Porous CrN thin films by selectively etching CrCuN for symmetric supercapacitors

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HIGHLIGHTS

- Porous CrN was prepared by magnetron co-sputtering and selective chemical etching.
- A maximum specific capacitance of $31.3\,mF\,cm^{-2}$ was achieved at $1.0\,mA\,cm^{-2}$.
- A symmetric supercapacitor exhibited both high energy density and power density.
- The preparation method can be extended to other porous transition metal nitrides.

GRAPHICAL ABSTRACT
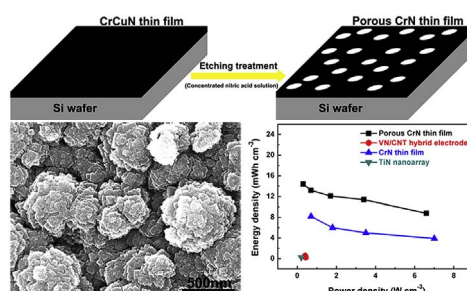
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ABSTRACT

Transition metal nitrides are regarded as a new class of excellent electrode materials for high-performance supercapacitors due to their superior chemical stability and excellent electrical conductivity. We synthesize successfully the porous CrN thin films for binder-free supercapacitor electrodes by reactive magnetron co-sputtering and selective chemical etching. The porous CrN thin film electrodes exhibit high-capacitance performance ($31.3\,mF\,cm^{-2}$ at $1.0\,mA\,cm^{-2}$) and reasonable cycling stability (94% retention after 20000 cycles). Moreover, the specific capacitance is more than two-fold higher than that of the CrN thin film electrodes in previous work. In addition, a symmetric supercapacitor device with a maximum energy density of 14.4 mWh cm^{-3} and a maximum power density of $6.6\,W\,cm^{-3}$ is achieved. These findings demonstrate that the porous CrN thin films will have potential applications in supercapacitors.

1. Introduction

With the rapid development of society and the growth of population, the increasing consumption of resources will inevitably result in energy crisis. Therefore, looking for clean and efficient new energy storage and conversion technologies has become a topic of concern [1]. Supercapacitors have been considered as new energy storage devices and have attracted much attention recently due to their higher specific power, good reversibility, fast charge/discharge rate, and long cycle lifetime [2,3]. Currently, the materials used for supercapacitors are mainly carbon-based materials and transition metal oxides [4]. Carbon-based materials have many advantages such as low cost, high surface area and outstanding cycling stability, however, the specific capacitance is generally low [5]. Whereas transition metal oxides have much

higher specific capacitances but suffer from low power density mainly resulted from their intrinsic poor electrical conductivity [6]. In addition to the above-mentioned materials, transition metal nitrides have emerged as alternative electrode materials on account of excellent electrical conductivity, superior chemical stability and ultrahigh cycling stability [7–9]. In fact, several nitrides such as CrN [10], TiN [11], VN [12], MnN [13], etc. have been investigated as electrode materials for supercapacitors. Note that nitrides are typically prepared by high temperature nitridation of corresponding oxides in NH_3 atmosphere. Further, the resulted products are normally in powder form and thus require additional polymer binders or conducting additives during electrode fabrication. These binders and/or additives could block the active sites and create "dead area" [14,15]. Direct deposition of active materials onto conductive substrates is an effective way to overcome the above mentioned drawbacks. We have previously demonstrated that CrN thin films prepared by reactive DC magnetron sputtering are a potential electrode material for supercapacitors yet still suffer from relatively low capacitance (12.8 mF cm^{-2} at 1.0 mA cm^{-2}) [9]. It is noted that the electrochemical reactions only occur on/near the electrode surface, to further improve the supercapacitor performance, it is essential to nanostructure the electrodes [16]. Porous nanostructures generally exhibit good electrochemical performance as the abundant pores can provide more active sites and promote the electrolyte diffusion [17]. Thermal decomposition is an effective way to produce porous structures, but is generally limited to the preparation of metal oxides, while the preparation of porous metal nitrides is less common and more difficult. Here, we suggest that selective chemical etching is an effective way to produce porous metal nitrides. Using CrN as a demonstration, we show that porous CrN thin films can be prepared by selectively etching Cu off CrCuN thin films. The resulted porous CrN thin film electrodes show a high areal specific capacitance of 31.3 mF cm^{-2} at 1.0 mA cm^{-2} in 0.5 M H_2SO_4 electrolyte, which is much higher than that of directly synthesized CrN thin films (12.8 mF cm^{-2}). In addition, the symmetric supercapacitor device based on the porous CrN thin films can deliver a high energy density of 14.4 mWh cm^{-3} at a power density of 0.3 W cm^{-3}, along with outstanding stability. Our work provides a new strategy to produce porous transition metal nitride thin films and further to significantly enhance their electrochemical performance for supercapacitors.

2. Experimental details

2.1. Preparation of the porous CrN thin films

CrCuN thin films were deposited on single polished silicon (100) wafers by reactive magnetron co-sputtering of Cr (99.95% purity) and Cu (99.99% purity) targets in an Ar/N_2 atmosphere (99.999% purity for each gas). During the deposition process, the working pressure was kept at 3.5 pa and the nitrogen flow percentage N_2/(N_2 + Ar) was fixed at 5.1%. The DC power (Advanced Energy, US) applied to the Cr target was maintained at 250 W, while the Cu target RF power (Advanced Energy, US) was set at 150 W. To get porous thin films, the as-prepared CrCuN thin films were etched in concentrated nitric acid solution for 3–4 days to selectively remove Cu. For comparison, CrN thin films were also directly synthesized by reactive magnetron sputtering following our previously reported recipe [9].

2.2. Material characterizations

To investigate the crystal structure and chemical bonding states of the thin films, X-ray diffraction patterns (XRD, Philips X'pert PRO) with Cu K$_\alpha$ radiation and X-ray photoelectron spectroscopy (XPS, PHI-Quantum 2000) with Al K$_\alpha$ radiation were employed. The surface and cross-sectional morphologies were observed by scanning electron microscopy (SEM, ZEISS Sigma). The elemental compositions of the thin films were determined by electron probe microanalysis (EMPA, JEOL

JXA-8100). Root mean square roughness of the thin films was measured by atomic force microscopy (AFM, Agilent 5500), which was operated in tapping mode. The reflective index of the thin films was obtained using an ellipsometer.

2.3. Electrochemical measurements

In order to investigate the electrochemical performance of the thin films, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed. All electrochemical measurements were carried out on a CHI 660E electrochemical workstation in a 0.5 M H_2SO_4 aqueous electrolyte using a conventional three-electrode setup and a two-electrode symmetric supercapacitor configuration. A three-electrode system consists of the thin films as both working electrode (exposed area 1×1 cm^2, mass loading ~ 0.26 mg cm^{-2}) and current collector, an Ag/AgCl as reference electrode, and a Pt wire as counter electrode, respectively. A symmetric supercapacitor device was assembled using a pair of porous CrN thin films and a Celgard 3501 separator.

3. Results and discussion

The synthetic procedures of the porous CrN thin films are shown in Fig. 1a. CrCuN thin films were first prepared by reactive magnetron co-sputtering, which were then treated by concentrated nitric acid solution to produce porous CrN thin films. Details of the preparation and characterization methods are given in the experimental details. The products were first investigated by scanning electron microscopy (SEM). As shown in Fig. 1b and c, the CrCuN thin films show a granular structure with a particle size of ~ 500 nm. After selectively etching, no significant particle size change occurs, and however some pores can be observed (Fig. 1d, inset and Fig. 1e). These additional pores can increase the specific surface area and improve the electronic and ionic transport channels in the aqueous electrolyte [18]. For comparison, we also directly prepared non-porous CrN thin films with same thickness (1.1 μm) by reactive magnetron sputtering. The CrN thin films also exhibit a granular structure but with much smaller particle sizes (Fig. 1f and g).

The products were then characterized by X-ray diffraction patterns (XRD) and X-ray photoelectron spectroscopy (XPS). The XRD pattern (Fig. 2a) of CrCuN shows three diffraction peaks at around 37.6, 43.7, and 63.5°, which can be indexed to the (111), (200), and (220) planes of the fcc CrN (JCPDS No. 76-2494), respectively. The minor variation is due to the existence of copper, as proposed by Öztürk et al. [19]. The introduction of copper causes an increase of compressive stresses in the thin films, resulting in a slight positive peak shift. The composition of CrCuN thin films was determined using electron probe microanalysis (EMPA) and the result shows that the Cu is about 19.36 at.%. After chemical etching, the XRD pattern doesn't show significant difference and can also be indexed to *fcc* CrN, however, the EPMA analysis indicates that Cu is almost completely etched away (0.006 at.%). This result confirms the efficacy of preparing porous CrN thin films by selective chemical etching. Interestingly, the XRD pattern of the directly synthesized CrN only shows one pronounced peak at 43.7°, indicating the relatively poorer crystallinity compared to porous CrN. XPS analysis was then carried out to further investigate the chemical bonding states of these three different thin films. No significant peak shift is detected, which is in concordance with the XRD results. The peak fitting analysis of N1s spectra (Fig. 2b) suggests there are two N species, namely CrN (396.7 eV) and organic or adsorbed N (399.0 eV) [20]. Fig. 2c shows the Cr 2p$_{3/2}$ spectra. A broad peak located at approximately 575.7 eV is observed, which can be assigned to the Cr species in CrN, further verifying the formation of CrN phase [21].

Three-dimensional atomic force microscopy (AFM) analysis was then employed to study the surface topography and roughness of the thin films. As shown in Fig. 3, all thin films are of the island growth type. The AFM analysis results further show that the porous CrN thin