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# Dependence of $NO_2$ gas sensitivity of $WO_3$ sputtered films on film density

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**Abstract**

Pure $WO_3$ films and $WO_3$ films doped with noble metals such as Au, Pt, and Ru were deposited on quartz substrates by dc reactive magnetron sputtering to investigate the $NO_2$ gas sensitivity. The temperature of the substrate and the pressure of the discharge gas were changed. The film structures were studied by X-ray diffraction, atomic force microscopy, and density measurements. The $WO_3$ films had a triclinic structure and seemed to be composed of columns surrounded by voids. The film density decreased as the discharge gas pressure increased and the substrate temperature decreased. Gas sensitivity was measured at an $NO_2$ gas concentration of 3 ppm. Low film density and Au doping caused a high sensitivity to $NO_2$ gas. The highest sensitivity was observed in a film with an Au concentration of 0.25 at.% and a density of 5.0 g/cm$^3$, which was significantly smaller than the bulk density of 7.3 g/cm$^3$.


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## 1. Introduction

In recent years, exhaust gas generation from automobiles and factories, etc., has created a serious air pollution problem all over the world. In particular, nitrogen oxide $NO_x$ ($NO_2$ or NO) is toxic in itself and, furthermore, is a main source of acid rain and photochemical smog [1]. In environmental monitoring, the threshold limit values for $NO_2$ and NO have been determined to be 3 and 25 ppm, respectively, as listed in the safety standards by the American Conference of Governmental Industrial Hygienists. Because NO gas tends to be oxidized into $NO_2$ gas in air [2], the development of a small $NO_2$ gas sensor with high sensitivity to low concentrations of $NO_2$ gas is strongly required.

Numerous attempts to use various metal oxide semiconductors as gas sensors have been made. Among those semiconductors, $WO_3$, an n-type semiconductor whose free electrons originate primarily from oxygen vacancies [3], shows excellent sensing properties with low concentrations of $NO_2$ gas. Therefore, $WO_3$ thin film is considered to be a promising $NO_2$ gas sensor [4–7]. Various attempts have been made to enhance the gas sensitivity of semiconductor gas sensors, one of which involved the doping of impurities in films. Penza et al. [8,9] have shown that a high sensitivity is achieved when noble metals such as Pt, Au, and Pd, etc. are deposited as activator layers on $WO_3$ films because of the effects of agglomeration of the noble metals on the surface of the $WO_3$ films. Zhao et al. [10] have reported that Al and Ti doping change the crystal structures of tungsten oxide films deposited by pulsed laser deposition from triclinic $WO_3$ to tetragonal $WO_{2.90}$. They have also mentioned that Al and Ti doping greatly improve the $NO_2$

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gas sensitivity due to the formation of fine crystallites in a tetragonal $WO_{2.90}$ film. Akiyama et al. [11] have reported that the NO gas sensitivity is improved by doping Pt, Au, and Ru to a $WO_3$ sintered sensor element, since the adsorption of the gas related to NO is increased. With regard to an Ag-doped $WO_3$ sintered sensor, Chen et al. [12] have found that Ag doping creates high concentrations of oxygen vacancies functioning as adsorption sites and improves the sensitivity to NO gas. Another attempt at improving gas sensitivity involved creating a porous film, as a porous film provides more surface adsorption sites for the detection gas. According to the microstructure model of sputtered films presented by Thornton [13], the sputtered films deposited under conditions of low temperature and high discharge gas pressure usually have a columnar structure and the columns are surrounded by voids. As the substrate temperature decreases and the discharge gas pressure increases, voids develop and the density of the film decreases. As such, Kunimoto et al. [14] and Yamazaki et al. [15] have investigated the influence of deposition conditions of $SnO_2$ sputtered films on the film structure and have discussed the relation between the film structure and $H_2$ gas sensitivity. They found that a porous film has a high sensitivity. In the present study, we investigated the effects of doping of noble metals (Pt, Au, and Ru) and the porosity of $WO_3$ films on $NO_2$ gas sensitivity.

## 2. Experimental details

$WO_3$ films were deposited on 15×15 $mm^2$ quartz substrates by reactive dc magnetron sputtering. A circular tungsten target 100 mm in diameter with a purity of 99.99% supplied by Furuuchi Chemical was used. For Au, Pt, and Ru doping, pieces of these metals 0.1 mm in thickness were placed on the tungsten target. The discharge gas was an argon–oxygen mixture with a ratio of $Ar/O_2$=1:1. Before deposition, the target was presputtered for 300 s with a shutter closed. The discharge gas pressure was changed between 1.3 and 10 Pa. The discharge current was fixed at 50 mA, and the discharge voltage took a value between 580 V and 480 V depending on the gas pressure. The substrate temperature was changed between room temperature and 673 K. The film thickness was approximately 100 nm. After deposition, the films supplied for the measurement of the sensing properties were annealed at 873 K for 14.4 ks in air to stabilize the sensing properties. Pt interdigital electrodes were then formed on the films.

The crystallographic structure and the surface morphology of sputtered $WO_3$ films were studied by means of X-ray diffraction (XRD) with Cu-$K_\alpha$ radiation and atomic force microscopy (AFM) in contact mode with silicon nitride tip, respectively. A diffractometer (Rigaku Rint 1000) and an atomic force microscope (Digital Ins. NanoScope III) were used in these measurements. The concentrations of the noble metals doped in the films were measured by an electron probe X-ray microanalyzer (Shimazu EPMA-1500). The film density was determined after annealing at 873 K by measuring the thickness and mass of the films using a mechanical surface roughness tester (Kosaka SE-30D) and an electronic balance (Mettler Toled MT5). The measurement error of the thickness and that of the mass were 3 nm and 1 μg, respectively; these values correspond to the uncertainty of 3% and 1%. Therefore, the uncertainty of the measured density is estimated to be about 4%.

To evaluate the sensitivities, sensor samples were installed in an aluminum vessel with a capacity of $13\times10^{-3}$ $m^3$ and were heated from the back of the quartz substrate using an electric heater. The heater was made of a nichrome wire wound around a mica plate and was

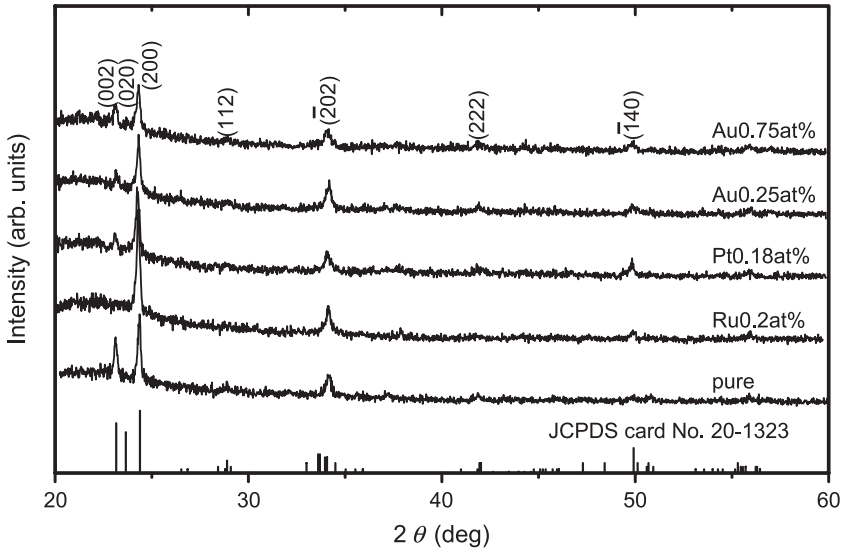


Fig. 1. XRD patterns of pure as well as Au, Pt, and Ru-doped $WO_3$ films after annealing at *873 K*. The discharge gas pressure and the substrate temperature during the deposition were 1.3 Pa and room temperature, respectively.