Radial growth of slanting-columnar nanocrystalline Si on Si nanowires

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1. Introduction

Si nanowires (SiNWs) have attracted a considerable amount of attention because they possess novel optical [1,2] and low thermal conduction [3,4] properties while retaining their semiconducting characteristics, which are useful for a broad range of energy related applications [5]. To achieve superior performance in solar cells, lithium ion batteries and thermoelectric devices, homo- or heterojunctions of NWs are preferred over intrinsic SiNWs in the construction of nanoscale building blocks and devices [6–8]. The bottom-up approach of chemical vapor deposition (CVD) via catalytic growth is one of the most popular techniques to synthesize high density [9] and good quality [10] Si nanowires under controllable [11] conditions. In CVD, decomposed silane radicals diffuse into the liquid catalyst due to its higher dissociative sticking coefficient [12] and induce the growth of NWs. This process is known as vapor–liquid–solid (VLS) or axial catalytic growth. During the growth of NWs, silane radicals can be adsorbed and deposited onto the NW surface, which results in uncatalyzed radial growth around the wall of the NWs. In general, radial growth occurs after the vapor–solid (VS) process [13]. The tapering [14,15], diameter expansion [16] and faceting [10,17] of NWs can be attributed to radial growth.

In conventional CVD, high temperatures (~600 °C) are required to decompose silane gas into reactive radicals to form SiNWs [18,19]. The use of plasmas or hot-wires (HW) in CVD enhances the decomposition rate of silane, even at low substrate temperatures [20,21]. Currently, these techniques show promise in the low temperature CVD synthesis of SiNWs [22–25]. However, the large quantity of reactive silane radicals produced by plasma and HWCVD techniques could promote the radial growth of SiNWs [26]. Recent studies suggest that controllable radial growth rates can be used to obtain the desired shape and tapering of SiNWs [27], and self-assembled radial growth structures may be employed to form core–shell NWs for photovoltaic applications [28]. Thus, to engineer the growth of SiNWs via low temperature CVD, a deeper understanding of the radial growth process must be obtained. In the present study, SiNWs were synthesized at a fast axial growth rate of ~300 nm/min via indium (In) catalyzed HWCVD, and the formation of radial growth structures on the sidewalls of the SiNWs was investigated. The deposition time (t d) was varied under constant deposition conditions to study the radial growth mechanism.

2. Experimental

SiNWs were prepared on p-type Si (111) substrates using a home built dual mode plasma-assisted HWCVD [29]. The substrates were heated to 400 °C in a vacuum chamber, and In catalyst islands were produced on the substrates by evaporating in wire using a tungsten filament. Evaporation was carried out in a H 2 plasma at a flow rate and radio frequency power of 50 sccm and 40 W, respectively. After evaporation, the plasma was terminated by switching off the rf supply. SiNWs were synthesized from H 2 diluted silane gas (H 2:SiH 4 ratio of 50:5 sccm) at a HW temperature of 1700 °C. The substrate temperature and chamber pressure were fixed at 400 °C and 0.7 mbar, respectively. The samples were characterized using a FEI Quanta 200 FESEM and a JOEL JEM 3100F HRTEM. XRD and Raman measurements were carried out using a SIEMENS D5000 X-ray diffractometer (Cu Kα X-ray radiation λ = 1.5418 Å) and a Horiba Jobin Yvon 800 UV micro-Raman spectrometer (514.5 nm Ar+ laser).

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3. Results and discussion

Figure 1a shows the FESEM image of In-catalyzed SiNWs grown on Si(111) via HWCVD at a t_d of 10 min. The SiNWs presented a tapering parameter [24] of ~40 nm/μm and were inclined at angles ranging from 40° to 70° from the substrate (supplementary materials, Figure S1). The NWs were slightly bent in the same direction, indicating a continuous transition toward the preferred orientation. A typical TEM image of the SiNWs is illustrated in Figure 1. HRTEM scans of the near end of the SiNWs (Figure 1b) revealed the single crystalline structure of the SiNWs. In addition, the Si(111) and Si(220) crystallographic planes presented a lattice spacing of ~0.31 nm and ~0.19 nm, respectively. The SiNW grew in the [−11 2] direction, as evidenced by the selected area electron diffraction pattern [inset of Figure 1b], thus, the preferred growth orientation of the NWs was (112). The radial growth of columnar structures was observed in the body of the NWs and was attributed to tapering. The diameter of the columnar structures was approximately 18 ± 3 nm. The HRTEM image of the columnar structures (Figure 1c) revealed that the material consisted of a mixture of amorphous Si and nanometer-sized Si crystalline grains. In addition, the preferential formation of the (1 1 1) Si crystal plane was observed. Thus, the HRTEM results showed that nanocolumns deposited on the walls of the SiNWs possessed nanocrystalline Si (nc-Si). The radial growth of columnar nc-Si structures was also evidenced in the TEM image of the sidewalls of the SiNWs. In the initial stages of the growth process, reactive silane radicals are adsorbed onto the surface of the NWs to form several monolayers of Si film. The nucleation and coalescence of the Si layer could lead to the formation of islands on the walls of the NWs, as shown in Figure 1d [30]. As the NWs grew, the walls of the NWs received an incident flux of silane radicals at a specific angle from the deposition source. Therefore, nucleated islands shielded the other sides of the film from growth [31]. Most of the silane radicals diffused into the Si islands, resulting in the growth of slanting-columnar structures, as shown in Figure 1e. Columnar nc-Si structures were slanted at an angle of ~66° toward the sidewalls of the NWs. Further investigation of the TEM micrographs revealed that the slanting angle of nc-Si columns from the sidewall of the NW ranged from 38° to 70° (supplementary materials, Figure S2). A possible mechanism for the formation of radially grown slanting-columnar nc-Si structures is illustrated in Figure 2. During the axial growth of SiNWs from the In catalyst, uncatalyzed silane radicals (SiH_x) become incorporated into the NW network through a VS growth process. Similar to oblique angle deposition [31], the islands shield other areas from growth and form columnar structures with a tilted geometry.

The axial growth of NWs is dependent on the catalyst. During axial growth, the In catalyst evaporates and condenses on the sidewalls of the NW [32,33] or becomes incorporated into the SiNW through diffusion [34,35]. As a result, the size of the catalyst gradually decreases, leading to the cessation of axial growth. According to the following expression [33], the length of the NW, L, is limited by the migration of the catalyst: \( L = \frac{a^2}{4 \pi \varphi_m} \), where \( a \) is the base radius of the NW, \( a^2 \) is the atomic volume of In (\( a = 0.30 \) nm) [36], and \( \varphi_m \) is the average coverage of In on the sidewalls of the NWs. To control the radial growth process, t_d was increased to terminate axial growth. Figure 3a and b shows FESEM images of the surface and tilted geometry of SiNWs prepared at a t_d of 20 min. The base diameter and length of the NWs increased from ~283 ± 20 nm to ~496 ± 34 nm and ~3.0 ± 0.5 to ~3.9 ± 0.4 μm, respectively. The morphology of SiNWs prepared at a t_d of 10 and 20 min are illustrated in Figure 3c and d, respectively. The In catalyst was completely consumed at a t_d of 20 min, and the majority of silane radicals contributed to radial growth. As a result, the diameter of NWs increased significantly at a t_d of 20 min. As shown in Figure 3d, the surface of the NWs was surrounded by a high density of slanting-columnar nc-Si structures, which formed a single crystalline Si core and columns of nc-Si shell NWs. Figure 3e shows a plot of the base radius (r) of the NWs as a function of t_d. The linearity of
the graph indicated that the growth rate of columnar nc-Si was constant and was not affected by the In catalyst. The core radius of the single crystalline SiNWs, $r_0$, can be deduced by extrapolating the linear graph to the $y$-intercept. If we assume that the nucleation time for the formation of islands is short ($\approx 0$), the growth rate, $R_d$ of columnar nc-Si can be calculated as $R_d = \frac{r_0}{t_d}$. The results showed that $R_d$ was approximately 2 Å/s. In contrast, HWCVD-deposited nc-Si films presented an $R_d$ of ~20 Å/s [37]. The observed difference in the growth rate was attributed to differences in the growth geometry. Normal nc-Si films show planar growth, while in this study, the nc-Si structures grew laterally on the sidewalls of the NWs. A large surface to volume ratio of SiNWs produces a high yield of nc-Si structures; however, compared to that of planar nc-Si films, $R_d$ is also reduced.

To confirm the growth of columnar nc-Si, XRD and Raman measurements were performed on the SiNWs. Figure 4a shows the XRD spectra of SiNWs prepared at $t_d$ of 10 and 20 min. Si diffraction peaks at 28.4°, 47.2° and 56.2° were attributed to (111), (220) and (311). Si crystallographic orientations were observed in both XRD spectra. The In catalyst capped the end of the NWs (Figure 3c), resulting in the formation of an In(101) diffraction peak. However, the In diffraction peak was completely suppressed at a $t_d$ of...
20 min. This result was in agreement with the FESEM images, which showed that In droplets were not present on the SiNWs. When \( t_d \) was increased to 20 min, an amorphous-like background was observed, and the Si peaks became broad. This result was quantitatively confirmed by an increase in the FWHM of the Si(111) peak from \( 0.36 \pm 0.01^\circ \) (\( t_d = 10 \) min) to \( 0.41 \pm 0.02^\circ \) (\( t_d = 20 \) min). Peak broadening was indicative of a reduction in the crystallite size [38]. In addition, the asymmetric broadening of the Raman peaks of crystalline Si TO phonon mode was more obvious at a \( t_d \) of 20 min as shown in Fig. 4b. Correspondingly, the FWHM of the TO mode of crystalline Si increased from \( 5.4 \pm 0.1 \) cm\(^{-1}\) (\( t_d = 10 \) min) to \( 6.6 \pm 0.1 \) cm\(^{-1}\) (\( t_d = 20 \) min), indicating that phonon confinement affected the structures due to the grain boundary and amorphous Si phases [39]. Because the NWs are single crystalline structures, the amorphous phase and smaller Si crystallites with grain boundaries provide evidence for the radial growth of nc-Si structures. However, the FWHM values were generally higher than the measured data of single crystal Si due to the confined size of the NWs [40]. Namely, the FWHM values were equal to 0.13\(^\circ\) for the Si(111) XRD peak and 4.6 cm\(^{-1}\) for the TO-phonon mode of c-Si.

4. Conclusion

In summary, the radial growth of slanting-columnar nc-Si structures on the sidewalls of NWs was achieved using HWCVD. The columnar structures displayed a constant growth rate of \( \sim 2 \) \( \AA \)/s. The radial growth of columnar nc-Si structures and axial growth of NWs resulted in the formation of a novel core–shell NW structure. In the future, the SiNWs produced in the present study could be engineered for various applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.08.046.