]. However, larger SE-measured i-a-Si thickness is confirmed on the (111)-oriented c-Si wafers with the ultra-thin SiO_x layers than those without SiO_x layers at substrate temperatures of more than 200 °C. This indicates that the formation

of SiO_x layers is also effective for (111)-oriented c-Si surfaces particularly at high substrate temperatures.

Figure 3 shows the τ_{eff} of (100)- and (111)-oriented c-Si wafers with Cat-CVD i-a-Si passivation films as a function of substrate temperature. τ_{eff} values are quite low for (100)-oriented c-Si wafers without SiO_x layers, while much higher τ_{eff} values are obtained for the c-Si wafers with SiO_x layer formation [11]. This fact shows the improvement in the quality of a-Si/c-Si interfaces by the introduction of the ultra-thin SiO_x films. On the contrary, there is no clear difference between the τ_{eff} values of (111)-oriented c-Si wafers with and without ultra-thin SiO_x films at low deposition temperatures. This is consistent with the result shown in Fig. 1, which indicates the absence of epitaxial growth at low deposition temperature. At high deposition temperatures (>200 °C), the τ_{eff} values of (111)-oriented c-Si wafers with the ultra-thin SiO_x layers are always higher than those without the SiO_x layers. This means the better a-Si/c-Si interface quality on the c-Si wafers with SiO_x layers resulting from the suppression of the epitaxial growth.

Figure 4 shows the cross-sectional TEM images of a-Si/Si(111) interfaces without and with ultra-thin oxide layers. The i-a-Si films were deposited at 240 °C in order to clearly see the effectiveness of the formation of SiO_x layers. An epitaxial layer is definitely seen in the vicinity of an a-Si/c-Si interface on the c-Si wafer without a SiO_x layer, while only much thinner epitaxial layer is observed on the c-Si wafer with a SiO_x layer. This is also a clear experimental evidence of the suppression of epitaxial growth by the usage of ultra-thin SiO_x layers.

Figure 5 shows the J - V characteristics of SHJ solar cells fabricated using Si(111) wafers without and with SiO_x oxide layers. We also used i-a-Si films deposited at

240 °C in the SHJ solar cells. Their performances are summarized in Table I. The short-circuit current density (J_{sc}) and fill factor (FF) of the SHJ cells are not sufficiently high. The low J_{sc} is because not alkali-textured but mirror-polished c-Si wafers were used for the SHJ cells and anti-reflection effect is imperfect. The insufficient FF is due to high series resistance, which is confirmed from high pseudo FF (pFF) values of >0.8 obtained by Suns-Voc measurement. One of the possible reasons for the high FFs is unoptimized ITO resistivity. The lower FF in the cell with SiO_x layers indicates that the SiO_x layers and/or thicker a-Si films can also act to increase series resistance. Similar tendency has also been confirmed for the cells with (100)-oriented wafers [11]. Note that this work does not aim at the realization of high-performance solar cells but simply focuses on the effect of oxidation process on the suppression of epitaxial growth. It should be emphasized that the SHJ cells with the ultra-thin SiO_x layers have higher τ_{eff} and V_{oc} than that without SiO_x layers. These values are ~ 2.5 ms and >0.7 V, respectively, indicating the excellent quality of a-Si/c-Si interfaces. Figure 6 shows the IQE spectra of the SHJ solar cells fabricated using Si(111) wafers without and with SiO_x oxide layers. Significantly low IQE region is confirmed in the wavelength of less than 600 nm, which is probably due to parasitic optical absorption in a-Si films formed on the illuminated side of c-Si wafers. Lower IQE is seen in the SHJ solar cell with SiO_x layers, which is consistent with the lower J_{sc} of SHJ cell with SiO_x layers shown in Fig. 5. This may be because of the existence of thicker i-a-Si films due to suppressed epitaxial growth. Note that this low J_{sc} will be easily improved by optimizing the thickness of i-a-Si and p-a-Si films. Based on the results obtained in this study, we can conclude that the oxidation of (111)-oriented c-Si by the simple H_2O_2 dipping prior to the deposition of Cat-CVD i-a-Si films is effective to suppress the epitaxial growth and

to improve the quality of a-Si/c-Si interfaces.

4. Conclusions

We have investigated the effectiveness of the H₂O₂ oxidation of (111)-oriented c-Si surfaces on the suppression of the epitaxial growth of Si films. The epitaxial growth can be prevented by the formation of ultra-thin SiO_x layers also on Si(111) surfaces particularly at substrate temperature of more than 200 °C during i-a-Si deposition. The suppression of epitaxial growth leads to better τ_{eff} values, indicating improvement in a-Si/c-Si interface qualities. The SHJ solar cell with the ultra-thin SiO_x layers shows better V_{oc} than that without SiO_x layers, demonstrating the effect of SiO_x insertion also on actual solar cell devices.

Acknowledgments

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References

- [1] M. Taguchi, A. Yano, S. Tohoda, K. Matsuyama, Y. Nakamura, T. Nishiwaki, K. Fujita, E. Maruyama, 24.7% Record efficiency HIT solar cell on thin silicon wafer, *IEEE J. Photovoltaics* 4 (2014) 96.
- [2] K. Masuko, M. Shigematsu, T. Hashiguchi, D. Fujishima, M. Kai, N. Yoshimura, T. Yamaguchi, Y. Ichihashi, T. Mishima, N. Matsubara, T. Yamanishi, T. Takahama, M. Taguchi, E. Maruyama, S. Okamoto, Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell, *IEEE J. Photovoltaics* 4 (2014) 1433.
- [3] J. Nakamura, N. Asano, T. Hieda, C. Okamoto, H. Katayama, K. Nakamura, Development of heterojunction back contact Si solar cells, *IEEE J. Photovoltaics* 4, 1491 (2014).
- [4] S. De Wolf, A. Descoedres, Z. C. Holman, C. Ballif, High-efficiency silicon heterojunction solar cells: a review, *Green* 2 (2012) 7.
- [5] J. L. Hernández, D. Adachi, D. Schroos, N. Valckx, N. Menou, T. Uto, M. Hino, M. Kanematsu, H. Kawasaki, R. Mishima, K. Nakano, H. Uzu, T. Terashita, K. Yoshikawa, T. Kuchiyama, M. Hiraishi, N. Nakanishi, M. Yoshimi, K. Yamamoto, High efficiency copper electroplated heterojunction solar cells and modules – the path towards 25% cell efficiency, *Proc. 28th European Photovolt. Solar Energy Conf.*, 2013, p. 741.
- [6] A. Descoedres, Z. C. Holman, L. Barraud, S. Morel, S. De Wolf, C. Ballif, >21% Efficient Silicon Heterojunction Solar Cells on n- and p-Type Wafers Compared, *IEEE J. Photovolt.* 3 (2013) 83.
- [7] M. Taguchi, A. Terakawa, E. Maruyama, M. Tanaka, Obtaining a Higher V_{oc} in HIT Cells, *Prog. Photovolt.: Res. Appl.* 13 (2005) 481.

- [8] D. Sarkar, E. U. Onyegam, S. Saha, L. Mathew, R. A. Rao, M. M. Hilali, R. S. Smith, D. Xu, D. Jawarani, R. Garcia, R. Stout, A. Gurmu, M. Ainom, J. G. Fossum, S. K. Banerjee, Remote Plasma Chemical Vapor Deposition for High-Efficiency Ultra-Thin ~25-Microns Crystalline Si Solar Cells, Proc. 38th IEEE Photovoltaic Specialists Conf., 2012.
- [9] H. Matsumura, K. Higashimine, K. Koyama, K. Ohdaira, Comparison of crystalline-silicon/amorphous-silicon interface prepared by plasma enhanced chemical vapor deposition and catalytic chemical vapor deposition, J. Vac. Sci. Technol. B 33 (2015) 031201.
- [10] H. Matsumura, Catalytic chemical vapor deposition method producing high quality hydrogenated amorphous silicon, Jpn. J. Appl. Phys. 25 (1986) L949.
- [11] T. Oikawa, K. Ohdaira, K. Higashimine, H. Matsumura, Application of crystalline silicon surface oxidation to silicon heterojunction solar cells, Current Appl. Phys. 15 (2015) 1168.
- [12] S. Tsuzaki, K. Ohdaira, T. Oikawa, K. Koyama, H. Matsumura, Improvement in passivation quality and open-circuit voltage in silicon heterojunction solar cells by the catalytic doping of phosphorus atoms, Jpn. J. Appl. Phys. 54 (2015) 072301.
- [13] Trinh Cham Thi, K. Koyama, K. Ohdaira, H. Matsumura, Drastic reduction in the surface recombination velocity of crystalline silicon passivated with Cat-CVD SiN_x films by introducing phosphorous Cat-doped layer, J. Appl. Phys. 116 (2015) 044510.
- [14] Trinh Cham Thi, K. Koyama, K. Ohdaira, H. Matsumura, Passivation quality of a stoichiometric SiN_x single passivation layer on crystalline silicon prepared by Cat-CVD and successive annealing, Jpn. J. Appl. Phys. 53 (2014) 022301.
- [15] T. Hayakawa, T. Ohta, Y. Nakashima, K. Koyama, K. Ohdaira, H. Matsumura,

Effect of radical-doped n^+ back surface field layer on the effective minority carrier lifetimes in crystalline Si with amorphous Si passivation Layer deposited by catalytic chemical vapor deposition, *Jpn. J. Appl. Phys* 51 (2012) 101301.

[16] Trinh Cham Thi, K. Koyama, K. Ohdaira, H. Matsumura, Passivation characteristics of $\text{SiN}_x/\text{a-Si}$ and $\text{SiN}_x/\text{Si-rich SiN}_x$ stacked layers on crystalline silicon, *Sol. Energy Mater. Sol. Cells* 100 (2012) 169.

[17] H. Matsumura, M. Miyamoto, K. Koyama, K. Ohdaira, Drastic reduction in surface recombination velocity of crystalline silicon by surface treatment using catalytically-generated radicals, *Sol. Energy Mater. Sol. Cells* 95 (2011) 797.

[18] K. Koyama, K. Ohdaira, H. Matsumura, Extremely low surface recombination velocities on crystalline silicon wafers realized by catalytic chemical vapor deposited $\text{SiN}_x/\text{a-Si}$ stacked passivation layers, *Appl. Phys. Lett.* 97 (2010) 082108.

[19] U. K. Das, M. Z. Burrows, M. Lu, S. Bowden, R. W. Birkmire, Surface passivation and heterojunction cells on Si (100) and (111) wafers using dc and rf plasma deposited Si:H thin films, *Appl. Phys. Lett.* 92 (2008) 063504.

[20] Qi Wang, M. Page, Y. Ai, W. Nemeth, L. Roybal, H.-C. Yuan, Hydrogenated amorphous Si deposition for high efficiency a-Si/c-Si heterojunction solar cells, *Proc. 39th IEEE Photovolt. Specialists Conf.*, 2012, p. 188.

[21] A. Matsuda, Thin-film silicon –growth process and solar cell application–, *Jpn. J. Appl. Phys.* 43 (2004) 7909.

[22] S. Tange, K. Inoue, K. Tonokura, M. Koshi, Catalytic decomposition of SiH_4 on a hot filament, *Thin Solid Films* 395 (2001) 42.

Figure captions

Fig. 1 τ_{eff} of bare c-Si wafers with ultra-thin SiO_x films as a function of H_2O_2 concentration.

Fig. 2 SE-measured thickness of Cat-CVD i-a-Si films deposited on (100)- and (111)-oriented c-Si wafers as a function of substrate temperature.

Fig. 3 τ_{eff} of (100)- and (111)-oriented c-Si wafers with Cat-CVD i-a-Si passivation films as a function of substrate temperature.

Fig. 4 Cross-sectional TEM images of a-Si/Si(111) interfaces (a) without and (b) with ultra-thin oxide layers.

Fig. 5 J - V characteristics of SHJ solar cells fabricated using Si(111) wafers without and with SiO_x oxide layers.

Fig. 6 IQE spectra of SHJ solar cells fabricated using Si(111) wafers without and with SiO_x oxide layers.

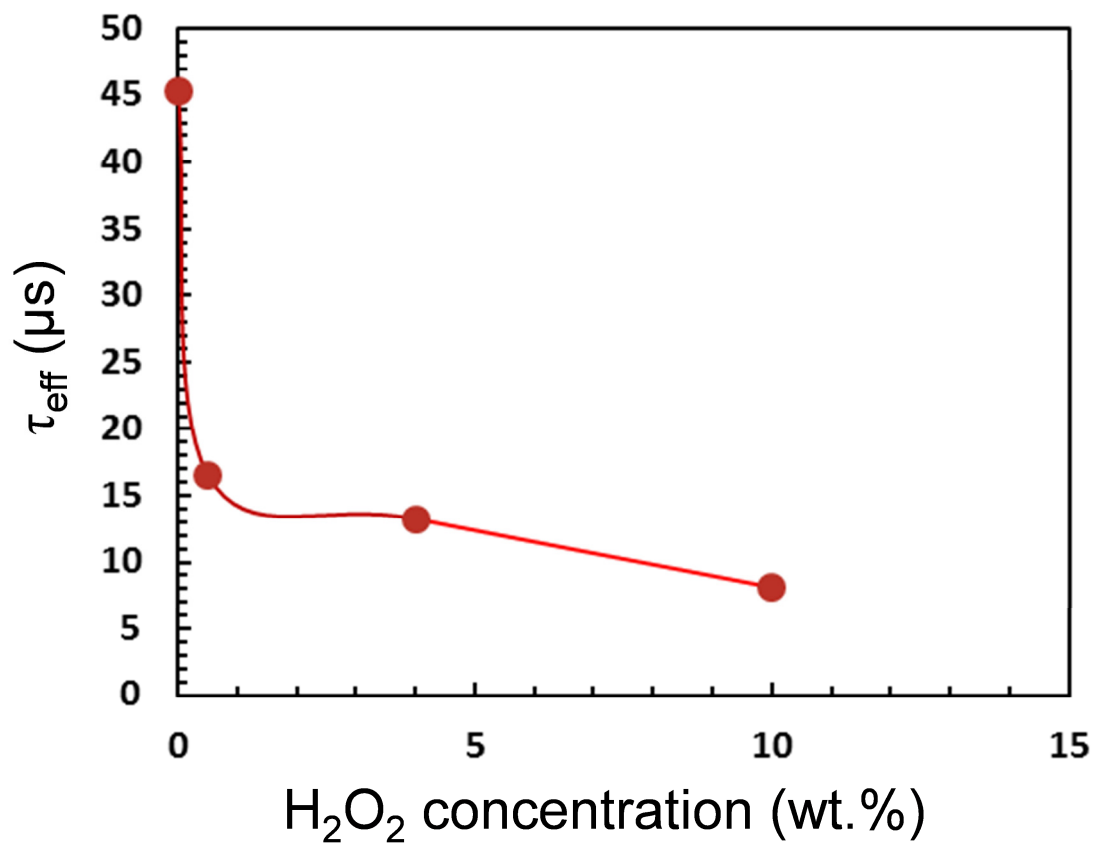


Figure 1 K. Ohdaira *et al.*,

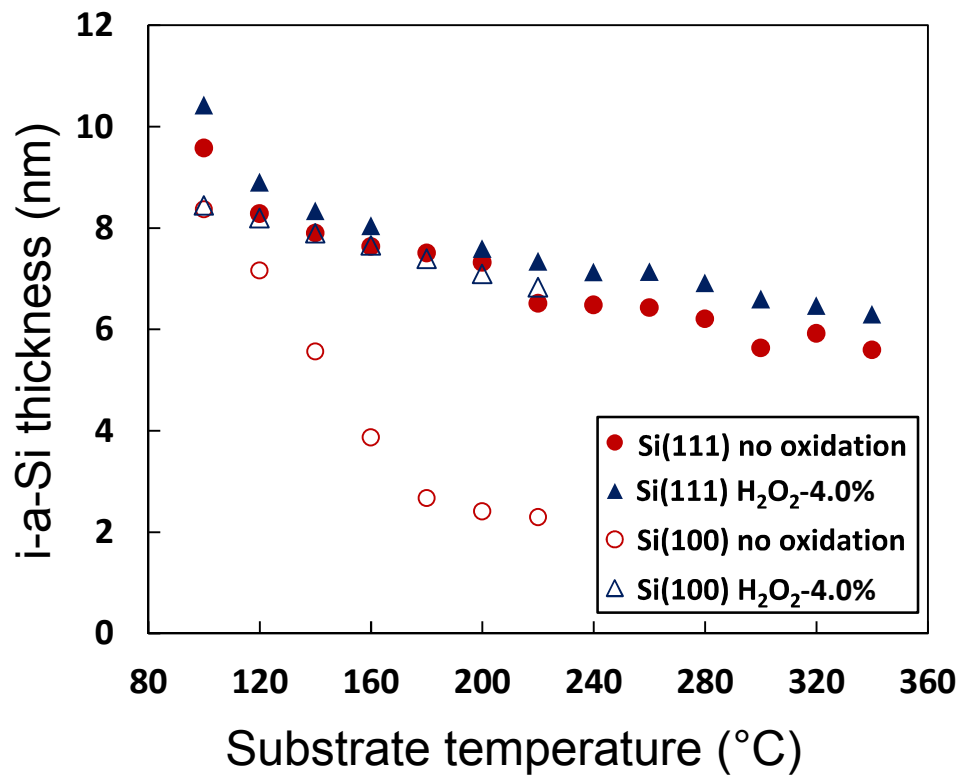


Figure 2 K. Ohdaira *et al.*,

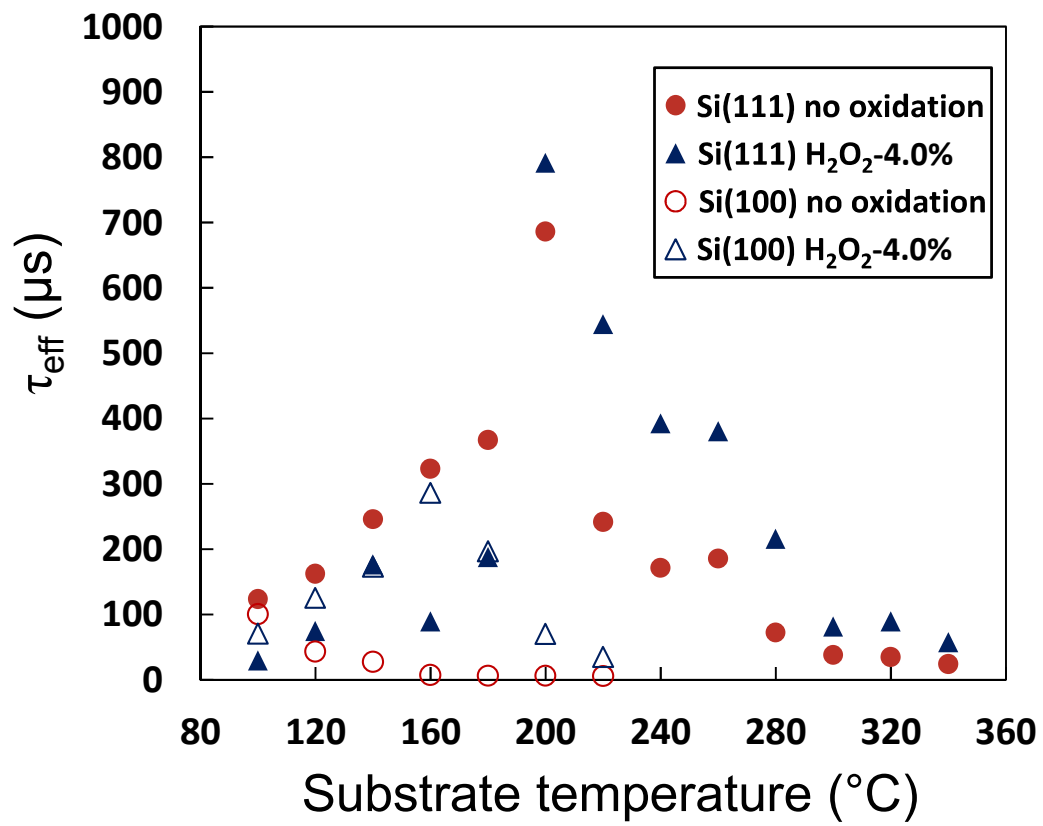


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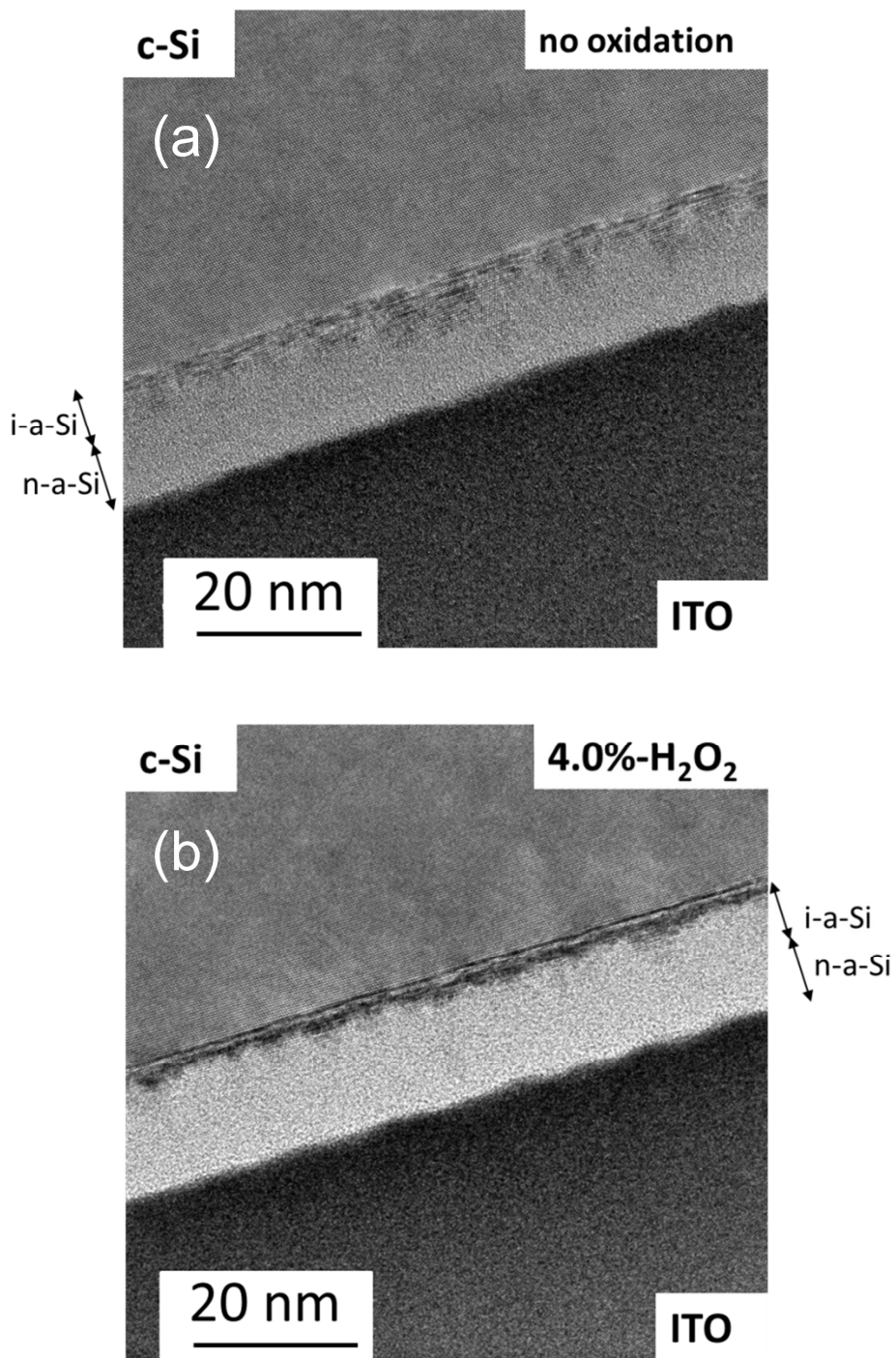


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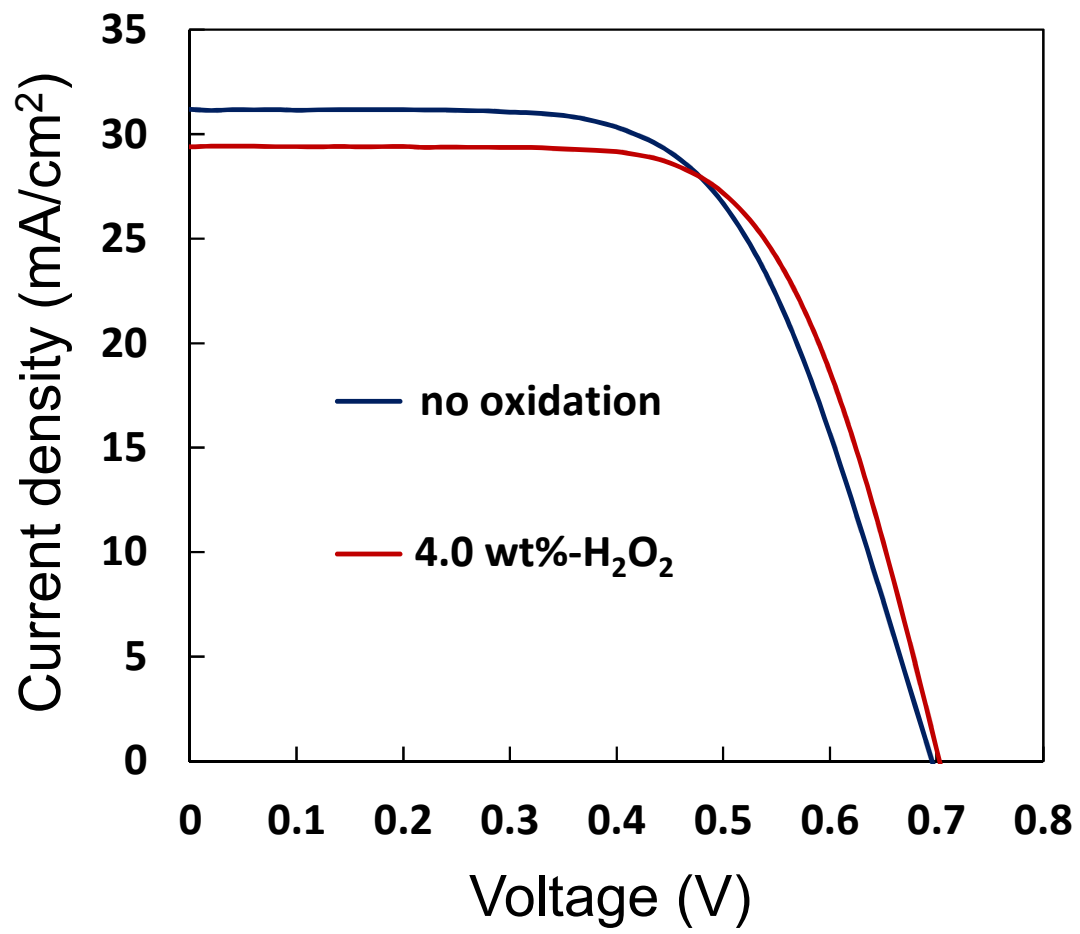


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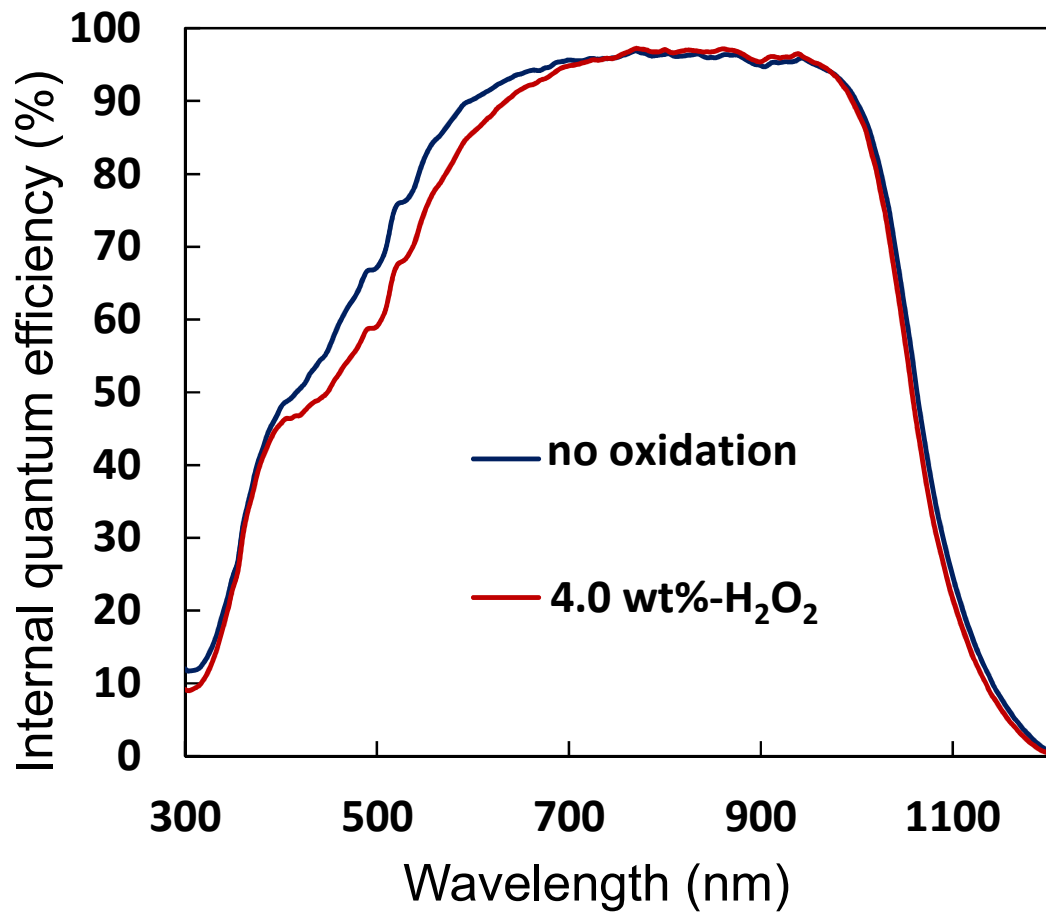


Figure 6 K. Ohdaira *et al.*,