Evidence for efficient passivation of vertical silicon nanowires by anodic aluminum oxide

Van Hoang NGUYEN¹, Shinya KATO², and, Noritaka USAMI^{1,3}

MEXT, FUTURE-PV Innovation, Japan Science and Technology Agency (JST)¹

Graduate school of Engineering, Nagoya Institute of Technology, 466-8555 Nagoya, Japan²

Graduate School of Engineering, Nagoya University, 464-8603 Nagoya, Japan³

Corresponding author: nguyenvanhoang1984@gmail.com

Abstract — We report on evaluation of effective carrier lifetimes of Si nanowires, which were selectively grown inside nanochannels of anodic aluminum oxide template using gas source molecule beam epitaxy. The carrier lifetime measurements were conducted under different injection level of irradiated photons at wavelength of 349 nm. It was found that anodic aluminum oxide template functioned not only as a mechanical guide of Si nanowires but also as an efficient passivation material. The effective carrier lifetime increased from 39 to 65.8 μ s upon postdeposition anneal of 400 °C. Furthermore, thermal treatment at 650 °C could enhance the excited carriers to diffuse inside Si substrate and yielded a promising effective carrier lifetime of 152 μ s. The Si nanowires embedded with anodic aluminum oxide templates are proved to be as potential candidate for fabrication of high efficiency solar cells.

Index Terms — AAO template, Si nanowires, effective carrier lifetime, selective growth

1. Introduction

Si nanowire (Si NW) arrays are intensively studied for solar cell fabrications owing to the quantum size effect to engineer the band gap [1]. The selective growth of Si NW assisted with anodic aluminum oxide template (AAO) using gas source molecular beam epitaxy (MBE) is advantageous compared with conventional methodology as electron beam lithography [2], metal-assisted chemical etching [3] in term of vertically epitaxial structures with controlled diameter, good mechanical stability supported by AAO template, availability of cheap passivation material and absence of metallic contamination. To achieve high-density Si NW by limiting the non-selective deposition of Si grains on AAO template, growth temperature, flow rate of gas source, AAO geometry and anodization process should be carefully controlled [4,5].

Carrier lifetime is one of the effective means to evaluate material quality for solar cells. A widely used tool is the microwave detected photoconductance decay (μ PCD) system, which is based on determination of the time decay of the excess carriers generated by irradiated photons [6–8]. To improve the effective carrier lifetime, surface recombination loss of carriers should be suppressed by somehow passivating the surface of Si NW. **Using chemistry PEDOT:PSS as a chemical passivation exhibited the effective carrier lifetime of Si NW at 8.5 μ s [9]. By controlling the deposition time and plasma power of hydrogenated amorphous silicon deposition, the effective carrier lifetime of 0.51- μ m-Si nanowires is around 6 μ s [10].** Recently, the Al_2O_3 thin film was considered as a promising candidate of surface passivation thanks to both reduction in interface defects and formation of fixed charges upon postdeposition anneal [11–13]. The Al_2O_3 thin film for passivation is generally deposited by means of plasma/thermal Atomic Layer Deposition (ALD) or Chemical Vapor Deposition (CVD). In this contribution, the abbreviation ALD will be used to stand for alumina thin film deposited by ALD. As an alternative low-cost method, AAO template fabricated by anodization process has been considered as an attractive passivation material [14,15]. Interestingly, AAO template is used as nanochannels for selective growth of vertically aligned Si NW. Therefore, the surface of Si NW could be effectively passivated by the AAO template, which might result in suppression of surface recombination loss.

In this paper, we report on characterizations of effective carrier lifetimes in Si NW obtained by selective growth assisted with AAO template using μ PCD at wavelength of 349 nm. Similar as conventional ALD, postdeposition anneal was used to study the passivation functionality of AAO template. Si NW embedded with AAO template and

ALD on the top (ALD/AAO/Si NW/Si substrate) yielded a promising effective carrier lifetime of 39 and 65.8 μs before and after thermal treatment of 400°C under injection level of $2.5 \times 10^{13} \text{ cm}^{-2}$. The possible explanation is that the diffusion of O ion from AAO to Si NW as well as the rearrangement of ions in Al sites under thermal treatment of 400°C could direct to a negative fixed charges to prevent the excited carriers from recombining at the interface. With increasing annealing temperature, an effective carrier lifetime increased up to 152 μs at 650°C followed by an abrupt decrease at 700°C. This increase of effective carrier lifetime can be due to enhanced diffusion of excited carriers inside Si substrate upon postdeposition anneal of 650°C. It revealed that the AAO template was considered as an excellent passivation material of Si NW, which yielded the promising effective carrier lifetimes. The Si NW embedded with AAO template can open a new path to fabrication of high efficiency solar cells.

2. Experiment

The experimental procedure of Si NW grown by selective growth was described in Figure 1. The Czochralski-grown P-doped Si (111) substrates with a resistivity of 2-4 $\Omega\cdot\text{cm}$ were employed for all experiments. The critical points of experimental process were to insert an Al thin film evaporated at low deposition rate before thickening Al for anodization to facilitate removal of the so-call “barrier layer” at the bottom of nanopores, and careful termination of the anodization process by monitoring an anodization current [16]. However, controlling the switch-off anodization current was still a challenge owing to its rapid drop at room temperature. Therefore, a cooling system was employed to slow down the electrochemical rate for more precise termination of the anodization process. The Al thin film acting as the anode electrode was positioned onto water block (cold plates), where flowing water was kept at 1°C. A Pt filament served as the cathode. The sample size ($\sim 1.2\text{ cm}^2$) and the distance between the electrodes were kept fixed. The net current resulting from the anodizing process was the same in all experiments. The anodization process was intended to be stopped when the anodization current decreased to 15 % of the steady-state current.

Regarding selective growth employing source gas Si_2H_6 , growth conditions were strictly considered to avoid the non-selective deposition of Si grains on AAO template. The presence of Si grains prevents the incoming laser from penetrating into Si NW for generating excess carriers inside Si NW. Therefore, non-selective deposition of Si grains should be as modest as possible to ease the incoming laser source to Si nanowires. The growth temperature was kept at 800 °C to avoid the conglomerated structures, which comprised the small grains piled up inside nanochannels. The flow rate of Si_2H_6 was altered to optimize the growth condition. Before epitaxial growth, the surface oxide was etched with 1% HF for 10 s at room temperature. The Si NW were grown using a gas source MBE system (Air-Water VCE S2020). The growth time was chosen as 90 min. All samples were annealed at 850 °C for 5 min before introducing Si_2H_6 into the growth chamber. After MBE growth, scanning electron microscope (SEM) (Hitachi, SU8230) was used to investigate morphology of as-grown samples as well as Si NW after removal of AAO template. The carrier lifetime measurement taken by microwave photo-conductivity decay (μPCD) method (KOBELCO, LTA1512EP) was employed for

all as-grown Si nanowires. A 5 ns laser pulse with a wavelength of 349 nm and a spot size of 2 mm was used to generate excess carrier density. Samples were measured at various excitation photon density levels of 2.5×10^{13} (L1), 5.0×10^{13} (L2), and 1.0×10^{14} (L3) cm^{-2} . A differential microwave antenna detection with frequency of 10 GHz was used to measure photoconductivity of sample. The microwave area was split into two parts with area of $5 \times 10 \text{ mm}^2$ for each part. The laser spot was irradiated on one part and signal from this part is taken as measured signal. Signal from another part without laser irradiation is taken as reference signal. The results of carrier lifetime measurements are resulted from difference between two signals. With such small size of samples as ours, the results of carrier lifetime measurements were more precise at the center. Carrier lifetime measurement at other points (0,1), (0,-1), (1,0) and (-1,0) were also taken into account. The unit is 1 millimeter. The results used in manuscript were resulted from average value of measured carrier lifetimes, which is not much different from the center point. The length of Si NW intended to be smaller than 1 μm ; therefore, the wavelength of incident source was selected as 349 nm, which penetrated into the samples at absorption depth of 10 nm [17]. To eliminate the recombination effect on top of Si nanowires, the as-grown samples were passivated by alumina thin film using thermal ALD. Finally, the Si nanowires were liberated by removing the AAO template with 5% H_3PO_4 at 30 °C for 20 minutes for additional SEM observation.

3. Results and discussion

3.1. Selective growth at different flow rates at growth temperature of 800 °C

Figures 2(a) and 2(b) show the top-view SEM images of samples grown at 800 °C with flow rates of 0.5, and 0.7 sccm, respectively. It was found that the selective growth was favorable at flow rate of 0.5 sccm, and only a few Si crystal grains were formed on the AAO template [Fig. 2(a)]. However, increasing the flow rate till 0.7 sccm caused poor selectivity and dense Si grains appeared on the AAO template [Fig. 2(b)]. Similarly in previous report [4], the impinging Si_2H_6 not only dissociated with active bare Si substrate but also AAO template at high flow rate. As a consequence, plenty of Si grains were produced on the AAO template. In fact, selectivity is quite sensitive to the flow rate of gas source at 800 °C, and a slight modification of flow rate directed to violation of selective growth. Figures 2(c) and 2(d) show the cross-sectional SEM images of samples after removal of the AAO template grown at flow rates of 0.5 and 0.7 sccm, respectively. At a flow rate of 0.5 sccm, 700-nm-long Si nanowires were observed on the Si substrate; whereas, the length of Si NW was about 300 nm using flow rate of 0.7 sccm. It can be explained that the Si thin film nonselectively deposited on top of the AAO template prevented the gas transport to nanochannels, which yielded short Si NW. Obviously, the samples with plenty of non-selective Si grains were unfavorable to characterize the effective lifetime in Si NW.

3.2. Carrier lifetime measurement under different Si NW geometries

Carrier lifetime measurement using wavelength of 349 nm, frequency of 10GHz and density of irradiated photon of $5 \times 10^{13} \text{ (cm}^{-2}\text{)}$ was applied for AAO template (AAO/Si substrate), 300-nm- and 700-nm-long Si NW (AAO/Si NW/Si substrate) [Fig. 3]. Herein, 300-nm-long Si NW was grown using flow rate of 0.5 sccm and growth time of 40min. The AAO/Si substrate, AAO/300-nm- and 700-nm-long Si NW/Si substrate exhibited the effective carrier lifetimes of 0.8 ± 0.02 , 5.2 ± 0.3 and $19.8 \pm 1.3 \text{ } \mu\text{s}$, respectively. These results indicate that the surface recombination velocity at the bottom

of AAO template is quite high presumably owing to defects appeared during anodization process. The effective carrier lifetime was improved with presence of Si NW and it induced a longer carrier lifetime with longer Si NW. With 700-nm-Si NW, the effective carrier lifetime is 4 times longer than that of 300-nm-long Si NW. The measured carrier lifetime is affected by extrinsic surface recombination in addition to intrinsic lifetime, which could comprise surface recombinations at AAO/Si NW, top of Si NW and Si NW/Si substrate. Assuming that the surface recombination of AAO/Si NW are similar in all samples and the recombination velocity of AAO/Si NW must be much smaller than that at the bottom/top of NW. The difference of effective carrier lifetime is due to only carrier diffusion lifetime, which is proportional to length of Si NW. Herein, the diffusion along Si NW was more considered than lateral diffusion. Therefore, longer Si NW are, longer carrier lifetime is. By simply assuming that the carrier diffusion lifetime is proportional to the square of the length of Si NW [18]. The lifetime in 700 nm-long-Si NW is roughly 5 times longer than that in 300 nm-long-Si NW. Rough estimation of carrier diffusion lifetime difference with a factor of 5 is quite approximate to that of experimental results, which reasonably approved that the recombination of AAO/Si NW is much smaller than that at top/bottom interface.

The decay curves of photo-excited carriers in Fig.3 consisted of two parts, which were fast decay and slow decay parts. The fast decay turned out the carrier lifetime of 0.6, 0.8 and 4.4 μs for AAO/Si substrate, AAO/300-nm-long Si NW and 700-nm-long Si NW/Si substrates, respectively. Furthermore, the carrier lifetimes resulted from slow decay component are 10.5, 58.7 and 53.3 μs for AAO/Si substrate, AAO/300-nm-long Si NW and 700-nm-long Si NW/ Si substrate, respectively. This slow component was usually attributed to emission/capture of minority/majority carriers at the carrier traps regarded as defect levels [19]. By observing the temperature dependence of slow components of photo-excited carrier decay curves, the factors contributed to slow components were deduced [20]. However, the measured carrier lifetime with AAO/Si NW/ Si substrate is affected by extrinsic surface recombination in addition to intrinsic lifetime, so the investigation of origin of the slow decay component is complicated and out of target in this contribution.

3.3. Impact of passivation material on carrier lifetime of Si NW

Figure 4 shows the decay curves of Si NW without AAO surround (Si NW/Si substrate), AAO/Si NW/Si substrate and Si NW embedded with AAO template and Al₂O₃ by ALD on the top (ALD/AAO/Si NW/Si substrate). The effective carrier lifetimes are 1.7 ± 0.03 , 19.8 ± 1.3 and 24.8 ± 4.2 μ s for Si NW/Si substrate, AAO/Si NW/Si substrate and ALD/AAO/Si NW/Si substrate, respectively. It demonstrates that the AAO template plays an important role as significant passivation of Si NW, which exhibited a carrier lifetime roughly 11 times higher than that of Si NW/Si substrate. However, employment of AAO as an applicable passivation material was studied in modest [14]. The impact of AAO utilization for solar cell fabrication can be from hydrogen incorporation during AAO fabrication on Si substrate, which can deactivate recombination-active sites at the bottom of AAO [21]. Furthermore, the effective carrier lifetime of Si NW was enhanced to roughly 24.8 ± 4.2 μ s once the top of Si NW was passivated by ALD. The AAO/Si NW/Si substrate without ALD is more recombination active than only ALD/AAO/Si NW/Si substrate.

Similarly in Fig.3, the decay curves of photo-excited carriers in Fig. 4 comprised of two components, which were fast decay and slow decay components. The carrier lifetimes deduced from fast decay curves were 0.8, 4.4 and 2.1 μ s for Si NW/Si substrate, AAO/Si NW/Si substrate and ALD/AAO/Si NW/Si substrate, respectively. Furthermore, the carrier lifetime extracted from the slow decay components are roughly 42.1, 53.3 and 100.0 μ s for Si NW/Si substrate, AAO/Si NW/Si substrate and ALD/AAO/Si NW/Si substrate, respectively.

3.4. Impact of incident irradiated photon on carrier lifetime of Si NW

Figure 5 shows the carrier lifetime of AAO passivated by ALD (ALD/AAO/Si substrate), ALD/AAO/Si NW/Si substrate and Si wafer passivated by ALD (ALD/Si substrate) as a function of density of irradiated photons. It is noted that the effective carrier lifetimes of ALD/AAO/Si NW were slightly varied in range of 1-1.5 μ s under any injection level. The effective carrier lifetimes of ALD/Si substrate increased with

increasing density of irradiated photons. With excitation intensity of 2.5×10^{13} , 5×10^{13} , and $1 \times 10^{14} \text{ cm}^{-2}$, the effective carrier lifetimes were recorded as 158 ± 15.0 , 183 ± 17.1 and $204 \pm 17.8 \text{ } \mu\text{s}$, respectively. In contrast, decrease of irradiated photons applied for ALD/AAO/Si NW/Si substrate resulted in gradually increasing carrier lifetime. Concretely, the effective carrier lifetimes were recorded as 12 ± 4.8 , 24.8 ± 4.2 and $39 \pm 7.7 \text{ } \mu\text{s}$ with density of irradiated photons of 1×10^{14} , 5×10^{13} and $2.5 \times 10^{13} \text{ cm}^{-2}$, respectively. Regarding as ALD/AAO/Si substrate, the anodization process with current ratio of 15 % could leave the defects at the interface or remaining barrier layer. Despite of injection level, the effective carrier lifetimes of ALD/AAO/Si substrate were low and unvaried due to fast recombination surface. In this case, ALD passivation was insufficient to suppress the recombination. For two remaining cases, the explanations are based on the dependence of carrier lifetimes on impurity energy level and injection level. In semiconductor, the recombination carrier lifetime comprised of Shockley-Read-Hall recombination lifetime τ_{SHR} , radiative recombination lifetime τ_{rad} and Auger recombination lifetime τ_{Auger} . Regarding as such c-Si material, Shockley-Read-Hall lifetime τ_{SHR} is dominant compared with τ_{rad} and τ_{Auger} when injection level is comparable with equilibrium carrier density. When impurity or defect density is negligible to either equilibrium carrier density or injection level, the effective carrier lifetime increased with increasing injection level [22]. The similar behavior of effective carrier lifetime under different injection level was seen with bare Si substrate passivated by ALD, which obviously introduced the impurity or defect density much smaller than equilibrium carrier density. In contrast, the impurity or defect density is much higher than both injection level and equilibrium carrier density, the effective carrier lifetime decreased with increasing injection level [22]. This could be used as an explanation for behavior of effective carrier lifetime of ALD/AAO/Si NW/Si substrate under different injection level. The defects or impurities can be formed at the interface of Si NW/Si substrate during selective growth assisted with AAO template since that AAO fabrication with current ratio of 15% left the Si substrate either the unintentional anodization or remaining barrier layer at the interface. Even though the defects at the interface were significantly reduced through baking of Si NW growth, the density of defects would be still high to reduce lifetimes.

3.5. Impact of annealing temperature on carrier lifetime of Si NW

Figure 6 shows the carrier lifetimes of ALD/AAO/Si NW/Si substrate and ALD/AAO/Si substrate under different annealing temperatures. It is noted that the effective carrier lifetimes of ALD/AAO/Si substrate slightly varied in range of 1-2 μs under annealing treatment from 400 to 550 $^{\circ}\text{C}$. As reported earlier, it can be due to dense defects at the bottom of AAO template after anodization process. In contrast, the ALD/AAO/Si NW/Si substrate yielded the increasing carrier lifetimes at annealing temperature of 400 $^{\circ}\text{C}$, which are 65.8 ± 6.9 , 57.4 ± 5.1 and 51.4 ± 4.2 μs under injection level of 2.5×10^{13} , 5×10^{13} and 1×10^{14} cm^{-2} , respectively. At annealing temperature of 450 $^{\circ}\text{C}$, ALD/AAO/Si NW/Si substrate resulted in similar results induced at annealing temperature of 400 $^{\circ}\text{C}$. It was turned out that efficiency of thermal treatment of around 400-450 $^{\circ}\text{C}$ can be relevant with satisfactory low interface defect density presumably thanks to field-effect passivation as well as chemical passivation. The presence of field-effect passivation using ALD on c-Si upon postdeposition anneal was vastly reported [11–13], which was based on the rearrangement of Al^{3+} in tetrahedrally coordinated Al sites while net negative charges of O diffused to Si interface and consequently, unintentionally interfacial SiO_x formed. Consequently, high negative charges localized in Al_2O_3 underlying Si substrate through an interfacial SiO_x , strongly reduced the electron concentration at the c-Si interface by means of electrostatic shielding [23–25]. To the best of our knowledge, field-effect passivation using AAO has not been studied yet. Noted that the negative charge in Al_2O_3 preferred to appeared at the unique tetrahedrally coordinated Al site as a net negative charge, in contrast to the octahedrally coordination site as a net positive charge of Al^{3+} [26] and the AAO was composed of 2/3 of aluminum in tetrahedral coordination and 1/3 aluminum in octahedral coordination [27]. It is probably that field effect passivation can be established by O ion diffusion from AAO or ALD to Si NW as well as rearrangement of Al site, which would postulate the negative fixed charges at interfaces between AAO wall/ALD and Si NW through an intentional interfacial layer SiO_x . It can be deduced

that mixture of AAO/ALD template contribute to efficient passivation of Si NW as field-effect passivation.

At annealing temperature of 500 °C, the effective carrier lifetimes of ALD/AAO/Si NW/Si substrate abruptly decreased. That can be due to increase of interface trap density of either Si NW/ALD or Si NW/AAO since an increasing H and O atoms would diffuse to Si NW and changed the physical state of Si NW surface. Diffusion of O and H atoms of AAO into Si NW is unknown for the time being. Kato *et al.* found that thermal treatment at 500 °C could direct to inflate the ALD from Si substrate since a number of O and H diffused to Si substrate and damaged the dangling bond on the Si surface[28]. Pierre *et al.* found that the negative fixed charge density induced from Al₂O₃ passivation on c-Si was stable after annealing at 450 °C and even, 870 °C with small variation of densities. However, the interface trap density are more spread out with thick Al₂O₃ passivation and some samples exhibited a rapid increase of interface trap density[29].

Continuing the thermal treatment of 550 °C led to an increase of carrier lifetimes of ALD/AAO/Si NW/Si substrate. The effective carrier lifetimes continuously increased at thermal treatment of 600 °C and at annealing temperature of 650 °C, they attained the maximum values at 152 ± 10.1 , 115 ± 14.2 and 88.4 ± 10.2 μ s with density of irradiated photons of 2.5×10^{13} , 5×10^{13} and 1×10^{14} cm⁻², respectively. For ALD/AAO/Si substrate, the effective carrier lifetime increased at annealing temperature of 650 °C and they exhibited the values of roughly 5.2 ± 0.9 , 2.8 ± 0.3 and 2.0 ± 0.2 μ s with injection level of 2.5×10^{13} , 5×10^{13} and 1×10^{14} cm⁻², respectively. It can be explained that thermal treatment of around 600 and 650 °C offered a significant reduction of defects at the interfaces, especially between Si substrate and Si NW, which eased the excited carriers to diffuse into Si substrate and generated long carrier lifetime despite of the increase of interface trap density upon annealing temperature. Till annealing temperature of 700 °C, the carrier lifetime of ALD/AAO/Si NW/Si substrate abruptly decreased while the effective carrier lifetimes of the ALD/AAO/Si substrate are same as those at annealing temperature of 650 °C. The possible explanations are that there would be a deterioration of passivation quality owing to the presence of blisters, which were considered as lifetime killing factor at high annealing treatment. The blisters strongly depended on the Al₂O₃ thickness [29]. It is obvious that the thickness of ALD in ALD/AAO/Si substrate

is thicker than that of ALD/AAO/Si NW/Si substrate. The annealing temperature of 700 °C was still unaffected with ALD/AAO/Si substrate. Another explanation of effective carrier lifetime behavior of ALD/AAO/Si NW/Si substrate at 700 °C is that interstitial Si was supplied from a growing SiO₂/ Si interface and consequently, vacancy was formed and increased with increasing annealing temperature [30], which effectively decreased the carrier lifetimes. This could be due to increase of interface trap density in either Si NW/ALD or Si NW/AAO which becomes dominant compared with other factors. The summarized results of carrier lifetime measurements are presented in Table 1.

4. Conclusions

Effective carrier lifetime measurements of Si NW grown by selective growth assisted with AAO were evaluated. It was found that AAO acted as an efficient passivation material in addition to guiding mechanically stable vertical Si NW. The effective carrier lifetime of AAO/Si NW/ Si substrate is 11 times higher than that of Si NW/Si substrate. Furthermore, postdeposition anneal at 400 °C enhanced the effective carrier lifetime of 65.8 μs under injection level of $2.5 \times 10^{13} \text{ cm}^{-2}$. Furthermore, increasing annealing temperature at 600-650 °C could promote the excited carriers to diffuse inside Si substrate, which yielded a promising effective carrier lifetime of 152 μs under injection level of $2.5 \times 10^{13} \text{ cm}^{-2}$. Postdeposition anneal at 700 °C directed to abrupt decrease of effective carrier lifetime. It was found that Si NW grown by selective growth assisted with AAO template are promising material for fabrication of high efficiency solar cells.

Acknowledgements

This work is supported by MEXT, FUTURE-PV Innovation (FUKUSHIMA Top-level United center for Renewable Energy research – PhotoVoltaics Innovation) Project. We acknowledge Dr. Thi Cham TRINH for her contribution and advice.

Reference

- [1] MEXT FUTURE-PV Innovation, <http://www.jst.go.jp/renewable/en/> (accessed November 16, 2015).
- [2] R. Juhasz, N. Elfström, J. Linnros, Controlled Fabrication of Silicon Nanowires by Electron Beam Lithography and Electrochemical Size Reduction, *Nano Lett.* 5 (2005) 275–280.
- [3] H. Han, Z. Huang, W. Lee, Metal-assisted chemical etching of silicon and nanotechnology applications, *Nano Today*. 9 (2014) 271–304.
- [4] V.H. Nguyen, Y. Hoshi, N. Usami, M. Konagai, Selective growth of vertical silicon nanowire array guided by anodic aluminum oxide template, *Jpn. J. Appl. Phys.* 54 (2015) 95003.
- [5] V.H. Nguyen, S. Tutashkonko, Y. Hoshi, N. Usami, Effects of anodization process of aluminum oxide template fabrication on selective growth of Si nanowire arrays, *Jpn. J. Appl. Phys.* 54 (2015) 08KA02.
- [6] K. Lauer, A. Laades, H. Übensee, H. Metzner, A. Lawrenz, Detailed analysis of the microwave-detected photoconductance decay in crystalline silicon, *J. Appl. Phys.* 104 (2008) 104503.
- [7] M. Kunst, G. Beck, The study of charge carrier kinetics in semiconductors by microwave conductivity measurements. II., *J. Appl. Phys.* 63 (1988) 1093–1098.
- [8] M. Kunst, G. Beck, The study of charge carrier kinetics in semiconductors by microwave conductivity measurements, *J. Appl. Phys.* 60 (1986) 3558–3566.
- [9] X. Yu, X. Shen, X. Mu, J. Zhang, B. Sun, L. Zeng, L. Yang, Y. Wu, H. He, D. Yang, High Efficiency Organic/Silicon-Nanowire Hybrid Solar Cells: Significance of Strong Inversion Layer, *Sci. Rep.* 5 (2015) 17371.
- [10] K. Li, X. Wang, P. Lu, J. Ding, N. Yuan, The influence of passivation and photovoltaic properties of α -Si:H coverage on silicon nanowire array solar cells, *Nanoscale Res. Lett.* 8 (2013) 396.
- [11] S. Kato, Y. Kurokawa, S. Miyajima, Y. Watanabe, A. Yamada, Y. Ohta, Y. Niwa, M. Hirota, Improvement of carrier diffusion length in silicon nanowire arrays using atomic layer deposition, *Nanoscale Res. Lett.* 8 (2013) 361.
- [12] J.J.H. Gielis, B. Hoex, M.C.M. van de Sanden, W.M.M. Kessels, Negative charge and charging dynamics in Al₂O₃ films on Si characterized by second-harmonic generation, *J. Appl. Phys.* 104 (2008) 73701.
- [13] S.-Y. Lien, C.-H. Yang, K.-C. Wu, C.-Y. Kung, Investigation on the passivated Si/Al₂O₃ interface fabricated by non-vacuum spatial atomic layer deposition system, *Nanoscale Res. Lett.* 10 (2015) 1–9.

- [14] P.H. Lu, K. Wang, Z. Lu, A.J. Lennon, S.R. Wenham, Anodic Aluminum Oxide Passivation For Silicon Solar Cells, *IEEE J. Photovolt.* 3 (2013) 143–151.
- [15] Y. Li, S. Dunham, S. Pillai, Z. Ouyang, A. Barnett, A. Lochtefeld, A. Lennon, Design of Anodic Aluminum Oxide Rear Surface Plasmonic Heterostructures for Light Trapping in Thin Silicon Solar Cells, *IEEE J. Photovolt.* 4 (2014) 1212–1219.
- [16] V.H. Nguyen, Y. Hoshi, N. Usami, Simple approach for improving gold deposition inside nanoporous alumina template on Si substrate, *Appl. Surf. Sci.* 305 (2014) 9–15.
- [17] Optical Properties of Silicon | PVEducation,
<http://www.pveducation.org/pvcdrom/materials/optical-properties-of-silicon>
(accessed November 16, 2015).
- [18] W.M. Bullis, H.R. Huff, Interpretation of Carrier Recombination Lifetime and Diffusion Length Measurements in Silicon, *J. Electrochem. Soc.* 143 (1996) 1399–1405.
- [19] M. Ichimura, Temperature dependence of a slow component of excess carrier decay curves, *Solid-State Electron.* 50 (2006) 1761–1766. doi:10.1016/j.sse.2006.10.001.
- [20] M. Hirano, M. Ichimura, E. Arai, Slow Decay of Excess Carrier Concentration in Bonded Silicon-on-Insulator Wafers, *Jpn. J. Appl. Phys.* 39 (2000) 6513–6514.
- [21] P.H.D. Lu, H. Strutzberg, S. Wenham, A. Lennon, Hydrogen Incorporation during Aluminium Anodisation on Silicon Wafer Surfaces, *Electrochimica Acta.* 133 (2014) 153–160.
- [22] D.K. Schroder, Carrier lifetimes in silicon, *IEEE Trans. Electron Devices.* 44 (1997) 160–170.
- [23] A.R. Chowdhuri, C.G. Takoudis, R.F. Klie, N.D. Browning, Metalorganic chemical vapor deposition of aluminum oxide on Si: Evidence of interface SiO₂ formation, *Appl. Phys. Lett.* 80 (2002) 4241–4243.
- [24] R.F. Klie, N.D. Browning, A.R. Chowdhuri, C.G. Takoudis, Analysis of ultrathin SiO₂ interface layers in chemical vapor deposition of Al₂O₃ on Si by in situ scanning transmission electron microscopy, *Appl. Phys. Lett.* 83 (2003) 1187–1189.
- [25] G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H.F.W. Dekkers, S. De Wolf, G. Beaucarne, Very low surface recombination velocities on p-type silicon wafers passivated with a dielectric with fixed negative charge, *Sol. Energy Mater. Sol. Cells.* 90 (2006) 3438–3443.
- [26] R.S. Johnson, G. Lucovsky, I. Baumvol, Physical and electrical properties of noncrystalline Al₂O₃ prepared by remote plasma enhanced chemical vapor deposition, *J. Vac. Sci. Technol. A.* 19 (2001) 1353–1360.

- [27] D. Losic, A. Santos, Nanoporous Alumina: Fabrication, Structure, Properties and Applications, Springer, 2015.
- [28] Shinya Kato, be submitted.
- [29] P. Saint-Cast, D. Kania, R. Heller, S. Kuehnhold, M. Hofmann, J. Rentsch, R. Preu, High-temperature stability of c-Si surface passivation by thick PECVD Al₂O₃ with and without hydrogenated capping layers, Appl. Surf. Sci. 258 (2012) 8371–8376.
- [30] K. Yoshioka, S. Ishikawa, M. Mimura, T. Saitoh, Relationship between thermal treatment conditions and minority carrier lifetimes in p-type, FZ Si wafers, Sol. Energy Mater. Sol. Cells. 65 (2001) 453–458.

FIGURES AND CAPTIONS

Figure 1: Experimental process of Si nanowire growth assisted with AAO template using selective growth techniques for carrier lifetime measurements

Figure 2: Top view SEM of as-grown samples by selective growth at 800°C with flow rate of, a) 0.5 and b) 0.7 sccm. Cross-sectional SEM images of etched samples grown by flow rate of c) 0.5 and d) 0.7 sccm.

Figure 3: Carrier lifetime measurement by μ PCD at wavelength 349 nm and frequency 10GHz of AAO/Si substrate, AAO/300-nm-long Si NW/Si substrate and AAO/700-nm-long Si NW/Si substrate.

Figure 4: Carrier lifetime measurement by μ PCD at wavelength 349 nm and frequency 10GHz of Si NW/Si substrate, AAO/Si nanowire/Si substrate and ALD/AAO/Si NW/Si substrate.

Figure 5: Carrier lifetime measurement of samples ALD/AAO/Si substrate, ALD/AAO/Si NW/ Si substrate and ALD/Si substrate under different density of irradiated photon.

Figure 6: Carrier lifetime of samples, ALD/AAO/Si NW/Si substrate and ALD/AAO/Si substrate under different annealing temperature.

Table 1: Summarized results of carrier lifetime measurements of all samples

Samples	AAO/ Si subs (L2) (μ s)	Si NW / Si subs (L2) (μ s)	AAO/ Si NW/ Si subs (L2) (μ s)	ALD/ Si subs (μ s)			ALD/ AAO/ Si subs (μ s)			ALD/AAO/Si NW/ Si subs (μ s)		
				L1	L2	L3	L1	L2	L3	L1	L2	L3
AT	0.8 $\pm$ 0.02	1.7 $\pm$ 0.03	19.8 $\pm$ 1.3	158 $\pm$ 15.0	183 $\pm$ 17.1	204 $\pm$ 17.8	1.2 $\pm$ 0.03	1.3 $\pm$ 0.06	1.4 $\pm$ 0.06	39 $\pm$ 7.7	24.8 $\pm$ 4.2	12 $\pm$ 4.8
400°C							1.6 $\pm$ 0.1	1.3 $\pm$ 0.03	1.4 $\pm$ 0.06	65.8 $\pm$ 6.9	57.4 $\pm$ 5.1	51.4 $\pm$ 4.2
450°C							1.9 $\pm$ 0.2	1.4 $\pm$ 0.03	1.3 $\pm$ 0.05	65.6 $\pm$ 5.7	56.8 $\pm$ 4.3	46.6 $\pm$ 2.3
500°C							1.9 $\pm$ 0.2	1.3 $\pm$ 0.03	1.3 $\pm$ 0.05	31.7 $\pm$ 2.7	32.3 $\pm$ 3.3	29.8 $\pm$ 2.1
550°C							1.7 $\pm$ 0.2	1.4 $\pm$ 0.06	1.3 $\pm$ 0.05	82.8 $\pm$ 5.1	71.6 $\pm$ 3.3	54.4 $\pm$ 5.4
600°C							3.3 $\pm$ 0.7	3.1 $\pm$ 0.3	2.7 $\pm$ 0.2	110.4 $\pm$ 12.8	87.6 $\pm$ 9.7	68.4 $\pm$ 9.1
650°C							5.2 $\pm$ 0.9	2.8 $\pm$ 0.3	2.2 $\pm$ 0.2	152 $\pm$ 10.1	115 $\pm$ 14.2	88.4 $\pm$ 10.2
700°C							5.2 $\pm$ 1.2	3.1 $\pm$ 0.4	2.2 $\pm$ 0.2	64.0 $\pm$ 4.7	50.4 $\pm$ 4.0	34.8 $\pm$ 5.3