ALD TITANIUM NITRIDE COATED CARBON NANOTUBE ELECTRODES FOR ELECTROCHEMICAL SUPERCAPACITORS

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ABSTRACT
We present titanium nitride (TiN) coated carbon nanotube (CNT) forest electrodes by means of atomic layer deposition (ALD) to store charges in the electrochemical supercapacitors for the first time. The specific achievements as compared with the state-of-art supercapacitor electrodes include: (1) 400 times higher capacitance than a flat-shape electrode; (2) conformal and uniform coating of TiN; and (3) greater than 500% enhancement of electrochemical capacitance at 81mF/cm² than CNT electrodes without TiN at 14mF/cm² due to increased oxygen vacancies on the TiN surfaces. As such, this work presents a new path to increase energy density of supercapacitors using TiN-based porous materials.

KEYWORDS
Titanium nitride; supercapacitor; atomic layer deposition; electrochemistry

INTRODUCTION
Electrochemical supercapacitors have recently gained attention for their quick discharge/charge ability. However, the limiting factor in supercapacitors is its storage capacity as compared to batteries or other high energy density storage devices. Early electrochemical supercapacitors achieved charge storage through double layer capacitance, achieved when ions from the electrolyte collect on the surface of the electrode. Since the number of ions that can gather at the surface is directly proportional to surface area, the energy storage of these electrodes can be further increased through texturization of electrode surface.

This is often achieved by using high surface area materials with high intrinsic capacities, such as porous carbon, activated carbon, or carbon nanotubes. These supercapacitors charge and discharge quickly, as the charge is highly mobile and the charge layer forms only at the surface of the material. In contrast, lithium ion batteries have relatively slow charge discharge cycles, as ions must intercalate themselves into the material. Moreover, in the process of intercalation, electrodes may become susceptible to damage. For example, silicon, known as one of the highest energy density lithium ion battery materials, can expand up for 400% upon intercalation. Damage in double layer supercapacitors is minimal, since charge simply gathers on the surface and does not insert itself into the electrode area.

The second mechanism of charge storage in an electrochemical supercapacitor is achieved by a faradaic redox reaction occurring at the surface of the electrode, or pseudocapacitance. In contrast to batteries, these reactions are much faster since they occur only on the surface layers of the electrode. However, many pseudocapacitors suffer from poor stability, since electrodes may experience damage from ion insertion. These two mechanisms of supercapacitor charge storage working in tandem can dramatically increase the charge storage capacity, depending on the device architecture and faradaic reaction. In our supercapacitor device, we increase the double-layer capacitance by using a vertically aligned carbon nanotube (CNT) forest, a high surface area material. We then further attempt to increase charge capacitance by conformally coating the CNT forest

Figure 1 Conceptual illustration of increasing capacitance through increased surface area and the pseudo capacitive effect. The storage and release of electrical charge occurs by adsorption and desorption of charge on the surface of TiN ("Double Layer charge storage") as well as oxidation of the surface layer. This surface layer of $\text{TiO}_2$-$\text{N}_x$, which forms as a native oxide layer, has a high nitrogen concentration, with a large number of oxygen vacancies in the surface. Both charge storage mechanisms combine to increase capacitance in the device. The current then flows through the ALD TiN and CNTs.
Figure 2 Process flow of substrate fabrication. Steps a-c show preparation of the CNT substrate before growth. This is carried out by evaporating a conductive layer and catalyst onto a silicon substrate with thermally grown oxide. When heated, the catalysts form droplets, which form the basis for CNT growth. In an ethylene environment, a vertically aligned CNT forest is grown by CVD (step d). Finally, in step e, TiN is deposited conformally onto the CNT forest using ALD.

with titanium nitride (TiN), which has previously been shown to exhibit faradaic redox surface reactions due to increased oxygen vacancies at the surface (see Figure 1).

Titanium nitride thin films have been widely used as the protection coatings in machinery and contacts in microelectronics due to its exceptional hardness, mechanical stability, biostability, and good electrical conductivity. Increased oxygen vacancies through surface behavior of the native oxide in TiN films have also led to usages in electrochemical supercapacitors for increased capacitance. For these applications, control over deposition upon irregular surfaces and nanostructures is central in optimizing performance. However, previous titanium nitride supercapacitors have been limited in geometry or surface functionalization due to the difficulty of precise fabrication. These electrodes are fabricated through a two-step, high temperature process, limiting selection of high surface area electrode materials [1] [2], or deposited by sputtering with poor conformality and coverage [3]. Here we present results from depositions of angstrom-level precision ALD TiN onto porous CNT forest electrodes and their outstanding performances in the supercapacitor electrode applications.

In our electrode as illustrated in Figure 1, we achieve

Figure 3 Characterizations: a) SEM image of TiN coated CNT forest showing conformal coating of the approximately 30μm tall forest. b) TEM image showing conformal and uniform coverage of TiN on CNTs.

Figure 4 Three electrode setup, with Pt wire as counter electrode vs. Ag/AgCl.
high capacitance by (1) increasing the surface area using the porous CNT forest architecture; and (2) allowing for redox reactions to occur in the oxygen vacancy rich TiN surface layer. These results are comparable to other supercapacitor materials deposited by ALD onto vertically aligned CNT structures [4][5]. Specifically, the large surface area helps the electric double-layer capacitance as storage/release of electrical charges occurs by the adsorption/desorption of charges on the surface of TiN. The oxidation of the surface layer, TiO$_{2-x}$N$_x$, forms a native oxide layer with high nitrogen concentration and a large number of oxygen vacancies for the redox reactions, which help the Faradaic electrochemical storages as the pseudo-capacitance for enhanced energy storages.

**FABRICATION AND METHODS**

**Electrode Preparation**

The CNT forest is grown as shown in Figure 2. First, a silicon substrate is prepared with 100nm thermally grown oxide. Next, a thin layer of molybdenum is deposited by electron-beam evaporation to form a conductive layer. The catalyst is a thermally evaporated mixture of 5nm iron and 5nm aluminum, with aluminum acting to prevent molybdenum and iron from forming an alloy. The substrate is transferred to a vacuum quartz tube furnace to grow the CNT forest by chemical vapor deposition (CVD), as outlined by Yingqi Jiang et al [6]. Once the temperature of the furnace is stabilized at 720°C, the process gases, hydrogen and ethylene are introduced in a 7:1 ratio with respect to volumetric flow rate. When heated to high temperatures, the catalysts nucleate and form droplets on the conductive surface, forming the basis for the CNT forest. At this high temperature, when placed in an ethylene rich environment, the CNTs are then grown by CVD.

TiN is ALD deposited using Tetrakis (dimethylamido) titanium (TDMAT) and nitrogen plasma as precursors. The process is highly dependent on ALD configuration, temperature, precursors, and is especially sensitive to atmospheric contaminants. A Cambridge Nanotech Fiji tool was used to deposit the TiN. ALD deposition was tested for 200°C, 250°C, and 300°C, as shown in Figure 5. Ultimately, TiN films deposited at 250°C were used as the temperature in Cambridge Nanotech’s standard TiN recipe. Additionally, as shown in Figure 5, films deposited at 250°C show the lowest oxygen to titanium ratio, indicating a higher amount of TiN in the sample. TDMAT heated to 75°C was pulsed for 0.25s, and N$_2$ plasma pulsed for 20s at an overall chamber temperature of 250°C, with purge steps of 6s and 5s, respectively, between the precursor steps. The pressure was on the order of millitorrs. The growth rate is roughly 6 Å/cycle. The as deposited film forms a native oxide in the presence of atmosphere, which is exacerbated in high temperature environments. Therefore, the deposited film is left to cool for 30 minutes-1 hour under vacuum environment.

Figure 3 shows SEM images of vertically aligned CNT forest coated with ALD TiN. As the images show, a CNT forest of roughly 30μm in height was successfully grown, corresponding to 20 minutes of growth time in an ethylene environment. Figure 3b is the TEM image of coated CNTs, showing conformal coating and uniform thickness of the ALD TiN, corresponding to 400 cycles of ALD. The CNT has diameter of 20nm and the TiN is roughly 20nm in thickness, consistent with the growth rate for this TiN recipe.

**Electrode Testing**

The electrode is tested using a three-electrode setup in aqueous electrolyte. Electrodes were used as prepared and tested with Pt wire as the counter electrode. In aqueous 0.5M H$_2$SO$_4$ solution, measurements were taken vs. Ag/AgCl reference electrode (see Figure 4).

**RESULTS AND DISCUSSION**

TiN-CNT, CNT, and planar TiN electrodes have been tested using a three-electrode setup with 0.5M H$_2$SO$_4$ as electrolyte, Pt wire as counter electrode, vs. Ag/AgCl as shown in Figure 6. The cyclic voltammetry curves shows an

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**Figure 5** XPS analysis of composition versus ALD temperature. Note the high oxygen content, a result of the TiO$_{2-x}$N$_x$ surface layer.

**Figure 6** Cyclic Voltammograms (CVs) of ALD TiN-CNTs as compared with bare CNTs and planar TiN, corresponding to 81mF/cm$^2$, 14mF/cm$^2$, and 0.2mF/cm$^2$, respectively.
 improvement of >500% in capacitance of the TiN-CNT device when compared to that of bare CNTs (81mF/cm² for TiN-CNT and 14mF/cm² for CNT electrodes), and an almost 400x improvement in capacitance when comparing CNTs with bare TiN electrodes (0.2mF/cm²).

In using a porous CNT framework, the almost 400x over a planar TiN electrode shows the significance of surface area on supercapacitor charge storage. Furthermore, the improvement of >500% in capacitance by conformal coating of TiN indicates that charge storage in the TiN device does not only take place by ion adsorption/desorption, but also through faradaic redox reactions, or pseudocapacitance. By increasing surface area (charge storage mechanism 1), one can drastically improve supercapacitor performance. However, using current methods of TiN deposition, one is limited to specific materials or surfaces. In contrast, our method of ALD TiN deposition is able to conformally coat with angstrom level precision, providing more flexibility in choice and architecture of the device.

In testing pseudocapacitive devices, stability must be considered, since damage to the electrode can occur with the insertion of ions, or damage to the electrode can occur in the case of non-reversible faradaic reactions. As can be seen in Figure 7, the device is relatively stable over charge discharge cycles. However, as can be seen in Figure 6, the reaction is not completely reversible. We hypothesize that this is due to irreversible oxidation at the surface of the TiN. Existing work on TiN supercapacitor devices have been able to show relatively stable oxygen vacancies in the presence of non-reversible oxidation due to simultaneous diffusion of nitrogen from the TiN bulk to the native oxide layer [2]. In the proposed system, the native oxide layer maintains the same number of oxygen vacancies, as the oxidation occurs through diffusion of oxygen into the bulk while nitrogen simultaneously diffuses from the bulk to the surface layer, implying that stability of the native oxide layer is also dependent on thickness of TiN film. Other existing work has mitigated stability issues through electrolyte choice. Preliminary testing in non-aqueous electrolyte of our TiN-CNT device show a more reversible and stable electrode, as elemental oxygen is not available to oxidize the active layer.

CONCLUSIONS

While current technology is limited to a two-step deposition process, or processes with poor conformality such as sputtering, we have achieved a conformal and precise coverage of TiN onto high aspect ratio porous CNT forests for supercapacitor applications. Analysis of our TiN-CNT architecture shows excellent performance and charge capacity, with the ability to increase performance by taking advantage of the flexibility offered by the precise ALD process. Furthermore, the electrode is relatively stable, with the potential for higher stability using different electrolytes or film thicknesses. Such stability studies are the subject of future work.

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REFERENCES


