



## Thin films of pure vanadium nitride: Evidence for anomalous non-faradaic capacitance



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### HIGHLIGHTS

- Pure oxygen-free VN films can deliver surface capacitance up to  $\sim 3 \text{ mF/cm}^2$  in KOH.
- In contrast to vanadium oxynitrides No redox reactions are involved.
- An alternative mechanism – subsurface space charge accumulation – is proposed.

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### ABSTRACT

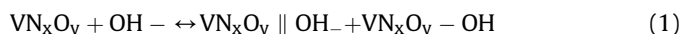
An impressive gravimetric capacitance of  $1300 \text{ F g}^{-1}$  (surface capacitance  $\sim 3.3 \text{ mF cm}^{-2}$ ) reported by Choi et al., 2006 for nanosized vanadium nitride has stimulated considerable interest in vanadium nitride as a potential electrode material for energy storing systems – supercapacitors. The postulated mechanism of charge storage in vanadium nitride materials involves redox reactions in the thin surface layer of vanadium oxide while the core vanadium nitride serves exclusively as a conducting platform. In this study we have synthesized pure oxygen-free vanadium nitride films and have found that they are capable of delivering a surface capacitance of up to  $\sim 3 \text{ mF cm}^{-2}$  at a potential scan rate of  $3 \text{ mV s}^{-1}$  and  $\sim 2 \text{ mF cm}^{-2}$  at a potential scan rate of  $1 \text{ V s}^{-1}$  in aqueous electrolytes. Combining electrochemical testing with X-ray photoelectron spectroscopy characterization has revealed that redox reactions play no or little role in the electrochemical response of pure VN, in contrast to the common wisdom stemming from the electrochemical response of oxygen-containing films. An alternative charge storage mechanism – space charge accumulation in a subsurface layer of  $\sim 100 \text{ nm}$  – was put forward to explain the experimentally observed capacitance of VN films in aqueous electrolytes.

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### 1. Introduction

Vanadium nitride has recently attracted considerable attention because of its possible application in electrochemical energy storage devices –supercapacitors. Choi et al. have demonstrated that nanosized VN can deliver an impressive gravimetric capacitance of up to  $\sim 1300 \text{ F g}^{-1}$  at a scan rate of  $2 \text{ mV/s}$  in  $1 \text{ M KOH}$  electrolyte. The demonstrated capacitance is comparable with the performance of

the benchmark -  $\text{RuO}_2$  [1–3]. However, in contrast to the latter, VN is less expensive and is more environmentally viable. In the seminal works of P.N. Kumta's group it has been postulated that the observed remarkable capacitance of nano-VN stems from reversible redox reactions occurring at the thin vanadium oxide shell [4,5]:



where component  $\text{VN}_x\text{O}_y \parallel \text{OH}^-$  represents electrical double layer (EDL) formed by the hydroxyl groups adsorbed on the surface and component  $\text{VN}_x\text{O}_y - \text{OH}$  represents oxidation of the  $\text{VN}_x\text{O}_y$  surface by the hydroxyl groups. The latter is considered as the major contributor to the observed specific (pseudo)capacitance [6]. Since

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then this pseudocapacitive mechanism of charge storage has been attributed to capacitance observed in various VN based materials studied later on [5] [7–10]. In this paradigm, a VN nanoparticle's core serves exclusively as a conductive platform for vanadium oxide surface phases, which are generally poor electrical conductors. But the question remains what would be a contribution of vanadium nitride if it was not encapsulated into the vanadium oxide shell? To the best of the authors' knowledge, the electrochemical activity of pure VN, in whatever form, has never been reported. The synthesis of oxygen-free VN is a challenging task. Indeed, for thermodynamic reasons, the formation of vanadium oxide phases is much more favorable than that of vanadium nitride (enthalpy of formation is  $-217 \text{ kJ mol}^{-1}$  for VN vs  $-1491$ – $1550 \text{ kJ mol}^{-1}$  for  $\text{V}_2\text{O}_5$  and  $-1093$ – $1218 \text{ kJ mol}^{-1}$  for  $\text{V}_2\text{O}_3$  and  $-371$ – $432 \text{ kJ mol}^{-1}$  for VO [11]. Moreover, the widely used ammonia-based synthesis of VN can also lead to the presence of an uncontrollable amount of hydrogen in the synthesized material, which, in turn, can affect the electronic properties of VN surface [12]. To elucidate the role of vanadium nitride in the charge storage mechanism we have chosen to use VN thin films as model systems. In this paper we report on a successful synthesis of oxygen-free VN thin films of various thicknesses employing ammonia-free process – direct nitridation of in-vacuo deposited metallic vanadium by annealing it in pure nitrogen at high pressure (1bar) and high temperature (800 °C). We have also shown that pure VN films grown on tantalum foil are electrochemically active demonstrating an unexpectedly high surface capacitance of  $\sim 2 \text{ mF cm}^{-2}$  when tested at a high potential sweep rate of  $1 \text{ V s}^{-1}$ . The observed surface capacitance exceeds the common values of EDL capacitance ( $\sim 10^{-2} \text{ mF cm}^{-2}$ ) by two orders of magnitude while no redox reactions on the VN films have been evidenced neither by cyclic voltammetry nor by recording X-ray photoelectron spectra before and after electrochemical testing. We argue that another capacitance mechanism, not considered before, is to be invoked to explain the observed surface capacitance of pure VN – space charge accumulation (SCA), when the accumulated charge ( $\sim 10^{16}$  electrons  $\text{cm}^{-2}$ ) is stored in an up to 100 nm-thick surface layer. Such an amount of electrons confined in a nanosized layer can behave as quasi 2D electron gas, which can result in quantized capacitance [13].

## 2. Experimental section

The experiments were carried out in an ultra high vacuum multichamber multitechnique system (SPECS GmbH) shown and described in Fig. 1.

### 2.1. Vanadium nitride film growth

The VN films were grown on Ta foil in 2-step process – pure vanadium metal deposition on the supporting Ta film followed by direct nitridation.

#### 2.1.1. Vanadium deposition

The pieces of Ta foil (Alfa Aesar) with size of  $10 \times 10 \times 0.125 \text{ mm}^3$  were used as substrate for vanadium deposition. In this work we have done deposition of metallic vanadium in two ways: e-beam assisted evaporation in the UHV chamber (in-situ) and D.C. magnetron sputtering (ex-situ) with deposition rate  $\sim 0.01 \text{ \AA/sec}$  and  $0.5$ – $0.7 \text{ \AA/sec}$  correspondently. In both cases the deposition rate was monitored by quartz crystal microbalance positioned in vicinity of the substrate. In the XPS system vanadium was evaporated from  $\varnothing 2 \text{ mm}$  vanadium rod (99.8%, Goodfellow) by means of an e-beam evaporator EBE-4 (SPECS GmbH). The deposition of thick metal films (30 nm and more) was performed ex-situ in a magnetron sputtering system Classic 500SP (Pfeiffer Vacuum).

Vanadium target (99.5%) from Kurt J. Lesker was used as a deposition source. Thickness of the deposited thick vanadium films was estimated by measuring the thickness of the “witness” film grown on a piece of masked Si wafer placed next to the Ta substrate during vanadium deposition. A piece of narrow Si bar ( $\sim 3 \text{ mm} \times 10 \text{ mm}$ ) cut out from the Si wafer was used as a growth mask clamped down to the silicon substrate. The depth of the trough created on the Si wafer upon vanadium deposition was measured with the help of stylus profiler DektakXT (Bruker). The precision of the described above method for film thickness measurements of films thicker than 10 nm was better than 20%. The substrate was kept at room temperature during vanadium deposition. In the case of ex-situ vanadium deposition the vanadium film was coated with a 1–2 nm graphite layer, using also DC sputtering before transferring it further to the XPS chamber for nitridation. This carbon coating was quite effective to prevent oxidation of the film during transferring it from the deposition chamber into the UHV chamber. The carbon coating layer was sputtered away by argon ions upon introducing the sample into the UHV chamber.

#### 2.1.2. Direct nitridation

Vanadium metal films were directly nitridated in the HPC by exposure to  $\sim 1$ bar of  $\text{N}_2$  (5X, Praxair) at elevated temperature of 800 °C for 30 min. To prevent unwanted oxidation of vanadium the HPC and gas line were thoroughly outgassed by prolonged bakeout until pressure  $1 \times 10^{-9}$  mbar or less was reached. The sample temperature during nitridation was controlled using a K-type thermocouple integrated into the sample holder (SPECS) to which the Ta foil was spotwelded. Upon heating and dwelling at high temperature the sample was cooled down to room temperature in nitrogen atmosphere.

Films with different thicknesses were grown. The thickness of the films varied from 1 nm to 400 nm. The surface capacitance was determined using formula (2) from the corresponding cyclic voltammetry (CV) recorded at a scan rate of  $30 \text{ mV s}^{-1}$  in 1M KOH electrolyte. In the case of the 1 nm film, the film was grown on an HOPG substrate. Ex-situ AFM imaging revealed clusters, which were 50–80 nm in diameter and 12–20 nm in height. All the CVs were recorded in the potential range of the electrochemical stability window, which was empirically established for each tested film separately.

## 2.2. Characterization of samples

### 2.2.1. Electrochemical characterization

Electrochemical characterizations of the synthesized VN films were performed in the Electrochemical Cell chamber (ECC) integrated to the XPS system. The ECC is schematically depicted in Fig. S1(A). During the electrochemical testing the ECC was back-filled with continuously flowing Ar gas. The 3-electrode setup for electrochemical tests is schematically depicted in Fig. S1(B). As a reference electrode was used an Ag/AgCl electrode (Sensortechnik Meinsberg). The counter electrode was made out of a Pt plate which measured  $25 \times 12.5 \times 0.3 \text{ mm}^3$ . The electrolytes used for testing were: 0.1M KOH, 0.3M KOH, 1M KOH, 3M KOH, 0.6M  $\text{K}_2\text{SO}_4$ , 1M LiOH and 1M  $\text{Li}_2\text{SO}_4$ . Electrochemical measurements were controlled by an SP200 potentiostat (Bio-Logic).

### 2.2.2. X-ray photoelectron spectroscopy (XPS) characterization

XPS characterization was used to follow changes in the film's composition and oxidation state of the film's constituent elements after electrochemical testing. The XPS spectra were acquired by means of a hemispherical electron energy analyzer PHOIBOS 150 (SPECS) and a twin Al/Mg anode X-ray source XR50 (SPECS) operated at 12 keV and power 100 W. The XPS spectra were acquired in

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