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Realization of effective light trapping and omnidirectional antireflection in smooth surface silicon nanowire arrays

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Abstract

We have successfully fabricated well-ordered silicon nanowire (SiNW) arrays of smooth surface by using a low-cost and facile Ag-assisted chemical etching technique. We have experimentally found that the reflectance can be significantly suppressed (<1\%) over a wide solar spectrum (300–1000 nm) in the as-grown samples. Also, based on our bundled model, we have used rigorous coupled-wave analysis to simulate the reflectance in SiNW arrays, and found that the calculated results are in good agreement with the experimental data. From a further simulation study on the light absorption in SiNW arrays, we have obtained a photocurrent enhancement of up to 425\% per unit volume of material as compared to crystalline Si, implying that effective light trapping can be realized in the as-grown samples. In addition, we have demonstrated experimentally and theoretically that the as-grown samples have an omnidirectional high-efficiency antireflection property.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Si nanowires (SiNWs) are very attractive nanomaterials in photovoltaic applications not only because of potentially low fabrication cost yet high power conversion efficiency but because of superior optical properties to bulk Si [1–12]. Among the many approaches to produce SiNW arrays such as vapor–liquid–solid growth [13], reactive ion etching combined with lithography techniques including nanoimprint and assembly [14, 15], metal-assisted chemical etching (MACE) technique [16–21], etc, the MACE technique appears to be the least costly and easiest approach to fabricate SiNW arrays to date. However, it still remains to resolve a rather rough surface problem in SiNW arrays fabricated by this technique [5, 6] for high-efficiency NW photovoltaic applications.

Recently, several light trapping methods have been reported to greatly enhance the optical absorption, such as by adding antireflective coating and nonabsorbing light scatterers in Si microwire arrays [9], by active surface area control in ordered SiNW arrays [10], by the optical antenna effect in semiconductor NWs [11], or by nonabsorbing dielectric coating in single SiNWs [12]. Also, SiNW solar cells have been demonstrated as a promising candidate to reduce both required quality and quantity of silicon material [1]. However, despite the great advantage of optical absorption, NW based solar cells still exhibit much lower power conversion efficiency than expected [3–7, 10]. This rather unexpected low efficiency in NW solar cells may come from the rough surfaces of NWs which can cause a high surface recombination velocity (i.e., a severe surface recombination), reducing the open-circuit voltage and the fill factor [5–7, 10]. It has been recently demonstrated that the surface recombination or the density of surface states can lead to poor electronic properties in
SiNW arrays, extremely limiting the performance of SiNW photovoltaic devices [22–24].

In this paper, we firstly show the realization of well-ordered SiNW arrays of smooth surface, fabricated by Ag-assisted chemical etching in aqueous H\textsubscript{2}O\textsubscript{2}/HF solution. From reflectance measurements on the as-grown SiNW arrays and simulation calculations on our modeled SiNW arrays, we then demonstrate that the light absorption can be enormously enhanced through effective light trapping in the as-grown SiNW arrays, through which the photocurrent can be enhanced by up to 425\% per unit volume of material as compared to crystalline Si. Finally, we show that the as-grown SiNW arrays have an omnidirectional high-efficiency antireflection property.

2. Experimental details

2.1. MACE technique

A Ag-assisted chemical etching technique (AgACE, but MACE will be used hereafter, if no confusion arises) in aqueous H\textsubscript{2}O\textsubscript{2}/HF solution has been employed to grow well-ordered SiNW arrays of smooth surface. It can be summed up as follows: (1) boron-doped (100) silicon wafers of 0.01–0.03 \(\Omega\cdot\text{cm}\) were cleaned via standard RCA procedure, and native oxide was then removed with 3 wt\% HF solution; (2) they were dipped in an aqueous solution of 4.0 M HF and 15 mM AgNO\textsubscript{3} for 60–100 s, forming Ag nanoparticle net-like films via the electroless metal deposition method [19]; (3) these Ag-deposited wafers were immediately immersed into oxidizing HF etching solutions, containing 5 M HF and various concentrations of H\textsubscript{2}O\textsubscript{2}, for a certain time; (4) lastly, the samples were washed with nitric acid (HNO\textsubscript{3}) to remove residual Ag nanoparticles and then rinsed with DI water.

The above process has been carried out over the range of 25–50\°C. In step (3), while obtaining SiNW arrays of desired lengths by controlling the etching time, we have been able to achieve SiNW arrays of very smooth surface by tuning the concentration of H\textsubscript{2}O\textsubscript{2}, as discussed later.

2.2. Methodology for morphology, photoluminescence, and reflectance

The morphology of the as-grown SiNW arrays has been characterized by field emission scanning electron microscopy (SEM, FEI SIRION 200) and transmission electron microscopy (TEM, JEOL JEM-2100) with 200 kV accelerating voltage. The photoluminescence (PL) measurements on as-grown SiNW arrays of various lengths have been carried out with a Jobin Yvon LabRAM HR 800UV micro-Raman system by using an exciting line of 514.5 nm from an Ar\textsuperscript{+} laser. The total hemispherical reflectance spectra have been measured with a UV/vis/NIR spectrometer (Perkin-Elmer Lambda 900) incorporated with a \(\Phi = 60\) mm integrating sphere. The angle-dependent reflectance for s- and p-polarized light has been also investigated with home-built equipment by utilizing the 514.5 nm laser line.

3. Results and discussion

3.1. Smooth surface SiNW arrays

We have used AgACE or MACE in aqueous H\textsubscript{2}O\textsubscript{2}/HF solution to obtain wafer-scale SiNW arrays, in which we have varied the oxidant (H\textsubscript{2}O\textsubscript{2}) concentration in a wide range of 0.02–8.0 M at a fixed HF concentration of 5.0 M. In figures 1(a)–(c),
we present side and top views of SEM images of as-grown samples etched for 30 min under H$_2$O$_2$ concentrations of 8.0, 2.0, and 0.1 M, respectively. From these figures, it can be clearly seen that the morphology of the samples strongly depends on the H$_2$O$_2$ concentration. For the high concentration of 8.0 M, there was no formation of SiNWs but there were random cone-shaped micropores of highly rough surface with large spacing ($\sim 11 \mu$m) between them, as shown in figure 1(a). For the intermediate concentration of 2.0 M, smaller micropores ($\sim 6 \mu$m spacing) were mostly yielded as shown in figure 1(b), but some nanowire-like bundles also began to appear between the micropores, as indicated by the red dashed circle in the figure. Note that although rather unclear from the figure, SiNWs were in fact formed in small parts of the area, as highlighted by the red solid circle in the inset, for this intermediate concentration. For the low concentration of 0.1 M, well-ordered SiNW arrays of $\sim 11 \mu$m length and 60–200 nm diameter were finally fabricated, as can be seen in figure 1(c). Here, we point out that these SiNW arrays are bended together (top view in the figure), which appears to be typical in such long SiNWs [19–21].

To investigate the surface morphology of SiNWs fabricated at low H$_2$O$_2$ concentrations, high resolution TEM studies have been performed on individual SiNWs grown at 0.4 and 0.1 M H$_2$O$_2$, as shown in figures 1(d), (f) and (e), respectively. In the case of 0.4 M H$_2$O$_2$, rather rough surface is evident from the low magnification TEM image in (d), as compared to the case of 0.1 M H$_2$O$_2$ in (e), and a $\sim 5$ nm porous silicon (PS) layer that appears to be the source of the rough surface can be seen from the high magnification TEM image in (f), where three regions of crystalline Si core (left), PS shell (center), and TEM carbon film (left) are clearly differentiated. Note that the shell is in fact composed of PS, as will be demonstrated by PL measurements below. In contrast, SiNWs fabricated at the lower H$_2$O$_2$ concentration of 0.1 M clearly have smooth surfaces as in (e) and no observable PS as in (g). Unlike in (f), there are only two regions of crystalline Si core (left) and TEM carbon film (left) seen in (g). No formation of PS at low H$_2$O$_2$ concentration will be clearly demonstrated from PL measurements below. We have also fabricated equally smooth surface SiNWs at even lower H$_2$O$_2$ concentrations such as 0.06 and 0.02 M, but found that the etching rate is considerably decreased: e.g., $\sim 270$ nm min$^{-1}$ (0.06 M) and $\sim 67$ nm min$^{-1}$ (0.02 M), compared to $\sim 370$ nm min$^{-1}$ (0.1 M). Also, from these TEM studies, we have confirmed by measuring the lattice distance that the growing orientation of the SiNWs is along the [100] direction, which is the perpendicular direction to the surface of the primitive (100) Si wafer.

With the fact that PS in a form of mesoporous silicon nanostructure, generated by anodization or chemical etching of Si in an oxidizing HF, gives rise to a strong visible emission [25], we have performed PL measurements on the as-grown SiNW arrays fabricated at various H$_2$O$_2$ concentrations. Figure 2(a) shows representative PL spectra of the as-grown samples for H$_2$O$_2$ concentrations of 8.0, 4.0, 0.8, 0.4, and 0.1 M. All these PL spectra except for 0.1 M H$_2$O$_2$ clearly show a broad band light emission with peaks around 690 nm, which is a typical luminescence characteristic of PS [25]. Also, as can be seen from the figure, the PL intensity considerably drops with decreasing H$_2$O$_2$ concentration and then shows almost no luminescence for 0.1 M H$_2$O$_2$, implying that the amount of PS becomes appreciably smaller for lower H$_2$O$_2$ concentration and finally there is no detectable amount of PS generated for the smallest H$_2$O$_2$ concentration.

In figure 2(b), we present the integrated PL intensity as a function of the H$_2$O$_2$ concentration, resulting from the
integration sum of the PL intensity in figure 2(a) over the wavelength from 550 to 900 nm. It slowly decreases with decreasing H₂O₂ concentration to ∼1.0 M and sharply drops below that concentration, indicating that PS generation is gradually reduced with decreasing H₂O₂ concentration and quickly becomes diminished below ∼1.0 M. From this PL investigation together with the TEM studies discussed above, we conclude that the H₂O₂ concentration, which is readily controllable, is a key parameter to fabricate our smooth surface SiNWs. These as-grown smooth surface SiNWs may provide a great opportunity to improve the electronic performance of NW photovoltaic devices, since NW solar cells have been experiencing rather poor electronic properties such as low open-circuit voltage and small fill factor, due to the rough surfaces of NWs [5–7, 10].

3.2. Growth mechanism and controllable length in SiNW arrays

According to the localized galvanic cell model [17–21], the MACE mechanism involves a localized microscopic electrochemical process in which net-like Ag nanoparticles (AgNPs, that are actually a cluster of Ag nanoparticles) serve not only as an etching mask but also as a catalyst to promote the anodic (the oxidation of Si or the hole injection into the valence band of Si) and, at the same time, cathodic (the reduction of H₂O₂ or electron-consuming) reactions. In aqueous H₂O₂/HF solution, a local oxidation of Si occurs underneath net-like AgNPs and this oxidized Si is then dissolved or etched by HF. This microscopic electrochemical process may turn the unmasked area to SiNWs [20].

In the previous study on SiNW growth in aqueous AgNO₃/HF solution, it has been reported that the oxidation of Si occurs through the injection of holes from the energy level of the Ag⁺/Ag redox potential into the valence band of Si, since the energy level of Ag⁺/Ag lies well below the valence band edge of Si [17]. This suggests that in our aqueous H₂O₂/HF solution, a certain concentration of Ag⁺ ions has to be maintained to promote the oxidation of Si that appears to be the most important precursor to fabricate SiNWs by the MACE method, which has not been considered in the previous works [18–20]. In the H₂O₂/HF solution, Ag⁺ ions are created by the oxidation of AgNPs due to H₂O₂ at the interface between Si and AgNPs. However, some of these created Ag⁺ ions are transformed back into Ag via spontaneous reaction with Si. So, Ag⁺ ions lacking in Si oxidation should be fed back into the solution. This backfilling can be done again by the oxidation of AgNPs. Thus, there should exist a cycling (Ag ↔ Ag⁺) between the oxidation of AgNPs by H₂O₂ (→Ag⁺) and the reduction of Ag⁺ by Si (→Ag) during the etching process to fabricate SiNWs.

Instead of H₂O₂, we have used other oxidants such as Fe(NO₃)₃, Zn(NO₃)₂, and FeCl₃ to fabricate SiNWs. We have found that SiNWs can be formed with Fe(NO₃)₃ and Zn(NO₃)₂, but not with FeCl₃ with which we have not observed any amount of etched SiNWs. These results can be understood by using the standard redox potentials of Fe³⁺/Fe²⁺ (0.771 V), NO₃⁻/NO (0.957 V), and H₂O₂/H₂O (1.776 V) [26]. Since the redox potential of Ag⁺/Ag is 0.799 V [26], the occurrence of the oxidation of Ag (→Ag⁺) is thermodynamically favored with NO₃⁻ or with H₂O₂, but not with Fe³⁺. Thus, there can be no reaction to provide continuous feeding of Ag⁺ ions with FeCl₃, i.e., no formation of SiNWs. Here, we point out that these experimental results clearly demonstrate the importance of the cycling (Ag ↔ Ag⁺) for the formation of SiNWs in the H₂O₂/HF solution. We also point out that NO₃⁻ rather than Fe³⁺ is a key ion in the formation of SiNWs in the case of Fe(NO₃)₃ oxidant, contrary to the previous discussion in the literature [18, 19].

The H₂O₂ concentration-dependent morphology as shown in figure 1 can be well explained by the above-discussed growth mechanism. In high H₂O₂ concentration as in figure 1(a), the dissolution of AgNPs by H₂O₂ is so acutely promoted that the size of net-like AgNPs quickly becomes smaller and smaller in time, and also the concentration of Ag⁺ ions sharply increases. These increased Ag⁺ ions, then, diffuse out and nucleate to form a great number of smaller AgNPs on other sites including the sidewall of the etched area, leading to a strong sidewall etching to form disordered cone-shaped micropores with a large amount of porous Si. Note that the strong etching is attributed to the highly promoted oxidation of Si at high H₂O₂ concentration. At decreasing H₂O₂ concentration, the acute reaction at the high concentration is expected to become retarded as can be seen in figure 1(b). Finally, for further decreasing H₂O₂ concentration, most of the Ag⁺ ions appear to be localized around the vicinity of AgNPs, which prevents the sidewall etching and the creation of porous Si occurring at the high H₂O₂ concentration. This sufficiently low H₂O₂ concentration can lead the localized Ag⁺ ions to sustain an appropriate oxidation reaction of Si, resulting in forming SiNW arrays of smooth surface as in figures 1(c), (e) and (g). Here, we should point out that the Si may be more etched due to a dense cluster of Ag nanoparticles in the beginning of the electrochemical process, and the cluster of Ag nanoparticles actually becomes smaller even at low concentration of H₂O₂ during the etching process, resulting in tapered SiNW arrays. In fact, most of our as-grown SiNW arrays showed negligible difference in diameter along individual SiNWs; however, we will take into account this tapering nature to build our bundled model, as will be discussed later. This tapering nature in SiNWs has been previously reported [21].

Now turning to the length control in SiNW arrays, we have been able to tailor the length of the as-grown SiNW arrays in a wide range by tuning the etching time. Figures 3(a)–(c) demonstrate the uniform lengths in SiNW arrays, fabricated at fixed 0.1 M H₂O₂ and 35 °C for the three representative etching times, 10, 30, and 60 min, respectively. As plotted in figure 3(d), the SiNW length exhibits an excellent linear behavior for a wide range of the etching time, giving the etching rate ∼0.5 μm min⁻¹. Also, we have observed that the SiNW length shows a similar linear behavior with respect to the etching time at different temperatures such that the higher temperature leads to the longer length at a fixed etching time. However, it turned out that the higher temperature (say, 50 °C) leads to rougher surface SiNWs. We shall, thus, discuss the
Figure 3. (a)–(c) SEM images of SiNWs (side view) etched for 10, 30, and 60 min at 0.1 M H₂O₂ and 35 °C, respectively. (d) Length of the SiNWs (L) versus etching time (t) at 35 °C, showing an approximately linear behavior.

reflection property of and light trapping in smooth surface SiNW arrays fabricated at 25 °C hereafter.

3.3. Length-dependent reflectance of SiNW arrays

As presented in figure 4(a), we have measured the reflectance of as-grown SiNW arrays of various lengths (250–6400 nm) over the wavelength range of \( \lambda = 300–1200 \) nm. They have been fabricated under the condition of 5.0 M HF, 0.1 M H₂O₂, and 25 °C for various etching times under which the etching rate was \( \sim 160 \) nm/min⁻¹. We have also measured the reflectance of polished and alkaline-textured Si wafers for comparison. As shown in the figure, the polished Si has over 35% reflectance as typically known [27, 28], and although the textured Si yields rather suppressed reflection due to the micron scale pyramidal structures [29], it still has over 10% reflectance. In contrast, the as-grown SiNW arrays exhibit a very different reflection behavior from that of conventional Si. Besides a different functional trend of their reflectance spectra as readily seen in the figure, the as-grown samples show a large suppression of the Fresnel reflectance over the entire wavelength range investigated. More importantly, this large suppression can be tailored simply with the length of the SiNW arrays such that it is greatly enhanced by increasing the length. For the 6400 nm long SiNW array, for example, the reflectance is almost suppressed (less than 1.0% for 300 nm < \( \lambda < 1000 \) nm). Thus, the as-grown SiNW arrays of appropriate lengths can serve as efficient antireflection layers for developing high-efficiency NW solar cells. Also, these measured reflectance spectra in the as-grown SiNW arrays contain small yet appreciable interference fringes, indicating that the as-grown arrays are to a certain extent of periodic nanostructure nature.

Figure 4(b) presents the normalized SiNW length-dependent reflectance \( (R/R_0) \) for wavelengths \( \lambda = 600, 800, 1000, \) and 1200 nm, extracted from the measured reflectance in figure 4(a), where \( R_0 \) is the reflectance of the polished Si. From the figure, one can see that the (normalized) reflectance rapidly decreases in the short SiNW length region and then gradually decays with increasing SiNW length, and also that the SiNW arrays yield lower reflectance at shorter wavelength. Also from the figure, we found that the normalized reflectance at the half-wavelength SiNW length is \( \sim 20, 27, 32, \) or 40% for \( \lambda = 600, 800, 1000, \) or 1200 nm, respectively, similar to the observation in tapered subwavelength structures [30, 31]. In figure 4(c), we show calculated reflectances for our modeled SiNW arrays of corresponding lengths to those in figure 4(a) by using the rigorous coupled-wave analysis (RCWA) that will be discussed below.

3.4. Numerical simulation for the reflectance of SiNW arrays

In order to understand the measured reflectance of as-grown SiNW arrays, we have implemented RCWA [32, 33] to calculate the reflectance of SiNW arrays of various lengths. RCWA is a simulation method to obtain the numerical solution
Figure 4. (a) Measured reflectance versus wavelength for SiNW arrays of various lengths and also for polished Si and textured Si. (b) Normalized reflectance ($R/R_0$) versus the SiNW length ($L$) for wavelengths of 600, 800, 1000, and 1200 nm, obtained from (a). $R_0$ is the reflectance of the polished Si. (c) RCWA-calculated reflectance versus wavelength for SiNW arrays of various lengths. Note that normally incident illumination was used for both measurement and calculation.

From the conglomeration of as-grown SiNWs as can be seen from the top view in figure 1(c), our SiNW arrays can be treated as bundled arrays as drawn in the middle of figure 5(a). Also, as discussed earlier, our individual SiNW appears to be a tapered cylinder. Considering the conglomeration and tapering natures together with the periodic behavior of the reflectance spectra in figure 4(a), we modeled our SiNW arrays as ideally periodic SiNW arrays, as illustrated in figure 5. For RCWA simulation, we used a periodicity of $D = 200$ nm, the top (bottom) radius of $r_t = 30$ nm ($r_b = 90$ nm) of each SiNW, and three tapered regions consisting of 10% (top), 80% (middle), and 10% (bottom) of the total length of the SiNWs, as shown in figures 5(b) and (c). Note that the periodicity and the top (bottom) radius have been realistically chosen based on our SEM studies. Note also that the multi-steps in these three tapered regions as in figure 5(c) do not come from the tapering nature of our SiNWs, but from a necessary procedure for RCWA simulation. In our simulation, we have employed the optical constants for bulk Si taken from [36], and transverse-electric (TE) and transverse-magnetic (TM) polarized plane waves. For each simulation for a given SiNW length, we have obtained not only the reflectance ($R$) but the transmittance ($T$), simultaneously, from which we can calculate the absorptance ($A = 1 - R - T$), that will be discussed later in section 3.5.

From this RCWA simulation, we have obtained the wavelength-dependent reflectance for our modeled SiNW arrays of various lengths, as presented in figure 4(c). These calculated results are to some extent consistent with the experimental results in figure 4(a), such that for short SiNW
arrays, the reflectance drops with increasing SiNW length as well as with decreasing wavelength. Note that the calculated reflectance spectra possess distinct interference fringes in comparison with the measured spectra, resulting from the ideally periodic modeling in the simulation. For long SiNW arrays, the comparison between simulation and experiment becomes rather difficult due to these large interference fringes. Hence, we calculated the integrated-reflectance that can show the overall suppression of the reflection under light illumination, as discussed below.

In figure 6(a), we plot the scaled integrated-reflectance ($R_{\text{int}}/R_{0-\text{int}}$), normalized to the integrated-reflectance of the polished Si ($R_{0-\text{int}}$), as a function of the SiNW length, which has been obtained by integrating measured and calculated reflectance spectra in figure 4 for $\lambda = 300–1200$ nm. As can be seen from the figure, the simulation is in good agreement with the experiment, implying that our modeled SiNW arrays can well represent the as-grown, bundled SiNW arrays. Also, the integrated-reflectance spectra from both experiment and simulation show a first order exponential decay ($R_{\text{int}}(L) \sim R_{0-\text{int}} \exp(-L/L_c)$) with the characteristic SiNW length $L_c = 206$ nm as plotted in the figure, implying that the reflectance of the SiNW arrays can be significantly suppressed by simply tailoring the SiNW length.

Such a significant reduction of the reflectance in SiNW arrays can be well understood in terms of the moth-eye effect [30, 31], that is an antireflection phenomenon of subwavelength structures on substrate (typically the same material as the subwavelength structures), in which they serve as a medium of a continuous gradient refractive index (i.e., effectively not a constant number) to effectively reduce a mismatch of the refractive indices between air and substrate. In our case, the SiNW arrays serve as such a buffer layer to reduce a large mismatch of the refractive indices between air and silicon substrate, resulting in the significant reduction of the observed reflectance spectra. Also, the SiNW length dependence of the observed reflectance can be readily understood, since a longer SiNW array can be thought of as a smoother gradient layer.

3.5. Light trapping in SiNW arrays

From the RCWA-calculated reflectance ($R$, in figure 4(c)) and transmittance ($T$, not shown in this paper), we have calculated the wavelength-dependent absorbance $A(\lambda) (=1 - R - T)$ to evaluate the short-circuit photocurrent density ($J_{\text{SC}}$) as $J_{\text{SC}} = q \int_0^{\lambda_g} F(\lambda) A(\lambda) \, d\lambda$, where $q$ is the electron charge, $\lambda_g$ (~1100 nm) is the wavelength at the band gap of bulk silicon, and $F(\lambda)$ is the spectral photon flux density corresponding to the air mass 1.5 spectrum [37]. In the calculation, we assumed that the internal quantum efficiency is 100%, actually yielding the ultimate short-circuit photocurrent density. In figure 6(b), we present calculated results of the $L$-dependent $J_{\text{SC}}$ for SiNW arrays, together with the $t$-dependent $J_{\text{SC}}$ for crystalline Si films of corresponding thicknesses ($t$) to the SiNW lengths ($L$). Note that as in the SiNW arrays, the top layers and bottom substrates for crystalline Si films are air and Si wafers, respectively. Note also that our calculated results for Si films ($J_{\text{SC}} = 3.31–12.12$ mA cm$^{-2}$ for $t = 250–3200$ nm) are consistent with the recently published results [11].

In order to see the photocurrent enhancement in SiNW arrays with respect to crystalline Si films, we have also calculated the photocurrent enhancement factor per unit volume (PEF) from the calculated $J_{\text{SC}}$, where PEF is defined as $(J_{\text{SC,SiNWs}}/V_{\text{SiNWs}} - J_{\text{SC,film}}/V_{\text{film}})/(J_{\text{SC,film}}/V_{\text{film}})$ with the short-circuit photocurrent density of SiNW arrays (crystalline Si films) $J_{\text{SC,SiNWs}}$ ($J_{\text{SC,film}}$) and the total material volume of SiNW arrays (crystalline Si films) $V_{\text{SiNWs}}$ ($V_{\text{film}}$). The PEF curve in figure 6(b) shows over 200% photocurrent enhancement for the entire investigated range ($L = 250–3200$ nm) with a maximum value of 425% at $L \sim 800$ nm. This implies that the short-circuit photocurrent density can be greatly enhanced, clearly resulting from a significant
absorption enhancement through light trapping in SiNW arrays.

Light trapping is an important technique to enhance the light absorption in solar cells. The effective light trapping in SiNW arrays mentioned above stems from the subwavelength nature of SiNWs and can be understood in terms of the multiple scattering of the incident light. According to the Lorenz–Mie light scattering theory [38], a strong light scattering will occur and dominate the transport of light when subwavelength structures are illuminated by the incident light. Our as-grown SiNW arrays that typically have 60–200 nm diameters can serve as subwavelength scatterers to scatter the incident light and thus to randomize the direction of the incident light, allowing the scattered, redirected light to be re-scattered. This multiple scattering process can prolong the optical path length of light, leading to a light absorption enhancement.

3.6. Angle- and polarization-dependent reflectance in SiNW arrays

Finally, we discuss the angle- and polarization-dependent studies of light reflection in SiNW arrays. In figure 7, we present measured (a) and calculated (b) reflectance as a function of the incident angle for s- (TE) and p-polarized (TM) light of $\lambda = 514.5$ nm, in the 800 nm long SiNW array as well as in the polished Si for comparison. For the reflectance calculation in the SiNW array, we have used the RCWA simulation method and our bundled model, as discussed in section 3.4 above. One can see from the figures that the simulated results are in good agreement with the experimental data, again implying that the as-grown SiNW arrays can be well represented by the bundled model. Also in the figures, one can see that the reflection property in the polished Si strongly depends on both the incident angle and the polarization of the incident light, and that the reflectance is about 40% for unpolarized light, which is not shown in the figures but is readily calculated as the average of the reflectances of TE and TM.

In contrast, the reflectance of the SiNW array is remarkably insensitive to both the incident angle and the polarization of the incident light to result in <4% (from experiment) regardless of TE or TM over a wide range of incident angle ($\theta = 0^\circ$–70$^\circ$), leading to the so called ‘omnidirectional antireflection’. Note that for high incident angles ($\theta > 70^\circ$), the reflectance shows a trivially increasing behavior since it must be 100% at $\theta = 90^\circ$. This omnidirectional antireflection property may lead to an effective light trapping effect in SiNW arrays over a wide range of the incident angle of light. This polarization insensitivity can also be understood by the strong light scattering in SiNW arrays as discussed above. If the incident TE or TM light is scattered through SiNW arrays, then the direction of light and the photon density of states are randomized, i.e., the polarization state becomes indistinguishable. Thus, there should be no difference in the reflection behavior with respect to the incident angle for different polarizations.

4. Conclusions

We have used a low-cost and facile Ag-assisted chemical etching technique to fabricate well-ordered and large-area SiNW arrays of smooth surface. We have shown that surface smoothness in SiNWs can be tailored by simply adjusting the $\text{H}_2\text{O}_2$ concentration, and that the length of the SiNW arrays can be controlled by the etching time. Based on the experimental reflectance of the as-grown SiNW arrays and the numerical simulation on modeled SiNW arrays, we have investigated the light absorption property in SiNW arrays, and found that
the light absorption can be significantly enhanced through strong light trapping in SiNW arrays, leading to a photocurrent enhancement of up to 425% as compared to crystalline Si films of equivalent active volume. Also, we have demonstrated experimentally and theoretically that the as-grown SiNW arrays exhibit a wide angle- and polarization-independent antireflection behavior. The strong light trapping and omnidirectional antireflection (leading to optical absorption enhancement) together with surface smoothness (leading to electronic property improvement) realized in the as-grown SiNW arrays can serve as powerful tools to develop high-efficiency NW solar cells.

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