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WO_3 Thin Films Prepared by Pulsed Laser Deposition

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We report the structural and gas sensing properties of tungsten trioxide (WO_3) thin films prepared by the KrF excimer pulsed laser deposition technique. The WO_3 thin films having amorphous, crystallized tetragonal and triclinic structures were fabricated at the oxygen pressure of 10–300 mTorr and the substrate temperature of 150–800°C. We revealed the effect of the oxygen pressure and substrate temperature during the deposition on the crystal phases of the WO_3 thin films. The atomic force microscopy measurement shows that the average grain size and the average number of grains are approximately 200 nm and 8/μm^2, respectively. The triclinic WO_3 thin film with a thickness of 1 μm showed high sensitivity of 254 in NO (60 ppm) gas at a low operating temperature of 150°C. [DOI: 10.1143/JJAP.41.5372]

KEYWORDS: WO_3, gas sensor, pulsed laser deposition, tetragonal, triclinic

1. Introduction

Electrical conductivity of *n*-type semiconductors such as ZnO, SnO_2, TiO_2 and tungsten trioxide (WO_3) changes when they are surrounded by oxidation or reduction gas. These materials are candidates for use as environmental gas sensors, detecting pollutant gases like sulphur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (CH_x) and nitrogen oxides (NO and NO_2: NO_x). According to the safety standard of the American Conference of Governmental Industrial Hygienists (ACGIH), the threshold limit values (TLVs) of NO and NO_2 in air are 25 ppm and 3 ppm, respectively. SnO_2 has been widely used as a detector of hazardous gases, however its sensitivity in such NO_x concentration is not sufficient to detect the TLVs. A reliable and compact thin film gas sensor, particularly for NO_x monitoring, is needed. Recently, WO_3 has attracted much interest due to its potential as a NO_x sensor. Several methods such as thermal evaporation,[1–4] sputtering,[5–8] chemical vapor deposition,[9] screen printing[10,11] and sol–gel[12] have been developed for synthesis of the WO_3 films. The films prepared by these methods need the postannealing to stabilize their gas sensing property. It is believed that oxygen vacancy, crystallinity, crystallite size and grain size of the WO_3 film influence electrical and gas sensing properties, however, it is difficult to control the film quality precisely in the above-mentioned process.

Pulsed laser deposition (PLD) technique is suitable for the preparation of WO_3 film because of its reproducibility and controllabilities of stoichiometry and crystal structure. The first study of the WO_3 films prepared using the PLD method was reported by Rougier *et al.* in 1999.[13] They investigated the effects of the processing temperature, pressure of atmosphere and postannealing on the structural and optical properties of the WO_3 films. However, the parameters varied coarsely. The conditions should be changed more finely to clarify influence of the conditions on the properties of the films in detail. In our work, we report the effect of the deposition conditions on the structural and gas sensing properties of WO_3 thin films deposited by the PLD method. In particular, the surface roughness, grain size, crystallite size and crystal structure were evaluated, because they have been considered to affect the gas sensing property.

2. Experimental

WO_3 thin films were deposited on quartz and Al_2O_3 crystal substrates by the PLD method. Before deposition, a chamber (Neocera, $\phi = 12$ inch) was pumped down to the base pressure of 1×10^{-5} Torr. A stoichiometric WO_3 target (Dowa, purity = 99.99%, $\phi = 30$ mm) was ablated by KrF excimer laser (Lambda Physik Compex 205, maximum energy = 650 mJ, $\lambda = 248$ nm, pulse duration = 25 ns) with the energy density of 2 J/cm^2 and the repetition rate of 5 Hz for 10 min. The distance between the target and substrate was 45 mm. The oxygen pressure (P_{O2}) and the substrate temperature (T_s) during the deposition were changed from 10 to 300 mTorr and from 150 to 800°C, respectively. After the deposition, the WO_3 thin films were cooled down to room temperature in oxygen atmosphere of 760 Torr.

The crystallinity of the WO_3 thin films was examined by means of X-ray diffractometry (XRD: Rigaku RINT2000/PC) with CuKα radiation. The surface morphology of the films was observed by atomic force microscopy (AFM: Seiko Instruments Inc. SPI3800N). The WO_3 thin films were deposited on Al_2O_3 substrates having Pt electrodes and the gas sensing properties were measured by a two-terminal resistance method.

3. Results and Discussion

WO_3 has a distorted cubic ReO_3-type lattice. The crystal structure of WO_3 bulk target measured by XRD was triclinic phase ($a = 7.33$ Å, $b = 7.54$ Å, $c = 7.71$ Å). Figure 1 shows P_{O2} dependence of XRD spectra of WO_3 thin films deposited on quartz substrates at T_s of 400°C. The P_{O2} was varied from 10 to 200 mTorr. The angular resolution was 0.01° in θ–2θ scan. The crystallite size of (*hkl*) phase ($D_{(hkl)}$) was calculated from Scherrer's equation: $D_{(hkl)} = K\lambda/\beta\cos\theta$. Where λ is the wavelength of the X-ray (1.54056 Å), θ is Bragg's diffraction angle, β is full-width at half maximum of a peak and K is constant (0.9). In the case of P_{O2} of 10 mTorr, the film was amorphous. The WO_3 thin film prepared at P_{O2} of 100 mTorr was composed of tetragonal phase (JCPDS card No. 05-0388). The *c*-axis lattice length estimated from (001) peak ($2\theta = 22.89°$) using Bragg's equation was 3.89 Å, which is close to that of the JCPDS card (3.90 Å). The diffraction peaks of the WO_3 thin

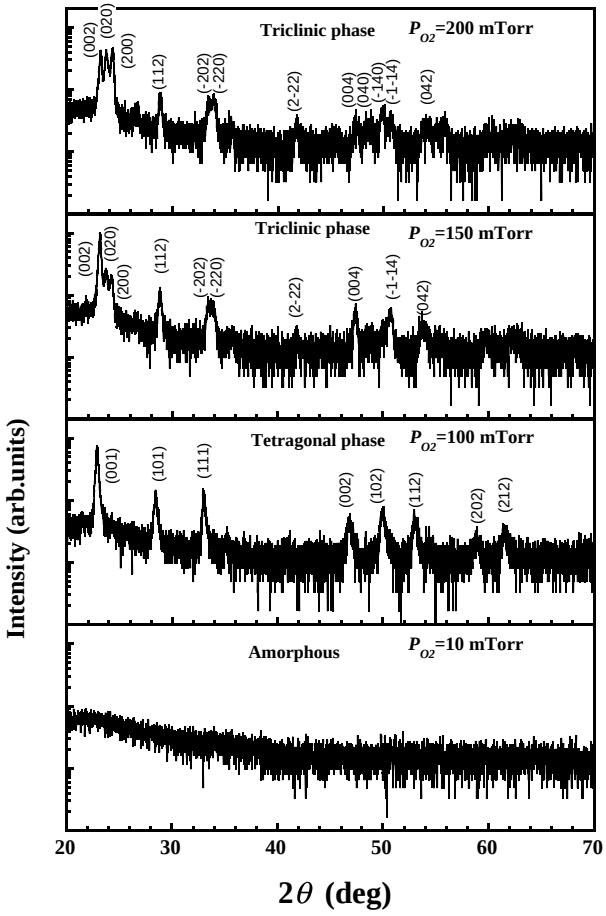

Fig. 1. The oxygen pressure P_{O2} dependence of the XRD spectra of the WO_3 thin films deposited at the substrate temperature T_s of 400°C.

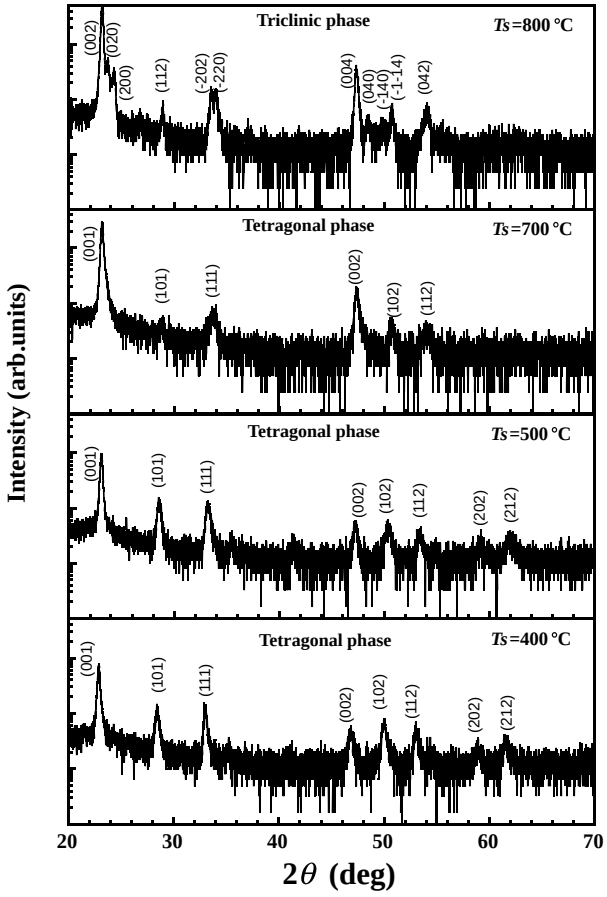

Fig. 2. The substrate temperature T_s dependence of the XRD spectra of the WO_3 thin films deposited at the oxygen pressure P_{O2} of 100 mTorr.

films deposited at P_{O2} of 150 and 200 mTorr were assigned referring triclinic structure (JCPDS card No. 20-1324). Strong (002), (020) and (200) peaks appeared around 2θ of 23–25°. The lattice lengths estimated from these strong peaks were $a = 7.33$ Å, $b = 7.50$ Å and $c = 7.68$ Å for the film deposited at P_{O2} of 150 mTorr and $a = 7.32$ Å, $b = 7.50$ Å and $c = 7.66$ Å for the film deposited at P_{O2} of 200 mTorr, respectively. These values are almost in agreement with the lattice lengths of the bulk target. The crystal structure of the WO_3 thin film fabricated in the P_{O2} range from 100 to 150 mTorr is easily influenced by the oxygen content. On the other hand, there was no remarkable P_{O2} dependence of the film qualities for the film deposited at P_{O2} over 150 mTorr. The $D_{(002)}$ of the film prepared at P_{O2} of 150 mTorr was 26 nm. In the case of P_{O2} of 200 mTorr, $D_{(002)}$ increased to 29 nm. These crystallite sizes are common in triclinic WO_3 thin films.[1)]

Figure 2 shows XRD spectra of WO_3 thin films deposited on quartz substrates at P_{O2} of 100 mTorr and different T_s (400–800°C). The crystal structure of the WO_3 thin films deposited at T_s from 400 to 700°C was tetragonal phase. However, the WO_3 thin film deposited at T_s of 800°C showed triclinic phase. This suggests that oxidation during the deposition is needed to obtain triclinic WO_3 thin film. The *c*-axis lattice lengths of the tetragonal films deposited at T_s of 400, 500 and 700°C were 3.89, 3.85 and 3.84 Å, respectively. The $D_{(001)}$ increased to 35 nm for the film deposited at T_s of 700°C, which is larger than that of the film deposited at T_s of 400°C (25 nm). The lattice lengths of the triclinic film (T_s of 800°C) were $a = 7.32$ Å, $b = 7.50$ Å and $c = 7.67$ Å. The *c*-axis lattice length of the tetragonal phase became shorter with the increase of T_s, which means the oxygen was taken into the lattice. The *c*-axis length of the film deposited at 700°C (3.84 Å) was very close to half the *c*-axis lattice length (7.67 Å) of the triclinic film. The lattice lengths of the triclinic WO_3 thin films are almost constant under the present deposition conditions.

Figure 3 shows the crystal structures of the WO_3 thin

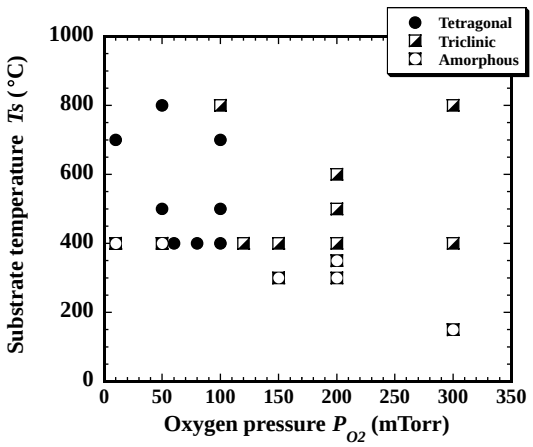

Fig. 3. The phase diagram of the WO_3 thin films deposited under various substrate temperatures T_s and oxygen pressures P_{O2}.

films deposited on quartz substrates under various T_s and P_{O2}. It was found that the films deposited at T_s lower than 350°C were amorphous. When the T_s exceeds the threshold temperature of 400°C, the amorphous structure changes markedly to triclinic phase as P_{O2} increases. The P_{O2} range from 60 to 100 mTorr provides tetragonal phase at T_s of 400°C. In the case of the preparation of the tetragonal WO_3 thin film, the P_{O2} is a more dominant factor than T_s. The triclinic WO_3 thin film can be obtained in the wide deposition range of the P_{O2} (120–300 mTorr) and T_s (400–800°C). It will be of interest to investigate the influence of the crystal structure on the gas sensing property. The estimated crystallite size were $D_{(001)}$ of 25 nm (T_s of 400°C, $P_{O2} = 100$ mTorr, tetragonal phase), $D_{(001)}$ of 35 nm (T_s of 700°C, $P_{O2} = 100$ mTorr, tetragonal phase), $D_{(002)}$ of 26 nm (T_s of 400°C, $P_{O2} = 150$ mTorr, triclinic phase) and $D_{(002)}$ of 29 nm (T_s of 400°C, $P_{O2} = 200$ mTorr, triclinic phase). Since these values are in the narrow range from 25 to 35 nm, it may be difficult to clarify the effect of crystallite size on the sensing property.

In addition, the grain size of the semiconducting gas sensor is considered to be one of the factors affecting its sensitivity.[11] The P_{O2} dependence of the surface morphology of the WO_3 thin films (T_s of 400°C) was observed by AFM. The scanned area was $5 \times 5\,\mu m^2$. Table I shows the average grain size, the average number of grains and the root-mean-square roughness of the WO_3 thin films deposited on quartz substrates under various P_{O2}. Since the film deposited at P_{O2} of 10 mTorr was amorphous, it was difficult to estimate the number of grains as well as the average grain size. The films deposited at P_{O2} higher than 100 mTorr had the average grain size of approximately 200 nm and the average number of grains of about $8/\mu m^2$. There was no remarkable influence of P_{O2} on the grain size of the WO_3 thin films. We propose that the most effective way to change the grain size of the film is not by means of P_{O2} during deposition but by postannealing after deposition. In fact, the film deposited at T_s of 400°C at P_{O2} of 100 mTorr was postannealed at 800°C in oxygen atmosphere of 600 Torr for 30 min. The average grain size of the postannealed WO_3 thin film increased to about twice that of as-deposited film.

The effect of crystal structure on the gas sensing property was investigated by using amorphous, tetragonal and triclinic WO_3 thin films. The sensing property was measured in 60 ppm NO gas. The sensitivity of the film is defined as R_{NO}/R_{N2}; here, R_{NO} and R_{N2} are resistance in NO gas and pure N_2 gas, respectively. The sensitivity of the triclinic WO_3 thin film was higher than that of the tetragonal film. The amorphous film could not detect NO gas. We assume that the amorphous film will have stoichiometric defects such as oxygen vacancy. Figure 4 shows the behavior of the non-postannealed triclinic WO_3 thin film ($T_s = 400$°C, $P_{O2} = 200$ mTorr, thickness $= 1\,\mu m$) sensor in NO (60 ppm) gas measured at the low operating temperature of 150°C. The resistance of the WO_3 thin film increased markedly in NO gas, because the potential barriers between the adjacent grains were built up by the adsorbed gas species. It takes 4 min to complete the interaction between the film and the gas. The resistance of this sensor was 95% recovered within 2 min. The maximum sensitivity of 254 was obtained. The sensitivity of the triclinic film is higher than that of thermally evaporated film having the sensitivity of 40–100 to NO_2 (1–10 ppm) gas at the operating temperature of 200–250°C.[1–3]

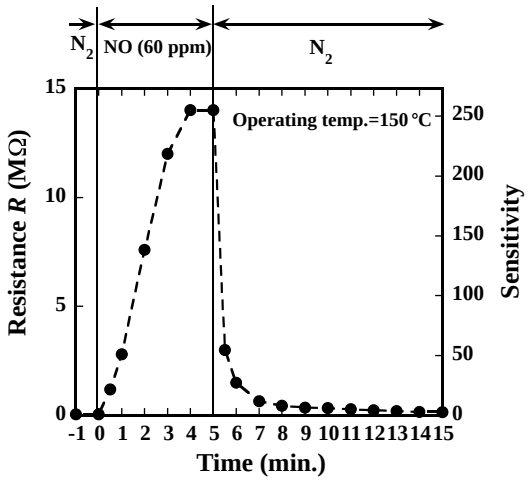

Fig. 4. The gas sensing property of the triclinic WO_3 thin film (1 μm) in NO gas (60 ppm).

4. Conclusions

In summary, the WO_3 thin films were deposited on quartz and Al_2O_3 substrates by the PLD method, changing the conditions of the P_{O2} (10–300 mTorr) and T_s (150–800°C). The tetragonal phase was prepared in the narrow range of P_{O2}. On the other hand, the triclinic WO_3 thin film was obtained in the wide range of P_{O2} (120–300 mTorr) and T_s (400–800°C). The lattice constant of the triclinic WO_3 thin films was close to that of the bulk target. No remarkable P_{O2} dependence of the grain size was observed under the present conditions. The average grain size and number of crystallized WO_3 thin films were approximately 200 nm and $8/\mu m^2$, respectively. The triclinic WO_3 thin film with thickness of 1 μm showed high sensitivity of 254 in NO (60 ppm) gas at low operating temperature of 150°C.

Table I. The oxygen pressure P_{O2} dependence of the average grain size, the average number of grains and the root-mean-square roughness of the WO_3 thin films deposited at the substrate temperature T_s of 400°C.

P_{O2} (mTorr)	Average grain size (nm)	Average number of grains ($/\mu m^2$)	R_{rms} (nm)
10	—	—	0.96
100	195	8.2	0.83
150	232	8.3	2.56
200	204	7.7	2.03
300	236	7.9	4.43

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