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Early stages of growth of Si nanowires by metal assisted chemical etching: A scaling study

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We have studied the kinetic roughening in the growth of Si nanowires (NWs) by metal assisted chemical etching (MACE) process as a function of the etching time using atomic force microscopy imaging. In the early stage of growth of Si NWs by Ag assisted MACE process, we have determined the scaling exponents α , β , and 1/z. In the formation of Si NWs, nascent Ag⁺ ions play an important role in diffusing through the Si surface by means of excess holes that control the size of the NWs. In this system, kinetic roughening of the growth front within the detectable range of lengths of Si NWs was observed. We have observed an $\alpha = 0.74 \pm 0.01$ at the early stage of growth of Si NWs. Interface width *w* increases as a power law of etching time (*t*), $w \sim t^{\beta}$, with growth exponent $\beta = 0.30 \pm 0.05$ and lateral correlation length ξ grows as $\xi \sim t^{1/z}$ with $1/z = 0.32 \pm 0.05$. These exponents α , β , and 1/z determine the universality class in which the system belongs to. The growth mechanism is explained by conventional shadowing instability model, which is common for columnar type of surface growth. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928714]

Roughening of growing surfaces and interfaces is a ubiquitous phenomenon in nature that is far from equilibrium condition. Surface roughening is observed in a wide range of phenomena from wetting front, bacterial growth, chemically etched surface, and different types of medium.¹⁻³ This surface roughening in growth has been shown to exhibit scaling properties characterized by some scaling exponents that enable one to understand similar behaviors independent of specified systems. Recently, study of physics associated with the formation and evolution of dynamic structures using a scaling description has attracted considerable interest in both experimental and theoretical studies.⁴⁻⁶ These studies relate with thin film growth mechanism by a set of scaling exponents describing the dependence of the surface roughness of film on their lateral length scale. While there has been a lot of research on the process of kinetic roughening leading to different surface morphology, there are many open questions and challenges related to the understanding of the growth mechanisms.^{3,5,7}

During the last decades, metal assisted chemical etching (MACE) has emerged as a promising and significant tool for producing large area, rapid, aligned, and well controlled Si nanowires (NWs) and is now adopted as a most cost effective alternative to other sophisticated tools for the production of high quality Si NWs.^{8,9} In principle, MACE involves two successive processes: surface nucleation of metal catalysts and anisotropic etching; these two processes take place in an aqueous etchant solution containing HF and metal salts.^{10–13} A plethora of articles have been published explaining the possible mechanisms of growth of Si nanostructures by MACE.^{10–15} Understanding and controlling the growth mechanism of Si NWs through MACE are of paramount importance for its tailored applications.

In this article, we investigate on the early stages of growth of Si NWs by MACE using high resolution AFM imaging. For the MACE grown Si NWs, we explore the different scaling exponents, e.g., roughness exponent, growth exponent, and dynamical exponents for the growth process. We have found that roughness exponent is constant within the detectable range and the local slope increases in the early stage of growth and it tends to saturate for the higher etching time. The etching mechanism of Si is explained by using the shadowing instability model suitable for columnar type of surface growth.

Si NWs were grown from boron-doped p-type Si(100) wafers with resistivity 1–10 Ω cm. The Si wafers were first cleaned by typical RCA process.⁸ For the growth of Si NWs, we have followed a one-step MACE process where the cleaned Si wafers were immersed in an etching solution containing HF and AgNO₃ for different time durations. After etching, the residual Ag dendrites are removed by dipping the samples in 10% HNO₃ solution for 5 min. The morphologies of the etched Si samples were characterized using atomic force microscopy (AFM) (Agilent SPM5500) in noncontact mode using Si tips (Nanosensors, PPP-NCH-20) and have been analyzed by Matlab programming. Raman scattering measurement was carried out with a 514 nm Ar^+ laser excitation using a micro-Raman spectrometer (HORIBA Scientific, T64000). Cross-sectional field emission scanning electron microscopy (FESEM) imaging was performed using Sigma, Zeiss.

Among the reported models on the growth mechanism of Si NWs,^{10–15} microscopic electrochemical cell model is considered very important for understanding the formation of vertical Si NWs array. In this self-assembled Ag induced selective etching process, continuous galvanic displacement of Si by Ag^+ via $Ag^+ \to Ag$ reduction occurs on the Si surface. $^{11-13,15}$ It results in a large density of local nanoelectrochemical cells being formed on the Si surface. In the cathode, the reduction of Ag⁺ ions produces metallic Ag deposits. It is considered that holes are injected following the capture of electrons by Ag⁺ ions, since Ag is more electronegative than the Si and hence providing an easy injection path for the hole. Consequently, the anodic reaction, oxidization of the atoms of Si surface, takes place by the release of electrons. The oxidized Si is then chemically dissolved in HF etchants (in the form of H_2SiF_6) allowing the newly exposed Si to come in contact with the Ag catalysts, which is further etched in the next cycle of the continuous process. The charge exchange and transport between anode (Si) and cathode sites (Ag particles) are more favorable at the Ag/Si interface as compared to the regions denuded of Ag particles (e.g., pore walls and Si regions not covered by Ag). Consequently, oxidation and dissolution of Si occur at the bottom of the pore where Ag particles reside and sink as the process proceeds with time, rather than at the pore walls. A schematic diagram of this growth process is shown in Figure 1(a).^{13,16} It has been reported that the MACE grown Si NWs are covered by a thin layer of the amorphous Si or Si-H layers that is believed to prevent the lateral etching of the Si NWs. In order to probe the quality of the Si NWs as well as the presence of amorphous Si or Si-H, we performed micro-Raman studies on the as-grown Si NWs. Figure 1(b) shows the Raman spectra of the Si NWs grown after different etching durations. Several multi-phonon bands are present in the spectra ($\sim 300, \sim 433, \sim 520, \sim 617, \sim 670, \sim 826, \text{ and}$ \sim 964 cm⁻¹), some of which are not detected in the bulk Si spectrum (i.e., before etching). The LO, 2LA, and 2LO modes shown in Figure 1(b) are mostly due to the amorphous

FIG. 1. (a) Schematic illustration of the growth of Si NWs in the MACE process in $HF/AgNO_3$ solution. (b) Comparison of the Raman spectra for the as-grown Si NWs etched for different time durations. The curves are vertically shifted for clarity of presentation.

Si or the surface chemical bonds (such as Si-H).^{17,18} The peak intensities are increased with increasing duration of etching. Note that the TO mode at 520 cm^{-1} , the first-order Raman mode of crystalline Si, is extended down to $\sim 460 \,\mathrm{cm}^{-1}$. The TO peak ($\sim 480 \,\mathrm{cm}^{-1}$) corresponding to the amorphous Si may be overshadowed by the high intensity 1st order Raman peak of crystalline (core) Si (\sim 520 cm⁻¹). Note that the broadening of the 1st order Raman mode can be explained partly in terms of quantum confinement and strain in the Si nanostructure.¹⁸ The earlier reports including our studies using various techniques suggest that the MACE grown Si NWs are covered by a thin layer of amorphous Si or Si-H. Due to the presence of the amorphous Si and Si-H layer on Si NWs surface, the Ag⁺ ions do not affect the sidewall of the as grown Si NWs and the etching occurs preferentially along the vertical direction. This leads to straight vertical pores on the Si surface resulting in array of vertical Si NWs. Note that the existing models mainly discuss about the etching mechanism in terms of mass transfer, hydrogen production, heat production, and the diffusion of metalcatalyst by means of excess holes (h^+) in Si.

Figure 2 shows representative AFM images of etched Si surface for different etching time. Here, all the images are taken in $5 \times 5 \,\mu\text{m}^2$ areal surface that exhibits a rough type of surface morphology. The high resolution image of each sample scanned over $2 \times 2 \,\mu m^2$ area is shown as an inset in each case. Height profile of each image along a line is shown at the bottom of the respective images. The length of the Si NWs in each case is independently measured using crosssectional FESEM imaging.¹⁹ We found that in the early stages of growth, with etching time the length of NWs grows nearly linearly.¹⁹ In general, FESEM analysis showed higher length than that measured by AFM and the difference in estimate of NW length using two techniques increased for higher etching time samples. This is due to the limitation of the AFM tip movement in the dense array of NWs, when the length of the NWs is high. It is obvious that full length of the NWs is not accurately probed by AFM analysis, particularly at higher etching times. However, we are dealing with the evolution of the surface feature of the Si wafer during etching at the early stages of NW growth and the AFM data provide 3D profile that is necessary for the scaling analysis.

In order to gain insight into dynamic behavior of the surface evolution and characterize the roughness of the observed surface/interface, we define the local height h(x,t)along the moving direction of the surface to determine the different scaling exponents. These quantities are ascertained from height-height correlation function G(r,t), which is defined as statistical average of the mean square of height difference between two positions in the interface separated by a distance ralong horizontal direction as $G(r,t) = \langle [h(r,t) - h(0,t)]^2 \rangle$, where h(r,t) and h(0,t) are the heights of the surface at the locations separated by a distance r and the brackets signify an average over pairs of points obtained from AFM image. In other way, for small length scale it also defined as G(r, t) $= [m(t)r]^{2\alpha}$ with $r \ll \xi(t)$, where ξ is the characteristic in-plane length scale, α is the roughness scaling exponent, and m(t) is the local slope of the surface profile.^{20–23} Lateral correlation length, ξ is the measure of the length beyond which surface heights are not significantly correlated and $m(\theta)$ is calculated

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FIG. 2. AFM images of etched Si surface, showing the surface morphology for different etching durations. Each image consists of $5 \times 5 \,\mu\text{m}^2$ scanned area and scale bar is $1.0 \,\mu\text{m}$. The inset shows the magnified image (scale bar 400 nm) corresponding $2 \times 2 \,\mu\text{m}^2$ scanned area in each case. Height profile of each image is shown at the bottom of the respective images.

from above mentioned relation.²⁰ Here, we have considered the dynamic behavior of the growth in terms of etching duration *t*, only at the early stages of growth. The height-height correlation function G(r,t) as a function of distance *r* calculated from the AFM images for different etching durations is plotted in Figure 3. In our analysis, we have checked about 9–12 AFM images for each sample, which were enough to give statistically reliable data to obtain G(r,t) plot, and in this way the sampling induced effect in the G(r,t) calculation was avoided. Figure 3 shows $G^{1/2}(r,t)$ versus *r* plots for different samples with different etching duration. The roughness exponent α was calculated from a fit to the linear part of the log-log plot of $G^{1/2}(r)$ versus *r* and we obtained the average α as 0.74 \pm 0.01. We observe an upshift in the curves when we plot $G^{1/2}(r,t)$ vs.



FIG. 3. Square root of height-height correlation function ($G^{1/2}$) as a function of lateral distance (*r*), as calculated from the AFM images for different samples etched for different time duration. Roughness exponent (α) is calculated from the power law fitting of the linear portion.

r for different etching times, as shown in Figure 3, and it confirms the roughening in the growth process. In order to monitor the roughening process quantitatively, we have measured the interface width w(t) as function of *t* following the conventional method.^{24,25} Here, w(t) is defined as the value of $G^{1/2}(r,t)$ at the first local maximum (shown by arrow marked in Figure 3); $w(t) = G^{1/2}(t/2)$, whereas ξ marked by an upward arrow is the position of *r* at the first local minimum of $G^{1/2}(r)$.²⁶ This definition of roughness amplitude is preferred over the large *r* limit of G(r), since artifacts at large length scales can affect the AFM data.

We have observed a power law behavior of interface width (w), as $w \sim t^{\beta}$. The exponent β characterizes the dynamics of the roughening process and is called growth exponent. Similar type of power law dependence is also observed in lateral correlation length ξ . It increases with t as $t^{1/z}$, where exponent 1/z is called dynamic exponent. The logarithmic variation of w as a function of t is shown in Figure 4(a) for all etched samples. The obtained value of growth exponent β is 0.30 ± 0.05. The dynamic exponent (1/z) is calculated as 0.32 ± 0.05 from the log-log plot of ξ versus t, as shown in Figure 4(b). Figure 4(a) shows the increasing nature of w with time t, which signifies the roughening nature of growth. In order to identify the growth mode, we have plotted local slope (m) as a function of etching time, as shown in Fig. 4(c). If m(t) is independent of etching time, it is called stationary type of growth. In stationary growth, for $r \ll \xi$ the height-height correlation function will merge



FIG. 4. Log-log variation of (a) interface width (*w*), and (b) lateral correlation length (ξ) with etching time (*t*). The growth exponent (β) and dynamic exponent (1/z) are calculated from the slope of the respective curve. (c) Variation of local slope (m) as a function of etching time (t).

for different t values. However, for the non-stationary case, $G^{1/2}(r)$ will shift upward as the local slope will change with etching duration.²¹ In present case, the growth is obviously non-stationary. We also observe that the local slope at first increase and then saturate. This signifies that in the present case the growth process is roughening. In the early stage of growth, size of the Si nanostructures is very small, and with time the size as well as local slope is increasing. However, after a certain time the diameter of the Si NW do not change (only vertical growth is dominated), as a result the local slope is saturated. For the nonequilibrium growth, the theoretically predicted values of the exponents are $\alpha = 2/3$ and β = 1/5²⁷ and for liner growth the exponents are $\alpha = 1$ and $\beta = 1/4$.²⁸ However, our exponent values ($\alpha = 0.74$ and $\beta = 0.30$) are different from the above values. Thus, none of the theoretical models can properly support the type of growth observed here. Interestingly, growth due to roughening is still not well understood.²¹ In case of nonequilibrium film growth, the growth equation is expressed as²³

$$\begin{aligned} \frac{\partial h}{\partial t} &= D_s \nabla^4 h(r,t) + D_\nu \nabla^3 h(r,t) + \nu \nabla^2 h(r,t) + \lambda (\nabla h(r,t))^2 \\ &+ R\Omega(h,t) + \eta(r,t), \end{aligned}$$

where D_s expresses surface diffusion, D_v volume diffusion, ν evaporation and redeposition, λ is a non-linear coupling term, R is the growth (or etching) rate, Ω is the shadowing solid angle (which is a non-local term), and η is a noise term, which generates the roughness. Here, each term plays different role in different growth models, such as KPZ and Lai-Das-Sharma.²⁰ Interplay between the parameters will generate different types of surface. However, for explaining columnar type of growth, shadowing instability theory may be more relevant, where either $D_s = D_v = 0$ or $D_v = v$ $=0.^{29-31}$ The shadowing mechanism, i.e., the primary nonlocal effect is very much applicable for mound type surface, where taller surface features block incoming flux to reach lower lying areas of the surface. As a result, surface with small height receive little or no particle flux, whereas the taller surface receive higher flux. Shadowing is an inherently nonlocal process, since the shadowing of a surface feature depends on the difference between the surfaces with different heights. In absence of lateral diffusion or evaporation, the surface evolves as a vertical structure.³² Here, our experimental results seem to closely resemble the shadowing instability model. In case of MACE process, chemically generated Ag⁺ ions create defect site at the outer surface of the Si substrate. The rate of formation of soluble H₂SiF₆ is accelerated at these defect sites as compared to the flat surface. This means that etching occurs preferentially at these sites due to lower binding energy of Si compared to the Ag of Ag⁺ ions. Thus, the bottom of the native column is etched preferentially over the top surface of Si. It is consistent with the columnar growth that occurs as a result of shadowing during Si NWs growth, where the top of the native column grows more quickly than the bottom, which is equivalent to a faster etching of the bottom. The shadowing of the native column also prevents the lateral etching. Interestingly, similar type of shadowing effect has been reported in plasma etched Si surface by Drotar *et al.*³³ It was shown that vertical structure can be grown on Si with $\beta < 0.5$ by shadowing effect in plasma etched Si surface. Yao and Guo theoretically predicated a $\beta = 0.33 \pm 0.02$ using shadowing instability model.²⁹ These values are very close to our experimental data, i.e., $\beta = 0.30 \pm 0.05$. The other growth exponents for columnar type or mound type surface growth under shadowing effect, as explained by Pelliccione *et al.*, are also comparable to our experimental data.³² Though the etching mechanism of Si by MACE is still under debate, shadowing instability theory explaining columnar growth of Si NWs by MACE provides an alternative understanding on the etching mechanism.

In conclusion, growth mechanism of Si NWs by Ag assisted MACE process has been studied in terms of the different scaling exponents acquired from the AFM images. We have observed the roughening in the early stage of etching of Si by MACE as Ag diffuses through Si via excess holes in HF/AgNO₃ solution. Though this type of growth cannot be explained well by earlier published atomistic models, our results showed that shadowing instability model can nearly explain the columnar growth of Si NWs in the MACE process. The diffusion of Ag ions produces different universality class. Our results might provide valuable clues to the dynamics of growth of Si NWs by MACE for a better control of growth and morphologies, which are crucial for its future applications.

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- ¹C. Guerrero, E. Reyes, and V. González, Polymer 43, 6683 (2002).
- ²T. Vicsek, M. Cserző, and V. K. Horváth, Phys. A 167, 315 (1990).
- ³D. Bonamy, L. Ponson, S. Prades, E. Bouchaud, and C. Guillot, Phys. Rev. Lett. **97**, 135504 (2006).
- ⁴F. Family and T. Vicsek, *Dynamics of Fractal Surfaces* (World-Scientific, Singapore, 1990).
- ⁵L. Ponson, D. Bonamy, and E. Bouchaud, Phys. Rev. Lett. **96**, 035506 (2006).
- ⁶M. Lütt, J. P. Schlomka, M. Tolan, J. Stettner, O. H. Seeck, and W. Press, Phys. Rev. B 56, 4085 (1997).
- ⁷K. A. Takeuchi, M. Sano, T. Sasamoto, and H. Spohn, Sci. Rep. 1, 34 (2011).
- ⁸R. Ghosh, P. K. Giri, K. Imakita, and M. Fujii, Nanotechnology 25, 045703 (2014).
- ⁹K. Q. Peng, Y. J. Yan, S. P. Gao, and J. Zhu, Adv. Mater. 14, 1164 (2002).
- ¹⁰K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee, and J. Zhu, Adv. Funct. Mater. **16**, 387 (2006).
- ¹¹N. Bachtouli, S. Aouida, and B. Bessais, Microporous Mesoporous Mater. 187, 82 (2014).
- ¹²Z. R. Smith, R. L. Smith, and S. D. Collins, Electrochim. Acta **92**, 139 (2013).
- ¹³W. K. To, C. H. Tsang, H. H. Li, and Z. Huang, Nano Lett. **11**, 5252 (2011).
- ¹⁴Z. Huang, N. Geyer, P. Werner, J. de Boor, and U. Gosele, Adv. Mater. 23, 285 (2011).
- ¹⁵K. S. Sanjay, K. Dinesh, S. W. Schmitt, K. N. Sood, S. H. Christiansen, and P. K. Singh, Nanotechnology 25, 175601 (2014).
- ¹⁶C. Y. Chen, C. S. Wu, C. J. Chou, and T. J. Yen, Adv. Mater. 20, 3811 (2008).
- ¹⁷V. A. Volodin and D. I. Koshelev, J. Raman Spectrosc. 44, 1760 (2013).

¹⁸R. Ghosh, A. Pal, and P. K. Giri, J. Raman Spectrosc. 46, 624 (2015).

- ¹⁹See supplementary material at http://dx.doi.org/10.1063/1.4928714 for FESEM images of Si NWs and the length of the Si NWs as a function of etching time.
- ²⁰M. Pelliccione and T.-M. Lu, Evolution of Thin Film Morphology: Modeling and Simulation (Springer-Verlag, New York, 2008).
- ²¹J. H. Jeffries, J. K. Zuo, and M. M. Craig, Phys. Rev. Lett. 76, 4931 (1996).
- ²²Y. Zhao, G. C. Wang, and T.-M. Lu, Characterization of Amorphus and Crystalline Rough Surface: Principles and Application (Academic Press, London, 2001).
- ²³L. Barabási and H. E. Stanley, Fractal Concepts in Surface Growth (Cambridge University Press, 1995).
- ²⁴I. J. Lee, M. Yun, S. M. Lee, and J. Y. Kim, Phys. Rev. B 78, 115427 (2008).

- ²⁵D. P. Datta and T. K. Chini, Phys. Rev. B 69, 235313 (2004).
- ²⁶J. Kim, D. Cahill, and R. Averback, Phys. Rev. B **67**, 045404 (2003).
 ²⁷Z. Lai and S. Das Sarma, Phys. Rev. Lett. **66**, 2348 (1991).
- ²⁸D. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990).
- ²⁹J. H. Yao and H. Guo, Phys. Rev. E 47, 1007 (1993).
- ³⁰R. P. U. Karunasiri, R. Bruinsma, and J. Rudnick, Phys. Rev. Lett. 62, 788 (1989).
- ³¹G. S. Bales, R. Bruinsma, E. A. Eklund, R. P. U. Karunasiri, J. Rudnick, and A. Zangwill, Science 249, 264 (1990).
- ³²M. Pelliccione, T. Karabacak, C. Gaire, G. C. Wang, and T. M. Lu, Phys. Rev. B 74, 125420 (2006).
- ³³J. T. Drotar, Y. P. Zhao, T. M. Lu, and G. C. Wang, Phys. Rev. B **62**, 2118 (2000).