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Orientation of silicon nanowires grown from nickel-coated silicon wafers

Feng Ji Li [a,b], Sam Zhang [a,*], Jyh-Wei Lee [c,d], Jun Guo [e], Timothy John White [f], Bo Li [g], Dongliang Zhao [g]

[a] School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] PVD Department of Plating Division, Singapore Epson Industrial Pte Ltd, Singapore 628162, Singapore
[c] Department of Materials Engineering, Ming Chi University of Technology, Taipei 24301, Taiwan, ROC
[d] Center for Thin Film Technologies and Applications, Ming Chi University of Technology, Taipei 24301, Taiwan, ROC
[e] Analysis and Testing Center, Soochow University, Suzhou 215123, China
[f] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[g] Central Iron and Steel Research institute, 76 South Xueyuanlu Road, Haidan District, Beijing 100081, China

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ABSTRACT

Growth orientation of silicon (Si) nanowires is the key in tailoring the optical and electrical characteristics of semiconductor devices. To date, however, the distribution and dictator are still unclear. In this work, Si nanowires are grown via thermal annealing of nickel (Ni) coated Si wafers. The morphology, growth orientation and the relation to the seeding Ni catalyst particles are examined via high resolution transmission electron microscopy and selected area electron diffraction pattern. Statistical results show that Si nanowires prefer to be along the $<112>$ orientation, followed by the ones in the $<110>$, $<111>$, $<001>$, $<113>$ and $<133>$ orientations. Besides surface energy that is commonly believed to control the nanowire's growth, this work found that the nanowire's growth follows certain structure-sensitive principle at the wire/catalyst interface to minimize the mismatch in lattice spacing and dihedral angle.

1. Introduction

Silicon (Si) nanowires are important nanotechnology building blocks in optical devices [1–3], field-effect transistors [4–6], lithium batteries [7,8], and power generators [9,10]. They can grow by laser ablation of Si and Fe powder mixture [11], chemical vapor deposition of $SiCl_4/H_2$ [12–14], or SiH_4 gases [15], thermal degradation of diphenylsilane in a supercritical hexane fluid [16,17], or thermal evaporation of bulk Si onto metal-covered substrates under ultrahigh vacuum [18,19]. In the growth process, Si atoms come from vaporization of powder mixture [11], decomposition of gaseous molecules [12–14], degradation of diphenylsilane [16,17], or sublimation of bulk Si [18,19], and then, melt into the metal-Si eutectic droplet. Upon supersaturation of Si, Si precipitates out to seed a nanowire, followed by growth of the nanowire with continuous supply of precipitating Si atoms from the liquid droplet. If the growth takes place on a crystal substrate, e.g., Si wafer, the droplet becomes displaced from the substrate and "rides" atop the grown nanowire [12]. Si nanowires also grow by thermal annealing of Si wafers that are covered with metallic catalyst (e.g., Ni, Fe or Au) without additional vapor or liquid Si source [20–27]. In the process, the metallic catalyst melts with the beneath Si wafer to form the metal-Si eutectic droplet. Si atoms continuously diffuse into the droplet. Upon supersaturation, Si is precipitated from the droplet to grow into nanowires. To facilitate the growth, Si from the Si wafer serves as the source and the liquid metal-Si droplet acts as the medium. The nanowire always grows out from the liquid droplet while the droplet always stays on the wafer (thus the catalyst droplet is always found at the "root" of the nanowire, i.e., at the wafer substrate). This is called solid–liquid–solid (SLS) growth. In SLS growth, Si atoms directly come from the solid Si wafer. Thus, diphenylsilane, supercritical hexane fluid or Si-containing flammable gases are not necessary. Moreover, the growth condition is simple, i.e., a motor pump, a heating unit and an Ar gas atmosphere, avoiding high energy laser, high vacuum atmosphere or special chemical reaction environment.

Growth orientation is crucial in tailoring Si nanowire's properties. For instance, the band gap, electrical conductance and mechanical properties are dramatically different in nanowires with different growth orientations [28–34]. The $<100>$ oriented

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[*] Corresponding author.
E-mail address: MSYZhang@ntu.edu.sg (S. Zhang).

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Si nanowires exhibit a significantly higher exciton energy than the < 110 > counterparts [16]. The < 110 > oriented wire has the lowest total energy, and the highest sensitivity to surface modification [29], whereas the < 111 > oriented is structurally stable to the change of diameter, and of the lowest sensitivity to surface modification [30]. The < 110 > oriented one displays a direct transition, the < 111 > oriented possess a competitive indirect–direct gap character, and the < 112 > oriented has an indirect band-gap [32]. Tetrahedral Si nanowires oriented in < 111 > are the most stable and the best suited for quantum confinement effects [33]. The < 112 > nanowires exhibit the highest tensile strength of 12.31 GPa, and the weakest link fracture is a by-product of orientation-dependent flaw populations [34]. To date, what really determines the growth orientation is still unclear, though lots of factors have been reported to have effect, including surface chemical treatment of substrate [35], nanowire diameter [15,36,37], composition of the initial alloy droplet [38,39], growth temperature [40–42], reaction pressure [16,43], and precursor molar ratios [44]. Most people believe the preferential orientation is controlled by the energetics at the solid–liquid interface of the nanocrystal emerging from the liquid droplet. It involves the surface energy of various nanocrystal planes [15,45,46]. As one of the metal-seeded Si nanowire growth methods, however, SLS growth involves (1) the formation of the metal-Si eutectic droplet from solid [20–23], and (2) the subsequent Si precipitation or a crystallization process. The first process requires thermal energy to melt the solid Si and Ni to liquid Si–Ni eutectic, i.e., an energy-consuming process. The subsequent crystallization process solidifies the liquid eutectic to solid Si nanowires, i.e., an energy-releasing process [47]. Therefore, energy may not be necessary in the second process. It is therefore concluded that there may be alternative determinant factors controlling the growth orientation.

In the growth of Si nanowires, Au was widely used as the catalyst; however, the incorporation of Au in Si nanowires would possibly induce a deep-level trap, causing a reduction in the efficiency of the solar cells [48]. In addition, the ionization energy level of Ni within Si is located far from the mid-band gap, offering a higher threshold level (5×10^{15} cm^{-3}) in impurity concentration compared with that (3×10^{13} cm^{-3}) of Au [49]. With these concerns, in this work, highly crystalline Si nanowires were grown via thermal annealing of Ni-coated Si wafers. The morphology, growth orientation, and the relation to the seeding Ni catalyst particles were examined through high resolution transmission electron microscopy and selected area electron diffraction pattern. The determinant factors for the growth orientation were explored.

2. Experimental details

The Ni catalyst layer is sputtered on N-type Si (100) wafers (10 mm × 10 mm in area, 475 μm in thickness and 0.5 nm in room mean square surface roughness) in an E303A magnetron sputtering system (Penta-Vacuum, Singapore) [50]. Before loading the wafers into the sputtering chamber, the substrates were ultrasonically cleaned in acetone for 20 min, followed by 10 min in alcohol. Once the base pressure reached 1.0×10^{-1} Pa, Ar was introduced at a flow rate of 50 standard cubic centimeters per minute (sccm). High energy Ar^{+} ions were generated at −300 V substrate bias for substrate cleaning for 15 min to remove the native silicon oxide. Then, 5 min sputtering of Ni target (purity, 99.99%) in 0.47 Pa pressure at room temperature deposited about 30-nm thick Ni catalyst layer on the substrate. And then, about 570 nm amorphous carbon was sputtered from a graphite target (purity, 99.999%) on the Ni layer in the same work pressure for 60 min to retard the oxidation of grown Si nanowires [23,24]. During the process, about 4.16 at% Si was co-sputtered from a near Si target (99.999% in purity) on the Ni layer [23]. The sputtering power densities for Ni, Si and C were respectively RF 1.85 W cm^{-2}, RF 2.47 W cm^{-2} and DC 12.22 W cm^{-2}. In this study, the top layer is labelled a-C layer because the top layer is only sputtered to retard oxidation and the amount of Si in the layer is very few.

The a-C/Ni films underwent rapid thermal annealing (RTA, Jipelec Jetfirst 100 rapid thermal processor, France) in an Ar ambient at 1100 °C for 1 min. To obtain a clean growth atmosphere, the RTA chamber was purged 10 times with Ar (purity, 99.999%) at 2000-sccm before ramping up to 600 °C at 58 °C s^{-1} , which is controlled by a thermocouple. After dwelling for 6 s at 600 °C, the chamber was further ramped up to 1100 °C at 42 °C s^{-1}, which is controlled by a pyrometer, and then held for 1 min for the growth of Si nanowires. After annealing, the chamber was cooled to 500 °C at 43 °C s^{-1} , and then naturally cooled down to room temperature. During the whole annealing process (ramping, holding, and cooling), the inflow of the Ar gas was maintained at 2000 sccm to keep the chamber pressure at 1.08×10^{5} Pa. Field emission scanning electron microscopy (FESEM, JEOL, JBM-7600F, JEOL Ltd., Japan, 5-kV operating voltage) shown that wire-like nanostructures were grown on the annealed film surface. A high resolution transmission electron microscope (HRTEM, JEOL 2010, 2100F, 200-kV operating voltage, Japan) was employed to examine the structure of the grown nanowires. The size of the wire was calculated by randomly taking the mean value of 20 wires. Electron dispersive X-ray spectroscopy (EDX, EDAX Inc., USA) and selected area electron diffraction pattern were carried out to characterize the chemical composition and the growth orientation of the grown nanowires and the seeding Ni catalyst particles. To determine the correct growth direction, the SAED pattern is indexed for a specific zone axis of Si. This requires the electron beam perpendicular to a specific plane family of the crystal, i.e., zone axis, which could generate the pattern. In the process, the SAED pattern or systematic spots were generated by careful adjusting the tilt angle along the x- and y-axes of the sample holder to match the standard database that is cited from software JEMS.

3. Results and discussion

3.1. Morphology

Fig.1a shows a bundle of primarily wire-like nanostructures entangling into each other with remarkably uniform diameter on the order of 80 nm, with length longer than 10 μm. Statistical calculation on 20 randomly selected coaxial Si nanowires reveals that the mean diameter of the Si core is 17.0 ± 6.3 nm, and the mean thickness of SiO_x ($x \approx 2$) sheath is 19.7 ± 3.7 nm. The nanowire diameter equals that of the Si core plus two times of the SiO_x sheath thickness. The nanowires terminate at the root in dark ball-shaped nanoclusters with diameter 1.2 to 1.5 times that of the connected nanowires (cf., Fig. 1b). But no nanocluster is observed at the tip (cf., Fig. 1c). Similar morphology is reported in another paper [51]. This is suggestive of the Ni-catalyzed SLS growth similar to the vapour–liquid–solid growth, except for the opposite seeding location of the nanoclusters. Upon annealing, the Ni layer collapses into particles due to surface tension. Ni particles melt with the beneath Si wafer to form Ni–Si eutectic, leading to the continuous diffusion of Si into the droplet. Upon supersaturation, Si is precipitated from the droplet to grow into nanowires. As Si is from the Si wafer and the liquid Ni–Si droplet acts as the medium, the nanowire always grows out from the liquid droplet while the droplet always stays on the wafer. Experimentally, Ni is not detected in the X-ray photoelectron spectroscopy and FESEM image of the annealed Si wafer surface [23]. Therefore, the Ni–Si eutectic droplet always stays at the root of the wire.