Chapter

CrN Sputtered Thin Films for Supercapacitor Applications

Mohammad Arif, Amit Sanger and Arun Singh

Abstract

The growing demand of energy storage device has attracted significant attention toward transition metal nitrides because of their remarkable mechanical, electronic, and catalytic applications. Here, sputtered chromium nitride thin films deposited on steel substrate have been used as a working electrode for supercapacitor application. The deposited columnar CrN thin films show (111) and (200) planes of cubic phase. The electrochemical properties of CrN working electrode exhibit high specific capacitance of 41.8 F/g at the scan rate of 5 mV/s with excellent capacitance retention up to 2000 cycles. The supercapacitive performance of the CrN films suggests the potential application for supercapacitors.

Keywords: energy storage, supercapacitor, chromium nitride, sputtering

1. Introduction

Increasing impetus for renewable energy has directed the extensive growth of semiconductor technology market during the last decade. Among various energy storage devices, supercapacitor (SC) and lithium-ion battery (LIB) are the most anticipated devices [1]. Comparatively, SCs have better power density, charging/discharging ability, and reversibility to LIBs. Based on the mechanism, SCs are categorized into electrical double-layer capacitors (EDLCs) and pseudocapacitors [2, 3]. Currently, metal oxides are extensively used for SCs because of their high pseudocapacitance. However, these materials suffer low electrical conductivity and fickle stability during long cycles [4].

Therefore, exploring new materials and design for future advancement of the electrochemical properties of supercapacitors is prime requirement. Recently, metal nitrides are found to be prospective contenders for electrochemical applications because of their exceptional thermal and mechanical stability, high melting point, hardness, and excellent electrical conductivity (4000–55,500 S/cm) [5–11]. Among various metal nitrides, cubic CrN films are widely used in optoelectronics and MEMS applications due to its large bandgap [12, 13]. However, electrochemical capabilities of CrN nanostructured films were not emphasized. CrN films can be synthesized by physical vapor deposition methods, chemical vapor deposition, and ammonolysis [14]. Among these, sputtered CrN films are uniform, reproducible, and highly pure.

Herein, sputtered CrN thin films were deposited on steel substrate. The supercapacitive behavior of CrN working electrodes were examined via cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2. Experimental details

In this study, supercapacitor working electrodes were fabricated using 304L stainless steel as current collector (0.5 mm thick, 9 cm^2 area) coated with sputter CrN thin film. Prior to deposition, the steel substrates were polished with SiC abrasive paper and ultrasonically washed with alcohol and acetone, respectively. The thin film deposition was carried out for 60 min by applying 50 W power and 5 mTorr ($Ar:N_2$::1:1) working pressure using Cr target (99.99% pure, Testbourne Ltd., UK), keeping the current collector at 5 cm and 300°C.

The sputtered CrN thin films were characterized via X-ray diffraction (Bruker AXS, D8 advance), FE-SEM (Carl Zeiss, Ultra plus), energy dispersive X-ray analysis (EDAX, Oxford Instruments), Raman spectroscopy (Renishaw, United Kingdom), and X-ray photoelectron spectroscopy (XPS, PerkinElmer model 1257). The supercapacitive behavior of CrN working electrodes was examined via electrochemical workstation (CHI-660D) in a three-electrode cell in 1 M Na_2SO_4 solution.

The specific capacitance (F/g) of working electrode was calculated from the CV curves using Eq. (1), respectively:

$$C_s = \frac{Q}{m \times \Delta V} = \frac{\int_{-V}^{V} I(V)dV}{m \times \Delta V \times v} \quad (1)$$

Where specific capacitance C_s is in F/g, Q is charge in coulomb, m is mass of the active material in gram, v is the scan rate in V/s, and ΔV is the potential window between the positive (V+) and negative (V−) electrodes in volt [3]. The loading mass of active material was around ~12 mg.

3. Results and discussion

As depicted in **Figure 1**, the XRD spectrum of sputtered cubic CrN thin films shows three characteristic peaks at 37.45°, 43.35°, and 63.37 corresponding to (111), (200), and (220) planes (JCPDS file no. 110065) [15]. The working electrode also shows three characteristic peaks at 44.54°, 50.56°, and 73.96° corresponding to (111), (200), and (220) planes of cubic phase of 304 L steel substrate (JCPDS file no. 10752128) [16].

As shown in **Figure 2**, the CrN thin film depicts two Raman active modes centered at 238 cm^{-1} corresponding to vibrations of metal atoms, and 619 cm^{-1} corresponding to vibrations of lighter nonmetal ions [17].

As depicted in **Figure 3**, XPS measurements were carried out to study the chemical structure of CrN film. The XPS spectra of N1 s depict two binding energies peaks at 396.96 and 398.56 eV, corresponding to the CrN and adsorbed nitrogen, respectively (**Figure 3a**). The XPS spectra of $Cr_2p_{3/2}$ depict a peak at 575.76 eV corresponding to CrN (**Figure 3b**), well corroborated with the XRD and Raman results [18].

As depicted in **Figure 4a** and **b**, the FE-SEM images represent columnar porous morphology of CrN working electrode. The EDS spectra represents the stoichiometric chemical composition (1:1) of CrN working electrode.

To compare the CrN film and current collector, the CV curves were measured at a high scan rate of 200 mV/s. The CV curve depicted that CrN film is key contributor in supercapacitive performance as working electrode swept a more area than that of the current collector (**Figure 5a**). The CV plots of working electrode were tested between 0 and 1.2 V range at scan rates 5–200 mV/s in 1 M Na_2SO_4

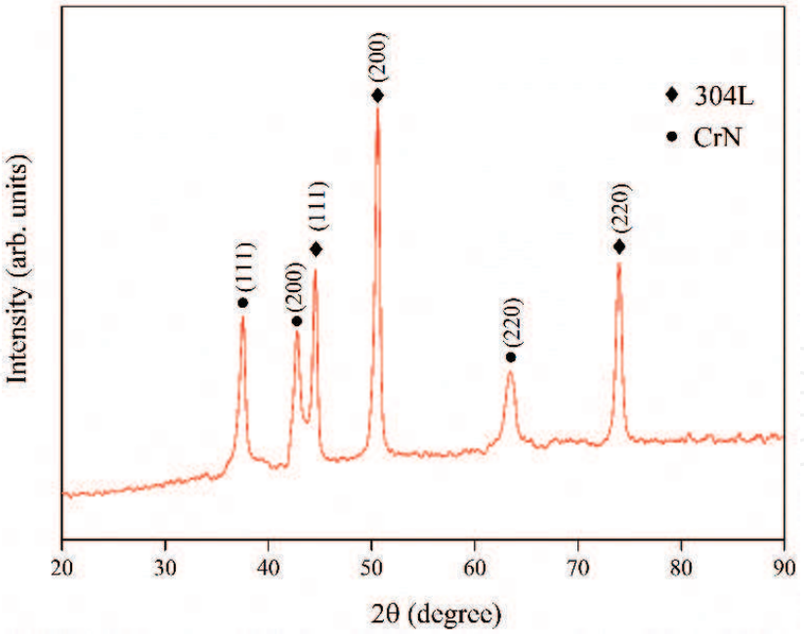

Figure 1.
XRD pattern of CrN working electrode. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23].

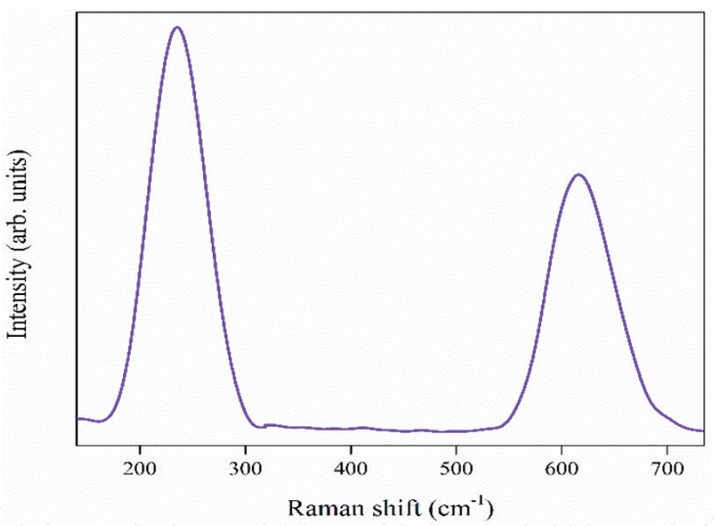

Figure 2.
Raman spectrum of CrN thin film. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23].

solution (**Figure 5b**). The CV curves of working electrode showed the symmetric and reversible plots with good capacitive behavior [19]. The plot between specific capacitance (Cs) versus scan rates is represented in **Figure 5c**, showing 41.66, 31.25, 16.7, 12.5, and 11.2 F/g at the scan rates of 5, 20, 50, 100, and 200 mV/s, respectively, well corroborated with the available literature [18, 20].

Table 1 shows the specific capacitance values of present case along with previously reported literature. As shown in **Figure 5d**, the CrN working electrode demonstrated excellent capacitance retention of 87% after 2000 cycles at a scan rate of 200 mV/s [21]. The reduction in capacitive retention is due to the dissolution of active sites of CrN films.

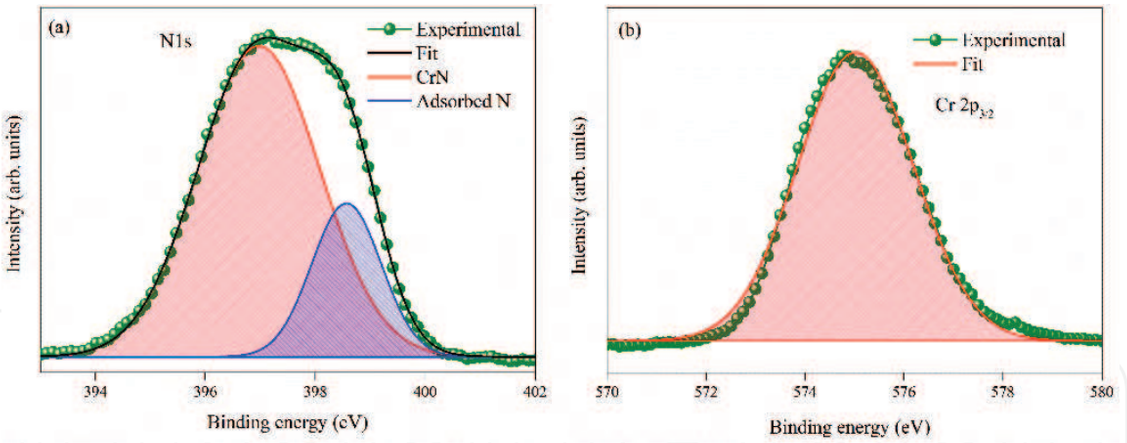

Figure 3.
(a) XPS spectra of N1 s, and (b) XPS spectra of $Cr_2p_{3/2}$. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23].

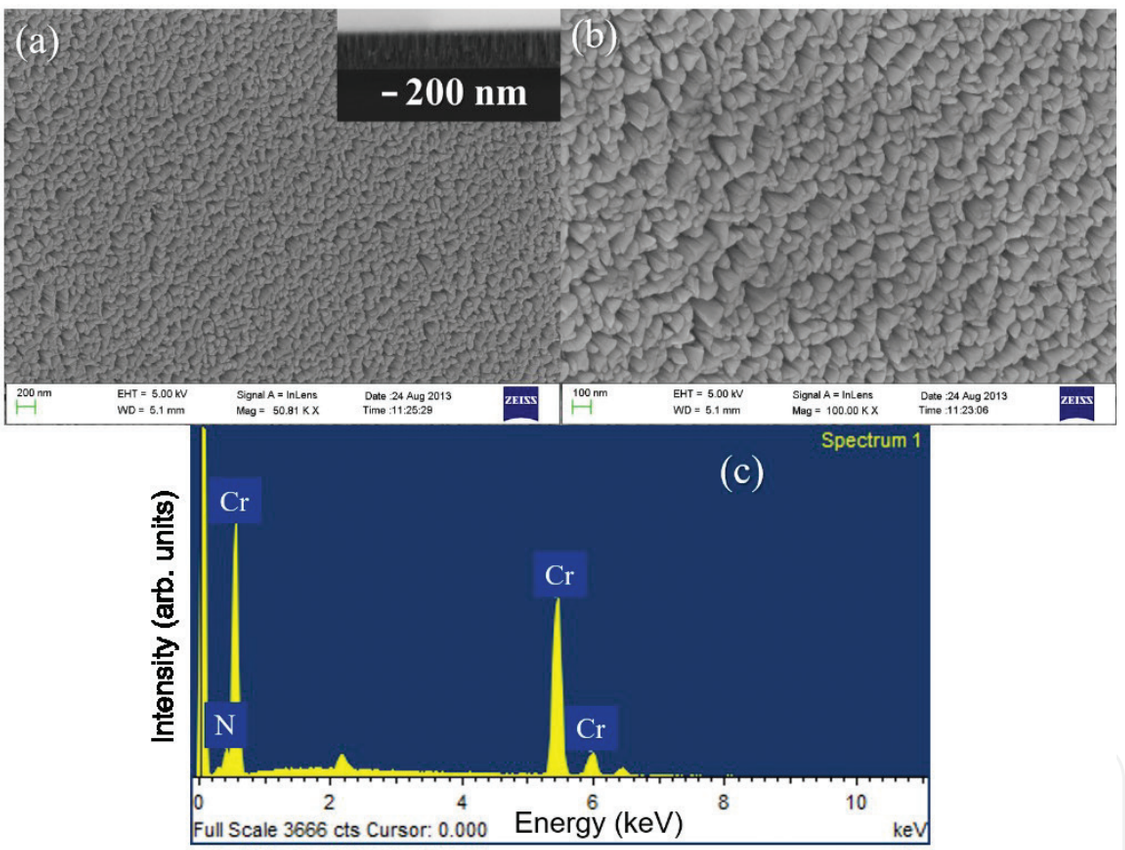

Figure 4.
(a and b) FE-SEM images of CrN thin film at different scales, 200 and 100 nm scales, and (c) EDS spectrum of CrN thin film. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23].

The EIS spectroscopy of CrN working electrode was measured between the frequency range of 0.01 and 100 kHz. As depicted in **Figure 5e**, the Nyquist plot of CrN working electrode showed a straight line in low frequency range, which represents the diffusion of ions at the electrode-electrolyte interface [22]. The Nyquist plot of CrN working electrodes showed a semicircle in high frequency range, which represents the electronic resistance and contact resistance between active material and current collector (inset of **Figure 5e**). The equivalent circuit model of working electrode is shown in **Figure 5f**. From the EIS circuit model, the electrolyte resistance (R_s) was found to be 1.77 Ω, corresponding to good ionic conductivity of the

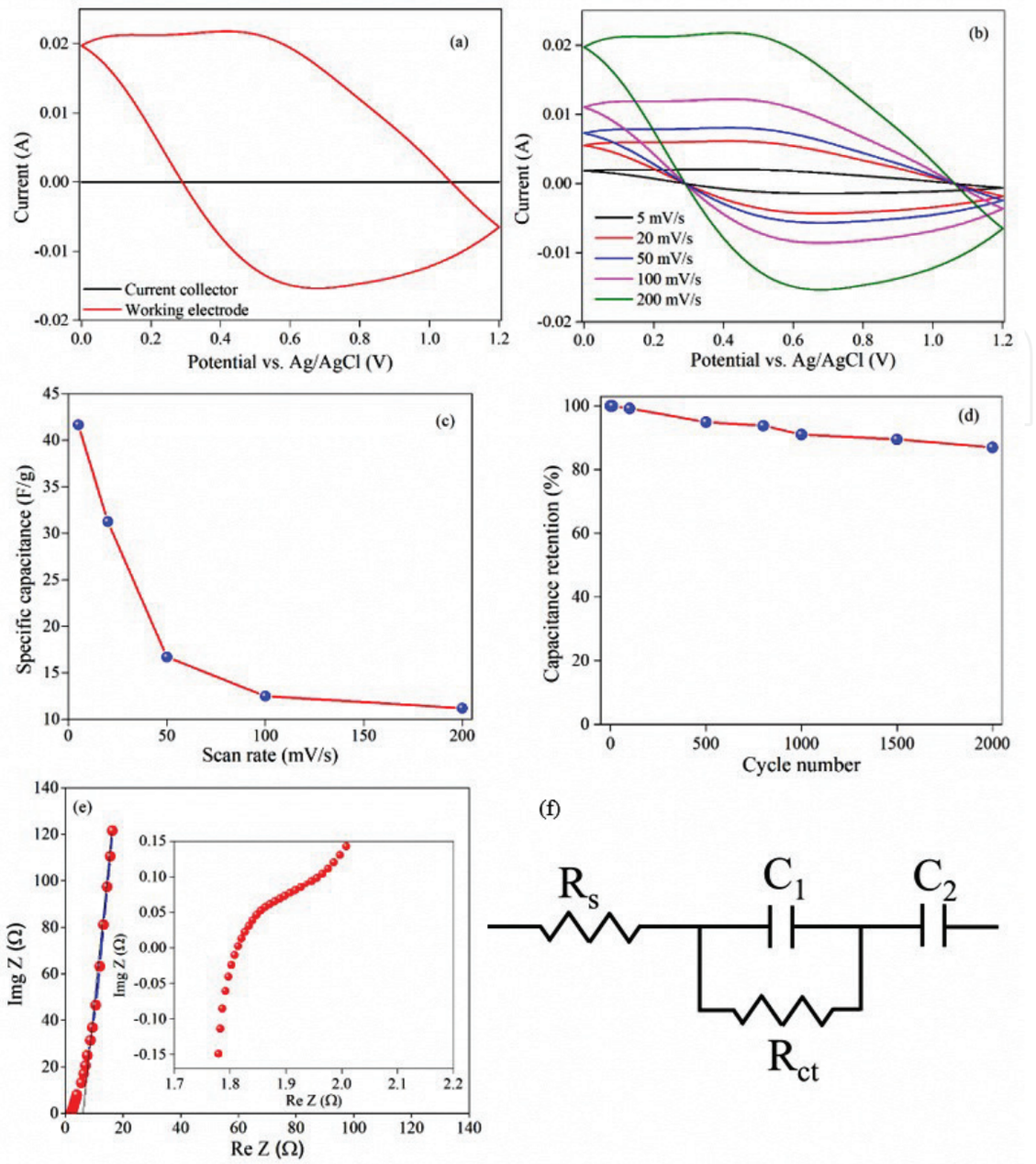

Figure 5.
(a) CV curve of CrN working electrode and steel current collector at 200 mV/s, (b) CV curve of CrN working electrode at different scan rates, (c) specific capacitance vs. scan rate graph, (d) capacitive retention curve of CrN thin film working electrode, (e) Nyquist plot (inset shows the enlarged Nyquist plot at the high frequency region), and (f) corresponding equivalent circuit model. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23.]

Sample	Method	Electrolyte specific	Capacitance	References
CrN thin film	Sputtering	0.5 M H_2SO_4	12.8 mF/cm^2 at 1 mA/cm^2	[17]
CrN/activated carbon nanoparticles	Chemical method	1 M $LiPF_6$	50 F/g at 1 mV/s	[19]
CrN thin films	Sputtering	1 M Na_2SO_4	41.6 F/g at 5 mV/s	This work

Table 1.
Comparison of the specific capacitance of chromium nitride-based supercapacitor electrodes reported in the literature. (Adapted from Mohd. Arif et al., with permission from Elsevier. Copyright 2018) [23].

electrolyte. The charge transfer resistance (R_{ct}) was found to be 6.15 Ω, owing to the contact between CrN film and steel substrate.

4. Conclusion

In summary, the supercapacitive behavior of sputter-deposited columnar-type cubic CrN-coated working electrode was tested. The CrN working electrode shows high specific capacitance of 41.6 F/g in 1 M Na_2SO_4 at the scan rate of 5 mV/s with the excellent capacitance retention (87% after 2000 cycles). These good electrochemical properties demonstrated that the CrN-based supercapacitor electrode has excellent potential in supercapacitor applications.

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Conflict of interest

The authors declare no conflict of interest.

Author details

Mohammad Arif[1], Amit Sanger[2] and Arun Singh[1*]

1 Advanced Electronic and Nanomaterials Laboratory, Department of Physics, Jamia Millia Islamia, New Delhi, India

2 Department of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), KIST-UNIST Ulsan Center for Convergent Materials (KUUC), Ulsan, Republic of Korea

*Address all correspondence to: arunsingh07@gmail.com

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