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Preparation and Characterization of Silicon Nanowires Catalyzed by Aluminum

H.F. Al-Taay\textsuperscript{1,2,*}, M. A. Mahdi\textsuperscript{3}, D. Parlevliet\textsuperscript{1}, Z. Hassan\textsuperscript{3}, P. Jennings\textsuperscript{1}

1. School of Engineering & Energy, Murdoch University, South St., Murdoch, WA 6150, Australia.
2. Department of Physics, College of Sciences for Women, University of Baghdad, Baghdad, Iraq.
3. Nano-Optoelectronics Research and Technology Laboratory (N.O.R), School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia.

*Corresponding author: H.F. Al-Taay, Tel:+61422411653, E-mail: hanaa_flayeh@yahoo.com

Abstract

Silicon nanowires (SiNWs) were grown on indium tin oxide coated glass substrates by a pulsed plasma-enhanced chemical vapor deposition (PPECVD) method using aluminum as a catalyst. The thin films of the catalyst, with thicknesses ranging from 10 nm to 100 nm, were deposited on the substrates by thermal evaporation. The effect of the thickness of the thin film catalyst on the morphology of the silicon nanowires was investigated. The surface morphology study of the prepared wires showed that the modal wire diameter increased as the catalyst film thickness increased. The X-ray diffraction patterns of the prepared silicon nanowires had no silicon peaks, indicating that the wires had low crystallinity. The photoluminescence spectra of the SiNWs showed that all samples had more than one emission band. The emission band location and shape were found to be dependent on catalyst thickness. The Raman spectra of the prepared nanowires showed that the first order transverse band shifted toward lower frequencies compared with the c-Si band location.

Keywords: Silicon nanowires, Al catalyst, Raman spectra.
1. Introduction

One-dimensional (1-D) nanomaterials, including nanorods, nanowires, nanotubes, and nanobelts, have attracted much attention and play an interesting role as candidates for future electronic components. Compared with conventional bulk phase or thin films, 1-D nanomaterials have several unique advantages, such as high surface-to-volume ratio, quantum confinement effects, and slow electron-hole recombination [1, 2]. Given the unique density of their electronic states, nanowires (NWs) of small diameters are expected to exhibit optical, electrical, and magnetic properties that are significantly different from their bulk crystalline counterparts [3].

Silicon nanowires (SiNWs) have acquired increasing attention in the development of a new generation of thin-film Si solar cells with enhanced light trapping [4]. The band gap in SiNWs turns from indirect into direct because of the quantum confinement effect at nanometre size [5]. In addition, the optical band gap of SiNWs increases with the decrease of the wire diameter; thus, they are potentially more useful in optoelectronics applications than bulk Si [6].

SiNWs can be prepared via various methods, such as thermal evaporation [7], laser ablation [8], molecular beam epitaxy [9], and chemical vapor deposition (CVD) [10]. Plasma-enhanced chemical vapor deposition (PECVD) is one of the most important methods of SiNW preparation because it significantly reduces the deposition temperature and increases the growth rate of SiNWs [11, 12]. In the CVD method of growing NWs, the vapor-liquid-solid (VLS) mechanism is the key growth process [13]. Thus, the synthesis of NWs via the CVD method almost always
requires a metal catalyst. Choosing a suitable catalyst for NW growth depends on the eutectic temperature of the metal-semiconductor system.

A variety of catalysts have been used to grow SiNWs, such as Au [14], Zn [15], In [16], Ga [17], and Sn [18], at different growth temperatures. Recently, the use of aluminum (Al) as a catalyst in growing SiNWs has attracted significant attention. However, using Al as a catalyst has been found to be more challenging because of the reactivity of Al with O₂ and H₂O that leads to the formation an oxide layer [19]. Moreover, Al metal can dope Si to form an acceptor level in the band gap of Si, which means that using Al as a catalyst is promising for obtaining a p-type SiNW [20]. The catalyst type has an impact on the nanowire properties, including on morphology, crystallinity, and on the carrier concentration of the SiNWs, because of the eutectic point of the catalyst with Si, which can determine the most suitable temperature required to synthesize SiNWs. Thus, if the growth temperature is less than the metal-Si eutectic point in the CVD, the growth of SiNWs can occur by the vapor-solid-solid (VSS) mechanism rather than by VLS [21].

In the present work, SiNWs were grown by the Pulsed PECVD method using Al metal of different thicknesses as a catalyst. The surface morphology, crystalline structure, and optical properties of the grown SiNWs were investigated.

2. Experimental details

Silicon nanowires were grown via the Pulsed PECVD method using Al metal as a catalyst. The catalyst thin films with various thicknesses ranging from 10 nm to 100 nm were deposited on indium tin oxide (ITO)/glass substrates by the thermal evaporation method. The substrates were loaded into the PECVD chamber and heated in the presence of 3 Torr argon to approximately 350 °C for 35 minutes. Afterwards, the substrate temperatures were increased to
400 °C, and SiH$_4$ gas was introduced as a Si source. The growth process was conducted under pulsed plasma with a frequency of 13.56 MHz supplied by a square wave pulse generator (SRS model DGS 35) using a modulation frequency of 1,000 Hz. The total preparation time was 45 min. After the deposition process was completed, the system was purged with argon and cooled to near room temperature; the samples were removed and prepared for analysis. All samples were grown under the same deposition conditions. The surface morphology of the products was investigated by field emission scanning electron microscopy (FESEM; model FEI Nova NanoSEM 450) and transmission electron microscopy (TEM- Philips CM 100 TEM). The TEM samples were prepared by placing the SiNWs in a beaker containing ethanol and placing the beaker in an ultrasound bath for 2 min to remove the wires from the substrate. The crystalline structure of the prepared SiNWs was investigated through X-ray diffraction (XRD) using a PANalytical X’Pert PRO MRD PW3040 instrument with CuK$\alpha$ radiation. The photoluminescence (PL) and Raman spectroscopy were conducted at room temperature using a Horiba Jobin Yvon HR 800 UV. The PL measurements were undertaken using 325 nm, 20 mW HeCd laser light for excitation while the Raman measurements were performed with a 20 mW argon ion laser at 514.5 nm, with a spot diameter of 100 µm.

3. Results and discussion

3.1 Morphology

The surface morphology of the SiNWs, prepared using the Al catalyst, with different thin-film thicknesses of 10 nm to 100 nm, was analyzed through FESEM images (Fig. 1). The SiNWs were significantly affected by the varying thicknesses of the thin-film catalyst. The SiNWs prepared using Al with thicknesses of 10 and 20 nm were characterized by a high wire density,
as shown in Figs. 1A and 1B. The nanowires became shorter in length and tended to aggregate when the Al thickness increased to 40 and 60 nm (Figs. 1C and 1D). Moreover, an 80 nm Al catalyst thickness resulted in the growth of short, aligned wires, as shown in the FESEM image in Fig. 1E. Small, circular types of particles were observed with a catalyst thickness of 100 nm, as shown in Fig. 1F.

Figure 2 shows the analysis of the diameter distributions of the SiNWs grown using different Al thin-film thicknesses. The modal wire diameter significantly increased when the Al thin-film thickness was increased. The wire diameters of the SiNWs prepared using 10 and 20 nm thick Al thin films ranged from 100 nm to 160 nm and from 110 nm to 170 nm, respectively (Figs. 2A and 2B). The modal diameters of the SiNWs catalyzed by layer thicknesses of 10 and 20 nm Al were about 115 and 125 nm, respectively. As shown in the FESEM images, the grown wires became shorter with increased diameter as the catalyst film thickness increased. Thus, the SiNWs catalyzed by 40 and 60 nm thick Al films, showed diameters ranging from 150 nm to 210 nm and 180 nm to 240 nm, respectively (Figs. 2C and 2D). Using an 80 nm Al catalyst thickness led to the formation of SiNWs with diameters reaching 270 nm (Fig. 2E). Furthermore, short wires with diameters ranging from 60 nm to 100 nm were also noticed in the sample which was prepared using the 80 nm thick Al catalyst. The reason for the appearance of these wires with such a small diameter is unknown. The maximum diameter of the grown SiNWs increased to about 300 nm as the Al catalyst thickness reached 100 nm (Fig. 2F).

From the FESEM images, the density (number of nanowires per µm²) of SiNWs grown using the Al catalyst was measured and found to decrease from 20 NW/µm² to 10 NW/µm² when the Al catalyst thickness increased from 10 nm to 100 nm, respectively (Fig. 3).
Figure 4 shows the cross-sectional FESEM of SiNWs synthesized using 20, 60, 80, and 100 nm Al catalyst thickness. The average length of the SiNWs catalyzed by a 20 nm layer of Al ranged from 2 to 2.5 µm and decreased when the thickness of the Al catalyst thin films increased. Moreover, short aligned wires are observed for SiNWs grown with an 80 nm thick layer of Al catalyst.

TEM images of the samples prepared using Al films of 20, 60, 80 and 100 nm thickness are shown in Fig. 5. These show that the aspect ratio of the grown SiNWs decreased as the catalyst thickness increased. Moreover, the grown SiNWs were relatively short when the 80 nm Al catalyst was used compared with the wires grown using thinner Al films. In addition, the TEM image shows that the SiNWs, prepared using an Al film of 100 nm thickness, consist of small circular particles which supports the observations of the FESEM image (see Fig 1F).

The eutectic point of the Al-Si system at 577 °C was at a low Si concentration of 12.6% [22, 23], as shown in the Al-Si phase diagram in Fig. 6. Two solid phases can be noted as the $\alpha$ and $\beta$ regions in the Al-Si phase diagram. Thus, depending on the growth temperature, two different growth mechanisms are possible when using Al metal to catalyze SiNWs, namely, VLS and VSS. In the VLS mechanism, the growth temperature should be higher than the eutectic point. Thus the growth temperature has to be higher than the eutectic temperature of 577 °C so that the Al–Si catalyst particle is a liquid [21, 24].

The growth temperature of SiNWs was 400 °C and less than the eutectic point of Al-Si, which means that the growth mechanism was VSS. The SiNWs grown via the VSS mechanism bring two benefits: reducing the growth temperature and reducing the solubility of Si in the catalyst to about one order of magnitude.
Wang et al. [21] also synthesized SiNWs by the CVD method using Al as a catalyst at temperatures between 430 °C and 490 °C (below the Al-Si eutectic point), indicating that their SiNWs were grown via the VSS mechanism. However, SiNWs were also grown via the VLS mechanism by Schmidt et al. [22] using an Al catalyst at temperatures between 580°C and 700°C. The VSS growth mechanism has been reported for the growth of SiNWs using other catalysts such as Ti [25].

Our results are in accordance with those presented by Wacaser et al. [19], who showed that varying Al layer thicknesses have an influence on the average SiNW diameter. The average diameters of the SiNWs grown by the low pressure chemical vapor deposition (LPCVD) method using Al thicknesses of 3, 5, and 7 nm increased to 58, 78 and 83 nm, respectively. Moreover, the diameter of SiNWs, prepared with 6 nm thick Al, ranged between 20 nm to 100 nm, and increased to about 100 - 120 nm with a 10 nm thick Al thin film [26]. Other studies also found that an increase in the catalyst thickness led to an increase in the diameters of the SiNWs [27, 28]. Figure 7 shows the EDX spectra of a SiNW sample that was catalyzed by using a 40 nm Al thin film thickness. The atomic ratio of Al metal in the sample was 2.81% while it was of 12.3% in the tip of a single SiNW. Moreover, the atomic ratio of Si in the tip was 72.7%. The EDX results confirmed that the SiNWs were catalyzed by Al metal.

3.2 Crystalline structure

The XRD patterns of SiNWs synthesized using various Al thin film thicknesses are shown in Fig. 8. The diffraction peak at 30.4° related to the (200) plane of the ITO coated glass substrate appeared conspicuously in the samples prepared using Al thin film thicknesses of 10, 20, 40 and 60 nm. The ITO peak became weaker in the SiNWs grown using 80 and 100 nm thick Al films.
This could be because of the increase in the wire diameters of these samples and the greater Al thickness that covered the substrates as shown in cross sectional FE SEM images in Fig.4. The Al diffraction peak was located at ~35° corresponding to the (110) plane of Al. This appeared clearly in the XRD patterns of the SiNWs prepared with 80 and 100 nm thick Al films. This peak was weaker in the other samples catalyzed by 10, 20 and 40 nm thick Al films. The strong peak at 24° for the 100nm thick Al film may be due to SiO₂. Moreover, other diffraction peaks related to the (111) and (220) planes of Al metal at 44.8° and 65°, respectively, were observed in some of the XRD patterns.

The diffraction peaks corresponding to the crystalline Si phase (which should occur around 28.5°) were absent, indicating that the prepared SiNWs had low crystallinity or amorphous structure. Iacopi et al. [24] used 10 nm Al particles prepared via PVD method to grow SiNWs by the PECVD. They found that Si layer that covered the catalyst is amorphous. Moreover, the SiNWs synthesized by pulsed PECVD with a Sn catalyst were entirely amorphous [29].

3.3 Photoluminescence spectra

The room temperature photoluminescence (PL) spectra of the grown SiNWs catalyzed by various Al thin-film thicknesses of between 10 nm to 100 nm are shown in Fig.9. These SiNWs showed three types of emissions: green, blue, and red bands. The SiNWs prepared using 10 nm thick Al catalyst showed a weak blue emission band centered at about 500 nm, and a broad red one peaking at around 770 nm. Two broad emission bands, located at 751 and 900 nm, were observed in the PL spectrum of the SiNWs catalyzed with 20 nm thick Al. The PL emission from the SiNWs catalyzed by a 40 nm thick Al film also contained two broad peaks at 782 and 900 nm as well as a weak blue emission at around 500 nm. The PL emission bands for the other
samples prepared using Al catalysts with thicknesses of 60, 80, and 100 nm are shown in Fig. 9 and listed in Table 1.

The Bohr radius of the free exciton of the bulk silicon was around 5 nm [30], and all prepared SiNWs had a diameter of more than 100 nm. Thus, the observed PL emission cannot be ascribed to the quantum confinement effect in the nanowires. The green and blue bands could have come from the recombination of free electrons with the oxygen defect in the silicon oxide layer which coated the SiNWs, while the red band was emitted from recombination at the interface between the amorphous sheath layer and the crystalline core [31, 32]. However, the absence of XRD peaks does not mean that the SiNWs had completely amorphous structure. They could have had a very low degree of crystallinity.

Bhattacharya et al. prepared SiNWs by pulsed laser vaporization of silicon using Au as a catalyst and found that red PL emissions peaked at 1.5 eV (826 nm) and 1.4 eV (886 nm) for different diameter distributions [33]. De Boer et al. [34] noticed an increase in PL intensity for Si nanocrystals and shifts to longer wavelength for small-sized nanocrystals. Our results conform with other studies that synthesized SiNWs using Au as a catalyst and obtained red emission peaks [35, 36].

3.4 Raman spectra

Micro-Raman spectroscopy is an analytical tool that provides information about doping concentration, lattice defect identification, and crystal orientation of nanostructured materials via the effect of phonon confinement [37, 38]. The micro-Raman spectra of SiNWs synthesized using an Al catalyst are shown in Fig.10. The SiNWs catalyzed by Al thin films with thicknesses
of 10, 20, 40 and 60 nm showed Raman peaks located at 500, 498, 495 and 493 cm$^{-1}$, respectively, corresponding to the first order transverse optical mode (1TO) of c-Si. Compared with the 1TO peak for c-Si, which is located at 522 cm$^{-1}$ [39], all the prepared SiNWs 1TO peaks shifted toward lower frequencies. A broad Raman peak was observed at 484 cm$^{-1}$ for the SiNWs prepared using 100 nm thick Al catalyst. The peak location and shape indicate that the wires were amorphous [40] and the broadening of this peak is indicative of oxidation. The SiNWs prepared using an 80 nm thick Al catalyst show a 1TO Raman band centered at 511 cm$^{-1}$, shifted from the c-Si band by about 11 cm$^{-1}$. The located 1TO band nearest to c-Si band could be due to the wires had small diameter which appeared in this sample as shown in FESEM image (Fig.1E). The broad peaks at 290 and 920 cm$^{-1}$ were related to the second order transverse acoustic phonon mode (2TA) and to the second order transverse optical phonon mode (2TO), respectively [41].

Campbell and Fauchet [42] proposed a model of phonon confinement to estimate the relationship between the Raman shift and the nanoparticle size. The decreases in the diameter of the Si nanospheres led to the shift in the 1TO peak toward the lower wave number. Qin et al. [43] noted that an a-Si layer covered the c-Si core of SiNWs prepared by inductively coupled PCVD using Au as a catalyst and concluded that the broad Raman peak at 480 cm$^{-1}$ corresponded to this amorphous Si layer. Moreover, they found that the amorphous layer thickness increased as the SiNW diameter increased due to using a thicker catalyst.

Individual SiNWs grown by CVD using 10 nm thick Al catalysts had diameters ranging from 50 nm to 500 nm. The micro-Raman spectra were taken at the nanowire tip and at the nanowire base, which both showed a sharp peak at 518 cm$^{-1}$, while the spectra near the base showed another broad peak at around 475 cm$^{-1}$ [44]. The Raman band location and curve shape depended
on the crystallinity, oxidation layer, size uniformity, and on the variation of crystal constants [45]. The shift in the 1TO peak towards lower frequencies could be caused by the decrease in the crystallinity of SiNWs when the wire diameter increased, except for the sample prepared by 80 nm thick Al. From the FESEM image, the SiNWs prepared by 80 nm thick Al were vertically aligned, which could be the reason the 1TO peak appeared nearest to the c-Si location. The enhancement of the crystallinity of SiNWs required a high preparation temperature. Ho et al. grew SiNWs by the CVD method at 850°C using Au as a catalyst and obtained a single crystal structure with vertical alignment. The 1TO Raman peak was strong and centered at 520 cm⁻¹ [46]. The SiNWs prepared at lower temperatures resulted in structures with lower crystallinity.

4. Conclusions

SiNWs were grown via the pulsed PECVD method using varying thicknesses of the Al catalyst ranging from 10 nm to 100 nm. Increasing the Al thin-film thickness has a strong effect on the morphology and dimensions of the grown wires. The wire diameter increased as the catalyst thin film thickness increased, resulting in the reduction of the density of the SiNWs. No diffraction peaks related to Si structure were observed in the XRD patterns, indicating the low crystallinity of the prepared wires. The PL spectra of the SiNWs prepared with various Al thicknesses showed emission bands in the green, blue, and red regions corresponding to recombination from the oxygen defect in the coated silicon oxide layer and from the interface between the amorphous layer and the crystalline core. Raman spectra confirmed that the crystallinity of SiNWs decreased as the catalyst thickness increased because the first order transverse band moved further away from the c-Si band location. The SiNWs catalyzed using 80 nm thick Al produced a 1TO Raman band nearest to c-Si because the wires were vertically
aligned. However, for SiNWs catalyzed by 100 nm thick Al, the 1TO Raman peak was found near the a-Si location.

Acknowledgment

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References


Table caption

Table 1: Peak locations of the Raman and PL bands for SiNWs grown with Al thin film catalyst of different thicknesses

Figurers caption

Fig. 1: FESEM images for SiNWs prepared using Al catalyst thickness of (A) 10 nm, (B) 20 nm, (C) 40 nm, (D) 60 nm, (E) 80 nm and (F) 100 nm.

Fig. 2: Diameter distribution of the SiNWs grown using an Al catalyst with various thin film thicknesses from 10-100 nm.

Fig. 3: The catalyst thin film thickness vs. wire diameter and density.

Fig. 4: Cross-sectional images for SiNWs synthesized using Al catalyst thickness of (A) 20 nm, (B) 60 nm, (C) 80 nm and (D) 100 nm.

Fig. 5: TEM images of SiNWs prepared by Al catalyst thin films with thicknesses of (A) 20 nm, (B) 60 nm, (C) 80 nm and (D) 100 nm.

Fig. 6: The Al-Si alloy binary phase diagram [24]

Fig. 7: EDX spectra of SiNWs catalyzed using 40 nm Al measured at (A) wide area of the sample and (B) on the tip of the SiNW.
Fig. 8: XRD patterns of the SiNWs grown using an Al catalyst with various thin film thicknesses from 10-100 nm.

Fig. 9: Room temperature PL spectra of the SiNWs grown using an Al catalyst with various thin film thicknesses from 10-100 nm.

Fig. 10: Raman spectra of SiNWs prepared using an Al catalyst with thickness of (A) 10 nm, (B) 20 nm, (C) 40 nm, (D) 60 nm, (E) 80 nm and (F) 100 nm.
Table 1:

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Fig. 1:
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Research highlight

SiNWs were prepared using PPECVD method. Al was used as a catalyst to grow the SiNWs. Catalyst thin films thickness ranging from 10 nm to 100 nm. The nanowire diameter increased and be shorter with increasing the catalyst thickness. Raman spectra confirmed that the crystallinity decreased as the catalyst thickness increased.