Influence of nanowires length on performance of crystalline silicon solar cell

Haofeng Li, Rui Jia,[a)] Chen Chen, Zhao Xing, Wuchang Ding, Yanlong Meng, Deqi Wu, Xinyu Liu, and Tianchun Ye
Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, China

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Silicon-nanowire (Si-NW) array, prepared by an electroless chemical-etching method, shows excellent optical antireflection property over a wide spectral bandwidth. The influence of the wire length on the optical antireflection property and the solar cell performance were studied for both the Si-NW array solar cells and the planar solar cells. The reflectance of NWs solar cells is almost invariable and much lower than that of the planar solar cells but the performance of planar solar cells is the best. Results show the performance of NWs solar cells is strongly affected by some other factors such as surface passivation and electrode-contact property. © *2011 American Institute of Physics*. [doi:10.1063/1.3574904]

Reducing reflectance is an important approach to enhance the performance of the solar cells.[1,2] Recently, the influence of the silicon-nanowire (Si-NW) array on the performance of the crystalline silicon (c-Si) solar cells has been raised to an unprecedented level.[3–5] Compared with the planar solar cells, the Si-NW array solar cells can reach ultralow reflectance.[6,7] However, the silicon NWs solar cell is still in its infancy. Moreover, most articles focus on the low reflectance and manufacturing process of NWs.[8–11] The length of NW is always long enough to obtain the low reflectance. But, there is still a distance to go in the aspect of detailed study of the effect of NWs on the solar cell.

In this letter, we apply the fabrication of NWs on silicon wafers. The NWs are made by an electroless wet-chemical etching method.[12] The length of NW of these solar cells is set corresponding changed with different etching time. Then the influence of the NWs on solar cells is under an intensive study by testing the electrical and optical performance of the solar cells. Meanwhile, the planar solar cells fabricated in the same technological conditions are chosen to compare with the NWs solar cells. The differences of the performances between planar solar cells and NWs solar cells are analyzed.

$\langle 100 \rangle$ 3 Ω cm p-type c-Si wafers with 125×125 mm^2 cell area were used. All wafers were well-cleaned and the surface native oxide layers were also removed. The NWs arrays were then formed adopting a developed silver-induced wet-chemical-etching process in an aqueous buffered HF and $AgNO_3$ etching solution at 25 °C. There were three contrast groups, of which the etching time was 30 min (NW-A), 60 min (NW-B), and 120 min (NW-C), respectively. The surface color of these wafers appeared black after removing the Ag remnants by immersing them in the concentrated HNO_3 solution for two hours. And the planar solar cells were textured with alkaline solution, called NW-D.

The cross-sectional views of the NWs and planar solar cells were analyzed using field-emission scanning electron microscopy (SEM), shown as Figs. 1. The length and diameter of NWs for different contrasting groups could be obtained. With the other conditions remained unchanged, the length of NW was proved to be determined by etching time. The NWs rose with an increase in the etching time. The length of NW in NW-C is about 6 μm, 4.5 μm in NW-B and 1 μm in NW-A. And the planar solar cells textured by alkaline solution had normal pyramid structure. The diameter of an individual NW was small and the surface of the solar cells became rough with the longer etching time, as shown in Figs. 1, which is the plane view of the NWs and planar solar cells. And the NW diameter is 800–900 μm, 500–600 μm, and 400–500 μm in NW-A, NW-B, and NW-C, respectively.

As shown in Fig. 2, the reflectance of the NWs array textured wafers of three groups ($R_{NW\text{-}A}$, $R_{NW\text{-}B}$, and $R_{NW\text{-}C}$)

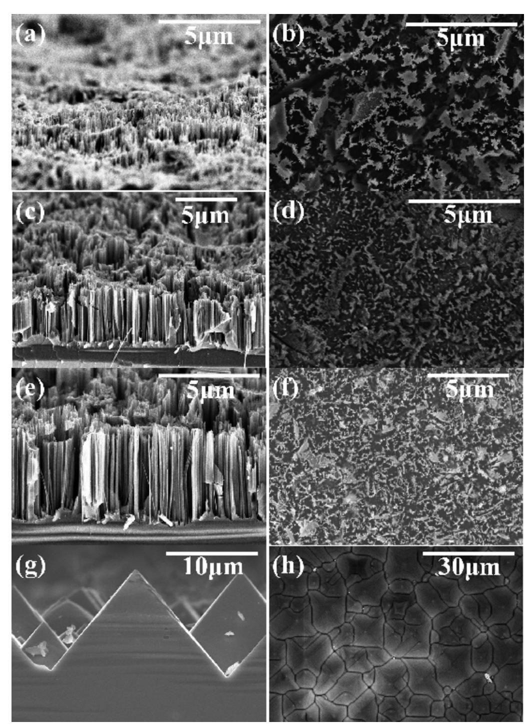

FIG. 1. SEM images of (a) the cross-sectional view for NW-A, (b) the plane view for NW-A, (c) the cross-sectional view for NW-B, (d) the plane view for NW-B, (e) the cross-sectional view for NW-C, (f) the plane view for NW-C, (g) the cross-sectional view for NW-D, and (h) the plane view for NW-D.

[a)]Electronic mail: jiarui@ime.ac.cn.

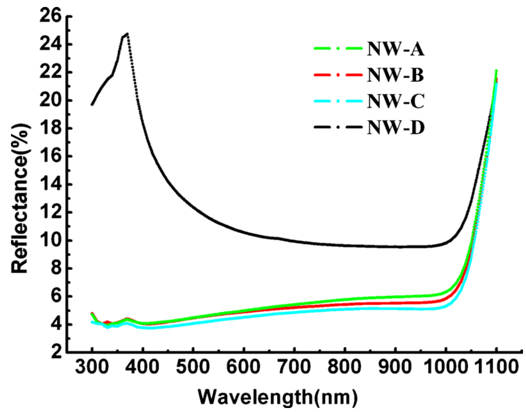

FIG. 2. (Color online) The reflectance of NWs solar cells (NW-A, NW-B, NW-C) and the planar solar cells (NW-D) with textured surface. The results show that the reflectance ranges in a diminishing sequence from $R_{NW\text{-}D}$, $R_{NW\text{-}A}$, $R_{NW\text{-}B}$ to $R_{NW\text{-}C}$. And there are slight difference among $R_{NW\text{-}A}$, $R_{NW\text{-}B}$, and $R_{NW\text{-}C}$, compared with $R_{NW\text{-}D}$.

is much lower than that of the planar solar cells ($R_{NW\text{-}D}$) with textured surface. Though the length of NW in NW-A is the shortest, $R_{NW\text{-}A}$ is slightly higher than $R_{NW\text{-}B}$ and $R_{NW\text{-}C}$, by 0.5%–1%. Compared with the previous work, the reflectance of the wafers with etching time 0.5 h is much lower.[13]

Then the NWs and planar solar cells were diffused under optimized condition using diffusion source of phosphorus oxychloride at 845 °C for 20 min. After the removal of phosphosilicate glass from the silicon surface with HF, and 50–100 Å silicon dioxide was thermally grown on the sample surface at 700 °C. It served as a passivation layer.[14] After edge isolation, an antireflection coating of nearly 800 Å silicon nitride was deposited by plasma-enhanced chemical vapor deposition. Then, the back and front sides were screen printed with silver-aluminum, aluminum, and silver pastes, followed by baking individual pastes of the printed wafers. Finally, dried wafers were cofired in belt furnace to achieve an Ohmic contact at both ends.

Table I shows the results of the current-voltage (I-V) measurements of the NWs solar cells and planar solar cells under the standard test condition (STC, air mass 1.5 irradiation, T=300 K, P=100 mW/cm^2). The maximum short circuit current (I_{sc}, the I_{sc} in NW-A and NW-D is referred to as $I_{sc\text{-}NW\text{-}A}$ and $I_{sc\text{-}NW\text{-}D}$) of NWs solar cells appears in NW-A, of which the mean value of I_{sc} is higher than NW-B by 1.12 A or 33.6%, and than NW-C by 3.18 A or more than twice.

Compared with planar solar cells, the reflectance of the NWs solar cells is low but the performance is disappointing. For example, the conversion efficiency (η) in NW-A is reduced by 10% contrasted with the sample in NW-D.

The reasons for this situation can be considered from the following aspects. The bulk and surface recombination may become one of the possible reasons for the degraded performance of the NWs solar cells. The length of NW in NW-C is the longest. Assuming that the hole diffusion constant and the minority carrier lifetime remain unchanged, the photogenerated carriers require to transport a longer distance before being collected, resulting in a large bulk recombination in NW-C group, although it possesses the lowest reflectance. The density of NWs becomes large as the etching time increases. So the surface area of the wafer, on which the surface recombination is strongly dependent, increases with an increase in the etching time, this renders a great surface recombination. The increase in the bulk and surface recombination may aggravate the short wave response of the solar cell, as shown in Fig. 4. From this point of view, the NWs solar cell requires an excellent surface passivation to offset the rough and enlarged surface. Second, the back surface of the solar cells is also destroyed in certain area. The back surface is rougher than the one of planar solar cells, especially for the NWs solar cells with a longer etching time. And the back-surface field (BSF) created by firing aluminum paste cannot form the good contact under this circumstance. As shown in Fig. 3, the BSF of the solar cell in NW-A remains intact. In contrast, a fraction of the back electrode in NW-B and NW-C peels off seriously, especially in NW-C, resulting in the absence of the BSF. Since the BSF is of great importance in passivating the back surface and forming the Ohmic contact, the absence of the BSF may cause the increase in the back surface recombination and thus affect the long wave response of the solar cell, as shown in Fig. 4. Similarly, on the front surface, the silver pastes which formed the electrode cannot form Ohmic contact due to the rough top plane of the wafer, as shown in Figs. 1(d) and 1(f). As the surface of the solar cells in NW-A is smoother than the others, the series resistance (R_s) in NW-A (the series resistance in NW-A, NW-C, and NW-D is referred to as $R_{s\text{-}NW\text{-}A}$, $R_{s\text{-}NW\text{-}C}$, and $R_{s\text{-}NW\text{-}D}$) was the lowest. As shown in Table I, $R_{s\text{-}NW\text{-}C}$ is higher than $R_{s\text{-}NW\text{-}A}$ by two orders of magnitude because of the bad contact. For the above reasons, the quantum efficiency and $I_{sc\text{-}NW\text{-}A}$ are the best in the three groups of NWs solar cell.

For the planar solar cells, the recombination and electrodes attachment characteristics are much less and better than the ones of NWs solar cells. For NWs solar cells, the

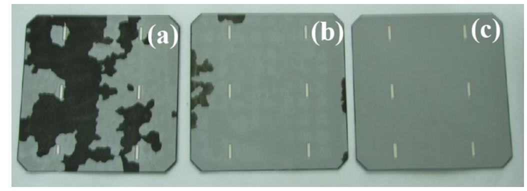

FIG. 3. (Color online) The photograph of BSF of different groups of NWs solar cells. The BSF of NW-C (a) peels off apparently. A little area of BSF comes off in NW-B (b). And the one of NW-A (c) remains intact.

TABLE I. Illuminated I-V measurements of p-type NWs-array solar cells under STC.

Group	V_{oc} (mV)	I_{sc} (A)	FF (%)	η (%)	R_s (Ω)
NW-A 4 cells	582±6	4.45±0.1	70.5±1.5	11.1±0.3	0.0023±0.005
NW-B 4 cells	578±3	3.33±1.2	64.1±2.4	7.70±0.2	0.0067±0.003
NW-C 4 cells	562±8	1.27±0.17	48.0±3	2.21±0.3	0.0988±0.02
NW-D 4 cells	586±8	4.9±0.1	77.3±1.2	12.6±0.1	0.0015±0.001

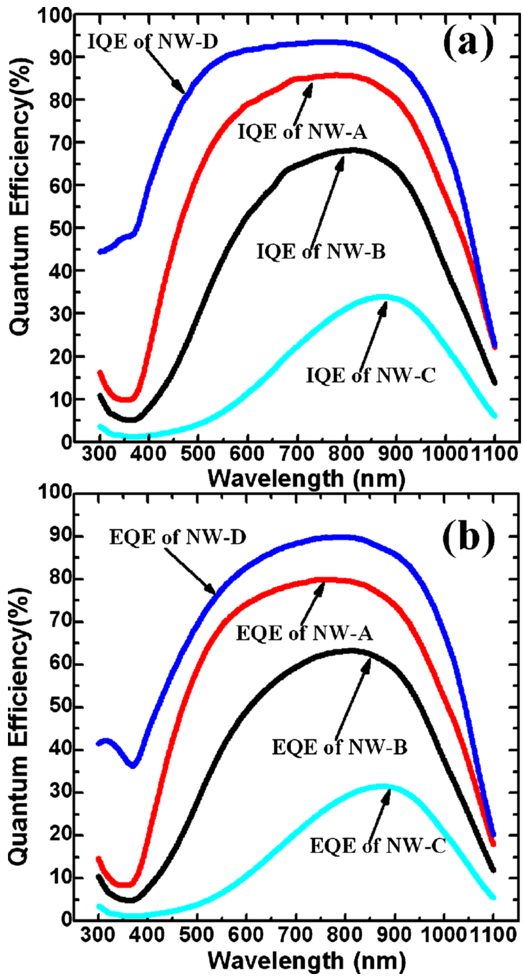

FIG. 4. (Color online) IQE (a) and EQE (b) as a function of the wavelength for NW-A, NW-B, NW-C, and NW-D. Corresponding to I-V measurement, the performance of NW-D is the best of all groups.

lost photons because of bulk and surface recombination are more than the extra absorbed photons owing to low reflectance. This is why the NWs solar cells have lower reflectance but poorer performance than the planar solar cells. With an increase in the NW length, the gap between planar solar cells and NWs solar cells increases.

The open circuit voltage (V_{oc}) of these groups has analogous trend with I_{sc}. According to the Eq. (1),[15] V_{oc} is a function of the saturation current (I_d) and I_{sc}. With an increase in the I_d and reduce in I_{sc}, the V_{oc} in NW-C is the lowest,

$$V_{oc} = \frac{k_B T}{q} \ln\left(1 + \frac{I_{sc}}{I_d}\right). \tag{1}$$

Fill factor (FF) can be described from Eq. (2),[16]

$$FF = FF_0 \times \left(1 - \frac{R_s I_{sc}}{V_{oc}}\right), \tag{2}$$

where FF_0 is the FF with the ideal characteristic and fixed under the condition that there is no huge difference of V_{oc} among the groups. Though $I_{sc\text{-}NW\text{-}D}$ is the highest, the $R_{s\text{-}NW\text{-}D}$ is lower than the others by one or two orders of magnitude. As a result, the term of $[1-(R_s I_{sc}/V_{oc})]$ in Eq. (2) of NW-D is higher than the other groups. This is the reason why FF in NW-D is the highest. From the reasons presented above, the η of NW-D is the best among the groups. So the low reflectance is a key point rather than a determinant of the high efficiency solar cell. And the optimized NW length is closely relevant to the silicon quality and the yielding technology, such as perfect surface passivation and enhanced electrode-contact property. The NWs solar cell cannot make use of the low reflectance because of the recombination of the electrons and holes under ordinary surface passivation.

In order to present a further verification, the internal quantum efficiency (IQE) and external quantum efficiency (EQE) are measured from 300 to 1100 nm, as shown in Fig. 4. The EQE of planar solar cells is much higher than that of NWs solar cells. In the low wavelength range, the reflectance of NWs solar cells is much lower than that of planar solar cells shown as Fig. 2 but the EQEs of the four groups have great difference. This result also shows that the front surface of NWs solar cells are not effectively passivated.

In this letter, the results show that the length of NW can be determined by controlling the etching time. The NWs array only reduces the reflectance of solar cells but does not improve the performance of the solar cells. The reason is that the longer NW causes the increase in bulk recombination, surface recombination, and the series resistance. And the increase in these parameters has a negative influence on the performance of the solar cells. The design principle of the NWs solar cell is that the low reflectance is not the only pursuit optimizing the surface passivation, improving the electrode-contact property and preventing the BSF peel off, should be considered together with NWs structure.

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