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Tungsten oxide nanowires locally grown on suspended carbon fibers

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One of the most studied metal oxide materials is tungsten oxide (WOX), numerous works have reported the use of this material for gas sensing applications [1] and also for fabrication of different useful devices e.g. display panels, smart windows and mirrors and many others [2]. This material has been synthesized by diverse methods such as thermal evaporation, sputtering, chemical vapor deposition (CVD), among others [3].

CVD is a technique in which a solid is volatilized in the presence of a transport agent and deposited on a substrate in the form of crystals, in this case the solid and the transport agent are a gas. The reactant and transport agent are placed at different temperature zone in the carbon fiber. In this approach, the morphology and density of the crystals are affected by growth temperature, transport direction, seed layer, gas flow rate and free energy of the reaction. In this case the growth was in one direction and is for this the WO3 growth in nanowires.

Nanowires sensors possess many advantages, but one of the main challenges for their implementation into functional devices is the challenge of how to integrate them to macroscopic elements in our system. Most frequently, the synthesis of NWs results in randomly oriented wires in a substrate, over which the connecting structures are fabricated by means of electron beam lithography, which is an expensive and specialized process. A different approach to integrate NWs is to grow them directly onto a supporting structure. For example, WOX-NWs have been directly grown on carbon paper [4] or directly electrospun into the connecting electrodes [5].

In this work, towards the development of CVD technique on suspended CNFs, the deposition process of tungsten oxide is optimized to increase the surface area by growing WOX-NWs directly on the surface of the carbon fiber.

1. Materials and methods

1.1. Carbon device fabrication

Supporting negative photoresist SU-8 2025 (MicroChem Inc., Westborough, MA, USA) structure is photolithographically defined. Second, the SU-8 2025 is deposited using the near-field electrospinning technique, to allow for the control necessary to deposit a single fiber at a precise location. Finally, the complete structure is pyrolyzed at a temperature of 900°C in an inert N2 environment. The result is a monolithic carbon structure were a suspended glassy carbon fiber is suspended over two carbon walls.

1.2. Chemical vapor deposition of tungsten oxide nanowires

The deposition conditions were controlled by placing the samples in a 3 L custom-made chamber connected to a Pfeiffer HiPace 80 vacuum turbopump (Pfeiffer Vacuum, Asslar, Germany), with the vacuum set at 1.6x10-2 torr. The precursor tungsten hexacarbonyl [W(CO)6] (Sigma-Aldrich) was placed on a pre-chamber, also at 1.6x10-2 torr, and heated to a temperature of 95 °C in order to vaporize it. The gas precursor was then let into the main chamber through a valve. Electrical feed-through connections were used to connect the carbon fiber to the voltage supply in order heat it up

2. Results and discussion

2.1. Tungsten oxide nanowires growth on CNFs

Once placed in the chamber under a vacuum of 1.6x10-2 torr, the deposition process consisted of electrically stimulating the CNF in order to take it to the temperature required for WOX-NW formation on it. Since at the moment the local measurement of the temperature at the CNF was not possible, the deposition was monitored by observing the changes in the electrical resistance on the CNF. As found in reference [6], the onset of WOX deposition can be observed as decrease on the resistance of the CNF, resulting in solid layer on the fiber, indicating that the rate of growth parallel to the fiber outpaced the rate of perpendicular growth of the WOX layer [7]. The protocol followed consisted on a controlled electrical stimulation of the carbon nanofiber and monitoring of the electrical resistance changes as described in reference [8]. In figures 1A and 1B SEM micrographs of the CNF before and after WOX NWs growth are shown. Furthermore, by careful control of the applied voltage, different morphologies of tungsten oxide layers were deposited over the CNF as shown in 1B, 1C and 1D.

The EDS (Fig. 2) results confirmed the presence of respective constituent elements in WOxNWs and the silicon detected came from of the substrate.

In this work, we demonstrated the deposition of tungsten oxide nanowires over a single suspended CNFs with potential application to low-power, fast response, gas sensors.

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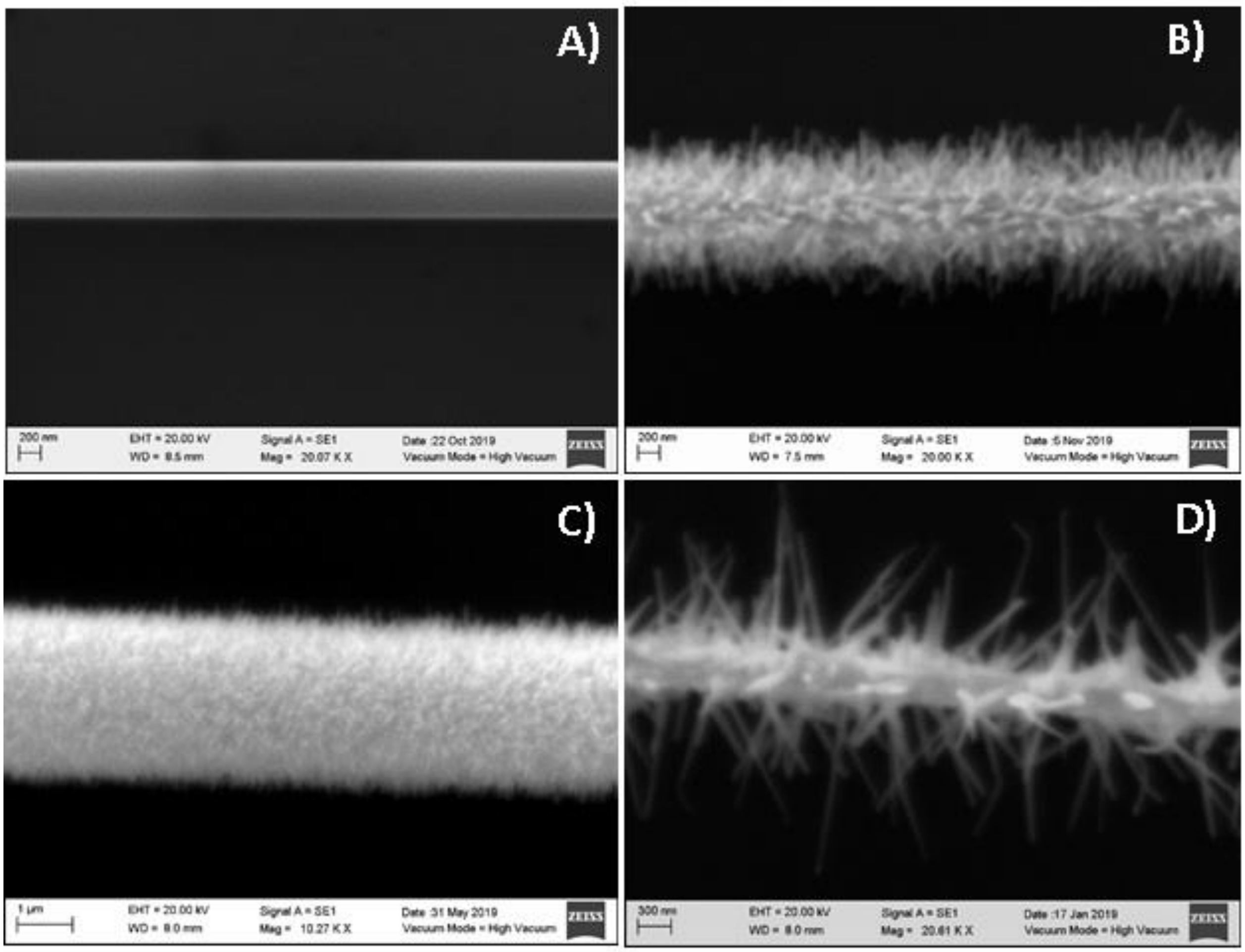

Figure 1. Figure 1. SEM micrographs of different deposition morphologies: A) CNF of 560 nm in diameter previous to the deposition process. B) WOX NWs grown on the CNF. C) short tungsten oxide nanowires. D) long tungsten oxide nanowires.

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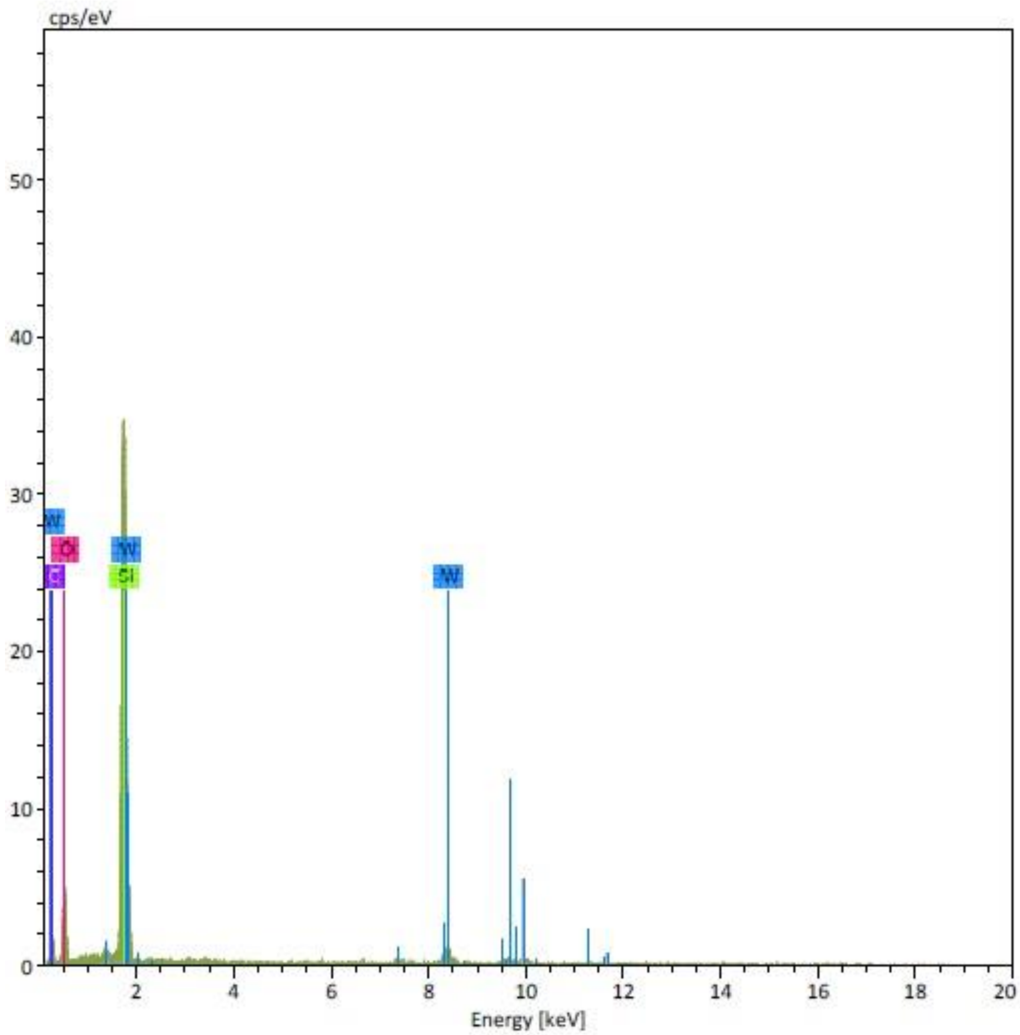

Figure 2. Figure 2. EDS spectrum of the WOxNWs

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