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Letter to the Editor

Forming-free resistive switching in a nanoporous nitrogen-doped carbon thin film with ready-made metal nanofilaments

Hao Chen [a,b], *Fei Zhuge* [b,*], *Bing Fu* [b], *Jun Li* [b], *Jun Wang* [c], *Weigao Wang* [c], *Qin Wang* [c], *Le Li* [c], *Fagen Li* [c], *Haolei Zhang* [b], *Lingyan Liang* [b], *Hao Luo* [b], *Mei Wang* [b], *Junhua Gao* [b], *Hongtao Cao* [b], *Hong Zhang* [a], *Zhicheng Li* [a,*]

[a] *School of Materials Science and Engineering, Central South University, Changsha 410083, PR China*
[b] *Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China*
[c] *Department of Physics, Ningbo University, Ningbo 315211, PR China*

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ABSTRACT

An amorphous carbon thin film, with through-pores of several tens of nanometers in size, has been synthesized by annealing magnetron sputtered nitrogen-doped carbon thin films at elevated temperature in an inert atmosphere. Based on this nanoporous carbon film, we first report forming-free resistive switching in a two terminal device containing ready-made metal nanofilaments. Such nanoporous carbon-based resistance memory device shows low operation voltages and good endurance and retention performance.

Resistive switching (RS) attributed to the formation/rupture of nanoscale metal (Cu, Ag, Au, or Ti) filaments has been reported in sputtered copper-doped carbon films [1–3], ion beam deposited hydrogenated carbon films [4], electron beam evaporated carbon films [5], and pulsed laser deposited nitrogen-doped diamond-like carbon films [6]. In these cases, an electrically [1–6] or thermally [7] induced metal filament formation process was necessary since no ready-made metal filaments existed in the pristine carbon films. Herein, we report forming-free RS phenomena in a nanoporous nitrogen-doped carbon thin film containing ready-made metal nanofilaments. The porous films have been synthesized by annealing magnetron sputtered N-doped carbon thin films at elevated temperature in an inert atmosphere.

Deposition of amorphous nitrogen-doped carbon thin films on commercial Pt/Ti/SiO_2/Si substrates was carried out by DC magnetron sputtering at room temperature (RT) in pure nitrogen. A high-purity pyrolytic graphite disc was used as the target. The composition of as-sputtered films was determined to be $CN_{0.25}$ by X-ray photoelectron spectroscopy (XPS). The atomic oxygen concentration was ~5 at.%. As-sputtered films were annealed at 600 °C in Ar ambient for 10 min. The annealed carbon films were still amorphous as determined by X-ray diffraction. The composition of annealed films was $CN_{0.15}$ with a very small amount of oxygen (~1 at.%). The thickness of as-sputtered ($CN_{0.25}$) and annealed ($CN_{0.15}$) carbon films was estimated to be ~60 and ~25 nm from the corresponding cross-sectional transmission electron

* *Corresponding authors.*
E-mail addresses: zhugefei@nimte.ac.cn (F. Zhuge), zhchli@csu.edu.cn (Z. Li).
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microscopy (TEM) images, as shown in Figs. S1a and b, respectively. The N 1s XPS spectra for $CN_{0.25}$ and $CN_{0.15}$ are shown in Figs. S2a and b, respectively. Both N 1s spectra can be deconvoluted into two distinct peaks at 398.6 and 400.2 eV. The peak at 398.6 eV can be assigned to N bonded to sp^3 coordinated C while the other peak at 400.2 eV can be assigned to N bonded to sp^2 coordinated C [8–10]. The N=Csp^2 bonds were found to be less stable than the N–Csp^3 bonds upon annealing [8,10]. In addition, a three-peak deconvolution of C 1s XPS spectra for $CN_{0.25}$ and $CN_{0.15}$ is shown in Figs. S2c and d. The peak at 284.4 eV corresponds to graphitic-like carbon while the peaks centred at 285.6 and 287.6 eV correspond to sp^2C=N and sp^3C–N bonds, respectively [8–10].

Atomic force microscopy (AFM) characterization was conducted to study the surface topography of as-sputtered and annealed carbon films. Fig. 1a and b shows the AFM images of $CN_{0.25}$ and $CN_{0.15}$, respectively. We see that the as-sputtered film has a smooth and dense surface without any pinhole whereas the annealed one contains numerous pores of several tens of nanometers in size. Further investigation on geometrical features of the nanopores in $CN_{0.15}$ films was provided by cross-sectional TEM (see Fig. 1c and d). The TEM specimen was prepared by focused ion beam (FIB) system using a finely focused beam of gallium ions. Protective layer of Pt was locally deposited on the $CN_{0.15}$ film to prevent beam-induced damage. More importantly, platinum, acting as the pore filler, could facilitate the TEM observation of nanopores. From the figure we can clearly observe an asymmetric through-pore filled with Pt with wider and narrower diameters of several tens of nanometers and several nanometers, respectively. We therefore conclude that numerous asymmetric nanosized through-pores were formed in annealed N-doped carbon thin films. For N-doped carbon films, it has been reported that a loss of N content accompanied by a film thickness reduction occurs as annealing at elevated temperatures due to the formation of volatile products such as N_2 and C_2N_2 [8–11]. Then, we can reasonably deduce that the formation of such volatile products also accounts for the growth of asymmetric through-nanopores.

In order to measure the electrical properties of $CN_{0.25}$ and $CN_{0.15}$ films, 50 nm thick Cu top electrodes of 100 μm in diameter were deposited at RT by electron-beam evaporation. To prevent Cu from oxidizing, ~20 nm thick Au protection layers were also deposited on the Cu electrodes. *I–V* characteristics of Cu/CN_x/Pt ($x = 0.25$ or 0.15) structures were measured at RT in air using a Keithley 4200 semiconductor parameter analyzer. The device structures are schematically illustrated in Fig. 2a and d. Fig. 2b and c plot the *I–V* curves of Cu/$CN_{0.25}$/Pt in linear and semilogarithmic scale, respectively. The *I–V* curves show typical bipolar RS characteristics. Based on our

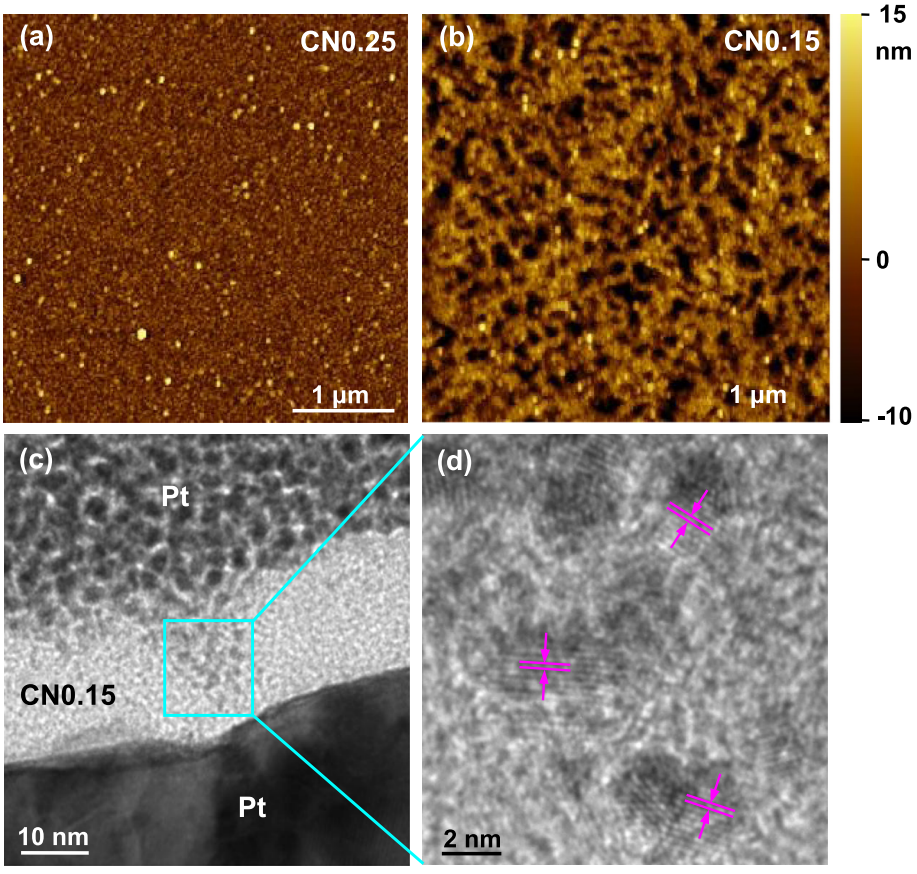

Fig. 1 – AFM images of (a) as-sputtered and (b) annealed nitrogen-doped carbon thin films. (c) Cross-sectional TEM image of the $CN_{0.15}$ thin film. The specimen was prepared by an FIB system. Protective layer of Pt was locally deposited on the film to prevent beam-induced damage. More importantly, Pt acts as the pore filler facilitating the observation of nanopores. A through-pore can be clearly observed. (d) High resolution TEM image for the area marked by the light blue rectangle. The lattice distance is 2.3 Å corresponding to the Pt (111) plane. (A colour version of this figure can be viewed online.)

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