Pulsed laser deposited WO$_3$ thin films for gas sensor

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Abstract

WO$_3$ has attracted attention because of its potential for NO$_x$ gas sensing. Thin films of WO$_{3-y}$ were prepared by KrF excimer pulsed laser deposition technique on quartz and Al$_2$O$_3$ with Pt electrode. The films were deposited at various substrate temperature, oxygen pressure and conditions of the post-annealing. The substrate temperature over 400 $^\circ$C was needed for the crystallization of the WO$_{3-y}$ thin film. The crystal structure of the WO$_{3-y}$ thin film deposited at oxygen pressure of 100 mTorr and the substrate temperature of 400 $^\circ$C was tetragonal phase, however, the films deposited at the oxygen pressure over 200 mTorr showed triclinic phase. The atomic force microscopy image of the WO$_{3-y}$ thin film post-annealed in oxygen atmosphere for 30 min showed an average grain size of 268 nm. It was approximately two times larger than that of the as-deposited film. The maximum sensitivity ($R_{NO}/R_{air}$) of the as-deposited triclinic WO$_{3-y}$ thin film gas sensor in the NO gas (60 ppm in N$_2$) was 4.2 at an operating temperature of 200 $^\circ$C.

Keywords: WO$_3$; NO$_x$; Gas sensor; Tetragonal; Triclinic; Pulsed laser deposition

1. Introduction

The n-type semiconductor gas sensing materials like ZnO, SnO$_2$, TiO$_2$ and tungsten trioxide (WO$_3$) are based on the electrical conductivity change due to the interaction with gas. When gas molecules are adsorbed on the surface of a semiconductor gas sensor, electron transfer occurs between the semiconductor and adsorbate. If the electron affinity of the oxidizing adsorbate such as SO$_2$ and NO$_x$ is larger than the work function of the n-type semiconductor, the adsorbate accepts electrons from the semiconductor. If the adsorbate is a reducing gas, the semiconductor accepts electrons from the adsorbates. This electron transfer results in the change of potential barrier at the grain or crystallite boundary of the semiconductor. Therefore, the electrical conductivity of the semiconductor decreases in the oxidizing gas. In the reducing gas, the electrical conductivity increases.

The NO$_x$ gas sensor is needed for emission control of the NO$_x$. SnO$_2$ has been widely used as detector of hazardous gases, however it has problems such as low reproducibility, stability and selectivity. The sensitivity of SnO$_2$ sensor is too low to detect a small amount of NO$_x$ in air. Recently, the WO$_3$ has attracted much attention due to its high sensitivity to the NO$_x$. In addition, the film type gas sensors have been studied. Several methods such as thermal evaporation [1–3], sputtering [4–6], chemical vapor deposition [7] have been used for synthesis of WO$_3$ films.

We assume that pulsed laser deposition (PLD) technique is suitable for preparation of WO$_3$ film because of its reproducibility and controllabilities of stoichiometry and crystal structure. We report the crystal structure, surface morphology, grain size, crystallite size, optical property and gas sensing property of the WO$_{3-y}$ thin films prepared by PLD method.

2. Experimental details

WO$_{3-y}$ thin films were deposited on quartz and Al$_2$O$_3$ substrates by PLD method. The WO$_{3-y}$/quartz thin films were for measurement of X-ray diffraction (XRD), atomic force microscopy (AFM) and optical transmission. The Al$_2$O$_3$ substrate on which Pt electrodes were printed was used to measure the gas sensing property. Before deposition, a chamber (Neocera, $\varnothing = 12$ inches) was pumped down to base pressure of $1 \times 10^{-5}$ Torr. A stoichiometric WO$_3$ target (Dowa,
purity = 99.99%, \( \phi = 30 \) mm) was ablated by KrF excimer laser (Lambda Physik Compex205, 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 the substrate was 45 mm. The substrate temperature \( (T_s) \) and the oxygen pressure \( (P_{O_2}) \) during the deposition were changed from 150 to 800 °C and from 10 to 300 mTorr, respectively. After the deposition, the WO\(_{3-x}\) thin films were cooled down to room temperature in oxygen atmosphere of 760 Torr.

The crystallinity of the WO\(_{3-x}\) thin films was examined by means of the XRD (Rigaku RINT2000/PC) with Cu K\( \alpha \) radiation. The surface morphology of the films was observed by the AFM (Seiko Instruments Inc. SPI3800N). The optical transmission was measured using a spectrophotometer (Shimazu UV-160, UV-vis light). The electrical resistance \( (R) \) of the WO\(_{3-x}\) thin film was measured using the two terminal resistance method. The sensitivity of the WO\(_{3-x}\) thin film was estimated from the resistance measurement in NO gas (60 ppm in N\(_2\)).

3. Results and discussion

The crystal structure of the WO\(_3\) is a distorted cubic ReO\(_3\) type lattice. The XRD measurement showed that the crystal structure of our WO\(_3\) bulk target was triclinic phase with the lattice lengths of \( a = 7.33 \) Å, \( b = 7.54 \) Å and \( c = 7.71 \) Å. The WO\(_{3-x}\) thin films deposited at \( T_s \) lower than 400 °C were amorphous within the \( P_{O_2} \) range of 10–300 mTorr. The optical transmittance of the amorphous WO\(_{3-x}\) thin film was less than 5% in the wavelength range of 200–800 nm. The \( R \) of the amorphous WO\(_{3-x}\) thin film was rather smaller than that of the crystallized WO\(_{3-x}\) thin film. The oxygen deficiency \( (x) \) will be large in the amorphous film.

Fig. 1 shows \( P_{O_2} \) dependence of XRD spectra (20° \(< \theta < 26°\)) of WO\(_{3-x}\) thin films deposited on the quartz substrates at \( T_s \) of 400 °C. The \( P_{O_2} \) was varied from 10 to 200 mTorr. The typical strong diffraction peaks of the WO\(_3\) appear approximately 20 of 23°. The WO\(_{3-x}\) thin film deposited at \( P_{O_2} \) of 100 mTorr had a (0 0 1) peak at 22.89° showing tetragonal phase (JCPDS card No. 05-0388). The c-axis lattice length estimated from (0 0 1) peak angle using Bragg’s equation was 3.89 Å, which is corresponding to that of the JCPDS card (3.90 Å). The tetragonal WO\(_{3-x}\) thin film can be obtained within very narrow \( P_{O_2} \) range from 60 to 100 mTorr. In the case of \( P_{O_2} \) over 150 mTorr, the strong (0 2 0) and (2 0 0) peaks corresponding with triclinic phase (JCPDS card No. 20-1324) were observed. 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 \( P_{O_2} \) of 150 mTorr and \( a = 7.32 \) Å, \( b = 7.50 \) Å and \( c = 7.66 \) Å for the film deposited at \( P_{O_2} \) of 200 mTorr, respectively. These values are almost in agreement with the lattice lengths of triclinic bulk target. This controllability of the crystallization will be useful to investigate the effect of crystal structure on the gas sensing property.

We studied the influence of the post-annealing on the properties of WO\(_{3-x}\) thin film. Fig. 2 shows AFM images (3×3 \( \mu m^2 \)) of (a) as-deposited film prepared at \( T_s \) of 400 °C and \( P_{O_2} \) of 100 mTorr (tetragonal phase) and (b) post-annealed film in \( P_{O_2} \) of 600 Torr at \( T_s \) of 800 °C for 30 min. The crystal structure did not changed by the post-annealing. However, the grain size of the post-annealed film increased approximately two times comparing to the as-deposited film. The average grain sizes of the as-deposited film and post-annealed film were 125 and 268 nm, respectively. Since the gas sensor having the large surface area is desirable, the as-deposited film consisting of smaller grains is expected to have higher sensitivity than the post-annealed film.

Whereas, the WO\(_{3-x}\) thin film deposited at \( T_s \) of 400 °C and \( P_{O_2} \) of 200 mTorr was post-annealed in vacuum (2×10\(^{-5}\) Torr) at \( T_s \) of 800 °C for 30 min. The crystal structure changed from the triclinic phase to the tetragonal phase with very broad peaks by the annealing. The annealed film had very low resistance. It suggests that the oxygen deficiency was enhanced by the post-annealing in vacuum. Fig. 3 shows the optical transmittance of the as-deposited film and the post-annealed film in vacuum measured by the spectrophotometer. The as-deposited film exhibited the transmittance over 80% in the visible region, but the post-annealed film showed the low transmittance at the wavelength range (400–500 nm). Zhuang et al. reported that the WO\(_{3-x}\) thin film with \( x = 0.3–0.5 \) was blue colored film showing electrical conductive property [8]. The grain sizes before and after annealing were almost the same value of 120 nm.

Fig. 4 shows the gas sensing property of the as-deposited triclinic WO\(_{3-x}\) thin film (\( T_s = 400 °C \), \( P_{O_2} = 200 \) mTorr) prepared on the Al\(_2\)O\(_3\) substrate as NO gas detector. Thickness of the film is approximately 300
The sensor property was measured in a quartz tube (Ω = 11 mm). The NO gas (60 ppm) flow was adjusted using mass flow controller. N₂ gas was used for balance gas. The WO₃₋ₓ thin film sensor was heated directly using an electrical block heater and temperature controller. The sensitivity is defined as \( R_{\text{NO}} / R_{\text{N₂}} \), where \( R_{\text{NO}} \) is the \( R \) in NO gas and \( R_{\text{N₂}} \) is the \( R \) in pure N₂ gas. The \( R_{\text{N₂}} \) decreased as increase of the operating temperature. The maximum sensitivity of 4.2 was obtained at the operating temperature of 200 °C. This temperature which give maximum sensitivity is approximately 200 °C lower than that of the SnO₂.

4. Conclusion

We prepared the WO₃₋ₓ thin films using PLD method for gas sensor. The threshold \( T_s \) for crystallization was 400 °C. The tetragonal phase was obtained in the \( P_{\text{O₂}} \) range of 60–100 mTorr. In the case of the \( P_{\text{O₂}} \) over 150 mTorr, the film became triclinic structure. The grain size of the tetragonal WO₃₋ₓ thin film post-annealed in \( P_{\text{O₂}} \) of 600 Torr was two times larger than that of the as-deposited film. The crystal structure of the triclinic WO₃₋ₓ thin film changed to the tetragonal phase by the post-annealing in vacuum, however there was no change as to the grain size before and after annealing. The optical transmittance of the WO₃₋ₓ thin film after post-annealing in vacuum was very low in the visible region.
and the color was slightly blue. The sensitivity of the triclinic $\text{WO}_3$ thin film to NO gas (60 ppm in $\text{N}_2$) was 4.2 at the operating temperature of 200 °C. It was found that the $\text{WO}_3$ thin film gas sensor has potential for the NO gas sensor working at lower temperature than other oxide semiconductor sensors.

References
