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Titanium Vanadium Nitride Electrode For Micro-Supercapacitors

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ABSTRACT

Here we report on the synthesis of binary transition metal nitride electrodes based on titanium vanadium nitride (TiVN) thin films. These films were deposited by a method compatible with micro-electronic processes which consists of DC co-sputtering of vanadium (V) and titanium (Ti) targets. TiVN films with different Ti/V ratio were deposited. A dependence of the capacitance and the cycling stability with the Ti/V atomic ratio in the films was established. While V rich sample exhibits a Faradic behavior that limits its cycling ability despite a high areal and volumetric capacity, the addition of Ti in the film drastically improves the cycling ability with virtually no fade in capacitance after 10 000 cycles. Furthermore, a 1.1 Ti/V ratio leads to an areal capacitance up to 15 $mF.cm^{-2}$ in 1M KOH electrolyte solution. Such electrodes shed light on the use of binary transition metal nitrides as candidate electrodes for micro-supercapacitor.

Keywords; Micro-supercapacitors, Transition metal nitride, Titanium nitride, Vanadium nitride

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1. Introduction

Electrochemical capacitors (ECs), also named supercapacitors, are energy storage devices that are being developed to fulfill the increasing energy demand of modern technologies and to complement other energy storage systems such as batteries [1-5]. Recently, transition metal nitrides (TMNs) such as RuN [6] , VN [7-11], TiN [12-14], or Mo_xN [14,15] have emerged as promising electrode materials for electrochemical capacitors. These materials are relatively inexpensive when deposited as thin films, they feature good chemical resistance, and most importantly, in contrast to oxides, they exhibit a very high electronic conductivity. Among these nanostructured TMNs , VN has shown impressive gravimetric capacitance up to 1340 F g^{-1} [7]. However, such high value seems to be due to faradaic reactions that strongly limits the cycling ability of vanadium nitride electrodes. Unlike VN, the electrochemical behavior of TiN [12, 13] seems to be mainly ruled by capacitive charge storage which confers to the thin film electrodes quite a high cycling ability. In this study, we aim at coupling titanium and vanadium in binary TMNs, in order to emphasize the role of both elements for micro-supercapacitor applications.

In this work, we present for the first time results on the synthesis and electrochemical storage properties of TiVN thin films deposited by co-sputtering and investigated in aqueous KOH electrolyte. Many researchers are focusing on improving the gravimetric performance of the electrodes of ECs, but for portable electronics and micro-devices, the surface is the most important, especially when the electrodes are in the form of dense

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films [16-18]. This allow a direct integration of micro-supercapacitor at micro-scale level in order to bring portability.

In this work, we propose to emphasize the use of binary transition metal nitrides, namely (Ti,V)N, for micro-supercapacitor applications, which couples the high cycling ability of TiN thin film electrode with the high areal capacitance of VN. Indeed, the capacitance and cycling stability of the TiVN thin film electrodes were found to be strongly dependent on Ti/V ratio. We demonstrate an areal capacitance value of the TiVN electrode (with a Ti/V ratio close to 1.1) of 15 $mF.cm^{-2}$ at 2 $mV.s^{-1}$ (corresponding to a volumetric capacitance of 500 $F.cm^{-3}$) with remarkable capacitance retention of more than 99% after 10 000 cycles.

2. Experimental Procedure

2.1 Deposition of the TiVN electrodes

Titanium vanadium nitride (TiVN) films were deposited directly on (001) oriented silicon substrates by reactive DC Magnetron Co-Sputtering of vanadium and titanium targets in a sputter machine described in Ref [13]. Vanadium and titanium metal targets were used (purity 99.9%). The reactive sputtering was carried out without substrate heating. The nitrogen and argon flux were kept constant at 2 and 19 sccm, respectively. The deposition time was fixed to 30 minutes at constant pressure of $2x10^{-3}$ mbar. The applied power on the targets were changed in order to obtain films with different Ti/V ratio. TiVN1 was deposited with an applied power of 90 watts on both Ti and V targets. TiVN2 was deposited with applied powers of 30 and 90 watts on Ti and V targets, respectively. Finally, TiVN3 was prepared with applied powers of 90 and 30 watts on Ti and V targets, respectively.

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2.2 Structural and surface characterizations

The samples were characterized by Scanning Electron Microscopy (SEM) performed on a JEOL JSM 7600F apparatus. X-ray diffraction (XRD) was performed on Siemens D5000 diffractometer using CuKα1 radiation in Bragg Brentano configuration. For surface analysis, 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.

2.3 Electrochemical measurements

Electrochemical measurements were performed in 1 M potassium hydroxide (KOH) (Alfa Aesar 99.99%) aqueous solution electrolyte. A conventional three-electrode cell was used for electrochemical characterization. Electrochemical measurements were controlled via a VMP 3 multi potentiostat/galvanostat (Biologic) monitored with EC-Lab software. A PTFE cell holder was used to limit the surface area of the working electrode. For cycling voltammetry experiments, ten cycles were performed prior to those provided in the manuscript in order to assume that the cycles were reproducible. Long term cycling experiments were conducted at a temperature of 27 °C.

3. Results and discussion

Surface micro-structures of TiVN electrodes are displayed in SEM images (Fig.1a to 1c). It can be noticed that all the films show the same pyramidal shaped grains. This nanostructured morphology is similar to that obtained in the case of TiN films we have recently reported [13]. The grain size of the TiVN1 film ranges from 20 to 50 nm, while the crystallites of TiVN2 and TiVN3 films are slightly lower (10-40 nm). The thicknesses

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of the electrodes are in the same order of magnitude as depicted from the cross section SEM images shown in Fig.1d (270, 240 and 220 nm for TiVN1, TiVN2 and TiVN3 films, respectively). The XRD patterns as shown in Fig.1e reveal that the three films are textured along (111) direction. The TiVN3 film shows a single phase and a preferential orientation according to the peak located at 36.9 ° which is very close to the (111) diffraction peak of TiN [13,19], with no peak related to VN. This similarity to TiN crystalline structure can be explained by the Ti/V ratio measured by XPS (Fig. 1f) which exhibits a larger amount of titanium compared to vanadium (Ti/V ≈ 1.8). As this ratio decreases, i.e. as the thin film incorporates more vanadium, this (111) peak shifts toward higher 2θ diffraction angles. Indeed, for a Ti/V ratio close to 0.7 (Fig. 1f), the (111) diffraction peak of TiVN2 film is located at 37.6 ° which is close to the (111) peak of VN [20], and there is no peak assigned to TiN which also evidences a single phase for TiVN2 film. For intermediate composition (Ti/V ≈ 1.1), TiVN1 film exhibits a preferential (111) orientation (at 37.2°) which is in-between the (111) peak of TiN and the (111) peak of VN. This peak can be assigned to a (Ti,V)N solid solution [21,22]. Thus it is expected that the electrochemical behavior of TiVN3 will be close to that of TiN and that of TiVN2 will look like that of VN thin film electrodes. An intermediate behavior is expected for TiVN1 sample.

Figure. 2 (a-f) show typical cycling voltammograms (CV) of TiVN electrodes measured in 1 M KOH electrolyte at different scan rates. The TiVN1 (Fig 2a-2b), TiVN2 (Fig 2c-2d) and TiVN3 (Fig 2e-2f) were cycled in potential windows of [-0.9 – 0.1], [-1.3–0] and [-0.6–0.3], respectively, which present the safe electrochemical stability windows of each electrode [7-13]. At moderate scan rates, the CV curves corresponding to TiVN1 (Fig.2a)

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and TiVN3 (Fig.2e) electrodes exhibit a nearly rectangular shape in 1 KOH electrolyte solution, indicative of a capacitive-like behavior. Furthermore, the CVs retain their rectangular shape even at higher scan rate (up to 500 $mV.s^{-1}$). The CV plots of TiVN2 electrode are quite different compared to those of the two other electrodes. Indeed, well-defined redox peaks can be depicted at -0.8, -0.5, -1.1 and -0.7 V. These peaks (which are highlighted at lower scan rate) originate from the faradaic behavior of VN involving protons in confined vanadium oxide/oxynitride that forms at the VN surface, as proposed by Choi *et al* [7]. However, this reaction mechanism has not been clearly evidenced up to now. It is worth mentioning that the electrochemical window of TiVN2 looks like that of VN in KOH electrolyte [5] and the electrochemical window of TiVN3 resembles that obtained for TiN in KOH electrolyte as previously reported by our group [5]. In Ref [5], we showed that the charge storage mechanism of TiN was mainly due to the double-layer capacitance of this material while for VN it was a mixture of capacitive (or pseudo-capacitive) behavior and faradaic behavior. In the latter case, the faradaic behavior seems to improve the capacity of the electrode but it is detrimental to its cycling ability. In the present work, the electrochemical behavior for TiVN2 and TiVN3 electrodes shown in Figure 2c-d and 2 e-f also looks like the electrochemical behavior of VN and a TiN phases, respectively, in good agreement with XRD patterns (Fig.1e). In the case of TiVN1 the CVs are similar to those of TiVN3, but with much higher capacitance. Since the thickness of both films are very close, this suggests that the electrochemical behavior of the binary titanium vanadium nitride possibly involves double layer capacitance and pseudo-capacitance when the Ti/V atomic ratio is close to 1.

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The areal capacitances of the different TiVN films versus scan rate are presented in Figure 3a. Since the film thicknesses is nearly the same for all the samples, a comparison of the areal capacitance is possible. The capacitance rapidly decreases for all the films when scan rates is increased from 2 $mV.s^{-1}$ up to 50 $mV.s^{-1}$. Then it stabilizes between 50 $mV.s^{-1}$ and 500 $mV.s^{-1}$. The highest capacitance is obtained for TiVN2 film with the highest V content (Fig.2a) mainly due to the Faradaic reactions related to the large amount of vanadium in this film (24 $mF.\ cm^{-2}$ at 2 $mV.s^{-1}$). According to the capacitive behavior of TiN, TiVN3 films which has the highest Ti/V ratio shows a limited capacitance of 5 $mF.cm^{-2}$ at 2 $mV.s^{-1}$. Despite a very similar electrochemical behavior, the intermediate composition sample TiVN1 exhibits a much higher capacitance than TiVN3, reaching 15 mF cm^{-2} at 2 $mV.s^{-1}$. This behavior emphasizes the role of vanadium substitution in TiN films, improving the capacitance by a factor of 3.

The long term cycling test of the vanadium rich sample TiVN2 (Fig.3b) at 100 $mV.\ s^{-1}$, shows moderate cycling ability with 30 % decay of the capacitance over 10.000 consecutive cycles. This fade in capacitance has been assigned to the presence of Faradaic reactions which probably irreversibly affects the structure and micro-structure of the film upon cycling. However, this has never been evidenced by in-situ analysis and some in-depth investigations are required in order to further highlight the charge storage mechanism and the changes occurring upon cycling VN electrodes. Unlike TiVN2 sample, TiVN1 and TiVN3 electrodes show an impressive cycling stability over 10.000 cycles with very low capacitance decay (less than 1%). Such cycling ability is crucial for micro-supercapacitor application for long term use of the corresponding device. It is worth mentioning that the cycling ability of the TiVN electrodes decreases with the

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increase of vanadium content in the films. Indeed, the presence of more titanium in the film stabilizes the cycling efficiency. This was expected for a titanium rich TiVN film since TiVN3 exhibits a capacitive like behavior with a low areal capacitance (1.5 mF. cm^{-2} at 100 $mV.s^{-1}$). However, it is an unexpected improvement to keep such excellent cycling behavior together with improved capacitance (6 $mF.cm^{-2}$ at the same scan rate). This is much higher than the areal capacitance reported for many 2D thin film electrodes designed with different materials reported in a recent review [16]. Furthermore, the cycling ability is quite impressive compared to existing literature in the field [16,18]. Many capacitance values are also reported as volumetric capacitance [17,18,23]. Despite the fact that this is not the right metric for comparison of thin film electrodes with different thicknesses, it can be noted that the volumetric capacitance of TiVN1 film reaches 500 $F.cm^{-3}$ at 2 $mV.s^{-1}$ which compares well for example with carbide derived carbon thin films recently reported in the literature (410 $F.cm^{-3}$ at 1 $mV.s^{-1}$) [23].

Conclusions

TiVN films with different Ti/V ratio were deposited on silicon for use as micro-supercapacitor electrodes. It was found that the capacitance and cycling stability of the electrodes depend on the Ti/V ratio in the films. High vanadium content in the films lead to an increase of capacitance but at the expense of the cycling ability, while low vanadium content improves the cycling behavior but strongly decreases the areal capacitance. However, a film with a Ti/V ratio close to 1.1 exhibits both improved capacitance up to 15 $mF.cm^{-2}$ together with excellent cyclability over 10000 cycles. These performances are comparable to the state of art of the best electrodes reported in literature. Our results can

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open new perspectives to explore other binary/ ternary transition metal nitride electrode for electrochemical storage applications, where the role of the different metal cations need to be investigated.

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Figure Captions

Fig.1 Top view SEM images of TiVN electrodes for (a) TiVN1, (b) TiVN2 and (c) TiVN3 (d) SEM cross section of the three samples, (e) XRD pattern of TiVN electrodes, (f) elemental atomic percentage of Ti and V probed from XPS analyses.

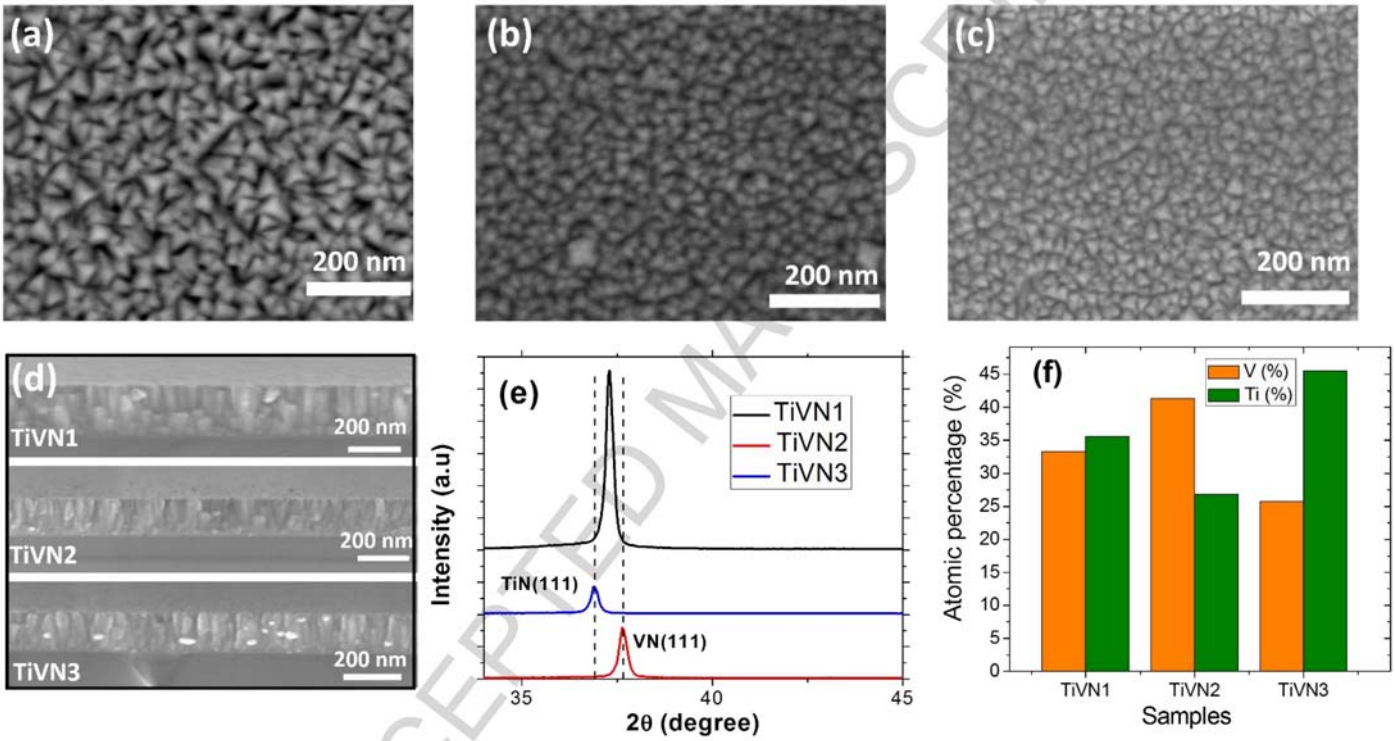
Fig.2 Cyclic voltamograms curves versus scan rate of (a-b) TiVN1, (b-c) TiVN2, (c-d) TiVN3 electrodes.

Fig.3 (a) Areal capacitance versus scan rate of TiVN electrodes, (b) Capacitance retention of the electrodes at scan rate of 100 $mV.s^{-1}$

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Fig.1



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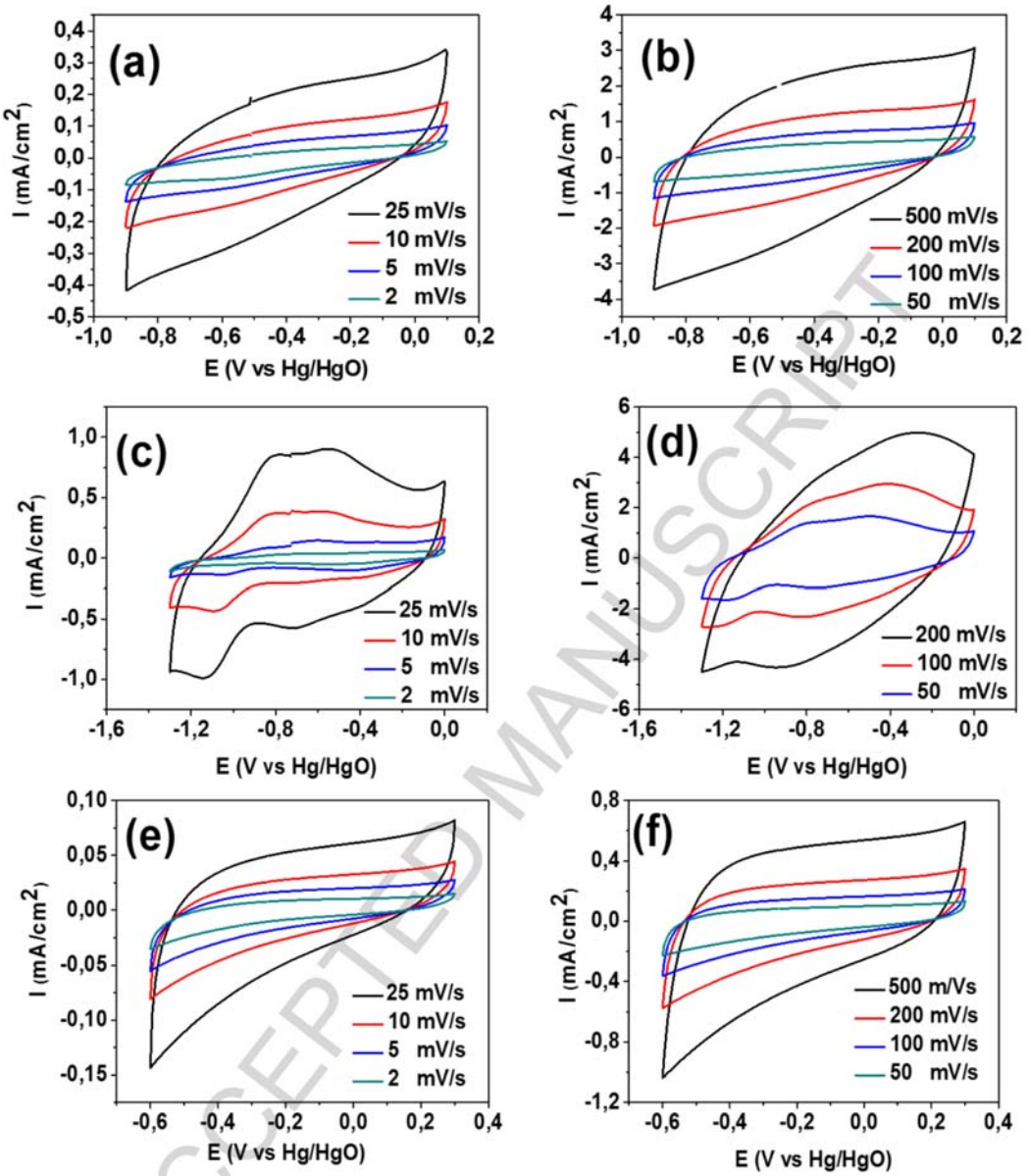


Fig.2

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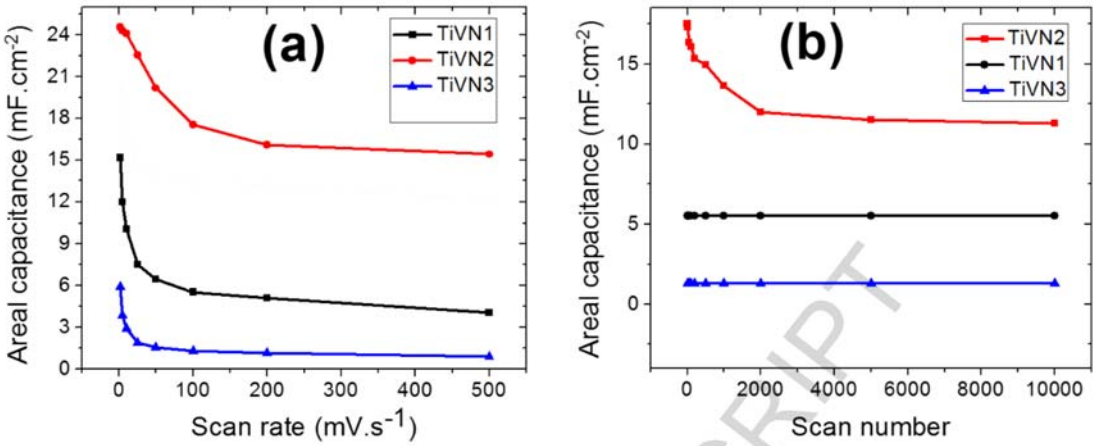


Fig.3

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Highlights

- TiVN electorchemical storage is reported for the first time
- Effect of Ti/V ratio on the electrode performances is demonstrated
- Enhancement of capacitance by factor of three without scarifying the cycling life
- Capacitance of 500 $F.cm^{-3}$ (15 $mF.cm^{-2}$) with no loss after 10 000 cycles

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