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EFFECT OF GROWTH TEMPERATURE ON THE CATALYST-FREE GROWTH OF LONG SILICON NANOWIRES USING RADIO FREQUENCY MAGNETRON SPUTTERING

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We have grown metal catalyst free, straight Si nanowires (NWs) with high aspect ratio of about 130 on Si(100) substrate using radio frequency magnetron sputtering. Thin Si seed layer on thermally oxidized substrate was used for catalyst-free growth. Then Si deposition was done on that substrate using sputtering technique followed by heat treatment at different temperatures (900°C−1100°C). Sample heated at 1000°C results in straight, long, and uniform cylindrical shaped Si NWs with diameter 62−74 nm and length up to 8 μm, whereas sample heated above 1000°C transformed toward nanorods with larger diameter. However, no significant growth of Si NWs took place at 900°C. Sputter deposition technique provides an alternate fabrication route for Si NW synthesis. For comparison, we have also grown Au catalyst assisted Si NWs on Si(100) substrate by similar process. These nanowires also show similar morphology with diameter 48−65 nm and aspect ratio about 165. Growth mechanism and effect of growth temperatures on the structure and morphology of Si NWs are discussed.

Keywords: Silicon nanowires; catalyst-free growth; sputtering.

1. Introduction

Crystalline nanostructures offer unique access to low-dimensional physics and can be used in large scale in the microelectronic industry to achieve higher device integration. Si nanowires (NWs) have great potential to use in electronic and photovoltaic devices.[1−3] Si NWs have strong ability to confine photo-energy from visible light.[4] Catalyst-assisted growth of Si NWs has been extensively studied, but there are few reports on catalyst-free growth of Si NWs.[5−7] Various sophisticated instruments have been used to grow Si NWs using silane gas or SiO powder as a source material. However, magnetron sputtering technique can be used to produce good-quality nanowires. To our knowledge, previously there were only two reports on use of magnetron sputtering for Si NW growth on two different substrates.[8,9] And these Si NWs structures were found to be bundled and fullerene/noncylindrical shaped. Further, these noncylindrical shaped NWs were grown at high substrate temperature (600 −850°C) using Au catalyst.

In this paper, we report an alternative easy-to-use approach to the successful growth of catalyst-free as well as Au catalyst-assisted straight Si NWs with uniform cylindrical shape and high aspect ratio on Si(100) wafer using radio frequency (RF) magnetron sputtering. Structure and surface morphology of the Si NWs were studied using X-ray diffraction, scanning electron microscope, transmission electron

microscope, and Raman scattering measurement. Growth mechanism of straight NWs is discussed based on the experimental observations.

2. Experimental Details

For the growth of Si NWs, here we have used two types of substrates. For metal catalyst-free growth, commercial Si(100) wafer was thermally oxidized at 900°C in pure O_2 atmosphere for 1 h followed by deposition of a thin Si layer (∼300 nm) by RF-sputtering at room temperature. All wafers were cleaned by sonication in acetone and then trichloroethylene for 15 min each and dried with N_2 gas blow. In addition, for catalyst-assisted NW growth, cleaned Si wafer was treated with 10% HF solution for 60 s to remove native Si oxide layer. Then 2 nm Au layer was deposited on the etched wafer for use as catalyst. Subsequently, it was dipped in 10% HF solution again for few seconds to remove ultrathin oxide layer on the top surface of catalytic particles. The Si-coated and Au-coated Si(100) substrates were placed in a RF-sputtering chamber and the substrate temperature was raised to 365°C. The final sputter deposition of Si layer was done with RF power of 80 W and Ar pressure 0.01 mbar for 1 h. An undoped Si sputter target (purity 99.999%, Kurt J Lesker) was used as source material. During second sputtering ∼45 μm Si layer was grown on both substrates. After the sputter deposition, the coated substrates were heat-treated at 900°C, 1000°C, and 1100°C for 1 h in 100 sccm Ar gas flow to grow the Si nanowires. Note that in catalyst-mediated growth of Si NWs, no NWs were formed if the ultrathin Au layer on Si substrate was not HF-treated.

After the growth of Si NWs, X-ray diffraction (XRD, Seifert 3003 T/T with Cu Kα radiation), scanning electron microscopy (SEM, LEO 1430VP) equipped with EDX, and transmission electron microscope (TEM, JEOL JEM-2100) were used to characterize the NWs. Raman scattering measurement was carried out with a 488 nm Ar^+ laser excitation using a micro-Raman spectrometer (LabRAM HR-800, Jobin Yvon).

3. Results and Discussion

After the heat treatment, all the samples were examined by SEM imaging. Sample treated at 900°C did not show any formation of Si NWs. Only Si droplets with different sizes are observed on noncatalytic substrate, as displayed in Fig. 1(a). In catalytic substrate small Si grains and Au droplets are observed at 900°C. This indicates that 900°C temperature is not sufficient for the growth of Si NWs in this process, whereas heat treatment at 1000°C results in the growth of straight, long and uniform cylindrical shaped Si NWs. Figure 1(b) shows the SEM image of the Si NWs grown on the noncatalytic Si seed layer substrate. NWs are grown horizontally on the substrate plane. These NWs are very long with length up to 8 μm with diameter 62−74 nm. Along with the NWs, some random size Si nanoparticles are also observed. This is likely due to high deposition rate of Si during sputtering. At 1100°C, we observed that NWs transformed toward nanorods. Figure 1(c) shows the SEM image of the Si nanowires/nanorods grown at 1100°C. Here we observed an increase in diameter of Si NWs, compared to the Si NWs grown at 1000°C. This is due to higher temperature growth of Si NWs. Similar to previous case, here also we observed the formation of spherical Si droplets along with Si nanowires. Au catalyst-assisted growth of Si NWs by similar process at 1000°C is shown in Fig. 1(d). These NWs have similar morphology to the catalyst-free Si NWs grown at the same temperature. These NWs are found to be straight, and highest length about 8 μm is observed and diameter varies from 48−65 nm. Similar to the earlier case, catalyst-assisted grown NWs are transformed to nanorods at 1100°C (not shown).

Figure 2 shows the TEM image of the Si NWs grown at 1000°C on catalyst-free Si(100) substrate. It is found that Si NWs have a core shell structure. Outer shell layer is a thin amorphous oxide layer, as confirmed from the EDX result. EDX result shows higher oxygen content at the edge of the Si NW compared to the center of the NW. Si NW core diameter is 50−60 nm as measured from TEM image and oxide layer thickness is measured of the SiNW (∼7 nm). Diameter distribution is shown in Fig. 3. It is found that majority of the as-grown NWs have diameter 68 nm, which is the average NWs diameter, whereas core diameter of the catalyst-assisted grown Si NWs is 35−50 nm. The aspect ratios of these NWs are ∼130 for the catalyst-free growth, while it is ∼165 for the catalyst-mediated growth. Inset shows selected area electron diffraction pattern of the corresponding Si NWs, which is a typical ring pattern similar to that of bulk crystalline Si(111) and (220) planes. This indicates the polycrystalline nature of the as-grown products or

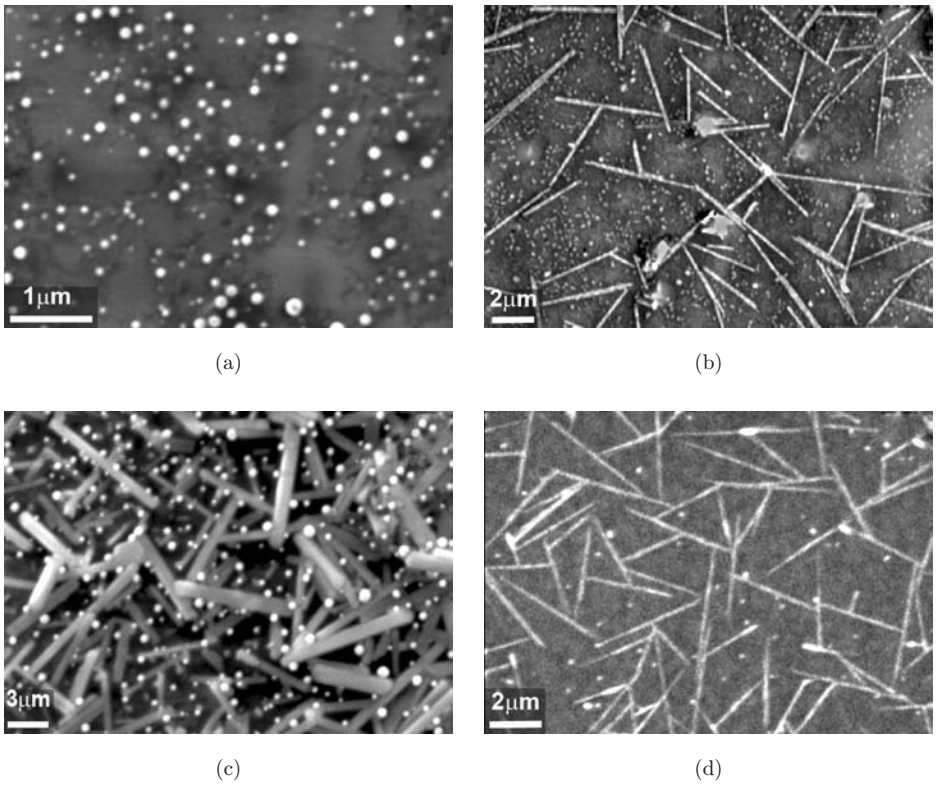

Fig. 1. SEM images of sputtered deposited Si layer on noncatalytic Si seed layer substrate after heat treatment at (a) 900°C, (b) 1000°C, and (c) 1100°C, respectively. Long and straight cylindrical shaped Si NWs were grown at 1000°C. At 1100°C Si nanowires/nanorods were grown. (d) Au catalyst-assisted grown Si NWs at 1000°C.

randomly oriented crystalline structure.[10] This may be due to fast growth rate of Si NWs or high sputter deposition rate.

Figure 4 shows the XRD pattern of the Si layer heat-treated at 900°C (a), along with catalyst-free Si NWs grown at 1000°C (b) and 1100°C (c), respectively. Due to microcrystalline structure, Si grains show distinct peaks corresponding to Si(111), (220), and (311) planes, whereas only one broad peak of Si(111) plane and a strong peak corresponding to Si(311) plane is observed from catalyst-free Si nanowires/nanorods.

In the present study, mechanism of catalyst-free as well as catalyst-assisted growth of Si NWs using sputtering process can be understood in the following way. In a catalyst-free growth of Si NWs, we believe that these NWs are grown by self-catalytic growth process. At higher temperature, Si droplets are

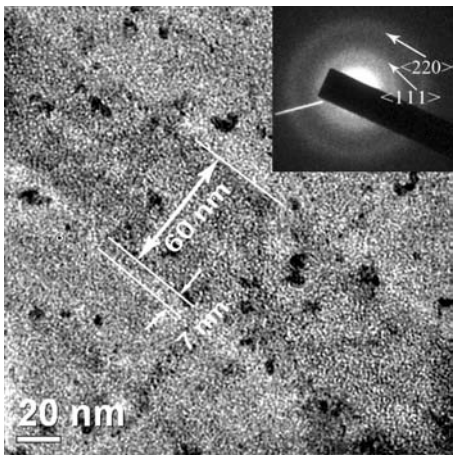

Fig. 2. TEM image of a catalyst-free single Si NW. Si NWs have a core-shell structure, where the shell is a thin amorphous oxide layer. The inset shows the SAED pattern of the Si NW. Arrow on the diffracted ring shows the corresponding crystal planes.

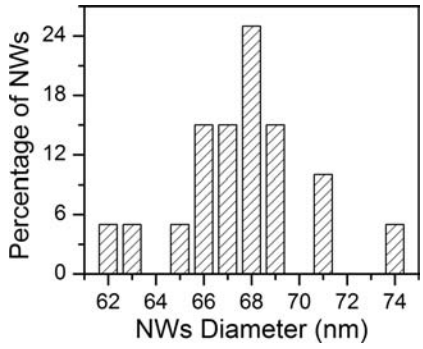

Fig. 3. Diameter distribution of catalyst-free Si NWs grown at 1000°C.

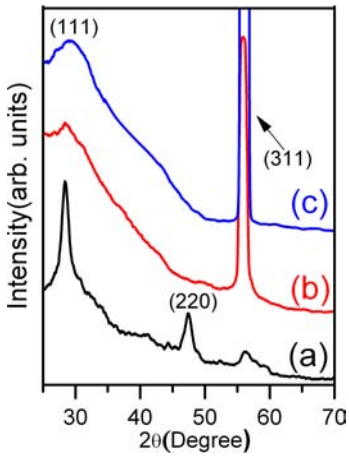

Fig. 4. XRD pattern of the Si droplets/catalyst-free Si NWs on Si(100) substrate grown at (a) 900°C, (b) 1000°C, and (c) 1100°C, respectively.

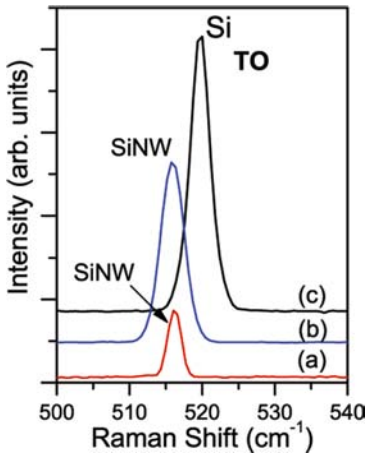

Fig. 5. Micro-Raman spectra of Si NWs: (a) catalyst-mediated growth, (b) catalyst-free growth, (c) bulk Si spectra shown for comparison.

formed on the oxide surface, which acts as nucleation site and guide the NWs growth as Au catalyst does in catalyst-assisted growth case. In this growth process there was no source of Si vapor for absorption, but liquid Si atoms were present along the substrate plane. These liquid atoms are stuck on the Si droplets and started the NWs growth along the horizontal direction, i.e., along the plane of the substrate. However, it may not be identical to the self-catalytic VLS process, suggested for catalyst-free growth of compound semiconductor.[11] In this mechanism multiple components are required for nucleation and growth. For catalyst-assisted growth, when substrate temperature reaches 365°C, Au−Si alloy nanodroplet forms on the Si substrate but it failed to supersaturate by the incoming Si atoms. This is due to the fact that Si atoms did not have enough time to diffuse on the droplets to start Si nanowire growth[9] at such a low temperature or arriving Si atoms did not have sufficient energy for supersaturation. During post-deposition heating, at 1000°C Au−Si droplets are supersaturated by surrounding liquid Si atoms and growth of Si NWs take place.

Raman spectra show good crystalline nature of the as-grown Si NWs, as shown in Fig. 5. For comparison, bulk Si Raman spectrum is also shown. Both the NW samples show strong characteristic first-order transverse optical phonon mode (TO) of Si at 516 cm^{-1} for first case and at 515.7 cm^{-1} for second case. High intensity and symmetric nature of these peaks indicate high crystallinity and uniform diameter of the NWs.[12] Compared to TO mode of bulk Si at 520 cm^{-1}, a redshift is observed for both the samples. This downshift is unlikely to be caused by phonon confinement effect, as the diameter of the Si NWs is relatively large compared to the excitonic Bohr radius of Si. Therefore, the downshift is most likely to be caused by the tensile strain experienced by the NWs due to the presence of an oxide shell over the crystalline Si NW core. This is consistent with the XRD results.

4. Conclusions

In conclusion, we report the catalyst-free and catalyst-mediated growth of straight Si NWs with high aspect ratio by using RF-magnetron sputtering. Crystalline Si NWs with diameter ∼50 nm and length up to 8 μm were synthesized by sputter deposition of Si layer followed by heat-treatment at 1000°C. Si NWs grown without Au catalyst have similar morphology except a slightly lower diameter of the NWs. This study demonstrated the use of sputter deposition technique for the growth of Si NWs in a single and less expensive way.

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