Solar Energy Materials & Solar Cells 157 (2016) 393–398

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

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

Van Hoang Nguyen [a,*], Shinya Kato [b], Noritaka Usami [a,c]

[a] *MEXT, FUTURE-PV Innovation, Japan Science and Technology Agency (JST), Japan*
[b] *Graduate school of Engineering, Nagoya Institute of Technology, 466-8555 Nagoya, Japan*
[c] *Graduate School of Engineering, Nagoya University, 464-8603 Nagoya, Japan*

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form
3 June 2016
Accepted 3 July 2016

Keywords:
AAO template
Si nanowires
Effective carrier lifetime
Selective growth

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 μs 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 μs. The Si nanowires embedded with anodic aluminum oxide templates are proved to be as potential candidate for fabrication of high efficiency solar cells.

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 (μPCD) 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 μs [9]. By controlling the deposition time and plasma power of hydrogenated amorphous silicon deposition, the effective carrier lifetime of 0.51-μm-Si nanowires is around 6 μs [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 μPCD 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 2.5×10^{13} 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

---

* Corresponding author.
E-mail address: nguyenvanhoang1984@gmail.com (V.H. Nguyen).

http://dx.doi.org/10.1016/j.solmat.2016.07.002
0927-0248/

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 Fig. 1. The Czochralski-grown P-doped Si (111) substrates with a resistivity of 2–4 Ω 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 (~1.2 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 5×10 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 mm. 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 min for additional SEM observation.

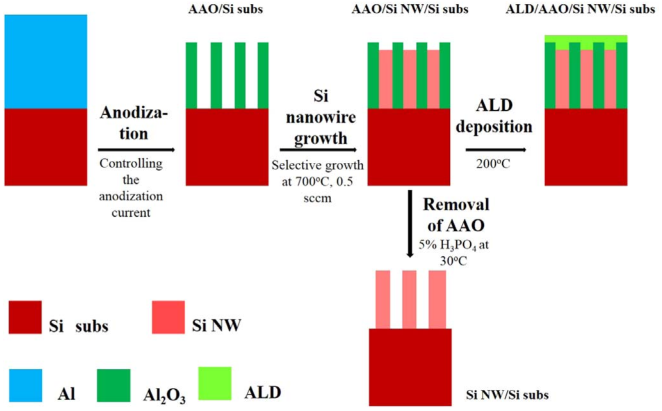

Fig. 1. Experimental process of Si nanowire growth assisted with AAO template using selective growth techniques for carrier lifetime measurements.

3. Results and discussion

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

Fig. 2(a) and (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. Fig. 2(c) and (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 10 GHz and density of irradiated photon of 5×10^{13} (cm^{-2}) was applied for AAO template (AAO/Si substrate), 300-nm- and 700-nm-long Si NW (AAO/Si NW/Si substrate)