Surface profile-controlled close-packed Si nanorod arrays for self-cleaning antireflection coatings

Yi-Ruei Lin, Hsin-Ping Wang, Chin-An Lin, and Jr-Hau He^{a)}

Department of Electrical Engineering and Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617, Taiwan

(Received 8 September 2009; accepted 12 October 2009; published online 4 December 2009)

We demonstrate the fabrication of surface profile-controlled close-packed Si nanorod arrays (NRAs), using a scalable and integrated circuit compatible process combining colloidal lithography and reactive ion etching. Si NRAs exhibit broadband, omnidirectional, and polarization-insensitive antireflection (AR) properties and enhance the hydrophobicity. The effect of surface profiles of periodic NRAs on the AR and hydrophobicity was investigated systematically. The Si NRAs function as both self-cleaning and AR layers, which offer a promising approach to enhance the solar cell energy conversion efficiency. © 2009 American Institute of Physics. [doi:10.1063/1.3267147]

I. INTRODUCTION

Recently researchers are increasingly turning toward nature to biomimic a variety of the functions of creatures for the design inspiration. For example, subwavelength structures (SWSs) for antireflection (AR)^{1–6} are inspired by the moth-eye corneas where it comprises of an array of protuberant structures.⁷ Because its periodicity is smaller than the wavelength of the incident light, the nanostructured array surface behaves like an effective homogeneous medium with continuous gradient of refraction index. There are several potential techniques for texturing Si solar cells to form SWSs. Conventionally, by taking advantage of the different etching rates between the $\langle 100 \rangle$ and $\langle 111 \rangle$ surfaces in an alkaline solution, the surfaces of single crystalline Si solar cells are textured with V-groove. The random nature of the crystal orientation of polycrystalline Si wafers makes such techniques much less effective. For polycrystalline Si, wet acidic texturing is utilized to fabricate rounded AR structures. However, an important problem with wet acidic texturing is that the feature growth needs to be initialized by surface defects;⁸ otherwise a planar surface will appear. Reactive ion etching (RIE) is an alternative method for the formation of textured structures on not only single crystalline but also polycrystalline Si solar cells without the use of large quantities of liquid solutions.^{9,10}

To obtain high-performance solar cells it is critical to fabricate periodic SWSs to eliminate all diffraction-order light. So far periodic SWSs have been patterned on Si through various methods, such as electron-beam lithography,¹¹ laser interference lithography,¹² nanoimprint lithography,¹³ and electrochemical etching technique.¹⁴ However, these techniques are restricted from the practical applications due to their expensive equipment, complex procedures, and disordered alignment. Therefore, a technique, such as colloidal lithography,^{4,9} is a desirable large-area self-assembly for patterning nanostructures due to its simplicity

and low cost. In addition, previous studies indicate that the optimum AR structures of solar cells are close-packed pyramidal or honeycomblike arrays.^{10,15}

It has been reported that the nanorod arrays (NRAs) fabricated by various methods have the significant influences on the AR properties.^{4,11,12,16} A detailed study on the surface profile-dependent AR properties of NRAs is demanded for the design and optimization of the SWS processes.

The self-cleaning effect due to the hydrophobic surface, which is observed on lotus leaves, is another biomimetic example. Controlling wettability of solid surfaces governed by the geometry of the surface has aroused much interest for both fundamental researches and practical applications.^{17–19} Understanding enhanced hydrophobicity of nanostructured surfaces could benefit optical and optoelectronic devices significantly due to self-cleaning effect.

In this study, we fabricate close-packed Si NRAs with tunable surface profiles using a method combining colloidal lithography and RIE. The effects of surface profiles of periodic NRAs on the reflection were investigated systematically, demonstrating the broadband, omnidirectional, and polarization-insensitive AR properties. The hydrophobic effect as a function of surface profile of Si NRAs was also discussed. The Si NRA SWSs combining AR and enhanced hydrophobic effects benefit optical and optoelectronic devices significantly.

II. EXPERIMENTS

A drop-coat method of close-packed polystyrene nanospheres (PS NSs) on Si substrates was employed. The patterns created by PS NSs were then transferred to the Si substrates to form close-packed Si NRAs by RIE procedure. The fabrication of Si NRAs involved a two-step etching process. 50 SCCM (SCCM denotes cubic centimeter per minute at STP) O₂ was used to shrink the PS NPs at a total pressure of 6 mTorr for the first step. For the second step, SF₆ gas was used to etch the surface at a total pressure of 1.33 mTorr for 45 s.

For morphological characterization, scanning electron microscopy (SEM) was employed with a JEOL JSM-6500

^{a)}Electronic mail: jhhe@cc.ee.ntu.edu.tw.

FIG. 1. (Color online) The SEM images of (a) 500 nm PS NS monolayer and Si NRAs with (b) 303 nm, (c) 200 nm, and (d) 145 nm in diameters. (e) The etching time of oxygen plasma for PS vs the diameter of PS.

field emission SEM with an electron energy of 10 kV. Reflection measurements were performed with a JASCO V-670 UV-visible spectrometer with integral sphere.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical SEM image of a monolayer colloidal crystal consisting of 500-nm-diameter PS NSs on Si substrates. The hexagonal arrangement is evident. The RIE conditions strongly influenced the morphology of Si nanostructures. The patterns of the PS NSs were transferred to the Si substrates to form close-packed Si NRAs using RIE. A two-step etching process was employed to control the surface profile of Si NRAs. For the first step O₂ plasma was used to minify the diameter of the close-packed PS NSs. The second step is that SF₆ plasmas etched the underlying Si substrates for 45 s. Due to the high etching selectivity, the shrinkage of templating PS NSs is not significant and consequently the unprotected Si is preferentially etched by reactive F ions during the second step, leading to the cylinderlike NRAs. The diameters of NRAs can be determined by the diameters of the templating PS NSs. Figures 1(b)–1(d) are the typical SEM images of the Si NRAs with different diameters via controlling the size of the PS NSs as a mask. The etching times of oxygen plasma were varied from 0 to 75 s for etching the NSs. The preservation of the hexagonal ordering and the interdistance of the original PS colloidal crystal are apparent for the nanostructured Si arrays. The diameters of NRAs with O₂ plasma etching durations were measured from SEM images and varied from 145 to 303 nm, as shown in Fig. 1(e). The height of Si NRAs is ~ 200 nm by fixing SF₆ etching duration. The coverage of the NRAs was decreased upon increasing the duration of oxygen plasma etching, leading to the different roughness values. The filling factors vary from 0.076 to 0.33.

For investigating geometrical factors on the AR behaviors of the Si NRAs, the total reflectance measurements at the angle of incidence (AOI) of 8° were performed, as shown in Fig. 2(a). The polished Si shows more than 35% reflectance

FIG. 2. (Color online) (a) Total reflectance over a range from 350 to 850 nm for diameter-controlled NRAs. The root mean square roughness is plotted as a function of the filling factor, which is related to the diameter of NRAs.

tance for the wavelengths from 350 to 850 nm, agreeing well with previous measurements.²⁰ The maximum at 370 nm in the reflectance for polished Si is caused by the interband transitions.²¹ This principal spectral feature is also seen for the nanostructured surfaces and not shifted substantially with the diameter of the nanorods, indicating that the Si NRAs were not extensively damaged by the RIE process.²² Compared to polished Si, the decrease in reflectance of periodic Si NRAs over a wide range of wavelengths can be explained by moth-eye effect, which is related to several factors. First of all, whether a reflection (i.e., backward diffraction) order propagates or not is determined by the diffraction grating equation.²³ As the wavelength of the incident light is comparable to or larger than the periodicity of the NRA structure (Λ) of 500 nm, the high reflection order is expected to eliminate, leading to the reduction in reflectance over the wavelength domains more than 500 nm. When considering all reflection orders, the reflectance increased dramatically at wavelengths less than Λ . The second factor to decrease the reflectance is stated as follows. A perfect pillar array should be equivalent to a homogeneous coating with a constant index of refraction which cannot be employed for AR coatings that operate over a broad range of wavelengths. For such a structure a minimum in the reflectance would be expected at a wavelength for which the optical thickness is $\lambda/4$. However, such behavior has not been observed in our samples. The reason is that the structure fabricated by using RIE is not a perfect cylindrical array. Due to imperfectly preferential etching by RIE process, the broadening of the nanorods beginning at about half the height and extending to the bottom appears to be sufficient to result in a height dependent on the effective index of refraction (n_{eff}); i.e., the NRA layers behave like an effective medium, in which n_{eff} changes continuously from refractive index of air to refractive index of Si, leading to the great reduction in the reflectance in a broad wavelength domain for Si NRA layers. The curves of all nanostructured samples are similar, verifying the universal behavior of the diminishing reflectance caused by the moth-eye effect.

Moreover, the magnitude of total reflectance for the NRA surfaces decreases with increasing diameter of NRAs over all wavelength ranges, as shown in Fig. 2(a). We attribute diameter-dependent reflectance to the surface roughness, which influences light trapping significantly.^{24,25} Physically speaking, the rough surface reduces the reflectance by increasing the frequency of reflected light bouncing back from the back surface, rather than out to the surrounding

FIG. 3. (Color online) The reflectance of diameter-controlled NRAs as a function of AOI using (a) unpolarized and (b) s-, and (c) p-polarized lights with 650 nm wavelength. (d) The reflectance ratio of polarization (I_s/I_p) as a function of AOI.

air.²⁶ Under the assumption that Si NRAs are a cylinder array for simplicity, the root mean square roughness (δ_{rms}) can be represented by

$$\delta_{\text{rms}} = \sqrt{F(h^2 - \bar{h}^2)}, \quad (1)$$

where F is the filling factor of the NRAs ($0 \leq F \leq 1$), h is the height of NRAs (~ 200 nm), and $\bar{h}$ is the average height of the surface.²⁷ $\bar{h}$ is equal to $h \times F$. According to Eq. (1), δ_{rms} is a function of the filling factor as h is fixed in Fig. 2(b), indicating that δ_{rms} of the Si NRAs with the diameter of 303 nm reaches 94.3 nm at $F \sim 1/3$. This represents that the rough surface of Si (i.e., large diameter of nanorods) enhances the light trapping, leading to the low reflectance. In addition, Chen *et al.*²⁸ numerically analyzed that when the diameter of the nanorod is comparable to or smaller than the wavelengths of incident light, a nanorod can actually absorb not only the portion of a wave incident directly on it but also the surrounding wave. Another well-known example is that a small single particle can have larger absorption cross section than its geometric cross section.²⁹ The low reflectance of the incident wave in the Si NRAs might be another example of this small size effect.

One of the desirable features of AR coatings for solar cells is AOI-insensitive reflection, which is so-called omnidirectionality. In order to examine the omnidirectional characteristics, the specular reflectance as a function of AOI for various Si NRAs at 650 nm wavelength was compared for unpolarized, s-, and p-polarized lights, where s and p denote planes of incidence perpendicular and parallel to the electric field of the incident light, as shown in Figs. 3(a)–3(c), respectively. The curves of all nanostructured samples are similar. In general, the reflectance can also be reduced by increasing diameter of NRAs over a wide range of AOI. The reflectances of NRAs with 303 nm in diameter for unpolarized, s-, and p-polarized lights remain below 4.53%, 5.97%, and 1.31%, respectively, for AOI up to 50° , indicating that the reflectance of Si NRAs is insensitive to AOI. The polarization-dependent characteristic can be characterized by the ratio of the reflectance of the s-polarization to that of the p-polarization (I_s/I_p), as shown in Fig. 3(d). The polished Si exhibits a maximum of $I_s/I_p = 133.35$ while a maximum of

FIG. 4. (Color online) The CAs for the diameter-controlled NRAs. The insets are corresponding photographs of water droplets on the surfaces of Si NRA layers.

I_s/I_p is decreased significantly to < 8 for all NRAs, suggesting that the reflection becomes polarization insensitive in Si NRA surfaces over the wide AOI.

It has been reported that enhanced hydrophobic surfaces can be conveniently fabricated through nanostructure constructing on hydrophobic materials.^{18,19} To investigate the effect of diameter-controlled Si NRAs on the wettability, the measurements of the water contact angle (CA) were performed. The CA on the flat surface of Si substrate was measured to be 95° . Si NRAs exhibit greater surface hydrophobicity with CAs between 101° and 118° , as shown in Fig. 4. Corresponding photographs of water droplets on the surfaces of Si NRAs are shown in the insets of Fig. 4. The CA increases with diameter of NRAs. The mechanism of the NRA diameter-dependent hydrophobic behavior can be explained by Wenzel's³⁰ model

$$\cos \theta_w = r \cos \theta_y \quad (r > 1), \quad (2)$$

where θ_w is the measured CA on a NRA surface, θ_y is the intrinsic CA on a flat surface, and r is the ratio of the actual contact area to the apparent area. Obviously, CA increases with actual contact areas with water droplets at the hydrophobic surface. Increasing diameter of nanorod makes the actual contact areas raise and then enhances the hydrophobicity of the surfaces.

IV. CONCLUSION

In summary, we synthesized the surface profile-tunable Si NRAs by a technique combining colloidal lithography and RIE. The AR properties and nonwetting ability could be enhanced via controlling diameter of NRAs. The Si NRAs exhibit excellent broadband and omnidirectional AR properties; for example, the reflectance of the NRAs with 303 nm in diameter remains below 10% over wavelength domains from 500 to 850 nm and below 5.5% for AOI up to 55° with unpolarized 650 nm light. I_s/I_p is decreased significantly to < 8 for all NRA layers, demonstrating polarization-insensitive AR properties. Moreover, hydrophobic properties could be enhanced by increasing the diameter of NRAs. The Si NRAs function as both self-cleaning and AR layers, which offer a promising approach to enhance the solar cell energy conversion efficiency.

ACKNOWLEDGMENTS

The research was supported by the National Science Council (Grant Nos. NSC 96-2112-M-002-038-MY3 and NSC 96-2622-M-002-002-CC3) and the Aim for Top University Project from the Ministry of Education.

- ¹Y.-F. Huang, S. Chattopadhyay, Y.-J. Jen, C.-Y. Peng, T.-A. Liu, Y.-K. Hsu, C.-L. Pan, H.-C. Lo, C.-H. Hsu, Y.-H. Chang, C.-S. Lee, K.-H. Chen, and L.-C. Chen, *Nat. Nanotechnol.* **2**, 770 (2007).
- ²J. Y. Huang, X. Wang, and Z.-L. Wang, *Nano Lett.* **6**, 2325 (2006).
- ³H. Xu, N. Lu, D. Qi, J. Hao, L. Gao, B. Zhang, and L. Chi, *Small* **4**, 1972 (2008).
- ⁴J. Y. Huang, X. D. Wang, and Z. L. Wang, *Nanotechnology* **19**, 025602 (2008).
- ⁵J. Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. Chen, S.-Y. Lin, W. Liu, and J. A. Smart, *Nat. Photonics* **1**, 176 (2007).
- ⁶S. L. Diedenhofen, G. Vecchi, R. E. Algra, A. Hartsuiker, O. L. Muskens, G. Immink, E. Bakkers, E. W. Vos, and J. E. Rivas, *Adv. Mater. (Weinheim, Ger.)* **21**, 973 (2009).
- ⁷D. G. Stavenga, S. Foletti, G. Palasantzas, and K. Arikawa, *Proc. R. Soc. London, Ser. B* **273**, 661 (2006).
- ⁸D. H. Macdonald, A. Cuevas, M. J. Kerr, C. Samundsett, D. Ruby, S. Winderbaum, and A. Leo, *Sol. Energy* **76**, 277 (2003).
- ⁹H. L. Chen, S. Y. Chuang, C. H. Lin, and Y. H. Lin, *Opt. Express* **15**, 14793 (2007).
- ¹⁰S. H. Zaidi, D. S. Ruby, and J. M. Gee, *IEEE Trans. Electron Devices* **48**, 1200 (2001).
- ¹¹S. A. Boden and D. M. Bagnall, *Appl. Phys. Lett.* **93**, 133108 (2008).
- ¹²K. Hadobás, S. Kirsch, A. Carl, M. Acet, and E. F. Wassermann, *Nanotechnology* **11**, 161 (2000).
- ¹³Z. Yu, H. Gao, W. Wu, H. Ge, and S. Y. Chou, *J. Vac. Sci. Technol. B* **21**, 2874 (2003).
- ¹⁴I. Montanari, A. Nogueira, J. Nelson, J. R. Durrant, C. Winder, M. A. Loi, N. S. Sariciftci, and C. Brabec, *Appl. Phys. Lett.* **81**, 3001 (2002).
- ¹⁵J. Zhao, A. Wang, M. Green, and F. Ferrazza, *Appl. Phys. Lett.* **73**, 1991 (1998).
- ¹⁶C. H. Chang, P. C. Yu, and C. S. Yang, *Appl. Phys. Lett.* **94**, 051114 (2009).
- ¹⁷W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Oner, J. Youngblood, and T. J. McCarthy, *Langmuir* **15**, 3395 (1999).
- ¹⁸W.-L. Min, B. Jiang, and P. Jiang, *Adv. Mater. (Weinheim, Ger.)* **20**, 3914 (2008).
- ¹⁹W.-L. Min, B. Jiang, and P. Jiang, *Nanotechnology* **19**, 475604 (2008).
- ²⁰Y. Kanamori, K. Hane, H. Sai, and H. Yugami, *Appl. Phys. Lett.* **78**, 142 (2001).
- ²¹S. Adachi, *J. Appl. Phys.* **66**, 3224 (1989).
- ²²N. Layadi, V. M. Donnelly, J. T. C. Lee, and F. P. Klemens, *J. Vac. Sci. Technol. A* **15**, 604 (1997).
- ²³J. Turunen and F. Wyrowski, *Diffraction Optics for Industrial and Commercial Applications* (Akademie, Berlin, 1997).
- ²⁴A. Poruba, A. Fejfar, Z. Remes, J. Springer, M. Vanecek, J. Kocka, J. Meier, P. Torres, and A. Shah, *J. Appl. Phys.* **88**, 148 (2000).
- ²⁵I. Ohlidal, F. Lukes, and K. Navratil, *Surf. Sci.* **45**, 91 (1974).
- ²⁶P. Beckman and A. Spizzichno, *The Scattering of Electromagnetic Waves from Rough Surfaces* (Pergamon, Oxford, 1963).
- ²⁷H. Yoshida, Y. Terada, H. Miyake, and K. Hiramatsu, *Jpn. J. Appl. Phys., Part 2* **41**, L1134 (2002).
- ²⁸L. Hu and G. Chen, *Nano Lett.* **7**, 3249 (2007).
- ²⁹G. W. Kattawar and M. Eisner, *Appl. Opt.* **9**, 2685 (1970).
- ³⁰R. N. Wenzel, *Ind. Eng. Chem.* **28**, 988 (1936).