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Titanium nitride films for micro-supercapacitors: Effect of surface chemistry and film morphology on the capacitance

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HIGHLIGHTS

- Titanium nitride films have been deposited with different morphologies.
- The electrode exhibits a specific capacitance in excess of 146 F cm^{-3}.
- The effect of TiN stoichiometry on film capacitance has been demonstrated.

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ABSTRACT

Electrochemical capacitors (EC) in the form of packed films can be integrated in various electronic devices as power source. A fabrication process of EC electrodes, which is compatible with micro-fabrication, should be addressed for practical applications. Here, we show that titanium nitride films with controlled porosity can be deposited on flat silicon substrates by reactive DC-sputtering for use as high performance micro-supercapacitor electrodes. A superior volumetric capacitance as high as 146.4 F cm^{-3}, with an outstanding cycling stability over 20,000 cycles, was measured in mild neutral electrolyte of potassium sulfate. The specific capacitance of the films as well as their capacitance retentions were found to depend on thickness, porosity and surface chemistry of electrodes. The one step process used to fabricate these TiN electrodes and the wide use of this material in the field of semiconductor technology make it promising for miniaturized energy storage systems.

1. Introduction

There is an increasing demand for miniaturization and boosting the performance of the wide spread multifunctional electronic devices and micro electromechanical systems (MEMS) for more challenging and smart environments [1,2]. An integrated micro-scale power source can play a major role in device reliability and performance enhancement during operation [3], underlining the need to develop such power sources. Electrochemical capacitors, also called supercapacitors, should be suitable for on-chip integration alongside the circuit they power because of their excellent charge–discharge rate and long operating lifetime as compared to the existing micro-batteries [1]. The key issues to be addressed in developing miniaturized supercapacitors, also referred to as micro-supercapacitors, are; improvement of volumetric/areal energy density, maintaining good cycling stability and use of electrode

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fabrication technique that is compatible with micro-fabrication processes [4]. Usually, powders (CNTs, activated carbon…) are processed in the form of packed films to fabricate micro-supercapacitor electrodes [5,6], a process that has many drawbacks such as bad adhesion to the current collector which adds to external resistance, loss of accessible volume to the electrolyte and incompatibility with standard micro-fabrication protocols [4]. Physical vapor deposition (PVD) techniques, widely used in the semiconductor technology manufacturing, can produce films with good adhesion, controlled thickness, composition and morphology. Thus, using PVD to fabricate electrodes for micro-supercapacitors would be the alternative solution to most of the problems faced during processing of powder into packed films. Chmiola et al. [4] have demonstrated that such technology can be used to manufacture mesoporous carbon films with high volumetric capacitance (~180 F cm^{-3}) by etching the DC-sputter deposited precursor titanium carbide film. Electrodes based on carbon materials called electrochemical double layer capacitors (EDLCs) have lower volumetric/areal energy density as compared to the so called pseudo-capacitors based on metallic oxides (RuO_2, MnO_2) [7,8] and polymeric materials [9]. Nevertheless, EDLCs are attractive as micro-supercapacitor electrodes due to long cycling life stability, thus allowing long-term use of the corresponding device.

Recently, transition metal nitrides (TMN) have been proposed as potential candidates for supercapacitors [10]. Using PVD techniques, TMN thin films such as VN [11] and RuN [12] have been proposed by our group as electrodes for micro-supercapacitors. Although these films offer high volumetric capacitance, their cycling life and power density need to be further improved for more challenging applications.

Titanium nitride (TiN) is a transition metal nitride material with remarkable properties including high electrical conductivity, high hardness and excellent thermal stability [13], making TiN films as one of the most extensively used material in semiconductor technology for electrical interconnects and diffusion barrier in MEMS devices [14]. Recently, we have demonstrated a high performance electrode for micro-supercapacitors based on TiN and carbon nanotubes (CNTs) composites (TiN/CNTs) with an outstanding cycling stability and an areal capacitance much larger than those of carbon based electrodes [15]. Producing sputter deposited TiN films as micro-supercapacitors electrode directly on a flat silicon substrates without the CNT template, while keeping performance attributes comparable to those of TiN/CNTs electrodes, will add flexibility to the design of micro-supercapacitors for practical application due to simplicity of the process and device structure as well as complementarities to EDLCs. In this work, we demonstrate that TiN, deposited on silicon substrate by reactive DC-sputtering, can be directly used as micro-supercapacitor electrodes. The volumetric capacitance value of the TiN electrodes can reach as high as 146.4 F cm^{-3} with an elegant cycling life stability of more than 20,000 cycles. Moreover, the porosity of the TiN electrode can be controlled by tailoring the deposition parameters inside the chamber during film growth, which affects both the volumetric/areal capacitance and power density of the electrodes.

2. Experimental

The TiN films were deposited over Si(100) wafers without intentional heating of the substrate holder using DC reactive magnetron sputtering technique. The deposition was carried out in a sputtering machine that is equipped with a turbo molecular pump which ensures base pressure of $<10^{-7}$ mbar in the vacuum chamber. Argon (99.999%) and nitrogen (99.999%) gases were used as sputtering and reactive gases, respectively. Titanium target (99.999%) was sputtered at different power values in order to obtain TiN films with different porosity levels and composition. The argon and nitrogen flow rates were maintained at fixed values of 18 and 2 standard cubic centimetres per minute (sccm), respectively. During deposition, the substrate holder was biased with a radio frequency generator at −75 V. A second series of TiN films, hereafter designed as T5, was prepared under similar conditions, but at a lower nitrogen partial pressure. The sample preparation conditions and their designations are summarized in Table 1. The film surface chemistry and composition as estimated by XPS, before and after in-situ erosion, are also presented in Tables 2 and 3, respectively.

Scanning electron microscope (SEM) analysis was performed using a JEOL JSM 7600 apparatus to observe morphology and to measure thickness of the deposited films. The images were recorded at an accelerating voltage of 5 kV. The films were also characterised using X-ray diffraction (XRD) machine with Bragg Brentano configuration in the range of 20–65°. Room temperature Raman spectra were recorded with a Jobin Yvon micro Raman spectrometer (T64000) at 514 nm wavelength and 200 mW power. The XPS measurements were carried out on a Kratos Axis Ultra using AlKα (1486.6 eV) radiation. High resolution spectra were acquired at 20 eV pass energy with energy resolution of 0.9 eV. The C1s line of 284.5 eV was used as a reference to correct the binding energies for charge energy shift. The Shirley background was subtracted from the spectra and signals symmetric Gaussian functions were used in the peak fitting procedure. The ellipsomertry analyses were performed using a Jobin Yvon UVISEL NIR Spectroscopic Phase Modulated Ellipsometer, with an automatic goniometer. Ellipsometric measurements were collected at an incidence angle of 70° across the spectral range 380–800 nm.

Electrochemical measurements were performed in 0.5 M K_2SO_4 (Alfa Aesar 99.99%) aqueous solution. The chemicals were used without further purification. A conventional cell with a three-electrode configuration was used for electrochemical characterization.

Electrochemical measurements were controlled via a VMP 3 multi potentiostat-galvanostat (Biologic) monitored with EC-Lab software at room temperature. A Teflon™ cell holder was used to define the surface area of the working electrode (exposed area 3 × 1 cm^2). For cyclic voltammetry experiments, ten cycles were performed prior to those provided in order to ensure that the cycles were reproducible.

3. Results and discussion

3.1. Structure and surface chemistry studies

Comparison of the XRD patterns of the T1-T4 films, shown in Fig. 1(a), indicates rock salt structure with (111) preferential orientation during films growth. The preferential orientation was found to be governed by contribution of surface energy and strain energy of the growing film. The (111) plan is known as having the lowest strain energy and the highest surface energy [16]. Therefore, it can be suggested that TiN films grew along the (111) plane in order to minimize their strain energy predominantly as a result of nitrogen excess. The XRD pattern of the T4 film was noticed to shift

Table 1
Sample identification scheme and processing conditions for TiN films.

Sample ID	T1	T2	T3	T4	T5
Power (W)	120	150	200	80	150
Nitrogen flux (sscm)	2	2	2	2	1
Argon flux (sscm)	18	18	18	18	18