# RAPID COMMUNICATIONS

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## Restructuring tungsten thin films into nanowires and hollow square cross-section microducts

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We report on the growth of nanowires and unusual hollow microducts of tungsten oxide by thermal treatment of tungsten films in a radio frequency $H_2$/Ar plasma at temperatures between 550 and 620 °C. Nanowires with diameters of 10–30 nm and lengths between 50 and 300 nm were formed directly from the tungsten film, while under certain specific operating conditions hollow microducts having edge lengths ~0.5 μm and lengths between 10 and 200 μm were observed. Presence of a reducing gas such as $H_2$ was crucial in growing these nanostructures as were trace quantities of oxygen, which was necessary to form a volatile tungsten species. Preferential restructuring of the film surface into nanowires or microducts appeared to be influenced significantly by the rate of mass transfer of gas-phase species to the surface. Nanowires were also observed to grow on tungsten wires under similar conditions. A surface containing nanowires, annealed at 500 °C in air, exhibited the capability of sensing trace quantities of nitrous oxides ($NO_x$).

Growth of nanostructures, such as nanowires,[1,2] nanotubes,[3,4] nanobelts,[5] etc., has attracted tremendous research interest recently. Due to their nearly one-dimensional structure, they possess unique electrical, thermal, optical, and mechanical properties, which may be exploited in a variety of applications. Advances in the growth of such high aspect ratio structures have been hampered by difficulties in growing them with controllable dimensions, morphology, and phase purity. The most common techniques to fabricate these nanostructures include e-beam lithography,[6] solution-phase synthesis,[7] vapor phase evaporation/condensation,[8] and template-directed synthesis.[9,10] In the case of nanowires, transition metals like tungsten find applications in electronic devices, sensors, and magnetic recording devices.[11,12]

Very recently, Lee et al.[13] reported the growth of tungsten nanowires of less than 100 nm in diameter and about 1 μm in length by thermal treatment of tungsten films in the presence of $H_2$, and demonstrated excellent field-emission properties. Gu et al.[14] grew tungsten oxide nanowires on metal tungsten tips (prepared by electrochemical etching of tungsten wires) heated in argon. They observed tungsten oxide nanowires between 10 and 30 nm in diameter and about 300 nm in length. Well-aligned nanowire arrays of molybdenum oxide were grown through thermal evaporation at 1100 °C by Zhou et al.[15] and subsequently reduced to molybdenum nanowires under a heated $H_2$ atmosphere. Using a similar approach, Liu et al.[16] synthesized large-scale arrays of aligned tungsten oxide nanorods by heating a spiral tungsten coil to ~1000 °C. Vaddiraju et al.[17] also demonstrated vapor-phase synthesis of tungsten and tungsten oxide nanowires in a hot-filament CVD reactor, at temperatures above the decomposition temperature of tungsten oxide (~1450 °C). Apart from nanowires, other nanostructures such as whiskers and hollow fibers of tungsten oxide have been studied in the past.[18–21] More recently, Li et al.[22] grew $W_{18}O_{49}$ nanotubes and nanowires by infrared irradiation on W foils under different vacuum conditions.

In this work, we show how a radio frequency (RF) $H_2$/Ar plasma can be used to substantially reduce the processing temperature required to restructure tungsten

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thin films into tungsten oxide nanowires. We also show a mode that we observe in regions of restricted gas-phase mass transfer in which the tungsten film is converted into novel hollow microducts of square cross-section. These microducts can be quite long (10–200 μm) with edge lengths of 0.5 μm. We also discuss the difference in growth mechanisms between nanowires and microducts, the former occurring by nucleation from the vapor phase and the latter involving surface restructuring of the thin film, and growth in regions of restricted gas-phase mass transfer. Finally, we present the gas-sensing capabilities of the nanowires annealed in air.

Tungsten films of 300–350 nm were deposited on a flat, polished substrate (1 cm × 1 cm) of sapphire by DC-magnetron sputtering from a high-purity tungsten (99.99% pure) target with pure argon (99.9995% pure) as the sputtering gas. The substrate was then secured to a heater-plate assembly using a ceramic clip and transferred (in air) to a low-pressure CVD chamber where argon and $H_2$ were metered with mass flow controllers, and chamber pressure maintained at 5 Torr during growth using a rotary mechanical rough pump. Ar flow rate was kept constant at 300 sccm for all experiments. The substrate temperature was then increased to 500–700 °C and monitored using a thermocouple in contact with the substrate. An RF plasma was easily generated within the chamber by winding a copper coil around the 7.5-cm cylindrical quartz chamber, and the plasma power (20 W) was controlled using a matching network. Growth times were typically 10 min, after which time the heater was turned off and the substrate was cooled to room temperature, while the chamber was continuously purged with Ar and $H_2$. The morphologies of all films were observed using a Hitachi S-4000 field emission scanning electron microscope (SEM).

Initially, experiments were conducted in the absence of the RF plasma. Heating the film in pure Ar to 750–800 °C without any $H_2$ resulted in the restructuring of the smooth tungsten surface into a grainy, nodular one [Fig. 1(a)]. However, when $H_2$ was introduced (30 sccm) along with Ar at these temperatures, nanowires appeared on the surface, similar to those observed by Lee et al.[13] With an RF plasma, it was found that a lower substrate temperature and a lower concentration of $H_2$ also produced nanowires. Fig. 1(b) shows the result of heating a tungsten film to ~550 °C with a reduced $H_2$ flow rate of 5 sccm for 10 min. A uniformly dense network of nanowires were observed to have grown with diameters between 10 and 30 nm and lengths between 0.5 and 1 μm. Increasing the substrate temperature to 600 °C [Fig. 1(c)], produced several larger tungsten crystallite structures in addition to nanowires. However, above ~620 °C, no evidence of wires could be found; rather, the

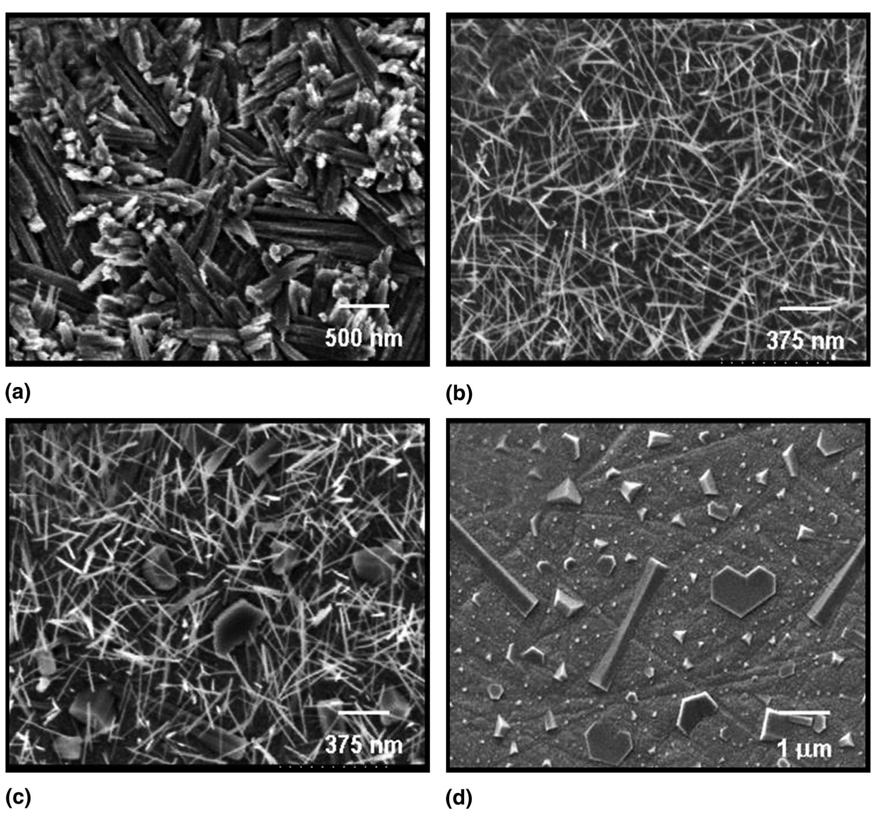



FIG. 1. Micrographs of tungsten film surface: (a) heated in the absence of $H_2$; (b) nanowires; (c) nanowires and crystallite structures; (d) crystallite structures and solid square nanorods.

films consisted of large crystallite structures of various shapes as well as solid square nanorods [Fig. 1(d)].

A significant finding was that, for samples that were heated to temperatures between 550 and 620 °C, several unusual hollow microstructures with a square cross-section (henceforth referred to as "microduct") had grown in the region of the substrate underneath the ceramic clip that was securing the sample. These microducts had average edge lengths of ~0.5 μm, wall thickness of about 20–30 nm, and lengths ranging from tens to a few hundreds of micrometers. The SEM images of the microducts are presented in Fig. 2. To test the generality of the process, we heated a 0.005-inch diameter tungsten wire (Alfa Aesar, Ward Hill, MA), as well as a tungsten coated TEM grid (200 mesh, Pacific Grid Tech, Sugar Land, TX) to 700 °C in Ar/$H_2$ within the chamber, and observed that nanowires grew over the entire surface of both the wire, and the TEM grid (Fig. 3).

Nanowires grown on the tungsten TEM grid were analyzed by transmission electron microscopy (TEM) to obtain phase information and growth direction. A TEM image of a nanowire and electron-diffraction patterns obtained from two different nanowires are shown in Fig. 4.

Upon inspecting several different nanowires, two different electron-diffraction patterns were observed [Figs. 4(b) and 4(c)]. The d-spacings of approximately 0.38 and 1.75 nm corresponded most closely to the d-spacings of $W_{18}O_{49}$. The streaked pattern obtained from some other nanowires, indicates the presence of disordered intergrowths, which may be due to varying oxygen stoichiometry within different nanowires.

Because no catalyst material was present to initiate the growth of nanowires, the VLS (vapor–liquid–solid) growth mechanism does not apply here. Growth of nanowires may be explained based on a modified versus (vapor–solid) mechanism, where the tungsten film deposited on the substrate acts as a self-catalytic layer. When the film is heated to 550 °C in a low-pressure plasma (~5 Torr), the volatile surface oxide evaporates. This vapor-phase oxide should be reduced in the $H_2$ plasma to a lower tungsten oxide, which then condenses again back on the film surface as a nanowire. The vapor-phase mechanism was confirmed, as nanowires were also seen to form on a pristine silicon wafer placed just above the heated tungsten sample. This mechanism implied that a source of oxygen (background from the rough vacuum-pumped chamber) played a necessary role in constantly oxidizing the tungsten film, thus creating a volatile tungsten-containing species. To test this hypothesis, we conducted experiments in a high-vacuum chamber. A tungsten sample heated to about 700 °C in pure $H_2$ and Ar failed to produce any nanowires. However, when a trace amount of air or oxygen (1–2 vol%) was bled into the system, nanowires appeared.

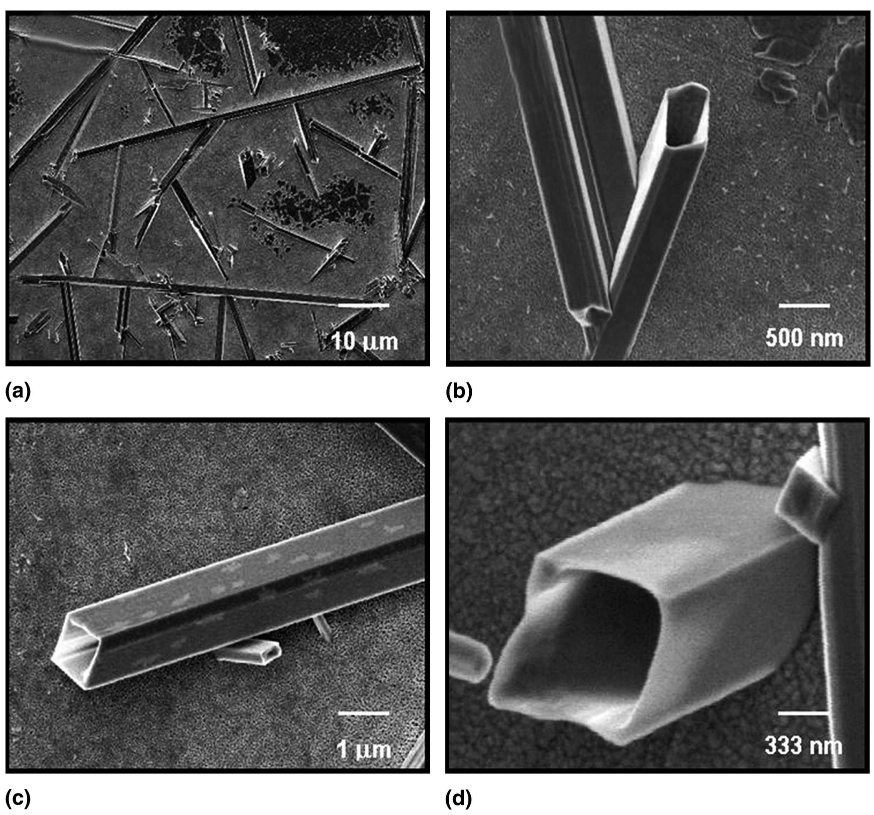



FIG. 2. Micrographs of hollow microducts grown from the tungsten film, at different magnifications.

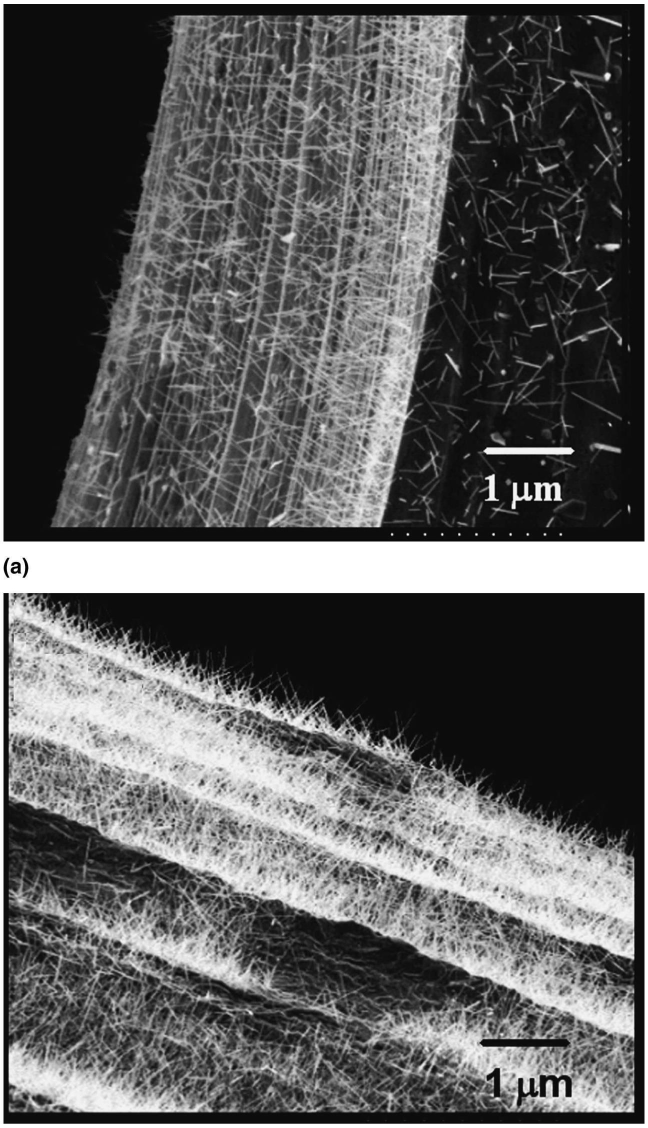



FIG. 3. Micrograph of nanowires grown on (a) a commercial tungsten TEM grid and (b) a commercial tungsten wire.

We believe that gas-phase mass-transfer rate of the reducing agent may play a pivotal role in determining whether growth of nanowires or microducts is preferred, since the latter grew only in specific regions underneath the clip. To test this hypothesis, we placed a ceramic substrate at a slight angle to the heated tungsten substrate as schematically illustrated in Fig. 5. The purpose was to impose a mass-transfer resistance of varying degree to the substrate and observe the resulting morphologies at different points along the length of the substrate. We discovered that the tungsten oxide nanowires grew over most of the sample, but with a higher density in the regions farthest from the contact point between the two substrates (Fig. 5, Region 1). Microducts and tungsten oxide crystallite structures were observed to grow

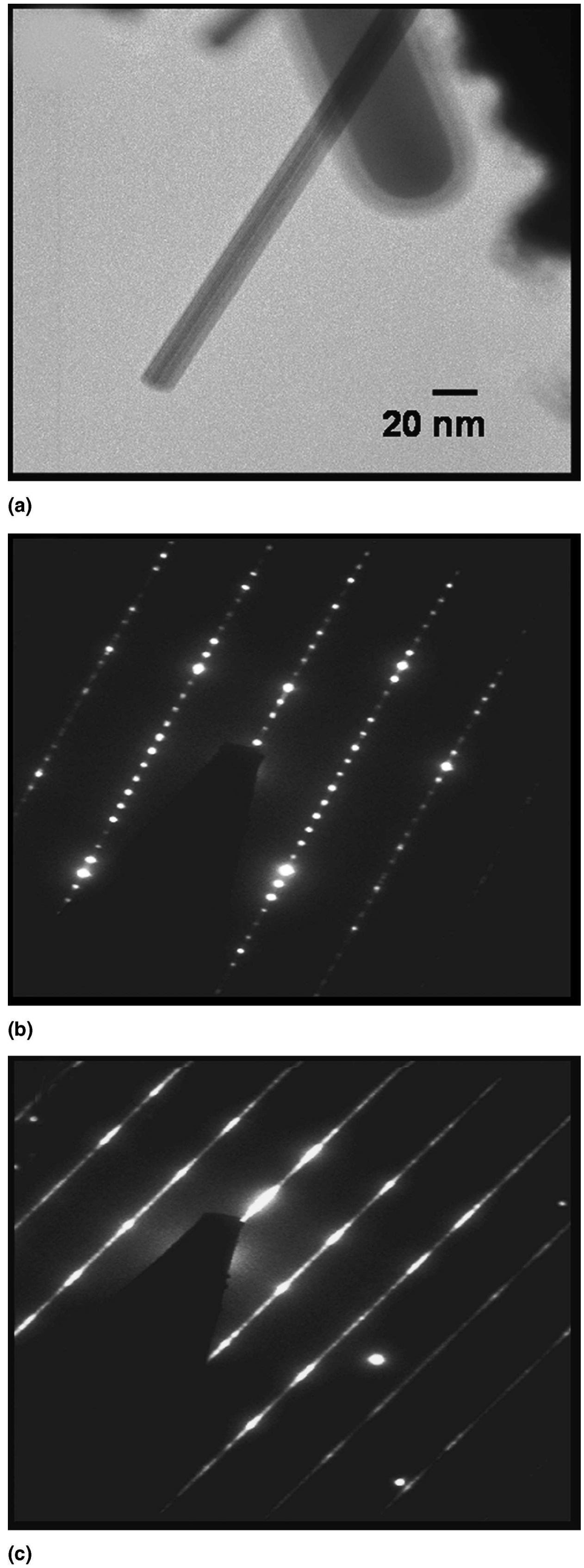



FIG. 4. (a) TEM image of a nanowire; (b, c) electron-diffraction patterns obtained from two different nanowires.

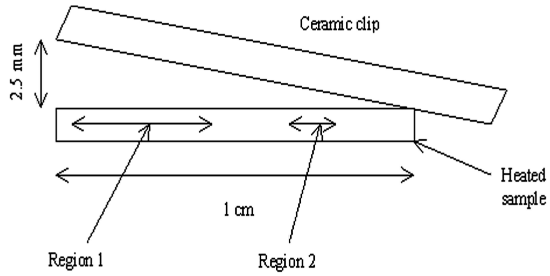


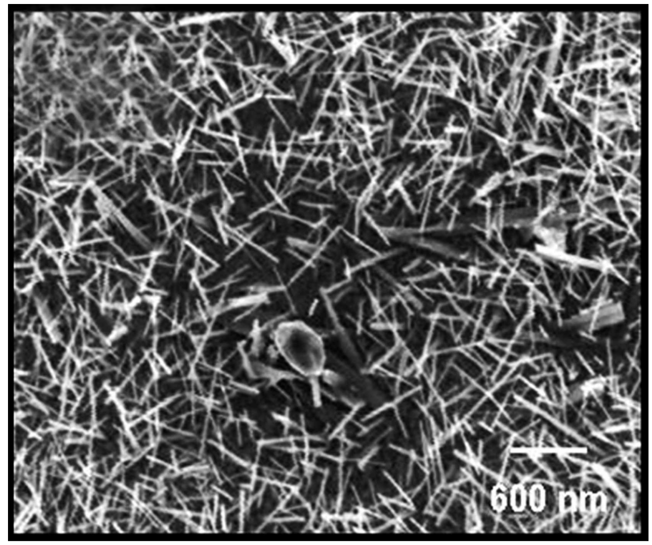

FIG. 5. Schematic of sample-clip assembly; Region 1 is covered with nanowires, while Region 2 contains microducts in addition to crystallite structures.

exclusively in the region where the gap between the substrate and sample was narrow (Fig. 5, Region 2). The appearance of nanowires with varying oxygen levels may also be explained through such an argument.

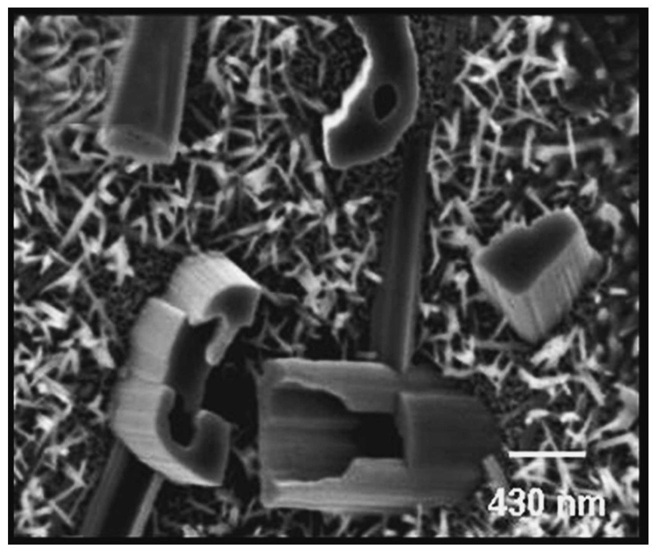
Mayers and Xia[23] recently reported on the growth of hollow nanotubes as well as solid nanorods of tellurium through a solution-phase approach. They observed that varying the mass-transfer rate of tellurium to the seed surface could control the type of nanostructure grown, a lower tellurium concentration resulting in the hollow nanotubes while a higher concentration resulted in solid nanorods. We believe that the hollow microducts of tungsten oxide grew only in regions on the substrate that offered maximum resistance to gas-phase mass transfer of $H_2$, which in turn influenced the rate of addition of tungsten oxide to the surface. At temperatures greater than 620 °C, the production rate of tungsten oxide atoms is enhanced, allowing uniform addition of tungsten oxide over the entire surface and resulting in solid nanorods and other stable crystallite structures.

To verify the role of $H_2$ as reducing agent rather than as an agent for creation of a $WH_x$ species, we replaced the $H_2$ with carbon monoxide (CO), and heated the sample to 550 °C in the RF plasma. The results were quite definitive in showing that $H_2$ was not necessary for the growth of nanowires as long as another reducing agent was present [Fig. 6(a)]. However, instead of hollow microducts with regular square cross-section, we observed several hollow nanostructures of irregular shapes [Fig. 6(b)]. This difference in nanostructures resulting from a different reducing agent may be due to the weaker reducing effect of CO in comparison to $H_2$ in addition to dissimilar mass-transfer rates.

We have done some preliminary tests on the application of these nanowires as gas sensors. Gas-sensing properties of $WO_3$ nanoparticle films have been studied in the recent past, showing excellent sensitivity to $H_2S$ gas and selectivity to other gases.[24] In our experiment, nanowires were grown on a microhotplate,[25,26] annealed in air at 500 °C for 30 min—which may completely oxidize them into $WO_3$—and then exposed to the test gas (20 ppm of $NO_2$/NO in air). In comparison with the sensor responses from a bare tungsten-coated surface annealed under similar conditions for the same length of time, the nanowire-coated surface was found to be much more sensitive to such low concentrations of $NO_x$ (Fig. 7), and the measurements could be repeated.




(a)




(b)

FIG. 6. Micrographs of tungsten film surface on heating in CO: (a) nanowires; (b) hollow nanostructures of irregular shapes.

In summary, we have developed a method of restructuring tungsten substrates into tungsten oxide nanowires and hollow microducts by simple thermal treatment in RF plasma at temperatures in the range of 550–620 °C, in the presence of a reducing gas like $H_2$ or CO. The nanowires have diameters between 10 and 30 nm and lengths up to 500 nm, while the microducts have square edge lengths of approximately 0.5 μm and lengths up to a few hundred micrometers. It is worth pointing out that the growth temperature of tungsten oxide nanowires in

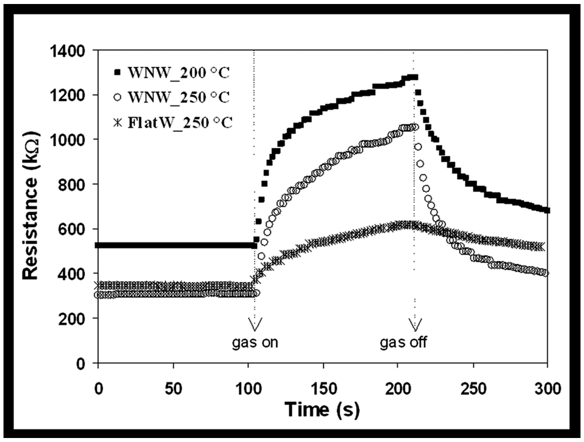



FIG. 7. Gas-sensor response curves from an annealed nanowire-coated surface and an annealed flat tungsten thin film surface, both exposed to 20 ppm of test gas $NO_2$/NO.

our work is significantly lower (by about 250 °C) than previous methods. A trace amount of background oxygen is essential for growth of these nanostructures, which can be grown preferentially by controlling the mass-transfer rate of gas-phase species to various regions on the substrate. Nanowires were also grown on commercial tungsten wires and tungsten-coated TEM grids, indicating the generality of the process. Apart from field emission sources,[13] these nanowires could be used as tips for STM and AFM. In addition, nanowires annealed in air are capable of sensing low concentrations of $NO_x$. The hollow microducts could find applications as building blocks for many functional devices like microbatteries, as microfluidic channels, and in microencapsulation for drug delivery.[23]

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