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WO_3 thin film prepared by PECVD technique and its gas sensing properties to NO_2

MAOSONG TONG, GUORUI DAI*, YUANDA WU, XIULI HE, DINGSAN GAO
Department of Electronic Engineering, National Integrated Optoelectronics Laboratory, Jilin University, Changchun 130023, People's Republic of China
E-mail: grdai@mail.jlu.edu.cn

Tungsten oxide films have been successfully fabricated from tungsten oxychloride ($WOCl_4$) precursor by using plasma enhanced vapor deposition (PECVD) technique. The films were deposited onto silicon substrates and ceramic tubes maintained at 100°C under a constant operating pressure of He-O_2 gas mixtures. The compositions and the structures of the thin films have been investigated by means of anaysis methods, such as XRD, XPS, UV and IR. The as-deposited WO_3 thin films were amorphous state and became crystalline after annealing above 400°C. The surface analysis of the films indicates that stoichiometry O/W is 2.77 : 1. The gas sensing measurements of the WO_3 thin film sensors indicate that these sensors have a high sensitivity, excellent selectivity and quick response behavior to NO_2.

1. Introduction

In recent years, demand for exact monitoring of nitrogen oxides (NO_x), which are air pollutants released from combustion facilities and automobiles has become more serious all over the world. Therefore, NO_x sensors for air-quality monitoring or exhaust-gas control are needed. For air-quality monitoring, NO_x is the main gas to be detected and its concentration range is about 0–10 ppm. Recently, sintered block or thick films of tungsten oxide (WO_3) have reported to be very sensitive to NO_2 [1, 2]. There are many methods to prepare WO_3 thin films such as conventional evaporation techniques [3], chemical vapor deposition [4, 5], sputtering [6–10] and anodic oxidation of metallic tungsten plates [11]. In this study we report on WO_3 thin films deposited from $WOCl_4$ and O_2 using plasma enhanced chemical vapor deposition (PECVD) method, which has a number of advantages, such as lower processing temperature, the ability to deposit on large-area substrates and the simple control of deposition. Optical properties of the WO_3 thin films have been investigated by infrared absorption spectra (IR) and ultraviolet spectroscopy (UV), while the structure and the composition of the films were studied by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). We also investigated the gas sensing properties of WO_3 thin film sensors to NO_2.

2. Experimental

2.1. Preparation of thin films

In this investigation, tungsten oxide films were prepared in a mixed He-O_2 atmosphere from tungsten oxychloride ($WOCl_4$) precursor. The experimental apparatus is a conventional PECVD reaction system. The same pumping speed was used throughout. The plasma frequency used was 13.56 MHz and the distance between two horizontal and parallel electrode plates was 20–30 mm. The substrates were mounted on the lower electrode plate and were heated by lamp banks above and below the reactor tube. The temperature was maintained at a fixed value in the range of 40–200°C during deposition and was measured by a chromelalumel thermocouple attached to the substrate holder. The reaction gases $WOCl_4$, transported by He, and O_2 were mixed to form the WO_3 films by the excited oxidation reaction.

$$WOCl_4 + O_2 \rightarrow WO_3 + 2Cl_2$$

The typical deposition conditions are as follows: an input r.f. power of 40–50 W, an deposition temperature of ca. 100, and a total pressure of the He-O_2 gas mixture of 250–500 Pa. In general, the deposition rate of the thin films was between 10 and 15 nm/min under these typical deposition conditions. The thickness of the obtained WO_3 films was about 100 nm.

2.2. Analysis of the thin films

The structure and crystal state of the thin films were determined on an X-ray diffractometer (Japan Rigaku D/MAX-RA) with a CuKα radiation (wavelength $\lambda = 1.542$ Å) operating at 150 mA and 50 kV. The data were collected by a step scanning method for $20^\circ \leq \theta \leq 60^\circ$, with a step width of 0.05° and a step time of 1s.

The composition and oxidation state of the WO_3 thin films annealed at 600°C for 5 h were investigated using

* Author to whom all correspondence should be addressed.

X-ray photoelectron spectroscopy (XPS). Measurements were made on a VG-spectrometer (ESCALAB MARK-II). The exciting radiation was CuKα radiation (wavelength $\lambda = 1.542$ Å). To eliminate below 5×10^{-7} Pa during the specimen analysis.

The optical characteristics of the films were determined by UV spectroscopy (Shimadzu UV-360) and by infrared absorption spectroscopy (FT-IR).

2.3. Measurements of gas sensing properties

The WO_3 films were deposited between interdigital gold electrodes on the outer wall of ceramic tubes. Electrical contacts were made with 0.05 mm gold wires attached to the gold electrodes. Then the deposited thin films were annealed at 600°C for 5 h. The obtained thin film sensors were set up in a glass test chamber with the volume of 0.18 m^3 and kept under a continuous flow of fresh air for 10 min before measurement. The operating voltage (V_H) was supplied to either of the coils for heating the sensors and the circuit voltage ($V_C = 10$ V) was supplied across the sensors and the load resistor ($R_L = 2$ kΩ) connected in series. The signal voltage across the load, which changed with sort and concentration of gas, was measured. The gas sensitivities to NO_2, C_2H_5OH gas, CH_4, CO and H_2S were measured. A given amount of each gas was injected into the chamber and mixed by a fan for 30 s. The sensitivity for gases, S, is defined as $S = V_g/V_a$, where V_g and V_a are the voltages drop across the load resistance in testing gases/air mixture and in air, respectively.

3. Results and discussion

3.1. The compositions and structures of the thin films

Fig. 1 shows the X-ray diffraction patterns for as-deposited tungsten oxide films on silicon substrates at 100°C (1a), for films annealed in air at 400°C (1b) and 600°C (1c) for 4 h. The figure shows that the as-deposited sample (1a) displays only very weak diffraction peaks, indicating an amorphous state or the presence of very small crystallites. For the specimens isothermally annealed, the relative intensities of the peaks in the diffraction pattern increases with increasing annealing temperature (cf. Fig. 1b and c). Comparing the experimental data with ASTM data, the characteristic peaks of the diffraction patterns of the films formed can be assigned to WO_3 (100), (200), (220) or (201), (221), (002), and (140) or (400).

Fig. 2 shows XPS spectra for a tungsten oxide film. In a wide scan spectrum (2a), a series of sample peaks are

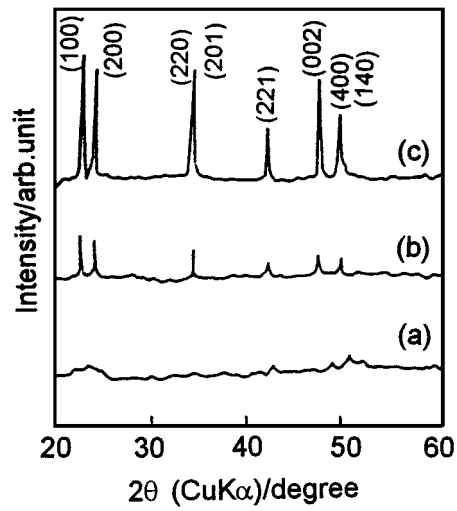

Figure 1 The XRD patterns of as-deposited and annealed films (a) As-deposited at 100°C, (b) Annealed 400°C, (c) Annealed at 600°C.

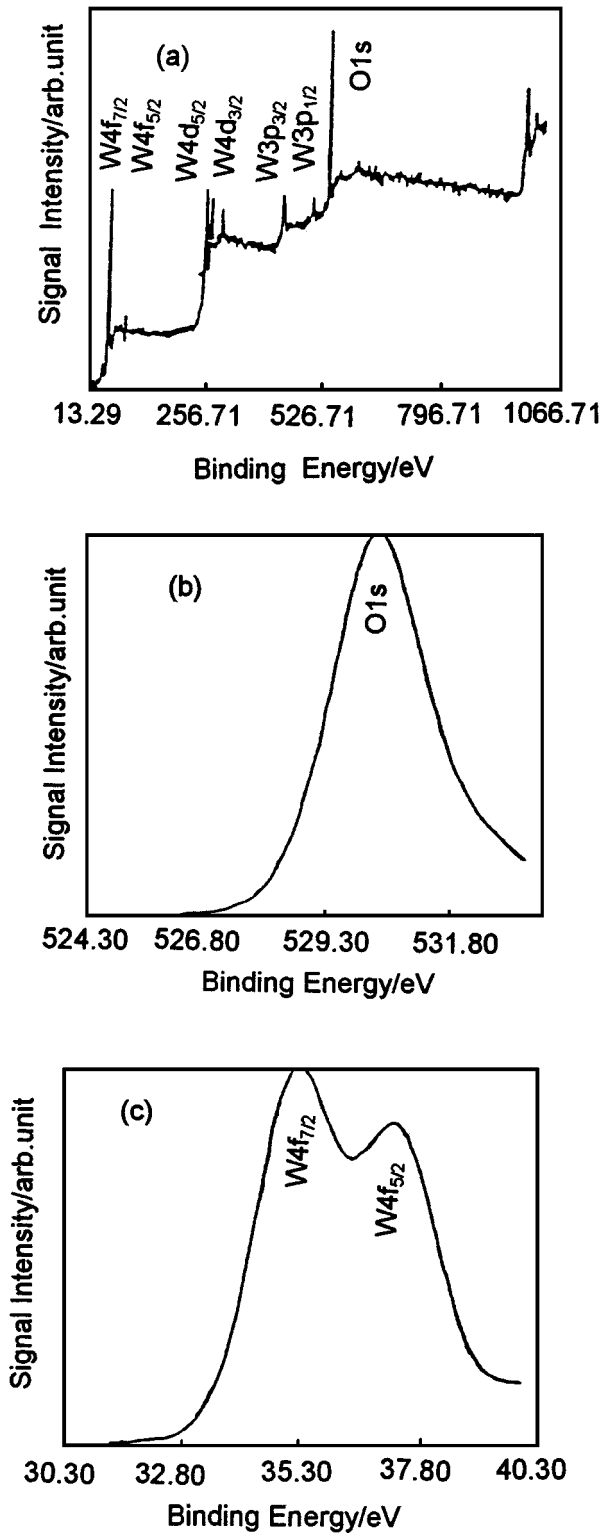

Figure 2 The XPS spectra of WO_3 films (a) Wide scan spectrum, (b) O1s Peak, (c) $W4f_{7/2}$ and $W4f_{5/2}$ peaks.

TABLE I Experimental results of XPS for a tungsten oxide film

Peak Identifier	Binding Energy/eV	Normalized Area	Sensitivity Factor	Atomic %	Stoichiometry
O1s	530.20	20147	2.930	73.65	2.77
$W4f_{7/2}$	35.20	7208	9.800	26.35	1.00
$W4f_{5/2}$	37.15				

observed on a background which generally increases as the binding energy increases, but which also shows some step increases on the high binding energy side of each set of significant peaks. The photoelectron peak of O1s (WO_3) is found (2b) to lie at 530.20($\pm$0.02) eV. The photoelectron peaks of $W4f_{7/2}$ and $4f_{5/2}$ (WO_3) are found at 35.20 and 37.15 eV, respectively. The other photoelectron peaks of $W4d_{5/2}$, $4d_{3/2}$, $4p_{3/2}$, $4p_{1/2}$ (WO_3) can be indentified in Fig. 2a. The 2p electron binding energy for Cl ($WOCl_4$) is 199.90 eV and its photoelectron peak is not observed in the WO_3 films. The experimental results, summarized in Table I, also indicated that the stoichiometric ratio of O/W of the tungsten oxide film was 2.77 : 1.

Fig. 3 shows the UV absorption spectra of as-deposited WO_3 films of three different thicknesses on glass, interference effects are evident in the spectra. The transmission edge is about the same, at 345 nm, for all of the samples. This edge when extrapolated to the spectrum (D) of the glass substrate gives the average value of the intrinsic absorption wavelength: $\lambda_0 = 392$ nm. The optical band gap (Eg) can be determined by the relation $Eg = 1.24/\lambda_0$, and it is found to have a value of 3.18 eV. This corresponds well with a value reported for sputtered WO_3 amorphous films.

For the IR analysis, the tungsten oxide films deposited on the highly resistive Si wafers. Fig. 4 shows the infrared absorption spectra (IR) of the films after annealing at 600 for 5 h. The IR spectra exhibit the bands

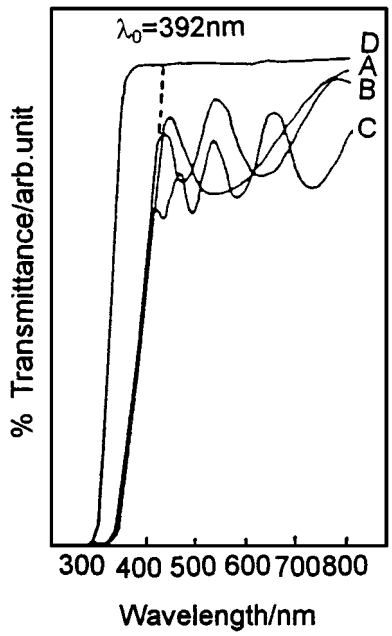

Figure 3 The UV absorption spectra of the as-deposited WO_3 films of different thickness A-1078 nm B-324 nm C-257 nm D-glass substrate.

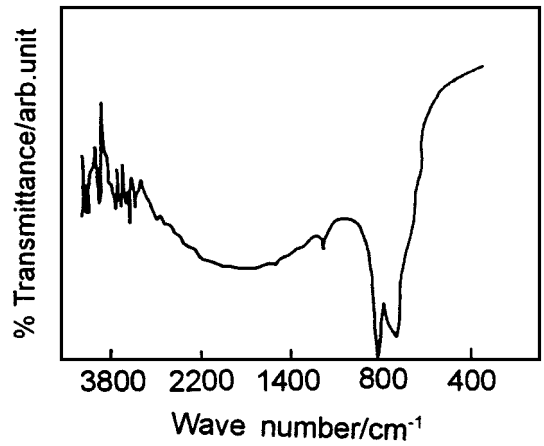

Figure 4 The IR absorption spectra of WO_3 films annealed at 600°C.

at 1080, 802 and 728 cm^{-1}. The band of 1080 cm^{-1} may be assigned to SiO_2, and the bands of 802 and 728 cm^{-1} may be attributed to W-O stretching vibration of WO_3.

3.2. Gas sensing properties of the thin film sensors

In general, the sensitivity of the sensors is affected by the operating temperature. The higher temperature enhances surface reaction of the thin films and gives higher sensitivity in a temperature range. Fig. 5 shows the relationship between the gas sensitivity and the operating temperature for 10 ppm NO_2. The results indicate that the gas sensitivity of the sensors increases with increasing operating temperature up to the optimum operating temperature of 200°C. Further increasing the operating temperature reduces the sensitivity. This type of thin film sensor was also tested for its sensitivity to other gases, such as C_2H_5OH, CH_4, CO and H_2S at the concentration of 500 ppm, as shown in Fig. 5. These experimental results indicate that the WO_3 thin film sensor was relatively insensitive to these gases. Furthermore, we have found that the gas sensitivity of the sensor increases with increasing NO_2 concentration, as shown in Fig. 6. A low detection concentration of NO_2 is 1 ppm and the gas sensitivity is approx. 4 at 200°C. Therefore, the WO_3 thin film sensors exhibit both high sensitivity and excellent selectivity to NO_2

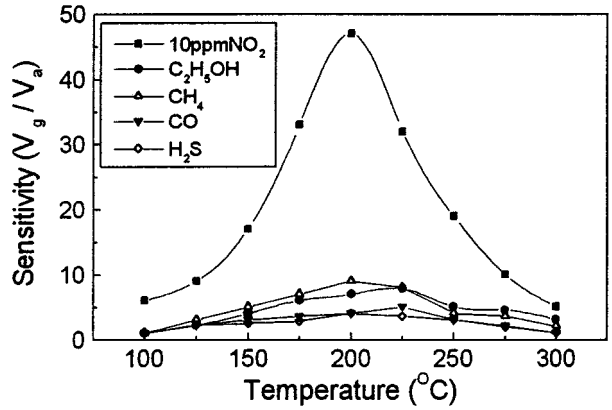

Figure 5 Gas sensitivity as a function of operating temperature to different gases.

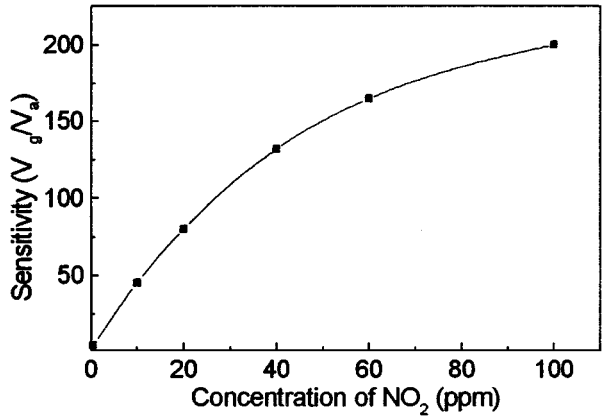

Figure 6 Gas sensitivity as a function of NO_2 concentration at 200°C.

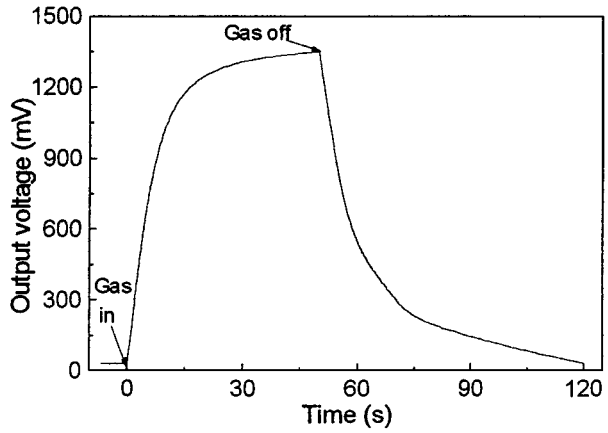

Figure 7 Response and recovery characteristic of WO_3 thin film sensor to 10 ppm NO_2 at 200°C.

gas. Fig. 7 shows the typical gas response characteristic of the WO_3 thin film sensors. After an introduction of 10 ppm NO_2 gas, the response appears immediately. The 90% response time and the 90% recovery time are 15 s and 25 s, respectively.

4. Conclusions

The WO_3 thin films are usually prepared by evaporation or sputtering. The aim of this work was to study a novel technique for the preparation of tungsten oxide films and to investigated the structure and gas sensing properties to NO_2. From the results presented in this paper the following conclusions can be drawn.

1. A technique has been developed using a solid precursor ($WOCl_4$) and PECVD. This precursors is safe to handle at room temperature and its use has obvious advantages over the CVD preparation of WO_3 films with more conventional and more hazardous precursors, such as WF_6 and $W(CO)_6$.

2. The XRD results show that the tungsten oxide films were amorphous on deposition, but when annealed at 400°C they became crystalline.

3. Surface analysis of the films by XPS shows that they had a stoichiometric ration of O/W of 2.77 : 1. The films were transparent as deposited and this is consistent with earlier observations that virgin films of WO_x are transparent for $x > 2.6$.

4. The UV spectroscopy results show that the band gap of the as-deposited WO_3 thin films is Eg = 2.95 eV. The IR spectra of the thin films annealed at 600°C exhibit the bands at 802 and 728 cm^{-1}, which may be attributed to W-O stretching vibration.

5. The gas sensing properties of the WO_3 thin film sensors indicate that these sensors exhibit high sensitivity, excellent selectivity and quick response behavior to NO_2 gas.

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