Growth and structural property studies on NiSi/SiC core-shell nanowires by hot-wire chemical vapor deposition

Nur Fatin Farhanah Binti Nazarudin, Siti Nur Azieani Binti Azizan, Saadah Abdul Rahman, Boon Tong Goh *

Low Dimensional Materials Research Centre (LDMRC), Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia

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A B S T R A C T
NiSi/SiC core-shell nanorods and nanowires grown on Ni-coated glass substrates by hot-wire chemical vapor deposition were studied. Nickel was used as a catalyst to induce the growth of these core-shell nanorods and nanowires at deposition pressures varying from 100 to 300 Pa. Increase of the deposition pressure to 300 Pa resulted in the growth of nanowires. These nanowires consisted of single crystalline NiSi and amorphous SiC as core and shell of the nanowires, respectively. Moreover, an increase in deposition pressure induces phase transition of the nanowires from the crystalline Si phase to amorphous SiC phase. 3C-SiC nano-crystallites embedded within an amorphous matrix were present in the nanowires shells, and broad photoluminescence emission spectra were observed within the visible region. The effects of the deposition pressure on the growth and structural properties of these core-shell nanowires are discussed.

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1. Introduction

One-dimensional (1D) semiconductor nanostructures such as nanowires and nanorods have attracted increasing attention recently due to their applications in mesoscopic physics and as the building blocks of nanoscale devices [1–3]. These 1D semiconductor nanostructure materials, mostly Si-based nanorods and nanowires, have demonstrated excellent structural [4], optical [5] and electrical [6] properties. These superior properties have enabled Si-based nanowires to achieve excellent performance in solar cells, lithium-ion batteries and thermoelectric devices [7–9]. However, due to their intrinsic material properties such as weak mechanical stability and associated side reactions resulting from unprotected surfaces, single-phased nanomaterials cannot fulfill certain application requirements [10,11]. Hybrid nanostructures such as core-shell nanowires have advantages that overcome the limitations of single-phased nanomaterials [12]. Hybrid core-shell nanowires composed of NiSi/SiC are expected to further enhance the mechanical, chemical resistivity, thermal stability and various optical properties of core-shell nanowires [13,14]. Furthermore, the highly metallic properties of single-crystalline NiSi nanowires could allow for their use as 1D electrodes for enhancing the efficiency of electron transfer between current collector supports and individual electrode materials, as well as that of ion transport to the electrode [15,16].

Hot-wire chemical vapor deposition (HWCVD) is one of the most promising techniques for the low-temperature, high deposition rate and large-area deposition of SiC-based thin film materials [17–19]. HWCVD has been demonstrated to allow for the low-temperature deposition (approximately 300 °C) of cubic SiC thin films [20,21]. In the HWCVD process, the decomposition of SiH4/CH4 molecules on the filament surfaces at a filament temperature above 2000 °C generates sufficiently higher densities of growth precursors (SiH3 and CH3) compared to plasma processes. Moreover, the decomposition of a high density of H radicals plays an important role in the low-temperature growth of nano-crystalline SiC thin films [22]. Recent studies on the growth of Si nanowires by HWCVD demonstrated that it is a promising technique for the growth of 1D Si-based nanostructure, owing to the lower production cost and the capability for large-scale production [23–25]. The HWCVD process has also been proven to enhance the growth rate of Si nanowires [26]. Compared to plasma-enhanced CVD, HWCVD does not utilize high-energy ions, leading to nanowires with superior crystallinity [27]. In this work, we studied low-temperature growth of nickel (Ni)-catalyzed NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures. The effects of the deposition pressure on the growth and structural properties of these core-shell nanowires were investigated primarily using field emission scanning electron microscopy (FESEM) combined with energy-dispersive X-ray (EDX), high-resolution transmission electron microscopy (HRTEM) combined with scanning transmission electron microscopy (STEM), micro-Raman scattering spectroscopy, X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy. The morphological change in the nanowires was observed to be significant for the samples prepared at 300 Pa. The effects of the deposition pressure on the growth and structural properties of these core-shell nanowires are also reported.

2. Experiments

NiSi/SiC core-shell nanowires were prepared on Ni-coated glass substrates by a home-built HWCVD system. Ni films measuring
approximately 30 ± 5 nm in thickness were deposited on the heated glass substrates under vacuum. Prior to deposition, the Ni films were treated by atomic hydrogen plasma for 10 min to form metal nano-islands. The substrate temperature, pressure, hydrogen flow-rate and radio-frequency power were fixed at 450 °C, 75 Pa, 100 sccm and 5 W, respectively. During deposition, the filament temperature and substrate temperature were fixed at 1900 °C and 450 °C, respectively. The filament temperature was measured using a pyrometer model Reytek Raynger 3i. The filament-to-substrate distance was fixed at 2 cm. The SiH₄, CH₄ and H₂ flow rates were fixed at 1, 2 and 100 sccm, respectively. The deposition pressure was varied from 100 to 300 Pa. The deposition time was fixed at 5 min.

FESEM images of the nanowires were obtained using a Hitachi SU 8000 SEM at a low electron-accelerating voltage of 2 kV. The EDX spectrum was collected by an Oxford Instrument at 15 kV. The working distances for imaging and EDX were fixed at 8 mm and 15 mm, respectively. TEM and HRTEM images of the nanowires were obtained using a TEM (JEOL JEM-2100F) with an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDS) elemental mappings of the nanowire were performed using STEM/high-angle annular dark-field and Oxford EDS detectors. XRD patterns were recorded over the 2θ range of 20° to 80° at a fixed grazing incidence angle of 5° using a SIEMENS D5000 X-ray diffractometer. The step time and step size of the scanning were fixed at 3 s and 0.02°, respectively. The Raman spectra of the films were recorded using an InVia Raman microscope with a charge-coupled device detector and grating of 2400 lines/mm. An argon-ion laser with an excitation wavelength and laser power of 514 nm and 10 mW, respectively, was used. The same spectrometer for the Raman measurement was used to obtain the PL spectra of the nanowires at room temperature, employing a HeCd laser with an excitation wavelength and laser power of 325 nm and 5 mW, respectively.

3. Results and discussion

Fig. 1 shows the FESEM images of the nanowires prepared by HWCVD at different deposition pressures. The samples prepared at deposition pressures below 200 Pa showed straight nanorods mostly vertically aligned and randomly distributed on the surface of the sample. The density and diameter of these nanorods increased and decreased, respectively, for the sample prepared at a deposition pressure of 200 Pa. The deposition time was fixed at 5 min.

Fig. 2. (a) FESEM image of the NiSi/SiC core-shell nanowires prepared by HWCVD at 300 Pa for EDX elemental analysis. (b) A typical EDX spectrum of the nanowires. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

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These nanorods showed superior alignment compared to the samples prepared at deposition pressures below 200 Pa, as shown in the insets of each figure. The average length and diameter of these nanorods were approximately 1.1 ± 0.1 μm and 268 ± 2 nm, respectively. As the deposition pressure increased to 300 Pa, the sample showed a high density of nanowires randomly distributed on its surface. The average length and diameter of these nanowires were approximately 2.6 ± 0.3 μm and 88 ± 1 nm, respectively. The increase in the growth rate of the nanowires with an increase in deposition pressure could be related to the hydrogen-etching effect. An increase in deposition pressure shortens the mean free path of the radicals and thus enhances gas-phase reactions. As a result, more H radicals are generated, and these energetic atomic H may reduce the thickness of the nanowires through the hydrogen-etching effect [28,29]. The results of EDX elemental analysis of the nanowires prepared at 300 Pa are shown in Fig. 2. The tip of the nanowire contained 40.2%, 24.4%, 30.1% and 5.3% of Si, carbon (C), Ni and oxygen (O), respectively, whereas the stem of the nanowire contained 40.7%, 25.3%, 28.2% and 5.8% of Si, C, Ni and O, respectively. There was an approximately 2% difference in Ni content between the nanowire tip and stem. The Ni nano-islands served as a template for the formation of NiSi and subsequently catalyzed the growth of these core-shell nanowires.

The microstructure of these nanowires was investigated by TEM, as shown in Fig. 3. A single nanowire of the sample prepared at 300 Pa was selected for TEM measurement. Fig. 3(a) shows a TEM image of the nanowire that clearly reveals the core-shell structure, with core and shell diameters of 22 ± 3 and 105 ± 12 nm, respectively, which are constant along the length of the nanowire. Fig. 3(b) shows a higher magnification of the nanowire TEM image along the sidewall of the nanowire. This image clearly illustrates the core-shell structure of the nanowire, which consists of a single crystalline core and an amorphous shell structure. HRTEM images of this core-shell structure are shown in Fig. 3(c) and (d). The microstructure of the nanowire shell reveals the presence of 3C-SiC nano-crystallites embedded within an amorphous matrix. Most of these nano-crystallites are less than 5 nm in size. The estimated lattice spacing is approximately 0.25 nm, corresponding to the 3C-SiC (111) crystallographic plane [30]. The crystalline structure of the nano-crystallites was further verified by applying a fast Fourier transform (FFT), as shown in the figure inset. The HRTEM scans obtained near the end of the nanowire sidewall clearly reveal the single-crystalline structure of the nanowire. The estimated lattice spacing is approximately 0.16 nm, corresponding to a Ni2Si (301) crystallographic plane [JCPDS card No. 00-065-1507], indicating that the Si nanowire’s core is actually formed by the NiSi nanowire. The NiSi crystalline structure of the core nanowire was further revealed by an FFT, as shown in the figure inset. An untilted selected area electron diffraction (SAED) image provides supporting evidence of the NiSi crystalline structure, as shown in Fig. 3(e). The appearance of diffraction rings is due to the nanowires’ amorphous shell.

The microstructure and composition of the nanowires were further investigated by STEM/EDS mappings, as shown in Fig. 4. The dark-field STEM image as shown in Fig. 4(a) displays a white layer surrounding the nanowire. This result could be due to the formation of SiOx on the surface of the nanowires, which generally occurs during nanowire growth. The microstructure of these nanowires is shown in Fig. 4(b). The EDS element maps of the core-shell nanowire are shown in Fig. 4(c-e). The image inset shows the growth direction of the nanowire from the root to stem. The STEM images of the nanowire are shown in Fig. 4(d-e). The EDS element maps of the core-shell nanowire are shown in Fig. 4(c-e).
growth using the CVD technique [31]. The average thickness of the SiO$_x$ layer was approximately 22 ± 3 nm. Moreover, the thickness of the SiO$_x$ layer decreased along the length of the nanowire, from root to stem, indicating that SiO$_x$ formation occurred at the initial stage of nucleation during nanowire growth. The compositions indicated by the EDS maps of the nanowire are shown in Fig. 4(b) to (e). Clearly, the presence of Ni along the center of the nanowire confirms the formation of the NiSi nanowire core. The estimated Ni-to-Si ratio is approximately 2. Again, the Ni layer surrounding the nanowire was verified by an O map. The C map is not clearly presented in this case, which could be due to the background of the C film of the copper grid. Because the formation of NiSi nanowires by metal-induced growth at temperatures of approximately 350–550 °C [16,32] has been widely reported, it is believed that the growth of the NiSi/SiC core-shell nanowires formed in this study follows the same mechanism. In this study, hydrogen plasma treatment was used to form Ni nano-islands at a lower substrate temperature than that reported in previous studies [16]. The shell of SiC could follow a radial growth mechanism during the nucleation of NiSi nanowires because no tapering was observed on the nanowires.

Fig. 5 shows the Raman spectra of the nanowires prepared by HWCVD at different deposition pressures. These spectra have been divided into three regions of Raman shift to clearly illustrate the Raman excitation bands. Fig. 5(a) presents typical Raman excitation bands of Si at 150, 300, 380–420 and 480–520 cm$^{-1}$, which are associated with transverse acoustic (TA), longitudinal acoustic (LA), longitudinal optical (LO) and transverse optical (TO) modes, respectively [33,34]. Moreover, the TO band of Si can be further divided into two components: TO$_1$ mode at 480 cm$^{-1}$ and TO$_2$ mode at 510–520 cm$^{-1}$, corresponding to amorphous and crystalline Si phases, respectively, as shown in Fig. 5(b). The Si TO band shifted to a lower wavenumber with an increase in pressure above 150 Pa. The shift in the Si TO band indicates a phase transition from crystalline Si to amorphous Si with increased pressure. This finding also reveals a decrease in size of the Si nano-crystallites embedded within an amorphous matrix [35]. The appearance of a Raman band near 500 cm$^{-1}$ for the sample prepared at 200 Pa indicates the formation of small Si nano-crystallites or grain boundaries in the matrix. Clearly, a transition from the crystalline to amorphous Si phase occurs in the shell of the nanowires. Fig. 5(c) shows the Raman spectra of the nanowires in the region of 550–1200 cm$^{-1}$. The appearance of a Raman excitation band at 980 cm$^{-1}$ is associated with a second-order Si TO band (2TO). The Si 2TO band shifted to a lower wavenumber, accompanying the appearance of a small Raman band at approximately 800 cm$^{-1}$, with an increase in deposition pressure. The appearance of Raman excitation bands at 780 and 910 cm$^{-1}$ reveals the formation of SiC nano-crystallites embedded within the amorphous matrix [36–38]. The red shifts and broadening of the Raman peaks, relative to the bulk 3C-SiC crystal [39], may be attributed to the quantum confinement effects of the SiC nano-crystallites [40]. The formation of 3C-SiC nano-crystallites embedded within an amorphous matrix in the shell of the nanowires is supported by the HRTEM images, as shown in Fig. 3(c).

Fig. 6 shows the XRD pattern of the nanowires prepared by HWCVD at deposition pressures of 100 and 300 Pa. At deposition pressure of 100 Pa, the nanowires’ XRD pattern only showed crystalline Si diffraction peaks at 28.4°, 47.3°, 56.1° and 68.7°, which correspond to c-Si orientations of (111), (220), (311) and (400) planes, respectively [23,41]. For the nanowires prepared at deposition pressure of 300 Pa, the crystalline NiSi and SiC diffraction peaks started to appear, as shown in the figure. The crystalline NiSi peaks located at 39.5°, 42.6°, 45.6°, 45.7°, 48.9° and 51.9° are associated with crystalline Ni$_3$Si orientations of (112), (103), (211), (013), (020) and (004) planes, respectively, according to JCPDS card number 00-065-1507. The crystalline SiC peak appears at approximately 35.7°, which corresponds to a crystalline 3C-SiC (111) plane. The phase of the nanowires was observed to change significantly from Si to SiC as the deposition pressure increased from 100 to 300 Pa, in agreement with the phase change indicated by the Raman spectra. The transition from the Si phase to SiC phase could result from the change in the gas-phase reaction for deposition pressures above 150 Pa. As reported by Wu et al. [42], this increase in deposition pressure enhances the generation of various radicals, especially H radicals. Creating a high density of H radicals enhances the decomposition of CH$_4$ and thus induces the nucleation of SiC nano-crystallites [42,43].

Fig. 7(a) shows the PL spectra of the nanowires prepared by HWCVD at different deposition pressures. These nanowires show broad PL emission spectra across photon wavelengths ranging from 400 to 800 nm, indicating that SiC nano-crystallites embedded within an amorphous matrix in the shell of the nanowires is supported by the Raman spectra.
The formation of Si nano-crystallites at the nc-Si/SiO₂ interface creates oxygen-related defects and/or surface and interface effects [46,47]. Approximately 590 nm are generally associated with emissions due to emissions from the quantum confinement effect of the Si nano-crystallites embedded within an amorphous matrix [44,45]. The emission bands located at approximately 590 nm are generally associated with emissions due to oxygen-related defects and/or surface and interface effects [46,47]. The formation of Si nano-crystallites at the nc-Si/SiO₂ interface creates an intermediate state for electron-hole radiative recombination, which leads to strong PL emissions in the visible region. The appearance of two small emission bands at 467 and 529 nm indicates the emission of SiC nanostructures [48–50]. The peak at 467 nm is comparable to PL emissions from SiC nanostructures [48,49] or PL emission spectra of SiC nanoparticles [50]. However, the emission peak for this core-shell nanowire is clearly blue-shifted compared to the emission peak of bulk 3C-SiC at 519 nm [48]. This phenomenon has been attributed to the quantum size effect of SiC nano-crystallites embedded within an amorphous matrix. The peak at 529 nm could result from the presence of defect centers within the band gap of the SiC shell, as previously reported by Gundiah et al. [51]. Various PL emissions from the core-shell nanowires indicate that luminescence characteristics depend greatly on the structure and size of the nano-crystallites embedded in the nanowires’ shells.

4. Conclusions

The growth and structural properties of NiSi/SiC core-shell nanorods and nanowires prepared by HWCVD at different deposition pressures was studied. These nanorods and nanowires were grown at deposition pressures below 300 and at 300 Pa, respectively. The hydrogen-etching effect plays an important role in forming these nanowires at higher deposition pressures. Moreover, these nanowires consist of single-crystalline NiSi and amorphous SiC as core and shell of the nanowires, respectively. The shell of the nanowires showed the presence of 3C-SiC nano-crystallites embedded within an amorphous matrix. The formation of the NiSi-core nanowires follows a metal-induced growth process at substrate temperatures below 500 °C, whereas the shell of the amorphous SiC could be due to radial growth. An increase in deposition pressure induced a phase transition of the shell of the nanowires from crystalline Si to amorphous Si and accompanied the transition which covers the entire visible region. A typical PL spectrum with Gaussian decomposition components is shown in Fig. 7(b). Among the decomposed components, there are two major constituents centered at approximately 590 and 665 nm, which are dominant in the entire spectrum. In addition, there are two small PL emission bands at approximately 467 and 529 nm. As demonstrated by previous studies, the emission band in the range of 650–750 nm is believed to originate from the quantum confinement effect of the Si nano-crystallites embedded within an amorphous matrix [44,45]. The emission bands located at approximately 590 nm are generally associated with emissions due to oxygen-related defects and/or surface and interface effects [46,47]. The formation of Si nano-crystallites at the nc-Si/SiO₂ interface creates an intermediate state for electron-hole radiative recombination, which leads to strong PL emissions in the visible region. The appearance of two small emission bands at 467 and 529 nm indicates the emission of SiC nanostructures [48–50]. The peak at 467 nm is comparable to PL emissions from SiC nanostructures [48,49] or PL emission spectra of SiC nanoparticles [50]. However, the emission peak for this core-shell nanowire is clearly blue-shifted compared to the emission peak of bulk 3C-SiC at 519 nm [48]. This phenomenon has been attributed to the quantum size effect of SiC nano-crystallites embedded within an amorphous matrix. The peak at 529 nm could result from the presence of defect centers within the band gap of the SiC shell, as previously reported by Gundiah et al. [51]. Various PL emissions from the core-shell nanowires indicate that luminescence characteristics depend greatly on the structure and size of the nano-crystallites embedded in the nanowires’ shells.

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