Fabrication of silicon nanowire on freestanding multiwalled carbon nanotubes by chemical vapor deposition

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ABSTRACT:

The multi-walled carbon nanotube-silicon nanowire (MWNT/SiNW) hybrids are important materials to meet the requirements of energy storage devices. We fabricated novel freestanding MWNT/SiNW hybrids by growing SiNWs directly on MWNT network via chemical vapor deposition. Gold (Au) was employed as catalyst and the influence of catalyst on the morphology of hybrids was investigated. The results indicated that tuning the thickness of Au layer could serve as a means to control the structure of MWNT/SiNW hybrids. The formation of SiNWs on the surface of MWNTs mainly depended on Au nanoparticles migrating into larger eutectic Au-Si alloy, and the abundant Si depositing on MWNTs improved the connections among MWNTs and SiNWs mechanically and electrically.

Keywords: Carbon nanotube, Silicon nanowire, Chemical vapor deposition, Gold nanoparticles, Nanocomposites

1. Introduction

Because of their unique characteristics, semiconductor nanowires have been used as the active roles in variety of devices including transistors, chemical sensors, emerging electronics [1, 2]. Silicon nanowires (SiNWs) are of particular interest due to their unusual properties to be the promising blocks for high performance devices [3]. More importantly, Si possesses high theoretical specific capacity of $\sim 4200 \text{ mAhg}^{-1}$ with mechanical integrity for lithium-ion batteries (LIB) as electrode material [4]. To date, various techniques such as chemical vapor deposition (CVD) [5], laser ablation [6], and oxide-assisted growth [7] have been developed to prepare SiNWs. Among these methods, CVD is the most widely used approach to realize precise control of morphology while providing high-quality and single-crystal nanowire growth [8]. However, significant challenges still remain for single-component Si anodes, which originate from their poor structural stability and low electrical conductivity. Notably, by integrating nano-Si with a conductive carbon matrix is considered the promising strategy for improving the device performance [9]. Among them, carbon nanotubes (CNTs) has been proven to be the primary candidate owing to its exceptional physicochemical properties in term of high electrical conductivity [10], excellent thermal conductivity [11], and superior mechanical properties [12]. For example, the hybrids consisting of SiNWs dispersing in CNT networks exhibit improved electrochemical performance in LIB [9]. It is expected that the performance can be further improved if the direct connection between CNTs and SiNWs is formed.

In this work, we present a new scheme to effectively deposit SiNWs onto multiwalled carbon nanotube (MWNT) sheet to form freestanding MWNT-SiNW hybrid materials. Here, the MWNTs bind SiNWs together to create the 3D network. The morphology and structure of the hybrids were characterized. The growth processes of SiNWs on MWNTs are discussed.

2. Experimental

A freestanding MWNT sheet was used as a substrate for SiNW growth. The freestanding MWNT sheet was produced by laterally drawing CNT from a CNT forest [13]. The CNTs in the sheet were well-aligned in the drawing direction (Fig. 1b) and they were MWNTs with 4–8 walls, 7–10 nm in diameter, and around 450 μm in length. The average thickness of the CNT sheet was approximately 18–20 μm [14]. The MWNT sheet consists of individual MWNTs and MWNT bundles (up to 150 nm in diameter). Gold (Au) was deposited via electron-beam evaporation onto the MWNT sheet in high vacuum ($\sim 5 \times 10^{-4}$ Pa) as the catalyst for fabricating SiNWs. The thickness sensor inside the electron-beam evaporator detected the thickness of Au deposition. Three different thickness, 2 nm, 4 nm, and 6.5 nm, were used for this study. The MWNT sheets coated with Au layer were placed on the quartz sample holder in the center of a horizontal tube furnace. The tube furnace was pre-evacuated to remove air and then filled with N_2 to 100 Torr. When the temperature of the furnace reached 460°C, the N_2 was replaced by H_2 and the substrates were annealed in H_2 ambient for 10 min at 20 Torr. Then a mixture of 90 sccm SiH_4 , 5 sccm PH_3 , and 90 sccm H_2 gases was introduced from one end of the quartz tube into the reaction zone. The gas flow is along the alignment direction of MWNTs in sheet. The SiNWs grow on MWNTs under 20 Torr and at 460°C for 10 min. The synthesized SiNWs were P-doped, N-type semiconductor wires.

The sample morphology was investigated using scanning electron microscopy (SEM) (JEOL 7400) at 10 kV and transmission electron microscopy (TEM) (JEM-ARM200cF). The X-ray diffraction (XRD) measurements were performed on a Bruker NanoSTAR system equipped with a micro-focus X-ray source operating at 45 kV and 650 mA with wavelength of $\text{Cu K}\alpha \lambda = 0.154$ nm. Image-Pro Plus software (Media Cybernetics, Silver Spring, USA) was used to characterize the diameter distribution of Au nanoparticles

and SiNWs.

3. Results and discussion

Fig. 1 presents the SEM images for the annealed Au nanoparticles and formed SiNWs when MWNT sheets deposited with 2, 4, and 6.5 nm thickness of Au layers. Au forms discrete nanoparticles on MWNT surface and its size increases as the increase of the deposition thickness (Fig. 1a-c). By the 6.5 nm deposition, the Au nanoparticles appear to be elongated along the axes of the MWNTs, which differs from the particles formed under 2 and 4 nm thickness. It has been established by research in the metal film deposition on planar substrates that, the structure of the film is dominated by the interactions between the deposited atoms and substrates [15]. Those two different Au nanostructures formed on MWNTs lead to the information about Au-MWNT interactions. According to a classical nucleation theory [15], the sticking coefficient for atoms infringing on a substrate from the vapor phase is proportional to $\exp(E_b/K_B T)$, where E_b is the binding energy of an metal atom with the substrate. The atoms diffuse around on the substrate and join critical nucleation centers for cluster growth. The diffusion rate is proportional to $\exp(-E_{diff}/K_B T)$, where E_{diff} is the diffusion activation energy. The Au nanoparticles appears highly discontinuous. This suggests weak Au – MWNT interaction and a small binding energy. As indicated from Fig. 1a – c, with the thickness of Au layer decreasing, the Au nanoparticles become smaller in size with a narrower size distribution. For Au deposition of 2 nm thickness, 77% of the particle size were smaller than 11 nm. For 4 nm thickness, 90% of the particle size were in the range of 11 to 20 nm. For the 6.5 nm thickness, 83% of the particles size were in the range of 15 to 50 nm. Due to the low nucleation density and high diffusion rate, Au atoms merge into isolated large particles.

Fig. 1. SEM images of Au layer with thickness (a) 2, (b) 4, and (c) 6.5 nm depositing on MWNT sheet, SEM images of formed SiNWs on MWNT surface grown from different thickness (g) 2, (h) 4, and (i) 6.5 nm of Au layer. The histogram (d-f) and (j-l) represent the diameter profile of Au nanoparticles and SiNWs, respectively.

SiNWs grow on MWNT sheet that keeps the structure and orientation as the pristine sheet. Fig. 1d-f show the morphology of formed SiNWs on MWNT sheet. The average diameter of fabricated SiNWs was 44.1, 50.3 and 55.4 nm according to the 2, 4, and 6.5 nm thickness of Au layer, respectively. It was speculated that the SiNWs morphology could be controlled by different thickness of Au layer. Based on the hypothesis, the nanowires should have the similar relative standard deviation of diameter as the Au catalyst particles to form their growth. The standard deviations of 2, 4, and 6.5 nm thickness of Au layer used are $\pm 28\%$, $\pm 26\%$, $\pm 29\%$ of the average diameter, respectively. The standard deviations of formed SiNWs are $\pm 25\%$, $\pm 18\%$, $\pm 15\%$ of the average diameter, respectively. These statistical results suggest more accurate diameter control of SiNWs grown from MWNT sheet is limited to small range of thickness of Au layer. It is also indicated by Fig. 1g-i that the density of grown SiNWs depends on the thickness of catalyst. There are

17.3, 21.4, and 28.4 wires per micrometer along MWNT axis for 2, 4 and 6.5 nm thickness of Au layer, respectively. By increasing the thickness of Au layer could result in more active catalysts for SiNW growth and narrow distributions of diameter of the SiNWs grown from MWNT substrate.

Fig. 2a depicts the XRD pattern of the SiNWs. All the diffraction peaks can be indexed to a diamond structure of crystalline silicon with a lattice constant $a = 0.357$ nm, which agrees with the literature values for silicon of an intense (111) peak along with minor (220), (311) peaks [16]. Consequently, vapor–liquid–solid theory was responsible for the formation of SiNWs on MWNT surface [6, 17, 18]. As Au and Si formed liquid droplet, the front end of the liquid was exposed to the SiH_4 to continuously absorb Si atoms into it, and SiNWs grew out of its rear where Si atoms are continuously consumed.

Fig. 2. (a) XRD pattern of the samples obtained with 6.5 nm thickness of Au layer after CVD growth, (b) TEM image of SiNWs grown on a MWNT, (c) HRTEM image of a SiNW.

A TEM image in Fig. 2b shows the representative morphology of the grown SiNWs on a MWNT. The high-resolution TEM micrograph of the SiNWs shown in Fig. 2c provides the direct evidence that the SiNW is composed of crystalline core and amorphous layer sheath with around 4 nm thickness. Natural oxidation of the SiNWs upon exposure to air after synthesis leads to the formation of the amorphous SiO_2 layer [6].

Fig. 3. SEM images of (a) freestanding MWNT sheet drawn from a CNT forest, (b) Au nanoparticles deposited on MWNTs, and (c) SiNWs grown on MWNTs, (d) the synthesis procedure of SiNWs on MWNT sheet.

As illustrated in Fig. 3d, possible fabrication process of SiNWs on MWNT is proposed based on structural characterization. No consistent relationship between Au particle size and SiNW diameter is mainly ascribed to the average time required for SiNW to grow a step height λ , which is approximately equal to the time for lateral – growth – merge process. Thus, longitudinal growth of the SiNW must be limited by the density of available growing island and island – lateral – growth process. Here, the Au nanoparticles diffusing at high migration velocity over MWNT surface, spreading and agglomerating with other Au nanoparticles, which is much faster than capturing Si atoms to get enough axial growth rate for SiNWs. Therefore, for the particular pressure, precursor flow rate, and temperature, the statistical results suggest that catalyst layer tends to form the SiNWs with ~50 nm in diameter. Thus, 6.5 nm thick Au layer effectively utilized the catalyst to form more SiNWs with ~50 nm in diameter. Au nanoparticles started to incorporate the Si atoms to form eutectic droplets at the initial stage. As the process proceeded, not all the

Au nanoparticles will induce the further growth of rod-like SiNWs. However, compared with no catalyst, the process of Au nanoparticles incorporating the Si atoms facilitated the Si deposition on the surface of MWNTs as illustrated in Fig. 2b, which benefits the connections among MWNTs and SiNWs. Meanwhile, SiNWs grow on MWNT sheet in all directions to form a 3D conductive network. The resultant hybrids with a good connection between MWNTs and SiNWs could better serve as the potential anode materials.

4. Conclusions

We demonstrated a simple approach to fabricate the freestanding MWNT/SiNW hybrids with Au layer as catalyst. The resultant hybrids were constructed by SiNWs grown on the surface of MWNT sheets with a diameter of about 50 nm. The SiNWs were directly connected with MWNTs and the abundant Si was formed on MWNTs and root of SiNWs to form stable 3D networks, which are promising electrode materials for energy storage. It is also anticipated that this method should be ideal for fabricating nanostructures that replicate other freestanding substrates.

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