Carbon Nanotubes on ITO/Silicon Substrate for Fabrication of Silicon Based Lithium Ion Battery

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Abstract

Carbon nano tubes are currently used in many modern devices for the improvement they can cause in different applications due to their unique properties. Especially in Lithium ion batteries that are today`s most common rechargeable batteries, CNTs have been utilized and offered certain advantages over commercial electrodes. Here we report utilizing carbon nanotubes grown on a silicon wafer with an ITO barrier layer, as the anode of a Lithium ion battery. CNTs with the average thickness of 90 nm and density of 14.5×10^8 cm^{-2} have been grown on the surface of the sample and used as the battery electrode. Fabrication of batteries on silicon wafer makes possible the integration of functional devices along with the power source on the same wafer, which is a considerable advantage. Surface of the sample remained intact after several charge and discharge processes, which is a very critical feature in lithium ion batteries based on silicon. High columbic efficiency of 98% and specific capacity of 0.08 mAh/cm^2 was achieved after 8 cycles for our structure.

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1. Introduction

Carbon nanotubes (CNTs) have proved great potential in modern technologies such as optical devices, transistors, displays, and energy devices. Among their vast applications in energy devices one can mention Lithium ion batteries (LIB) that are the most common type of rechargeable batteries used for providing energy of the portable electronic devices. Many reports are available on using nanostructures and especially CNTs as the active anode material in lithium ion batteries [1–9], which claim good specific capacity and aging characteristics due to CNTs unique structure and properties. According to these reports, carbon nanotubes which are simply one-dimensional cylindrical tubes made of concentric graphene sheets can improve the performance of Li-ion batteries due to their high conductivity (10^6Sm−1 at 300K for singlewalled CNTs (SWCNTs) and >10^5Sm−1 for multi-walled nanotubes (MWCNTs)) [10,11], low density, high rigidity (Young's modulus of the order of 1 TPa) [12,13], and high tensile strength (up to 60 GPa) [14].

Due to the above stated facts, CNTs are uniquely suited to replace graphite which is the active anode material used in current commercial Lithium-ion batteries [8]. Carbon nanotubes not only have a higher capacity than graphite, but also can be used as a support matrix to form novel CNT and metal composites that can take advantage of the higher capacity of metals too [13].

Furthermore, Growing CNTs on Silicon wafer and then using the grown CNTs as the active anode material in a LIB has the considerable advantage of integrating both the functional devices and the power source on the same silicon wafer.

In this regard, we aimed to fabricate lithium ion batteries on silicon substrate using CNTs as the active anode material. However, some challenges existed in order to achieve this purpose. The main challenge in using carbon nanotubes on a silicon wafer as the LIB active anode material is cracking of silicon substrate while operation of the LIB. This is because of the Lithium insertion/extraction into/from the silicon substrate during the charge and discharge processes. The solution for this problem is using a barrier layer. However, there were some requirements about the proper barrier layer. First of all, the barrier layer is needed to be conductive so that the charge transport can be

done properly. Besides, the barrier layer needed to be compatible with the CNT growth process. Finally, the barrier and discharge process. Regarding the stated requirements, we used an ITO barrier layer of 300nm between the silicon wafer and the CNTs. ITO is a conductive material, and also can be used as a stable material during both the CNT growth and the battery charge and discharge processes. As a result, both the proper growth of CNTs and using the grown CNTs on the Si wafer as a LIB active anode material are satisfied. Scanning Electron Microscopy was used to characterize the sample before and after the battery test. SEM pictures revealed that the Substrate remained intact after several charge and discharge cycles, and so this structure can be used as a good anode in LIBs.

layer required to be stable during the battery charge

2. Experimental details

For this experiment, we used a P type silicon wafer. First the surface of the sample was cleaned using RCA#1 solution. The schematic of the sample fabrication steps are illustrated in Figure 1. After cleaning the surface, an ITO barrier layer of the thickness about 300nm was deposited on the surface of the silicon substrate using a RF sputtering system (f=13.56 MHz). Next, using an electron beam evaporation system, a 9 nm Ni layer that is the catalyst for growth of CNTs was deposited on the ITO layer, as shown in Fig. 1(a). Finally, DC Plasma Enhanced Chemical Vapour Deposition (DC-PECVD) was used for the CNT growth (Fig. 1(b)). In this process, upon heating to 680 °C under a hydrogen atmosphere, the Ni film was annealed. The hydrogen flow rate during the annealing process was set to 15 sccm and the corresponding pressure was 43 torr. After one hour of annealing, hydrogen plasma with dc bias of 500 V and current of 30 mA was applied for 5 minutes. As a result, the Ni catalyst layer was activated and Ni nanoparticle islands were formed. Then, C_2H_2 gas with the flow rate of 6 sccm was added to the chamber. In this stage, The DC plasma voltage was set to 600 V and the corresponding current was about 32 mA. The duration for this stage that is the growth stage, was 10 minutes. At the end of the

growth period, samples were slowly cooled, within the furnace, under H_2 gas environment.

For testing the sample as a LIB anode, we have fabricated a Lithium ion battery, with Lithium as the other electrode of the battery as illustrated in Fig. 1(c). Also, a separator layer immersed in the electrolyte was placed between the two electrodes
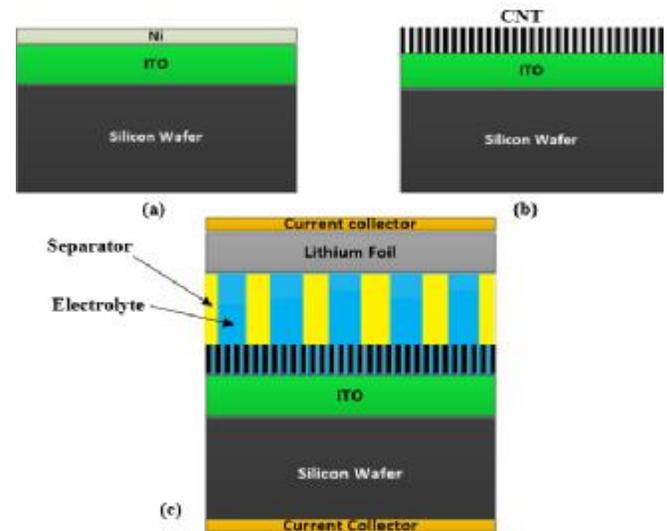
to isolate them from each other. 1M $LiPF_6$ in (Ethylene carbonate: Dimethyl carbonate (1:1 vol.%)) solution was used as the electrolyte of the battery.

Figure 1. Schematic of the fabricated Lithium ion battery. (a) deposition of ITO barrier layer and Ni catalyst layer on Silicon substrate. (b) CNTs grown on the sample. (c) using CNTs on Si/ITO surface as one of the electrodes to fabricate a Lithium ion battery.

3. Results

SEM image of the grown CNTs on the Si/ITO/Ni substrate is shown in Fig. 2. Arrays of vertically aligned carbon nanotubes with the thickness of around 90 nm, height of 600 nm, and density of 9.6×10^8 #/cm^2 are obtained. CNT parameters were calculated from the average values of CNTs in the SEM images of as grown CNTs (before battery test). We have previously grown CNTs directly on the silicon substrate using Ni as the catalyst, but now it can be seen that using a barrier layer such as ITO can also result in good growth of CNTs on the sample. As explained earlier we chose a barrier layer like ITO on the silicon surface in order to prevent the silicon surface from cracking and pulverization in the consequent steps of charge and discharging the Lithium ion battery. The critical

point in our experiment was the proper growth of CNTs on the barrier layer which was achieved according to Fig. 2. This sample was used as the integrated anode active material and current collector in the fabrication of Lithium ion battery while bulk lithium metal was used as the other electrode of the battery. The details of this process are explained in the previous part of this paper.

Fig. 3 shows the SEM image of the CNTs after several charge and discharge cycles.
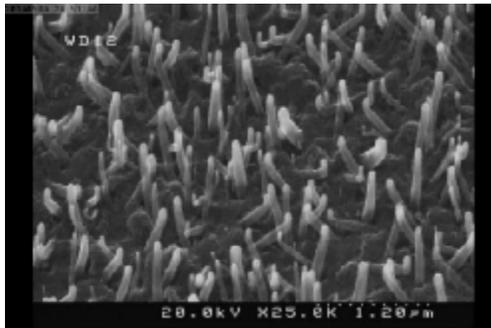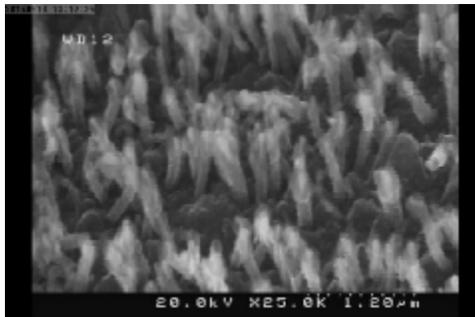

Figure 2. CNTs grown on Si/ITO/Ni surface.

Figure 3. CNTs grown on Si/ITO/Ni surface battery test up to 15 cycles.

Insertion of Li in the anode of LIB leads to expansion of the anode material that would change the diameter and side wall quality of CNTs. This effect can be seen in the SEM images of Figures 2 and 3. In Fig. 3 CNTs that have been used as the anode of the battery are clearly thicker than as grown CNTs of Fig. 2. Also it can be seen in Fig. 3 that CNTs do not lose their connection with the substrate that is an important characteristic for being used as the anode of the battery. As another noticeable point, this figure approves that during this test, the substrate remain intact. This is the result of protection of substrate by ITO layer against insertion of Li into silicon wafer. To

emphasize the roll of ITO layer, in Fig. 4 SEM image of silicon surface without this barrier layer and after battery test is illustrated, showing extreme degradation and cracking of the substrate.
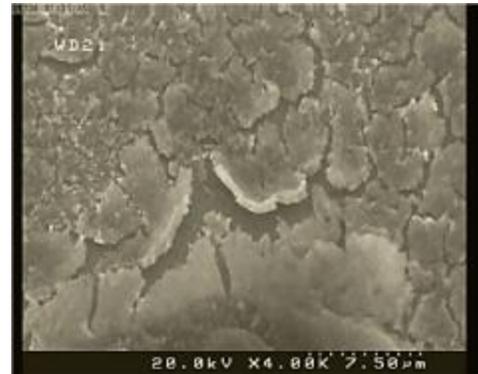

Figure 4. SEM image of silicon surface after battery test.

Columbic efficiency of the fabricated lithium-ion battery versus the cycle number is shown in Fig. 5. The sample was tested for 8 charge-discharge cycles in the voltage range of 50 mV to 3.7 V, and the current density of 0.4 mAh/cm^2. As can be seen in Fig. 5, the remarkable columbic efficiency of 98% after 8 cycles is obtained, which is a considerable efficiency for lithium ion batteries. The significant increase in the columbic efficiency of the battery from cycle 4 to cycle 5 can be explained as follows. In the first cycles of the battery test, as a result of the reactions between the electrolyte and anode, usually an intermediate layer form on the surface of anode material. This layer is known as Solid-Electrolyte-Interphase (SEI) layer. It consumes some of the Lithium ions and so reduces the amount of Lithium ions that contribute in the charge/ discharge process, decreasing the amount of columbic efficiency. As the battery test proceeds, this SEI layer becomes nearly stable, increasing the columbic efficiency. The rise in the efficiency of the battery from cycle 4 to cycle 5 can be related to this phenomena.
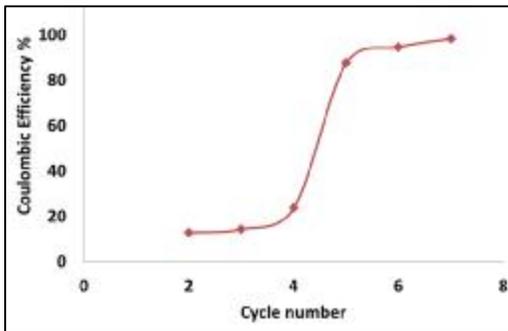
Figure 5. The results of coulombic efficiency for the fabricated Lithium ion battery. It can be seen that after 8 cycles of charge and discharge, a columbic efficiency of 98% is achieved, which is considered as a proper efficiency for lithium ion batteries.

The discharge specific capacity versus the cycle number for the above cell is shown in Fig. 6. This experiment was performed in the voltage range of 50 mV to 3.7 V, and current rate of 0.4 mA/cm^2 (equal to 5C). The specific capacity level of around 0.08 mAh/cm^2 is achieved after 8 cycles of charge and discharge, which is an acceptable result for the fabricated battery. For this experiment, the current rate was around 5C which is a high current level, and so shows that higher values for specific capacity can be obtained with lower current levels. We had previously tested the battery with ITO anode (without CNTs) in another experiment, showing significant lower specific capacitance in comparison with CNTs on ITO anode. Therefore the capacity seen in Fig. 6 can be attributed mainly to CNTs as the anode material of the battery.

Conclusion
Here, we have reported growth of CNTs on silicon wafer with an ITO barrier layer. The proper growth conditions for vertically aligned carbon nanotubes on this barrier layer is obtained, resulting in arrays of CNTs with the average thickness of 90 nm and the density of the array was 14.5×10^8 cm^{-2}. Furthermore, fabrication of Lithium ion battery with this CNT array electrode was reported. The battery tests showed almost stable specific capacity around 0.08 mAh/cm^2 after 8 cycles of charge and discharge with the current density of 0.4 mA/cm^2 (equal to 5C). After 8 cycles, the remarkable columbic efficiency of 98% was achieved which is a very good efficiency for lithium ion batteries. These results indicate that this structure can be used as an effective Lithium ion

battery anode on the silicon substrate. It is worth mentioning that the fabricated battery is on Silicon substrate, having the advantage of making possible the integration of other electronic devices on the same substrate.

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