



## **W18O49-Type Tungsten Oxide Nanomaterial and Applications Thereof in Light Sensor, Mosfet and Solar Cell US 20150075594 A1**

### **ABSTRACT**

The invention proposes W18O49-type tungsten oxide nanomaterial, which is fabricated with a precursor comprising WS<sub>2</sub> and formed by thermal oxidation from the precursor. Applications using W18O49-type tungsten oxide nanomaterial in light sensor, MOSFET and solar cell, are also disclosed.

### **BACKGROUND OF THE INVENTION**

#### **1. Field of the Invention**

The present invention relates to a tungsten oxide nanomaterial, and more particularly, to a sulfur-doped W18O49-type tungsten oxide nanomaterial and applications thereof.

#### **2. Description of the Prior Art**

Tungsten oxide (WO<sub>x</sub>) is a metal oxide with photoconductivity as well as a semiconductor. With the exciting of the photo energy, the valence electron can transit to the conduction band resulted in generating light current, and therefore can be applied as the light sensor. The tungsten oxide material is also characterized in gas absorption, and its resistance may change corresponding to gas absorption or desorption. Therefore, detecting the change of the resistance of the tungsten oxide material can be applied for gas detection.

The conventional WO<sub>3</sub> is a canary yellow rhomboidal crystal in the room temperature, and has about 2.6 eV band gap. Light sensors or gas detectors made of tungsten oxide nanomaterial semiconductor material have increased surface-to-volume ratio in terms of enhanced surface activity, photoconductivity gain, detector sensitivity or improved reaction time of detecting gas. The tungsten oxide material reveals characteristics of semiconductor, and can be also applied as MOSFET (metal-oxide-semiconductor field-effect transistor) material. For example, WO<sub>3</sub> Nanowires on Carbon Papers: Electronic Transport, Improved Ultraviolet-light Photo detectors and Excellent Field Emitters (Liang Li, Yong Zhang et al., on J. Mater. Chem., 2011, 21, 6525-6530), Ultraviolet Photoconductance of a Single Hexagonal WO<sub>3</sub> Nanowire, by Kai Huang, Qing Zhang et al, published on Nano. Res. (2010) 3:281-287.

Since tungsten oxide nanomaterial can be applied to the detector, MOSFET and photoconductive devices, it's an important goal to increase the surface-to-volume ratio, and improve the sensitivity and photoconductivity gain so as to improve the photovoltaic efficiency.

### **SUMMARY OF THE INVENTION**

In one embodiment of the present invention, a sulfur-doped W18O49-type tungsten oxide nanomaterial is represented by a chemical formula (I): W<sub>18</sub>O<sub>(49-x)</sub>S<sub>x</sub> . . . (I),



wherein  $x$  ranges from 0.5 to 5.5. The W18O49-type tungsten oxide nanomaterial of the present invention utilizes a precursor containing WS<sub>2</sub>, and fabricated by a deposition process after a thermal oxidation reaction.

In another embodiment of the present invention, a light sensor comprises a substrate, an electrode unit, a photoelectric conversion unit, and a current detecting unit. The electrode unit is configured on the substrate and has a first electrode and a second electrode. The photoelectric conversion unit is configured on the substrate, electrically connected to the first electrode and the second electrode. The photoelectric conversion unit comprises the sulfur-doped W18O49-type tungsten oxide nanomaterial. The photoelectric conversion unit is illuminated by a light to generate light current. The current detecting unit is electrically connected to the first electrode and the second electrode and configured for detecting the light current passing through the first electrode and the second electrode.

In yet another embodiment of the present invention, a metal-oxide-semiconductor field-effect transistor comprises a substrate, an oxide layer, a source/drain electrode, a semiconductor channel layer, and a gate electrode. The oxide layer is formed on the substrate, and the source/drain electrode is formed on the oxide layer. The semiconductor channel layer is configured on the oxide layer and a channel is formed between the source/drain electrodes. The channel comprises the sulfur-doped W18O49-type tungsten oxide nanomaterial. The gate electrode is configured on the lower surface of the substrate.

In still another embodiment of the present invention, a solar cell comprises a first substrate, a second substrate, a light absorption layer, and an n-type semiconductor layer. The first substrate has a first electrode, and the second substrate has a second electrode. The light absorption layer is located between the first substrate and the second substrate, wherein the light absorption layer comprises the sulfur-doped W18O49-type tungsten oxide nanomaterial. The n-type semiconductor layer is located between the light absorption layer and the second substrate.

The sulfur-doped W18O49-type tungsten oxide nanomaterial of the present invention is a new semiconductor material that dopes the sulfur to increase the light absorption rate and spectrum. The light absorbing wavelength is between 300-1400 nm, and the light absorption efficiency is about 80%. The band gap is modulated and reduced to 1.7 eV by doping the sulfur, and the lower band gap may improve the photoconductivity gain. The W18O49-type tungsten oxide material has the characteristics of photoconductivity as well as gas absorption so as to be applied in light/gas detectors, MOSFET and solar cell to improve the sensitivity and power conversion efficiency.

Other advantages of the present invention will become apparent from the following descriptions taken in conjunction with the accompanying drawings wherein certain



embodiments of the present invention are set forth by way of illustration and examples.

## BRIEF DESCRIPTION OF THE DRAWINGS

### DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is directed to providing a sulfur-doped W18O49-type tungsten oxide nanomaterial having the chemical formula (I):

$W_{18}O_{(49-x)}S_x$  . . . (I), wherein x ranges from 0.5 to 5.5, and x ranges from 2 to 4, preferably.

The sulfur-doped W18O49-type tungsten oxide (hereinafter abbreviated as  $W_{18}O_{(49-x)}S_x$ ) nanomaterial of the present invention utilizes a precursor comprising  $WS_2$ , and is fabricated by a deposition process after a thermal oxidation reaction. As shown in FIG. 1 a, a precursor containing  $WS_2$  is put in the chamber 1.  $O_2$  and Ar are put into the chamber 1 where  $O_2$  is the reaction gas and Ar is the carrier gas. The chamber 1 is heated to a conditional temperature  $400-1200^\circ C.$ , and then the  $O_2/Ar$  gas carries the precursor vapor and the reactant to the substrate 10 to form the sulfur-doped W18O49-type tungsten oxide nanomaterial to be deposited on the substrate 10.

The precursor may also comprise other reductants such as  $SnCl_2$ , and the doped ratio of sulfur in the W18O49-type tungsten oxide nanomaterial may be adjusted with the  $SnCl_2/WS_2$  ratio in the precursor. During the process,  $WS_2$  is oxidized to  $WO_3$ , and partial  $WO_3$  is reduced to  $WO_2$  by  $Sn^{2+}$  from  $SnCl_2$ , wherein W18O49 composed of  $WO_2$  and  $WO_3$  is formed on the substrate 10 and prevents from over-oxidization. When operated in the same process conditions (temperature, pressure and  $O_2$  flow rate), the higher ratio of  $WS_2$  in the precursor (in terms of lower  $SnCl_2$ ), the more sulfur doped in the W18O49-type tungsten oxide. The X in the  $W_{18}O_{(49-x)}S_x$  may reach 5.5 for the highest value. In a preferred embodiment, the  $WS_2$  ratio in the precursor is 20-80% and the x of the fabricated  $W_{18}O_{(49-x)}S_x$  may range from 2 to 4. Besides, factors such as the temperature, pressure and  $O_2$  flow rate may also be operated to adjust the doped ratio of sulfur.

In the above-mentioned process, the precursor is mainly composed of  $SnCl_2$  and  $WS_2$ . Here, it is known that the sulfur is a VI element and accordingly, the precursor may also contain other the chemical compounds having other VI elements (such as Se or Te), such as  $WSe_2$  or  $WTe_2$ . In the above-mentioned process, partial O in W18O49 may be replaced by Se or Te in the precursor comprising  $WSe_2$  or  $WTe_2$  in the thermal oxidation reaction so as to fabricate  $W_{18}O_{(49-x)}S_x$  nanomaterials doped with Se or Te, in addition to sulfur.

The sulfur-doped W18O49 fabricated in the present invention is blue in color and the chemical formula is  $W_{18}O_{49-x}S_x$ . The doped ratio of sulfur in  $W_{18}O_{(49-x)}S_x$  may be determined by process parameters such as chamber temperature (high temperature



area), the substrate temperature (low temperature area), ratio of the precursor ( $\text{SnCl}_2$  and  $\text{WS}_2$ ), and gas flow rate ( $\text{O}_2$  and  $\text{Ar}$ ). For example, when the substrate temperature is raised to 500, the  $\text{W}_{18}\text{O}_{49-x}\text{S}_x$  formed on the substrate is determined to be  $\text{W}_{18}\text{O}_{45.96}\text{S}_{3.04}$  based on quantitative chemical composition analysis. When the substrate temperature is raised to  $600^\circ\text{C}$ ., the  $\text{W}_{18}\text{O}_{49-x}\text{S}_x$  formed on the substrate is  $\text{W}_{18}\text{O}_{47.63}\text{S}_{1.37}$ .

Among the process parameters mentioned above, the structure and morphology of the  $\text{W}_{18}\text{O}_{49}$ -type tungsten oxide may be affected by the ratio of  $\text{WS}_2$  in the precursor and the substrate temperature, and the different types of nanomaterials such as nanowire, nanorod,

nanotube or thin film structure may be formed specifically by adopting different parameters such as composition ratio of the precursor and substrate temperature.

The first embodiment of the present invention utilizes the chemical vapor deposition (CVD) process to fabricate the sulfur-doped  $\text{W}_{18}\text{O}_{49}$ -type tungsten oxide nanomaterial. As shown in FIG. 1 a, first, the  $\text{WS}_2$  and  $\text{SnCl}_2$  powder are placed in the high temperature area of the chamber as a precursor, the ratio of  $\text{WS}_2$  in the precursor is 20-80% and the temperature is  $600\text{-}1200^\circ\text{C}$ . to obtain the vapor. The substrate 10 is placed in the low temperature area of the chamber, and the temperature is controlled to  $300\text{-}700^\circ\text{C}$ . Then, trace amount of  $\text{O}_2$  is put into the chamber 1 and the  $\text{Ar}$  is used as the carrier gas, the gas flow rate is 10 sccm (standard-state cubic centimeter per minute), and the pressure in the chamber 1 is about 0.1-1 Torr. When the substrate temperature is raised to  $300\text{-}700^\circ\text{C}$ ., the substrate temperature is maintained for 1 hour and then cooled down to the room temperature. During the cooling process, as shown in FIG. 1 b, the  $\text{W}_{18}\text{O}_{(49-x)}\text{S}_x$  nanomaterial grows on the substrate 10.

FIG. 1 c is an X-ray diffraction pattern of the  $\text{W}_{18}\text{O}_{(49-x)}\text{S}_x$  nanomaterial fabricated according to the first embodiment of the present invention. The diffraction peak in the FIG. 1 c is compared to the JCPDS database (Joint Committee on Powder Diffraction Standards), and the corresponding  $2\theta$  substantially matches that of the  $\text{W}_{18}\text{O}_{49}$  lattice plane in the database No. 71-2450. Three main diffraction peaks match to the corresponding lattice planes (010), (404) and (014). In the JCPDS database, the  $\text{W}_{18}\text{O}_{49}$  in database No. 71-2450 is a monoclinic structure, and the lattice constant  $a=18.334\text{ \AA}$ ,  $b=3.786\text{ \AA}$ ,  $c=14.044\text{ \AA}$ , and  $\beta=115.20^\circ$ . Therefore, the lattice plane of the nanomaterial of the present invention matches the lattice plane in the database No. 71-2450 of JCPDS, and the tungsten oxide of the present invention may be viewed as the  $\text{W}_{18}\text{O}_{49}$ -type tungsten oxide.

TABLE 1

The comparison of the  $\text{W}_{18}\text{O}_{49}$  lattice plane and corresponding  $2\theta$  in JCPDS database and the



measurement result in XRD of the W18O49-xSx

2θ from XRD

lattice 2θ from JCPDS measurement

plane (degree) (degree)

(002) 13.93 13.98

( 304) 14.48 14.54

(010) 23.48 23.72

(103) 23.78 24.28

( 404) 27.11 27.96

(004) 28.07 28.74

(113) 33.66 34.02

(014) 36.90 36.92

(020) 48.02 48.24

(405) 49.35 49.40

(123) 55.43 55.44

(017) 56.15 56.72

The effects of different factors, such as weight ratio of WS<sub>2</sub> and SnCl<sub>2</sub> in the precursor to W18O<sub>49-x</sub>S<sub>x</sub> nanomaterial structure are now described. With other process variables fixed, namely substrate temperature=500° C., chamber temperature=700-900° C., and ratio of O<sub>2</sub> and Ar=0.2%, the single variable, the ratio of WS<sub>2</sub> in the precursor, was changed and the W18O<sub>49-x</sub>S<sub>x</sub> with different structures was then obtained. Refer to FIG. 2 a-2 d, which are scanning electron microscope (SEM) images showing the W18O<sub>49-x</sub>S<sub>x</sub> nanostructure of the present invention, using WS<sub>2</sub> as 100%, 66.7%, 40%, and 10% precursors, respectively. FIG. 2 a shows the 100-200 nm sheet structure when using the precursor containing 100% WS<sub>2</sub> (only WS<sub>2</sub> in the precursor, no SnCl<sub>2</sub>). FIG. 2 b shows that, when using the precursor containing 66.7%, more amounts of nanomaterial structures were obtained, where there are most amount of nanorod structure with wider external diameter (100-200 nm) and shorter length (2-5 μm) and fewer amount of thin and long nanowire structure with 10 nm external diameter and 6-10 μm length. FIG. 2 c shows the dense nanowire structure with 10 nm external diameter and 3-10 μm length when using the precursor containing 40% WS<sub>2</sub>. FIG. 2 d shows the plank structure with 1 μm width when using the precursor containing 10% WS<sub>2</sub>.

The optical characteristics of the W18O<sub>49-x</sub>S<sub>x</sub> nanomaterial of the present invention are now described. Regarding light absorption, the measurement method is using a blank glass slide for baseline correction first to prevent the effect of glass slide in reflection and absorption spectrum. The measured transmission of the slide is  $Abs \% = 100 - Trans \% - Ref \%$ , where Abs is the absorption efficiency of the present material, Trans is the transmission of the glass slide, and Ref is the reflection. As shown in FIG. 1 d, the measured absorption of W18O<sub>45.96</sub>S<sub>3.04</sub>, for example, is about 80% to 95% in the wavelength range 300-1400 nm, and it therefore shows that the



W18O49-xSx nanomaterial of the present invention is an excellent light absorption material.

In FIGS. 3 a and 3 b, the band gap value of the W18O49-xSx nanomaterial is further described. FIGS. 3 a and 3 b are diagrams showing  $(\alpha h\nu)^2 - h\nu$  relation of the W18O45.96S3.04 and W18O47.63S1.37 nanowires of the present invention to calculate the band gap. Utilizing a linear zone in the  $(\alpha h\nu)^2 - h\nu$  relation diagrams of the W18O45.96S3.04 and W18O47.63S1.37 nanowires, the  $h\nu$  value on the X-axis is the band gap value of the W18O45.96S3.04 and W18O47.63S1.37 nanowires by using the intersection of the tangent line and the Y-axis ( $\alpha=0$ ), where  $\alpha$ ,  $h$  and  $\nu$  represent absorption coefficient, Plank constant, and frequency, respectively. In FIGS. 3 a and 3 b, band gap of the W18O45.96S3.04 nanowire is 1.7 eV, and band gap of the W18O47.63S1.37 nanowire is 1.8 eV. The absorption coefficient  $\alpha$  may be obtained by using the formula  $I=I_0 e^{-\alpha t}$ , where  $\alpha$  is absorption coefficient,  $t$  is material thickness (cm), and  $I$  and  $I_0$  are intensity of the emitting light and transmitted light. After calculation, the absorption coefficient of the W18O45.96S3.04 nanowire is  $7.8 \times 10^4 \text{ cm}^{-1}$ , and the absorption coefficient of the W18O47.63S1.37 nanowire is  $5.5 \times 10^4 \text{ cm}^{-1}$ . Using the above optical analysis (FIGS. 2,

3 a and 3 b), the W18O49-xSx nanomaterial of the present invention has great light absorption, and may have lower band gap by doping sulfur. Further, the W18O49-xSx nanomaterial is a semiconductor material and has gas absorption property. Applications in light/gas detectors, semiconductors and solar cells using the W18O49-xSx nanomaterial of the present invention are further explained in the following second to fourth embodiments.

Please refer to FIG. 4 a which shows a light sensor according to the second embodiment of the present invention. The light sensor comprises a substrate 10, an electrode unit, a photoelectric conversion unit 14, and a current detecting unit 16. As the process described in the first embodiment, the W18O49-xSx nanomaterial is formed on the substrate 10 to be the photoelectric conversion unit 14, and the focused-ion beam (FIB) is used for depositing the electrode unit. The electrode unit comprises a first electrode 12 a and a second electrode 12 b. The focused-ion beam dissociates the metal gas into metal (such as Pt) according to the depositing position of the first and second electrodes 12 a, 12 b, and then the metal Pt is deposited to form the first and second electrodes 12 a, 12 b and electrically connected to the photoelectric conversion unit 14. The photoelectric conversion unit 14 including the W18O49-xSx nanomaterial generates light current after light illumination. The current detecting unit 16 is electrically connected to the first electrode 12 a and the second electrode 12 b, for detecting the light current fabricated by the photoelectric conversion unit 14 passing through the first electrode 12 a and the second electrode 12 b.

The W18O45.96S3.04 nanowire of the present invention is characterized in full



spectrum light absorption according to the above analysis and in the second embodiment, the light sensor utilizes the photoelectric conversion unit 14 with W18O45.96S3.04 nanowire. The illuminating light is 532 nm green light, and has about 20W/m<sup>2</sup> intensity. FIG. 4 b shows the relation of light intensity and light current when the photoelectric conversion unit in the light sensor of the present invention is illuminated. Here, the photoconductivity gain (G) is used to evaluate the photovoltaic efficiency of the photoelectric conversion unit 14, and defined as the electron amount (Nel) received by the electrode unit in a period and divided by the photon amount (Nph) received by the photoelectric conversion unit 14 in a period. It is also represented by  $G=Nel/Nph$ , and may be further simplified as

wherein Iph is the light current, q is the elementary charge, P is the light intensity, h is the Plank constant, and  $\nu$  is the light frequency. After calculation, the light sensor using the W18O45.96S3.04 nanomaterial as the photoelectric conversion unit 14 has a photoconductivity gain about 107.

The photoelectric conversion unit 14 comprising W18O49-xSx nanomaterial of the light sensor in the second embodiment 1 also has the characteristic of gas absorption; therefore, the light sensor in the second embodiment may also be used as a gas detector. Here, the resistance value of the photoelectric conversion unit 14 changes after absorbing gas and may be used for detecting gas. In the case of detecting NO<sub>2</sub>, the photoelectric conversion unit 14 comprising the

W18O49-xSx nanomaterial is an n-type semiconductor. After absorbing NO<sub>2</sub>, an oxidative gas with electron affinity higher than O<sub>2</sub>, the space charge of the sulfur-doped tungsten oxide may be increased with electrons captured NO<sub>2</sub> and the resistance of the photoelectric conversion unit 14 is thus increased. The current detecting unit 16 may be used for monitoring the light current passing through the first electrode 12 a and the second electrode 12 b to determine whether the gas has been detected by the photoelectric conversion unit 14.

In the third embodiment of the present invention, a metal-oxide-semiconductor field-effect transistor comprises a substrate 10, an oxide layer 11, a source electrode S, a drain electrode D, and a semiconductor channel layer 13. The oxide layer 11 is an insulation layer formed on the substrate 10, and the source electrode S and the drain electrode D are formed on the oxide layer 11. The semiconductor channel layer 13 is configured on the oxide layer 11 to form a channel between the source electrode S and the drain electrode D, and a gate electrode G is configured on the lower surface of the substrate 10.

Please refer to FIG. 5 a for describing the fabrication process of the MOSFET of the third embodiment. The oxide layer 11 is made of SiO<sub>2</sub>. The fabrication process of the semiconductor channel layer 13 includes placing the W18O49-xSx nanomaterial into



isopropanol (IPA), using ultrasonic shaker to disperse, sucking the IPA having W18O49-xSx nanomaterial with pipetman and dripping to the substrate 10, heating to dry the substrate 10, and using the focused-ion beam to deposit metal and connect the source electrode S and the drain electrode D. The voltage value applied to the gate electrode G of the MOSFET can be used to control the conductance of the channel formed between the source electrode S so as to determine the conductivity characteristics of the channel. In the third embodiment, the W18O49-xSx nanomaterial is a p-type semiconductor. The conductive channel between the source electrode S and the drain electrode D may be formed and the electron hole with positive voltage may then flow into the drain electrode D from the source electrode S through the channel when a positive voltage is applied to the gate electrode G. FIG. 5 b shows the relation of  $I_{ds}$ - $V_g$  measured in the MOSFET using W18O49-xSx according to one embodiment of the present invention.

In the fourth embodiment of the present invention, a solar cell comprises a first substrate 21, a second substrate 22, a light absorption layer 23, and a semiconductor layer 24. A first electrode 211 is configured on the first substrate 21. The light absorption layer 23 comprises W18O49-xSx nanomaterial. The semiconductor layer 24 is configured on the light absorption layer 23. Then, a second electrode 222 is configured on the second substrate 22.

Please refer to FIG. 6 for describing the fabrication process of the solar cell of the fourth embodiment. First, the Pt with thickness 150 nm is deposited as the first electrode 211 on the first substrate 21 by sputtering, and then the W18O49-xSx nanomaterial of the present invention is deposited on the first substrate 21. The W18O49-xSx nanomaterial is a p-type semiconductor used as the light absorption layer 23. For forming the PN junction, n-type ZnS or n-type CdS is used as n-type semiconductor layer on the light absorption layer 23. Finally, a transparent

conductive layer is formed on the n-type semiconductor layer 24 as the second electrode 222, where the transparent conductive layer is Aluminum doped ZnO with 1  $\mu$ m thickness. The light absorption layer 23 of the solar cell comprises the sulfur-doped W18O49-xSx nanomaterial. The light absorption layer 23 is capable of absorbing the solar light and transform to electric energy (arrow in FIG. 6 represents the illumination direction), and then the voltage difference is formed between the first and second electrodes 211, 222 to generate light current. In this embodiment, the W18O49-xSx nanomaterial is a p-type semiconductor and is used as the light absorption layer 23. Furthermore, the W18O49-xSx nanomaterial of the present invention may also be provided with properties of an n-type semiconductor by adjusting the process factors. Similarly, for forming the PN junction, when n-type semiconductor W18O49-xSx nanomaterial is used as the light absorption layer 23, and the semiconductor layer 24 with the p-type semiconductor material is used as p-type semiconductor layer 24 is assembled to the substrate and electrodes to form the solar cell.





The sulfur-doped W18O49-xSx nanomaterial tungsten oxide with nanowire structure in has a minimum external diameter about 10 nm, a high surface-to-volume ratio, a wide light absorption spectrum, a wave length in the range of 300-1400 nm, a light absorption rate about 80% (95% maximum). In the case of W18O45.96S3.04 nanowire, it may reach  $7.8 \times 10^4 \text{ cm}^{-1}$  absorption coefficient, and a low band gap 1.7 eV by doping sulfur. The sulfur-doped nanomaterial tungsten oxide of the present invention is provided with great photovoltaic transforming efficiency. Therefore, photoconductivity gain of the fabricated light sensor may reach 107 and is much higher than that ( $G=4.6 \times 10^3$ ) in conventional WO<sub>3</sub> nanomaterial. With the above characteristics, the sulfur-doped nanomaterial tungsten oxide of the present invention may be applied in light/gas detector and solar cell and highly improve the sensor sensitivity and the photovoltaic transforming efficiency of the solar cell.

While the invention can be subject to various modifications and alternative forms, a specific example thereof has been shown in the drawings and is herein described in detail. It should be understood, however, that the invention is not to be limited to the particular form disclosed, but on the contrary, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the appended claims.