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Growth and Characterization of Silicon Nanowires Catalyzed by Zn Metal Via Pulsed Plasma-Enhanced Chemical Vapor Deposition

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Abstract

High-density silicon nanowires (SiNWs) were grown via Pulsed Plasma-Enhanced Chemical Vapor Deposition at 400°C. Zinc (Zn) metal thin films with varying thickness from 10nm to 100nm were used as a catalyst to synthesize the SiNWs. The surface morphology, crystalline structure, and optical properties of the grown SiNWs were investigated. Results indicated that increasing the Zn thickness from 10nm to 100nm led to an increase in wire diameter from 65nm to 205nm, resulting in a reduction of SiNW density. The wires grown with Zn thicknesses of 10 and 80nm exhibited high crystallinity as shown by the X-ray diffraction patterns. Three emission bands (green, blue, and red) were observed in the photoluminescence spectra of the SiNWs prepared using various Zn catalyst thicknesses. The SiNWs prepared using 10 and 80nm Zn thicknesses displayed a sharp Raman peak that corresponded to the first-order
transverse optical phonon mode in contrast to the other samples that produced SiNWs with a broad Raman band.

Keywords: Silicon nanowires, zinc catalyst, PECVD.

1. Introduction

One-dimensional (1D) nanomaterials including nanorods, nanotubes, and nanowires have attracted attention as potential electronic components because of their unique physical and chemical properties. Compared with conventional bulk phase or thin films, 1D nanomaterials have several unique advantages including high crystallinity, self-assembly, high surface-to-volume ratio, quantum confinement effects, and slow electron–hole recombination [1, 2]. Moreover, these nanostructures have high electrical mobility, which can provide direct and efficient pathways from the light-absorbing material to the conductive substrate by avoiding a series of particle-to-particle hopping transports that occur in nanoparticles [3]. Silicon nanowires (SiNWs) are one of the most interesting 1D nanostructure materials as they have unique physical properties, making them a promising option for a variety of nanotechnology applications [4-6]. SiNWs have interesting optical and structural properties that make them significantly different from bulk Si. SiNWs likewise exhibit a visible light emission at room temperature, which is absent in bulk material even at low temperatures [7]. High-density SiNWs with single crystalline structure have been grown via the Vapor–Liquid–Solid (VLS) mechanism proposed by Wagner and Ellis [8]. The catalyst plays an important role in growing nanowires, particularly in controlling the wire diameter [9, 10]. Gold (Au) metal is the most frequently used catalyst in growing SiNWs through VLS [11]. Various nanoparticle metals have similarly been used as alternative catalysts, including iron, copper, gallium, and indium [12-15]. Several reports have been published on the use of zinc (Zn) metal as a catalyst to grow SiNWs [16, 17]. Chemical
vapor deposition (CVD) is a widely used method for SiNW synthesis [18]. Plasma-Enhanced Chemical Vapor Deposition (PECVD) is another deposition method that has been used to produce SiNWs [19]. In PECVD, the plasma is used to promote the decomposition of precursor sources into reactive species [20]. The objective of the present work is to synthesize SiNWs via pulsed PECVD using Zn as a catalyst and to study the effects of varying catalyst thickness on the morphology and structural properties of SiNWs. The photoluminescence (PL) and Raman spectra of the prepared SiNWs are likewise investigated.

2. Experimental Details

2.1 Catalyst Preparation

Zn metal was deposited successfully via thermal evaporation using Bell Jar equipment under a pressure of $10^{-5}$ torr on ITO-coated glass substrates, and then used as a catalyst to grow SiNWs. Zn catalyst layers of varying thickness in the range of 10 to 100nm were deposited on the substrates. The thickness of the Zn thin films was monitored using a quartz crystal microbalance.

2.2 Growth of SiNWs

The prepared substrate was loaded into a Pulsed Plasma-Enhanced Chemical Vapor Deposition (PPECVD) system chamber to grow SiNWs. Argon (Ar) gas was introduced under a pressure of 3torr for 35min when the substrate temperature was fixed at about 350°C. Next, silane (SiH₄) gas was introduced to the preparation chamber as a source of Si and the substrate temperature was increased to approximately 400°C. Pulsed plasma with a frequency of 13.56 MHz and 30W power was used to generate the plasma. This was modulated with a square signal (SRS model DG 535) with a modulation frequency of 1000 Hz. The growth process of SiNWs was completed after 45 min. Finally, the chamber was purged with Ar and cooled to room temperature.
2.3 Characterizations

The morphology of the prepared SiNWs was characterized using Field Emission Scanning Electron Microscopy (FESEM; model FEI Nova NanoSEM 450) and Transmission Electron Microscopy (TEM; model Philips CM 100). The structural properties of the grown SiNWs were examined using X-ray diffraction (XRD) (X'Pert Pro MPD X-ray diffractometer, PANalytical Company) with CuKα radiation. Raman spectroscopy and PL were carried out at room temperature using Horiba Jobin Yvon HR 800 UV equipment.

3. Results and discussion

3.1 Surface Morphology

The surface morphologies of SiNWs synthesized via PPECVD and catalyzed using various thicknesses of Zn are depicted in the FESEM images shown in Figure 1. The as-grown SiNWs appear to be distributed randomly on the ITO substrate with a curved shape. The 10 and 20nm-thick Zn catalysts produced thin and short curved SiNWs as shown in Figures 1A and 1B respectively. When the thickness of the Zn catalyst was increased, the wire shapes gradually changed and the wires grew randomly, overlapping each other and increasing in diameter as shown in Figures 1C to 1E. The as-grown SiNWs became thicker and their diameters reached 240nm. Moreover, the wires appeared to be more curved when a 100nm thick Zn catalyst was used (Figure 1F). Thus, catalyst thickness appears to affect the diameter, shape and density of the as-grown SiNWs. Figure 2 shows the analysis of the diameter distributions of the synthesized SiNWs using different Zn thicknesses. The diameter of SiNWs prepared with 10nm thick Zn catalyst varied from 60nm to 110nm, whereas using a 20nm thick Zn catalyst led to SiNWs with diameters that ranged from 60nm to 120nm, as shown in Figures 2A and 2B respectively. The diameters of the SiNWs prepared using 40 and 60nm thick Zn catalysts were in the range of
120nm to 130nm and 130nm to 140nm respectively. A similar trend was found for SiNWs grown with 80 and 100nm thick Zn catalysts. The SiNWs had larger diameters of 165 and 175nm respectively (see Figures 2E and 2F). Yu et al. [16] and Chung et al. [17] synthesized SiNWs with diameters between 15 and 35nm using CVD at temperatures of 440°C to 500°C using Zn as the catalyst. The Zn catalyst was created through the deposition ZnCl₂/ethanol solution on a Si substrate and heating the substrate at 450°C. They found that SiNW synthesis via the gas-phase reaction of SiCl₄ with Zn at 1000°C resulted in SiNWs with diameters in the range of 40nm to 80nm. Zn metal was likewise observed at the end of the NWs, indicating that SiNWs could be grown via the VLS mechanism [21]. The results are in accordance with the results obtained by Al-Taay et al. [22, 23], who found that using Sn and Al catalysts with varying thickness in the range of 10nm to 100nm led to an increase in the diameter of as-grown SiNWs by PPECVD. Other studies similarly found that catalyst thickness plays an important role in determining the NW diameter and that an increase in catalyst thickness leads to an increase in SiNW diameter [24-26]. The densities of SiNWs grown using Zn catalysts with varying thicknesses were measured from the FESEM images. Figure 3 presents the relationships among catalyst thickness, average diameter, and density of SiNWs. An increase in Zn thin-film thickness from 10nm to 100nm led to an increase in the average diameter of grown SiNWs from 65nm to 205nm. The densities of synthesized SiNWs likewise decreased from 15NW/µm² to 7NW/µm² when the Zn thin-film thickness increased from 10nm to 100nm, as shown in Figure 3. Figure 4 shows the cross-sectional images of SiNWs catalyzed using Zn with 20 and 60 nm thicknesses. The height of the grown wires using 20 and 60nm of Zn catalyst was 420 and 350nm, respectively. Al-Taay et al. [27] noted that the increasing of the Au catalyst thickness from 20 to 100nm lead to decrease the wires height from 12 to 10 µm. Energy dispersive X-ray (EDX) measurement was conducted for SiNWs catalyzed with 40 nm-thick Zn during the FESEM observations (Figure 5).
The EDX spectra were collected from a large part of the SiNWs. Analysis showed the presence of Si with an atomic ratio of 54% and of Zn metal with an atomic ratio of 8.6%, indicating that the Zn catalyst is involved in the growth of SiNWs. The small amount of oxygen shown was due to the exposure of the samples to the atmosphere during preparation. Further microstructure characterization was carried out using TEM. The TEM images of SiNWs catalyzed with 20, 60, 80, and 100nm-thick Zn catalysts are shown in Figure 6. The Zn catalyst particle was clearly observed at the tip of the NWs, indicating that Zn catalyzed the growth of SiNWs via the VLS mechanism. The TEM images confirmed that an increase in catalyst thickness results in an increase in wire diameter. The phase diagram of Zn–Si shown in Figure 7, is dominated by a single eutectic point at 420°C at a Si concentration of 10% and despite its high vapor pressure of 0.2 mbar at 420°C [28]. Zn metal has an advantage in that Zn contamination can be removed easily compared with Au metal contamination [29].

3.2 Crystalline Structure

The XRD patterns of SiNWs synthesized with varying Zn thickness in the range of 10nm to 100nm are shown in Figure 8. The XRD patterns for all the prepared samples show a diffraction at peak about 30.6°, which corresponds to the (200) plane of the ITO-coated glass substrate. Figure 8 further shows that diffraction peaks appeared at 28.4°, 47.3°, and 56.1° corresponded to the (111), (220) and (311) planes of the crystalline Si phase, respectively. These peaks were most pronounced for SiNWs catalyzed with 10 and 80nm-thick Zn films, indicating that the prepared SiNWs had good crystallinity. Zn metal diffraction peaks from the (111) plane were also detected at 36°, indicating the catalyzed growth of SiNWs via the VLS mechanism. The absence or low intensity appearance of XRD peaks could be due to the low temperature used in the SiNW preparation, which in turn led to the growth of wires with low crystallinity. Using
the PECVD to prepare an amorphous layer over the wire, which led to a reduction in the crystallinity of the as-grown SiNWs [30-32]. Another reason for the weak crystallinity is that the wires were grown with a polycrystalline structure and the strength of the diffraction peaks in the XRD pattern is dependent on the particle size and the larger particles dominate[33].

3.3 Optical Properties

3.3.1 Photoluminescence Spectra

Figure 9 shows the room-temperature PL spectra of the SiNWs catalyzed using Zn metal with varying thicknesses in the range of 10nm to 100nm. Green, blue, and red emission bands were observed from the SiNWs. The PL spectrum of the SiNWs catalyzed with 10nm-thick Zn displayed a broad emission band with peaks at 500, 750, 850 and 920nm, whereas the 20nm-thick Zn catalyst produced SiNWs with three broad emission bands located at 540, 750 and 900nm. Two broad emission bands at 450 and 750nm were observed in the PL spectrum of the SiNWs grown with 100 nm-thick Zn. The PL emission for SiNWs catalyzed with 40, 60 and 80nm-thick Zn are listed in Table 1 and shown in Figure 9. In nanocrystalline materials, two emission peaks can usually be observed, a sharp one from the band-to-band recombination and a broad emission peak at a longer wavelength, due to a surface state or defect [34]. However, the emission peak could be related to the electron–hole recombination that occurred near the band edge. Based on the theoretical prediction of Sanders and Chang [35], the quantum confinement effect appears when the nanostructure dimension becomes comparable to or less than that of the free excitons of c–Si. The prepared SiNWs presented a huge NW diameter of about 50nm, indicating quantum confinement. Moreover, when the NW diameter becomes smaller, the energy band gap between the occupied and non-occupied states of electrons is enlarged, thereby leading to a blue shift [36]. Furthermore, for oxide-passivated SiNWs, a specific red PL at 745 nm was
observed, and this peak may originate from the Si–O–Si bridge bonds along the crystalline direction (111) based on the theoretical calculation and this peak is not observed from other structures such as (110) or (112) SiNWs, implying its dependence on the crystalline configurations [37].

3.3.2 Raman spectra

Raman spectra of the SiNWs catalyzed via different Zn metal thicknesses ranging from 10nm to 100nm are shown in Figure 10. The spectra for all the prepared samples had two broad peaks located at 920 and 290cm$^{-1}$, which corresponded to the second-order optical phonon mode and the second-order transverse acoustic phonon mode of crystalline Si respectively [38]. In contrast, the Raman spectrum of c–Si could be attributed to the first optical phonon peak at 520 cm$^{-1}$ [39]. The first-order Raman peak of the SiNWs catalyzed with 10 and 80nm-thick Zn exhibited a sharp peak located at 496cm$^{-1}$ with a down shift of about 24cm$^{-1}$. On the other hand, SiNWs prepared using 20, 40, and 60nm-thick Zn displayed broad band Raman peaks at 482, 476 and 475cm$^{-1}$ respectively. The Zn catalyst with 100nm thickness also produced SiNWs with a broad Raman peak that peaked at 468cm$^{-1}$. The SiNWs catalyzed with 10 and 80nm-thick Zn displayed a sharp Raman peak that could be attributed to c–Si, whereas broad peaks were observed for other samples catalyzed using different Zn thicknesses, which could originate from amorphous Si. Raman spectroscopy is an effective tool for estimating the amount of crystalline and amorphous phases in nanomaterials. Thus, the crystalline material presented a sharp Raman peak located at 520cm$^{-1}$, whereas the amorphous material displayed a broader peak at a lower frequency [40]. The location and curve shape of the Raman band depend on the crystallinity, size uniformity, oxidation layer and variation of crystal constants [41]. Our results are a good match with the results reported in literature [42, 43]. The relationship between nanoparticle size and
Raman shift assumed that the phonon confinement effect occurs when the particle diameter exceeds the phonon mean free path, resulting in the 1TO Raman band shifting towards a lower wave number [44]. The increase in wire diameter leads to a shift in ITO band toward the lower wave numbers because the wires become less crystalline as the diameter increases. The SiNWs prepared using 80nm-thick Zn catalyst displayed a Raman peak located at 495cm$^{-1}$ because this sample showed good crystallinity compared with other catalysts shown in the XRD pattern. The crystallite size $D_r$, can be estimated, depending on the value of the shift in the 1TO phonon mode [45]:

$$D_r = 2\pi \sqrt{\frac{B}{\Delta \omega}}$$

where B is 2.24cm$^{-1}$ nm$^2$ for Si and $\Delta \omega$ is the shift of the 1TO peak from the c-Si peak location.

Table 1 presents the crystallite size values of SiNWs catalyzed using different Zn catalyst layer thicknesses. The SiNWs catalyzed with 10 and 80nm-thick Zn had larger crystal sizes of approximately 1.9nm diameter.

4. Conclusions

Zn metal with various thicknesses was successfully used as a catalyst to grow high-density SiNWs through PPECVD on ITO-coated glass substrates. The FESEM images show that Zn catalyst thickness can affect and control the morphology and diameter of as-grown SiNWs. The diameters of the NWs increased from 65 to about 205 nm as a result of increased catalyst thickness from 10nm to 100nm. X-ray diffraction patterns reveal that SiNWs prepared using 10 and 80nm-thick Zn have good crystallite sizes compared with the SiNWs prepared using other thicknesses. Green, blue, and red emission bands are observed in the PL spectra of the SiNWs
catalyzed with various Zn thicknesses. Raman spectra show that the first-order band is sharp and is located nearest to the c–Si location for SiNWs catalyzed using 10 and 80nm-thick Zn. In comparison, a broad Raman band is observed for other prepared samples, indicating that SiNWs grown using 10 and 80nm-thick Zn catalysts have higher crystallinity. These results are confirmed by the XRD.

References

Figure captions

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

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

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

Fig. 4: Cross-sectional images of SiNWs synthesized using Zn catalyst thicknesses of (A) 20nm and (B) 60nm.

Fig. 5: EDX spectra of SiNWs catalyzed using a 40 nm thin film of Zn.

Fig. 6: TEM images of SiNWs prepared by Zn catalyst thin films with thicknesses of (A) 20nm, (B) 60nm, (C) 80nm and (D) 100nm.

Fig. 7: The Zn- Si alloy binary phase diagram [10].

Fig. 8: XRD patterns of SiNWs prepared using various Zn catalyst thicknesses in the range of 10-100nm.

Fig. 9: PL spectra of SiNWs prepared using Zn catalyst layers with thicknesses of 10-100nm.

Fig. 10: Raman spectra of SiNWs prepared using Zn catalyst layers with thicknesses of 10-100nm.
Figure 1:
Figure 2:
Figure 3:
Figure 4:
Figure 5:
Figure 6:
Figure 7:
Figure 8:
Figure 9:

[Graph showing intensity vs. wavelength for different nanometer thicknesses]
Figure 10:
Table captions

Table 1: Raman, PL peaks locations and crystal size of the grown SiNWs using Zn catalyst.

<table>
<thead>
<tr>
<th>Zn thickness (nm)</th>
<th>Raman peak (cm$^{-1}$)</th>
<th>crystallite size D$_r$ (nm)</th>
<th>PL bands (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>496</td>
<td>1.9</td>
<td>500, 750, 850, 920</td>
</tr>
<tr>
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<td>482</td>
<td>1.55</td>
<td>540, 760, 900</td>
</tr>
<tr>
<td>40</td>
<td>476</td>
<td>1.41</td>
<td>540, 750, 850, 900</td>
</tr>
<tr>
<td>60</td>
<td>475</td>
<td>1.4</td>
<td>590, 750, 900</td>
</tr>
<tr>
<td>80</td>
<td>495</td>
<td>1.9</td>
<td>550, 750, 900</td>
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<tr>
<td>100</td>
<td>468</td>
<td>1.3</td>
<td>450, 750</td>
</tr>
</tbody>
</table>

Highlights

High-density SiNWs were grown via Pulse PCVD method at 400°C> Zinc metal was used as a catalyst to synthesize the SiNWs> Increasing the Zn thickness led to an increase in wire diameter> The wires grown with Zn thicknesses of 10 and 80nm exhibited high crystallinity> Three emission bands (green, blue, and red) were observed in the PL spectra>