W$_{18}$O$_{49}$ Nanowires as Ultraviolet Photodetector

Feng Yang · Kai Huang · Shibing Ni · Qi Wang · Deyan He

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Abstract Photodetectors in a configuration of field effect transistor were fabricated based on individual W$_{18}$O$_{49}$ nanowires. Evaluation of electrical transport behavior indicates that the W$_{18}$O$_{49}$ nanowires are n-type semiconductors. The photodetectors show high sensitivity, stability and reversibility to ultraviolet (UV) light. A high photoconductive gain of $10^4$ was obtained, and the photoconductivity is up to 60 nS upon exposure to 312 nm UV light with an intensity of 1.6 mW/cm$^2$. Absorption of oxygen on the surface of W$_{18}$O$_{49}$ nanowires has a significant influence on the dark conductivity, and the ambient gas can remarkably change the conductivity of W$_{18}$O$_{49}$ nanowire. The results imply that W$_{18}$O$_{49}$ nanowires will be promising candidates for fabricating UV photodetectors.

Keywords W$_{18}$O$_{49}$ nanowires · Field effect transistor · Ultraviolet photodetector · Photoconductive gain · Near-surface depletion region

Introduction

Nowadays, ultraviolet (UV) photodetectors play very important roles in many fields such as missile tracking, ozone monitoring, flame detection, imaging techniques and lightwave communications [1–3]. One-dimensional nanostructures of high-performance oxides have attracted considerable attention as a class of potential optoelectronic materials. So far, UV nano-photodetectors based on ZnO nanowires, SnO$_2$ nanowires and Ga$_2$O$_3$ nanowires have been investigated, and some remarkable characteristics such as wavelength selectivity and photoresponse have been revealed [4–7].

As a kind of important transition metal oxides, tungsten oxides have been extensively researched for their distinctive properties including electrochromism, photochromism, gaschromism and photosensitivity [8–13]. Among the substoichiometric phases of WO$_x$, monoclinic W$_{18}$O$_{49}$ has attracted much attention for their photoluminescence, gas sensing and field emission properties [14–19]. However, to our knowledge, the photoconductivity characteristics of the W$_{18}$O$_{49}$ nanostructures have not been reported until now.

In this paper, we report a systematic study on UV photoconductivity characteristics of single W$_{18}$O$_{49}$ nanowires. The conductivity of W$_{18}$O$_{49}$ nanowires is extremely sensitive to UV light exposure, allowing us to reversibly switch the photoconductors between “OFF” and “ON” states with $I_{\text{light}}/I_{\text{dark}}$ ratios of two orders of magnitude, excellent stability and reproducibility. The results indicate that the W$_{18}$O$_{49}$ nanowires are a potential candidate for applications in high sensitivity nano-photodetector and nano-photoelectronic switch.

Experimental Section

The W$_{18}$O$_{49}$ nanowires were synthesized on ITO glass substrates by thermal evaporation of tungsten trioxide powders without catalysts or additives [20]. To fabricate single-nanowire detectors, seven parallel Ti/Au (10 nm/150 nm) electrodes spaced about 2 µm apart were fabricated with photolithography on a p$^{++}$-type Si substrate with a 500 nm SiO$_2$ layer. The as-prepared W$_{18}$O$_{49}$ nanowires were dispersed in deionized water by ultrasonic. An ac voltage with a frequency of 1 MHz and a peak to
peak voltage $V_{p-p} = 16$ V was applied between the two electrodes when a droplet of the W18O49 nanowires suspen-
sion was dropped to cover the electrodes area using a
micropipette. A fast thermal annealing at 300°C was car-
ried out in N2 atmosphere for 2 min to form the ohmic
contacts between the electrodes and nanowire.

The as-prepared nanowires were characterized by X-ray
powder diffraction (XRD) on a Rigaku RINT 2400 X-ray
diffractometer with Cu Kα radiation. Agilent B1500a
measurement system was used for electrical measurements.
Spectroline E-series Ultraviolet hand lamps were used as
the UV light sources. All measurements were performed at
room temperature.

Results and Discussion

The Typical XRD pattern of the as-prepared nanowires is
shown in Fig. 1. All the characteristic peaks can be indexed
to monoclinic W18O49 phase with the lattice constants $a =
18.280$ Å, $b = 3.775$ Å, $c = 13.980$ Å and $\beta = 115.20°$,
which is in good agreement with the JCPDS, No. 05-0392.
The sharp peaks confirm the high crystallinity of the
material.

Figure 2a, b respectively, show a schematic illustration
and a SEM image of the nanowire photoconductor in a
configuration of field effect transistor (FET). Under dark
condition, the current–voltage ($I_{sd}$–$V_{sd}$) characteristics of
the FET at different gate voltages (from +20 to −20 V
with a 10 V step) are shown in Fig. 2c. The conductivity of
W18O49 nanowire increases with increasing the gate volt-
age, which indicates that the nanowire is an n-type semi-
conductor. The n-type conduct behavior in nominally
undoped tungsten oxide can be attributed to the presence of
oxygen vacancies [18].

Optoelectronic characteristics of the device were
investigated under 312 nm UV illumination with an

intensity of 1.0 mW/cm². As shown in Fig. 3a, the nano-
wire is highly insulating in the dark. The conductivity of
the nanowire increases from 2 nS in the dark to 37 nS
under the UV light illumination, which shows its potential
application as UV photodetector. The current flowing
between Au electrodes without the nanowires connecting
has been measured to exclude the possible contribution of
the electrodes and the substrate.

The photoconductance of the W18O49 nanowire is
dependent on light intensity. Figure 3b shows the photo-
current as a function of the light intensity for a single
nanowire irradiated with the 312 nm UV light. The pho-
tocurrent ($I_p$) can be expressed by a simple power law [21]:

$$I_p \propto P^{0.94}$$

(1)

where $P$ is the intensity of UV illumination. The non-unity
exponent is a result of the complex process of electron–
hole generation, trapping and recombination within the
material. To change the power of illumination, the con-
ductance can increase by 10 times without damaging the
nanowire. Because the UV light intensity is relatively low,
no saturation photocurrent can be observed as shown in
Fig. 3b. It suggests that the hole-traps present on the sur-
face of the nanowire haven’t absolutely been released.
at low light intensity, leading to unsaturation of the photocurrent.

As a critical parameter for photoconductors, the gain $G$ was defined as the number of electrons collected by electrodes due to the excitation by one photon. $G$ can be expressed as

$$G = \frac{N_e}{N_p} = \frac{\tau}{t_{\text{tran}}}$$

where $N_e$ is the number of electrons collected in unit time, $N_p$ is the number of absorbed photons in unit time, $\tau$ is carrier lifetime, and $t_{\text{tran}}$ is the transit time between the electrodes. Take the obtained photocurrent value under 312 nm UV light with an intensity of 1.0 mW/cm$^2$ and the exposure area about $4 \times 10^{-9}$ cm$^2$ of the nanowire into Eq. (2), the corresponded gain of the nanowire photoconductor is about $10^4$.

The response of photoconductivity is very important for a photodetector. Figure 4a shows the response of the device to 312 nm light at a bias of 0.5 V. The real-time by ON/OFF switching was measured with an intensity of 1.6 mW/cm$^2$. The measured photocurrent shows a rapidly increase to 60 nA upon exposure to UV light with 1.6 mW/cm$^2$ and decreases back to the initial value when the UV light was turned off. The change on the photocurrent shows excellent stability and reversibility. The enhanced conductivity under UV light illumination is attributed to the photogenerated carriers in the semiconducting nanowire. As shown in Fig. 4b, detailed data analysis reveals a rise time ($t_r$) and fall time ($t_f$) of 35 and 100 s, respectively. It is worth mentioning that the time constant for the rise time is always faster than the fall time, which is believed that traps and other defect states were involved in the process.

For their large surface-to-volume ratio, chemisorption on the surface of nanowires may play an important role on the conductivity. To study the adsorption effect, we investigated the response of the $W_{18}O_{49}$ nanowires in air and vacuum under dark condition. Due to the presence of oxygen vacancies, as-synthesized nanowires are usually $n$-type semiconductors as demonstrated in Fig. 2. These vacancies serve as active sites for adsorption of ambient oxygen, which can create a depletion layer in the near-surface region of the nanowires by capturing free electrons, and result in a decrease of conductivity of the nanowires [6]. The conductivity of the $W_{18}O_{49}$ nanowire device increases obviously in vacuum compared to that measured in air under the same bias voltage, as shown in Fig. 5. In vacuum, some oxygen molecules could be desorbed from the surface of the nanowire, and some captured free electrons can be released from the near-surface depletion region, leading to an increase of the conductivity. Therefore, the ambient would be an important factor to the photodetector of the $W_{18}O_{49}$ nanowires.
Conclusion

In summary, the photoconductor devices were fabricated based on the single W$_{18}$O$_{49}$ nanowires. The photoelectrical properties have been characterized systematically and shown the highest light sensitivity at UV light. A simple power-law dependence on UV light intensity was observed at room temperature. The W$_{18}$O$_{49}$ nanowire photodetectors exhibit superior performance in sensitivity and reversibility. Absorption of oxygen on the surface of the W$_{18}$O$_{49}$ nanowires can significantly influence their conductivity. The results will open up some new possibilities of using W$_{18}$O$_{49}$ nanowires for fabricating nanodevices such as high-performance UV detectors, optical keys and optical memory.

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