



OPEN

SUBJECT AREAS:
SURFACE CHEMISTRY
NANOSCALE MATERIALSReceived
12 November 2013Accepted
6 March 2014Published
25 March 2014Correspondence and
requests for materials
should be addressed to
X.C. (xinchen@mail.
sitp.ac.cn)

Application of three-dimensionally area-selective atomic layer deposition for selectively coating the vertical surfaces of standing nanopillars

Wenjing Dong, Kenan Zhang, Yun Zhang, Tiaoxing Wei, Yan Sun, Xin Chen & Ning Dai

National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China.

We describe a strategy for selectively coating the vertical surfaces of standing nanopillars using area-selective atomic layer deposition (ALD). Hydrophobic self-assembled monolayers (SAMs) are utilised to selectively inhibit the coating of oxides on the modified horizontal regions to ensure that only the vertical surfaces of vertical standing nanorods are coated using ALD processes. This method makes it possible to fabricate vertical nanodevices using a simple process of depositing oxide layer on a vertical surface, and can also be applied to the area-selective surface passivation of other standing structures.

Surface coating and passivation are critical for optics¹, microelectronics², optoelectronics^{3,4} and catalysis⁵. Atomic layer deposition (ALD) is one powerful surface nano-engineering technique and has also demonstrated practical capability in microelectronics and photovoltaics^{6,7}. Recent achievements in nanowire-based sensors and field-effect transistors have promoted an escalation in ALD requirements in surface functionalisation and passivation^{8,9}. For example, ALD coats almost all surfaces that are exposed to the precursor gases, making it fundamentally difficult to coat desired surfaces in an area-selective manner. This restriction hinders the use of ALD in the selective passivation and coating of the lateral surfaces of vertically standing nanopillars on substrates, which are very common in microelectronic fin devices and vertical nanowire field-effect transistors^{10,11}. Although the inner walls of cylindrical nanopores have been selectively coated^{12,13}, the goal of attaining a three-dimensionally area-selective surface coating on standing nanopillars or vertical nanowires via flexible routes has yet to be achieved. In this letter, we demonstrate a feasible three-dimensionally area-selective ALD (3DAS-ALD) process by artfully exploiting hydrophobic self-assembled monolayers (SAMs) to tune the area-selective formation of ALD films on the vertical surfaces of standing pillars on substrates.

Surface activation plays an important role in the deposition of thin films on substrates using essential ALD processes^{14–16}. However, SAMs have been widely exploited to tune the chemical and physical properties of solid surfaces using alkanethiols and alkylsilanes^{17–19}. Hydrophobic SAMs have been used to inhibit the formation of ALD films, making it possible to achieve the two-dimensionally area-selective ALD of desired materials^{20–23}. The combination of SAMs and ALD has also been applied to selectively coat the inner walls of cylindrical nanopores to produce hybrid nanotubes^{12,13}. However, it is important but difficult to use 3DAS-ALD to construct hydrophilic and hydrophobic regions on standing nanopillar structures (e.g., vertical nanorods or nanowires) because existing methods such as lithography^{20,24} and microcontact printing^{25,26} for 2D planar films or nanopores are inherently difficult to apply in this case. In addition, the processes for selective ALD coating on cylindrical nanopores^{12,13} and lithography on nanowires^{27,28} do not appear to apply to the area-selective coating of the vertical surfaces of standing nanopillars on substrates.

Our experimental design and fabrication processes for achieving 3DAS-ALD on standing nanopillar structures are illustrated in Figure 1. During our fabrication, the cleaned and hydrophilic standing Si structures (step 1) are first coated with an Au film of several nanometres in thickness on the horizontal surfaces (step 2). Subsequently, SAMs of 1-dodecanethiol (DAT) form on the Au films to create hydrophobic surfaces (step 3). Because of the resist effect of hydrophobic SAMs, the precursor reactions will occur not on the hydrophobic horizontal surfaces but only on the vertical surfaces (step 4) during the ALD processes. In the end, the 3DAS-ALD will have coated only the vertical surfaces of the nanopillars with oxides (e.g., ZnO) once the Au films are removed. We observed

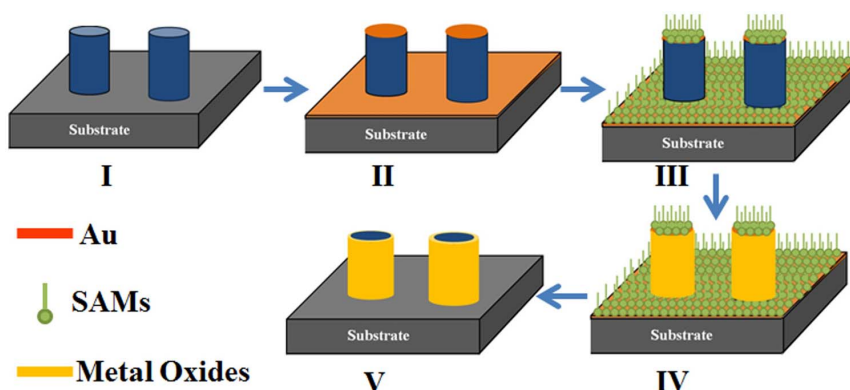


Figure 1 | Schematic diagrams of the 3DAS-ALD of a metal oxide on the vertical surfaces of standing nanopillar structures. The surfaces parallel to the substrate are referred to as horizontal surfaces in the text, and the perpendicular ones are referred to as vertical surfaces in the text.

that the DAT SAMs on Au films act as obstacles and can effectively hinder the ALD process (Figure S1), while ALD can still occur on Si substrates immersed in DAT solution (Figure S1c). This result indicates the possibility of using the above processes to realise 3DAS-ALD on standing structures.

Figure 2 shows the area-selective ZnO coating of the vertical surfaces of vertically oriented Si nanopillars (i.e., nanorods), proving that this fabrication technique is feasible. The original standing Si nanorods were nearly perpendicular to the horizontal surfaces (both the top surfaces of the nanorods and the substrates) and were fabricated in accordance with a modified process that has been reported elsewhere²⁹. The nanopillars (i.e., nanorods) were approximately 500 nm in length and approximately 250–350 nm in diameter, and the bottom part was a slightly wider than the top (Figure S2a). Then, a 6 nm thick Au film and a 4 nm thick Ti adhesion layer, which were used to form hydrophobic SAMs, were coated onto the top surfaces of the nanorods and the substrates.

Figure 2a presents a false-colour transmission electron microscopy (TEM) image of Si nanorods with DAT-modified Au films after the 3DAS-ALD process had been performed. In this figure, we note that there are no ZnO films on the Au film, although some ZnO particles are present because of initial imperfect structures or SAM defects, indicating that the DAT successfully acted as a resistant layer to prevent the ALD coating of ZnO onto the Au film. In addition, uniform ZnO film of approximately 30 nm in thickness appears only on the vertical surfaces of the Si nanorods. The magnified image in Figure 2b further confirms that no ZnO films were present on the Au, while a dense ZnO film covered only the vertical surfaces of the standing Si nanorods when the Au film on the top surfaces of the nanorods was not removed. In addition, when the Au film on the top surfaces of the nanorods was removed, as shown in Figure 3a and Figure S2, bare Si was exposed on the horizontal surfaces, and there were no ZnO films present on either the top of the nanorods or

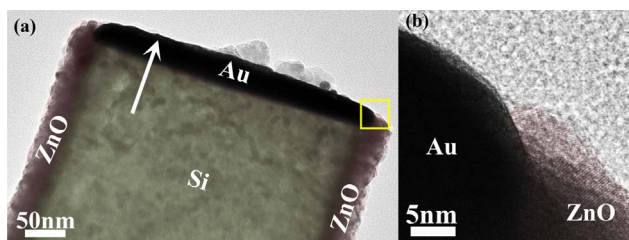


Figure 2 | (a) False-colour TEM images of nanorods after the 3DAS-ALD of ZnO films onto their vertical surfaces, before the Au films on the top surfaces of the nanorods were removed; the arrow points to the top of a nanorod. (b) False-colour HRTEM image of the region outlined in (a) with a yellow square.

the bottom of the Si substrates. As the ZnO particles were on the Au films and did not grow on the Si layer, these particles were removed when the Au films were removed.

Figure 3b presents an elemental profile acquired using line-scanning energy-dispersive X-ray spectroscopy (EDS); the Zn/O signals are much higher at the edges of the nanorods than in the other regions, while the signals corresponding to the Si element are lowest at the edges, indicating that ZnO films were present only on the vertical walls of the Si nanorods. In addition, the electrons injected onto the top surface are most likely to diffuse to the ZnO walls, which then produce Zn/O signals. However, when detecting the Zn/O elements at the bottom, the ZnO walls do not affect the result. Consequently, the background signals of Zn/O are higher at the top than at the bottom.

We further attempted to apply the 3DAS-ALD coating method on standing Si stripe arrays (Figure 4), although the results presented in Figure 3 already confirm that the concept is feasible for standing nanorods. The stripes were approximately 80 nm in width and approximately 400 nm in depth with a spacing of 150 nm (Figure S3a), as previously reported³⁰. As presented in the false-colour scanning electron microscopy (SEM) image of Figure 4a, the vertical surfaces were covered with ZnO film grown via ALD, whereas the horizontal surfaces were not coated. The line-scanned EDS spectrum in Figure 4b further confirms that the vertical surfaces were selectively coated with ZnO film via ALD. When no hydrophobic SAMs were present on the top surfaces of the Si stripes, all surfaces of the stripes and the substrate were completely coated with uniform ZnO film by the ALD process (Figure S4). The EDS spectrum reveals that when all surfaces were uniformly coated with ZnO, the Zn/O signals at the top surfaces had the form of a line; however, the Zn/O signals exhibited apparent peaks at the edges of the stripes when 3DAS-ALD was performed. This comparison is consistent with the SEM image in Figure 4a, indicating that this fabrication concept is feasible for long, standing, structured arrays.

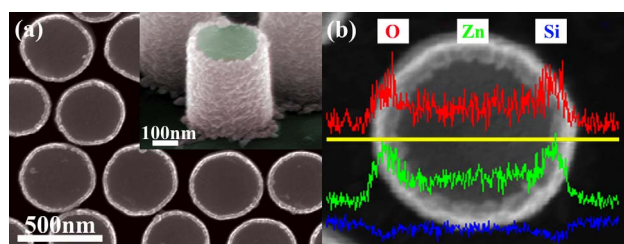


Figure 3 | (a) False-colour SEM image of nanorods after area-selectively depositing ZnO onto their vertical surfaces (top view); the inset is a 45°-tilted SEM image. (b) EDS elemental line scan of the area-selectively treated nanorods in the top view; the yellow line depicts the scanning route.

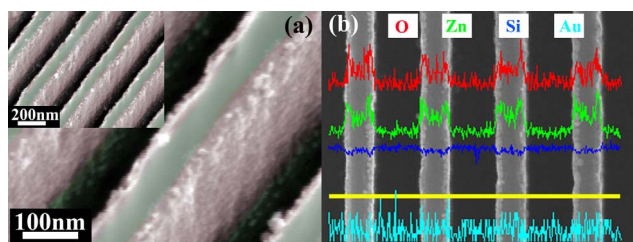


Figure 4 | (a) False-colour SEM images (tilted by 45°) of three-dimensional Si stripes with only the vertical surfaces selectively deposited with ZnO via ALD. (b) EDS elemental line scan of the stripes with vertical surfaces coated with ZnO; the yellow line depicts the scanning route.

Using a combination of ALD and SAMs, we achieved 3D area-selective ALD on standing structures (e.g., vertical nanorods and stripes). As mentioned above, the selective formation of stable hydrophobic SAMs^{23,31,32} is critical for area-selective ALD coating on the vertical surfaces of standing nanopillars. Thus, Au films play an important role in this process and are usually obtained via electron beam evaporation⁶, thermal evaporation or other processes¹⁹. In fact, most standing nanopillars are not strictly perpendicular to the substrates, which may cause the vertical surface to be unexpectedly coated with Au film during the deposition process (Figure S2b). The Au coated onto the vertical surfaces of the nanorods (Figure S2a) can be deposited in particle form by controlling the thickness of the Au films because of the much lower coverage on the vertical surfaces than on the horizontal surfaces (Figure S2b).

Figures S2c and S3b demonstrate how these Au particles on the vertical surfaces can be removed using a diluted HF solution with a simple dipping process, after which only the vertical surfaces remain active for ALD after the hydrophobic SAMs form on the horizontal Au films. Area-selective ALD can even be applied on the sharp edges of gathered standing nanorods, as illustrated in Figure S2d. In addition, subsequent ALD cycles result in slight coverage with ZnO film on the edges of the horizontal surfaces, as shown in Figures S5a and S5b. During the first several ALD cycles, the deposition occurs only on the vertical surfaces because of the DAT resistance. With an increasing number of ALD cycles, the diethylzinc/ H_2O precursors begin to react with the as-grown ZnO films, in accordance with the essential ALD process, once the thickness of the ZnO surpasses the total thickness of the metal films and SAMs^{11–13,23}. This reaction is available not only for the vertical direction but also for all directions in which the ZnO films are present. Figure S5c shows how the edges of the horizontal surfaces become slightly covered with ZnO film. All these results provide us with more opportunities for the design and fabrication of 3DAS-ALD coatings on the vertical surfaces of standing nanopillars.

We have demonstrated a feasible 3DAS-ALD process for standing nanopillar structures. Hydrophobic SAMs are utilised to selectively inhibit the coating of oxides onto the modified regions, making it possible to coat only the vertical surfaces of vertical standing nanorods and stripes during ALD processes. This 3DAS-ALD method can also be applied to vertical surface coating and passivation on other standing structures. We believe that this solution protocol will open up more opportunities and new perspectives for three-dimensionally area-selective surface coatings and passivation for use in advanced fabrication and nanodevices.

Methods

The Si substrates with standing nanopillar structures were cleaned with acetone, ethanol and water. The Si nanorod arrays were fabricated using a modified colloidal lithography and catalytic etching process²⁹. The Si stripes were obtained following a previously reported method³⁰. The Si structures were boiled in a piranha solution ($H_2SO_4:H_2O_2 = 3:1$ by volume) for 10 min and then washed with deionised water. A 3–10 nm thick Au film with a 1–5 nm thick Ti adhesion layer was deposited on the Si structures using Ar ion-beam sputtering. The structures that had been coated with

Au were then chemically treated with a 10% diluted HF solution during a dipping process. Subsequently, the samples were immersed in an ethanol solution that contained 20 mM 1-dodecanethiol (DAT) for 24 h and then thoroughly washed with ethanol. Finally, the samples were placed into the ALD (Picosun R100) cavity for surface coating in 3D mode.

During the ALD process, diethylzinc (DEZ) and H_2O were used as precursors, and N_2 was used as a carrier gas, while the reactor temperature was set to $90^\circ C$ because of the temperature sensitivity of DAT SAMs^{31,32}. The pulse time was 0.1 s for both DEZ and water; the purge times were 0.5 s and 15 s for DEZ and 0.5 s and 20 s for water. The samples were finally immersed in LiI/I_2 solution to remove the Au, thereby obtaining standing nanopillar structures with an area-selective ALD coating of ZnO on the vertical surfaces. Scanning electron microscopy (SEM) images and EDS spectra were obtained using an FEI Sirion200 SEM instrument. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F operated at 200 kV. The TEM specimens were prepared by scraping the samples off the substrate onto a carbon-coated copper grid.

- Shi, E. *et al.* Colloidal antireflection coating improves graphene–silicon solar cells. *Nano Lett.* **13**, 1776–1781 (2013).
- Arulkumar, S., Egawa, T., Ishikawa, H., Jimbo, T. & Sano, Y. Surface passivation effects on AlGaIn/GaN high-electron-mobility transistors with SiO_2 , Si_3N_4 , and silicon oxynitride. *Appl. Phys. Lett.* **84**, 613–615 (2004).
- Choi, H. *et al.* Versatile surface plasmon resonance of carbon-dot-supported silver nanoparticles in polymer optoelectronic devices. *Nat. Photon.* **7**, 732–738 (2013).
- Lao, C., Li, Y., Wong, C. P. & Wang, Z. L. Enhancing the electrical and optoelectronic performance of nanobelt devices by molecular surface functionalisation. *Nano Lett.* **7**, 1323–1328 (2007).
- Dasgupta, N. P., Liu, C., Andrews, S., Prinz, F. B. & Yang, P. Atomic layer deposition of platinum catalysts on nanowire surfaces for photoelectrochemical water reduction. *J. Am. Chem. Soc.* **135**, 12932–12935 (2013).
- Kim, S. *et al.* High-mobility and low-power thin-film transistors based on multilayer MoS_2 crystals. *Nat. Commun.* **3**, 1011 (2012).
- Schmidt, J. *et al.* Surface passivation of high-efficiency silicon solar cells by atomic-layer-deposited Al_2O_3 . *Prog. Photovolt. Res. Appl.* **16**, 461–466 (2008).
- Won-Sik, K. *et al.* SnO_2 nanotubes fabricated using electrospinning and atomic layer deposition and their gas sensing performance. *Nanotechnology* **21**, 245605 (2010).
- Tang, J. *et al.* Oxide-confined formation of germanium nanowire heterostructures for high-performance transistors. *ACS Nano* **5**, 6008–6015 (2011).
- Thelander, C. *et al.* Nanowire-based one-dimensional electronics. *Mater. Today* **9**, 28–35 (2006).
- Kim, H., Lee, H.-B.-R. & Maeng, W. J. Applications of atomic layer deposition to nanofabrication and emerging nanodevices. *Thin Solid Films* **517**, 2563–2580 (2009).
- Shin, H., Jeong, D. K., Lee, J., Sung, M. M. & Kim, J. Formation of TiO_2 and ZrO_2 nanotubes using atomic layer deposition with ultraprecise control of the wall thickness. *Adv. Mater.* **16**, 1197–1200 (2004).
- Bae, C. *et al.* Multisegmented nanotubes by surface-selective atomic layer deposition. *J. Mater. Chem. C* **1**, 621–625 (2013).
- Knez, M., Niesch, K. & Niimisto, L. Synthesis and surface engineering of complex nanostructures by atomic layer deposition. *Adv. Mater.* **19**, 3425–3438 (2007).
- Ras, R. H. A., Sahramo, E., Malm, J., Raula, J. & Karppinen, M. Blocking the lateral film growth at the nanoscale in area-selective atomic layer deposition. *J. Am. Chem. Soc.* **130**, 11252–11253 (2008).
- George, S. M., Ott, A. W. & Klaus, J. W. Surface chemistry for atomic layer growth. *J. Phys. Chem.* **100**, 13121–13131 (1996).
- Laibinis, P. E. *et al.* Comparison of the structures and wetting properties of self-assembled monolayers of n-alkanethiols on the coinage metal surfaces, copper, silver, and gold. *J. Am. Chem. Soc.* **113**, 7152–7167 (1991).
- Färm, E., Vehkamäki, M., Ritala, M. & Leskelä, M. Passivation of copper surfaces for selective-area ALD using a thiol self-assembled monolayer. *Semicond. Sci. Technol.* **27**, 074004 (2012).
- Lee, W. H. *et al.* Control of graphene field-effect transistors by interfacial hydrophobic self-assembled monolayers. *Adv. Mater.* **23**, 3460–3464 (2011).
- Lee, J. P. & Sung, M. M. A new patterning method using photocatalytic lithography and selective atomic layer deposition. *J. Am. Chem. Soc.* **126**, 28–29 (2003).
- Kobayashi, N. P., Donley, C. L., Wang, S.-Y. & Williams, R. S. Atomic layer deposition of aluminium oxide on hydrophobic and hydrophilic surfaces. *J. Cryst. Growth* **299**, 218–222 (2007).
- Chen, R. & Bent, S. F. Chemistry for positive pattern transfer using area-selective atomic layer deposition. *Adv. Mater.* **18**, 1086–1090 (2006).
- George, S. M. Atomic layer deposition: An overview. *Chem. Rev.* **110**, 111–131 (2010).
- Lee, W. & Prinz, F. B. Area-selective atomic layer deposition using self-assembled monolayer and scanning probe lithography. *J. Electrochem. Soc.* **156**, G125–G128 (2009).
- Yan, M. *et al.* Selective-area atomic layer epitaxy growth of ZnO features on soft lithography-patterned substrates. *Appl. Phys. Lett.* **79**, 1709 (2001).



26. Jiang, X. & Bent, S. F. Area-selective ALD with soft lithographic methods: Using self-assembled monolayers to direct film deposition. *J. Phys. Chem. C* **113**, 17613–17625 (2009).
27. Yan, R., Liang, W., Fan, R. & Yang, P. Nanofluidic diodes based on nanotube heterojunctions. *Nano Lett.* **9**, 3820–3825 (2009).
28. Liu, C., Hwang, Y. J., Jeong, H. E. & Yang, P. Light-induced charge transport within a single asymmetric nanowire. *Nano Lett.* **11**, 3755–3758 (2011).
29. Wang, H.-P., Lai, K.-Y., Lin, Y.-R., Lin, C.-A. & He, J.-H. Periodic Si nanopillar arrays fabricated by colloidal lithography and catalytic etching for broadband and omnidirectional elimination of Fresnel reflection. *Langmuir* **26**, 12855–12858 (2010).
30. Chen, X. *et al.* Aligned horizontal silica nanochannels by oxidative self-sealing of patterned silicon wafers. *Chem. Mater.* **19**, 3–5 (2007).
31. Prathima, N. *et al.* Thermal study of accumulation of conformational disorders in the self-assembled monolayers of C8 and C18 alkanethiols on the Au (111) surface. *Langmuir* **21**, 2364–2374 (2005).
32. Chandekar, A., Sengupta, S. K. & Whitten, J. E. Thermal stability of thiol and silane monolayers: A comparative study. *Appl. Surf. Sci.* **256**, 2742–2749 (2010).

Acknowledgments

This work was funded by the National Basic Research Programme of China (2012CB934301 and 2011CBA00905), NSFC (61376016, 61290304 and 61275114) and CAS (KSZD-EW-Z-018).

Author contributions

W.J.D., C.X. and N.D. performed the design, experiments and theoretical simulations and analysis and wrote the manuscript. T.X.W. and Y.Z. contributed the ALD process and spectroscopy measurements. K.N.Z. and Y.S. contributed to the deposition of the Au and Ag films and the SEM measurements.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Dong, W.J. *et al.* Application of three-dimensionally area-selective atomic layer deposition for selectively coating the vertical surfaces of standing nanopillars. *Sci. Rep.* **4**, 4458; DOI:10.1038/srep04458 (2014).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>