Pt- and TiO_2-doped Nb_2O_5 Thin Film by Ion-Beam-Enhanced Deposition

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ABSTRACT

This paper describes the preparation of Pt- and TiO_2-doped Nb_2O_5 thin film by Ion-Beam-Enhanced Deposition. Platinum and titanium doping, and Nb_2O_5 deposition were carried out in situ. The dependence of oxygen sensing properties on the amounts of Pt and Ti dopant in the Nb_2O_5 film was investigated. There were the highist sensitivity, the lowest temperature coefficient and the shortest responce time at doping of 5 mol % TiO_2 and 0.3 mol % Pt

1. INTRODUCTION

Oxygen sensors that can operate at elevated temperatures have found wide use in monitoring and control of combustion processes, for example, control of the air-to-fuel mixture of an internal conbustion engine. In the most widespread application, the oxygen sensors are used to feedback control the air-to-fuel ratio, A/F, of an engine at the stoichiometric value, $(A/F)_{stoich}$, by detecting the large change in the thermodynamic equilibrium oxygen partial pressure of the exhaust gas that occurs at this A/F value. To date, two different types of these so-called stoichiometric exhaust gas oxygen sensors have been developed. One is an electrochemical oxygen concentraation cell made from yttria or calcia-stabilized zirconia (ZrO_2). The other is a MOS (metal Oxide semiconductor)-based resistive-type device which utilizes the fact that the resistivity of MOS depends on the oxygen partial pressure in the ambient. Among MOS materials, TiO_2 has been under the most investigations [1-3]. Kondo et al [4] have reported that Nb_2O_5 exhibits the better sensing properties than TiO_2 as an A/F sensing material. Michitaka Chtaki et al [5] also reported that TiO_2-doped Nb_2O_5 ball mill exhibits the maximum sensitivity and the smaller temperature dependence on the electrical conductivity at the low doping level of Ti. This paper describes the preparation and characterization of Pt- and TiO_2-doped Nb_2O_5 Thin Film by IBED (Ion-Beam-Enhanced Deposition) . The better performances for oxygen sensing were obtained.

2. EXPERIMENTAL

Using the IBED technique and microelectron planar technology, automotive A/F sensors were produced on Al_2O_3 substrates consisting of an oxygen-sensitive Pt- and TiO_2- doped Nb_2O_5 element, a platinum temperature sensor and a Pt heater. (see Fig. 1). The Pt thin film with a thickness of 1μm was deposited by IBED, and was patterned using a conventional lift-off photolithographic process.

The Pt- and Ti-doped Nb_2O_5 thin film was deposited on a cooled Al_2O_3 substrate by IBED using a single ion source with Ar ion from a combined target of Pt, Ti and Nb_2O_5(purity concentration 5×10^{-3} % w/w). The amount of Pt and Ti dopant in Nb_2O_5 could be changed by changing area ratio of Pt and Ti to Nb_2O_5 target (see Fig. 2). The doping dose of Pt and Ti in Nb_2O_5 could also be finely adjusted by varying IBED parameters such as ion beam energy, ion beam current density and incident angle. The patterns of the Nb_2O_5 thin film were again delineated using the lift-off technique.

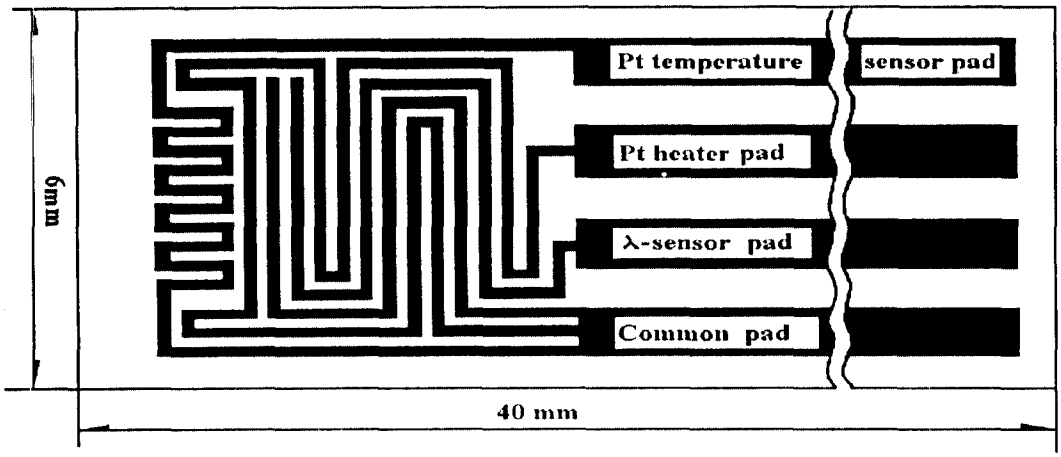

Fig 1. The structure of the λ-sensors

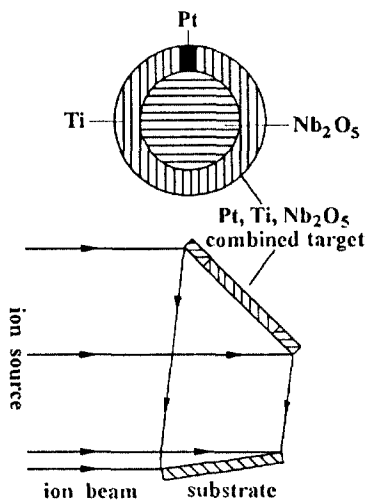

Fig 2. The principle of doping and simultaneous deposition in the IBED system

During deposition, the total pressure in the operation chamber of the sputtering system was approximately 1.6×10^{-2} Pa using 66.7% Ar and 33.3% O_2. The average sputtering power was approximately 2W/cm^2, which resulted in a deposition rate of 24nm/min. The films with a thickness between 0.5 and 1.5μm were then tempered in air for 2h at 1000 °C to obtain a structure, that was stable under high temperatures. The films were investigated by electrical measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). Analysis of the amount of TiO_2 dopant was carried out using inductively coupled plasma atomic emission spectrometry (ICP-AES). The dependence of the electrical resistance of the film on temperature was measured using a quartz vessel in a tube furnace either in nitrogen or oxygen. The R-T characteristic of the specimen was measured in the exhaust gas of an oxygen-propane combustion in the temperature range of 550 to 750°C. Propane, oxygen and nitrogen were mixed in appropriate ratios to obtain the desired λ value, then the gas mixture was burned at 450°C over a combustive catalytic case. The exhaust

gas was introduced into the quartz vessel in which an yttria-stabilized zirconia (YSZ) oxygen sensor was installed to monitor the equilibrious partial pressure of oxygen. The resistance of the specimen was measured using a 8840A MULTIMETER. Figure 3 shows the schematic diagram of the measurement system of the sensors.

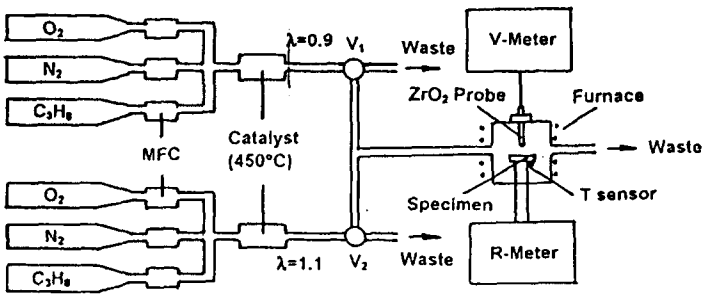

Fig 3. Schematic diagram of the measurement system of the sensors

3.Results and discussion

3.1 Spectra of XRD for the films

The results examined by XRD indicated that the TiO_2-Nb_2O_5 films with different ratio exhibit amorphous state. Figure 4 shows the spectra of XRD for the films after annealing at 1000°C in air for 2h. Besides the pure TiO_2 film is rutile, the Nb_2O_5 films with various amount of TiO_2 dopant belong to monoclinic system while not to found any TiO_2 crystal phases until the amount of TiO_2 dopant up to 34mol %. However, It is confirmed by the spectrum of XPS that Ti in Nb_2O_5 films appear as TiO_2 bond even through anealing at the range of 900-1100°C (Figure 5).

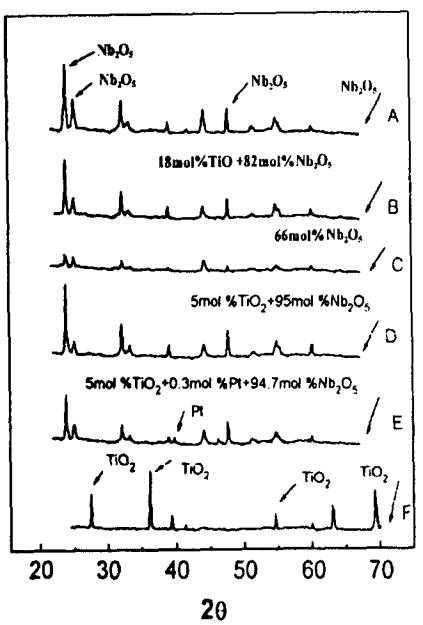

Fig. 4 Spectra of XRD for the films with different component.

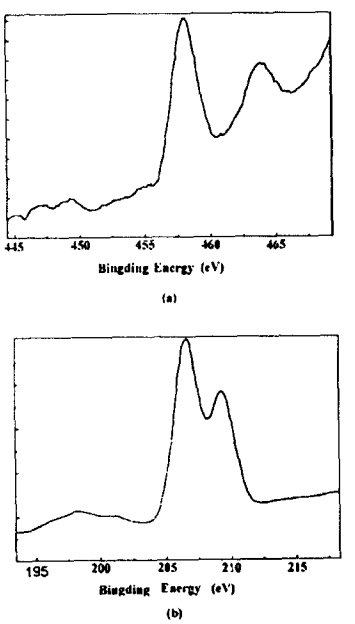

Fig. 5 Spectra of XPS for TiO_2 (a) and Nb_2O_5 (b).

3.2 Characteristic factor and activation energy

It is common knowledge that the electrical resistance of metal oxide semiconductor film depends on pO_2 according to the following equation:

$$R = R_0 \exp(E/KT)\left(P_{O_2}\right)^{1/m}, \qquad (1)$$

where m is a characteristic factor as a measure of the sensitivity to oxygen. E the activation energy, k the Boltzman constant. T the substrate temperature and pO_2 the partial oxygen pressure.

The measured data of the resistance of TiO_2-doped Nb_2O_5 thin film [$TiO_2/(TiO_2+Nb_2O_5)$=75mol%] and the calculated m values are listed in Table 1.

Table 1 Dependence of the resistance of the sensor on the partial pressure of oxygen at 700°C and the calculated m values.

Atmosphere	pO_2 (KPa)	R (KΩ)	m	$\bar{m}$
O_2	100	1050	4.896	
N_2	0.01	160	4.896	
O_2	100	1010	4.880	4.9
N_2	0.01	153	4.880	
O_2	100	963	4.918	
N_2	0.01	148	4.918	

The characteristic factor m, the activation energy E and the constant Ro of the films for various mol % of TiO_2 to Nb_2O_5 are listed in Table 2.The results shown in Table 2 indicate that the characteristic factor m decreased, i.e., the sensitivity to oxygen increased and the activation energy E decreased, so that the effect of temperature on the resistance of the film decreased as the ratio of TiO_2 to Nb_2O_5 decreased. Thus we chose 5 mol % TiO_2 as the film composition for the remaining experiments. The dependence of the characteristic factor m on the ratio of TiO_2 to Nb_2O_5 is similar to that found by Ohtak et al [5].

Table 2 m, E and Ro of the film depends on the ratio of TiO_2 to Nb_2O_5.

$TiO_2/(TiO_2+Nb_2O_5)$(mol%)	m	E (eV)	Ro (Ω)
75	4.9	0.74	0.24
25	4.9	0.20	4030
5	4.3	0.10	4467

3.3 Resistance-λ Characteristic curves

The resistance-λ characteristic curves at different temperatures are shown in Fig. 6. The jump in the curves at the stoichiometric point is greater than 3 orders of magnitude. There is a greater effect of temperature on the resistance of the sensor in the lean-burning region and little effect in the rich-burning region in the temperature range of 600 to 750 °C. Hence, the resistance jump of the sensor at low temperatures is larger than at high temperatures.

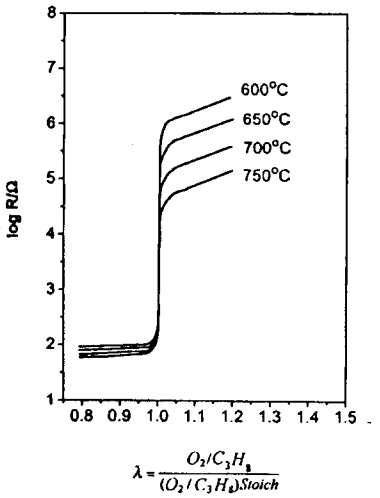

Fig 6 Resistance-λ characteristic curve of the λ-sensor at different temperatures.

3.4 Response time

The response time of the sensor depends not only on the temperature of the substrate and the thickness of the sensitive film (diffusion within a solid), but also on various other factors, including gas diffusion, absorption, reaction and porous diffusion as well as on the gas species of environment and the catalyst in the film. There were no significant differences for response time between the sensor without the catalyst Pt and that with Pt when the atmosphere changed between nitrogen and oxygen and between propane and oxygen. It took 3.5 min to establish a stable response when the atmosphere changed from nitrogen to oxygen However, the response time of the sensor is shorter than 0.1 min when the atmosphere changed from propane to oxygen. When the atmosphere changed from λ=1.1 to 0.9, the response time of the sensor with 0.03mol% of Pt was shorter than that without Pt. Compared with ZrO_2 oxygen sensor (LSH 23 Bosch, Germany), the response time of the Nb_2O_5 film sensor (10 ms) is shorter than that of the ZrO_2 sensor (20 ms)when the atmosphere changes from λ=0.9 to 1.1, which is contrary to that when λ=1.1 to 0.9 (100ms and 20 ms, respectively) (Fig. 7).

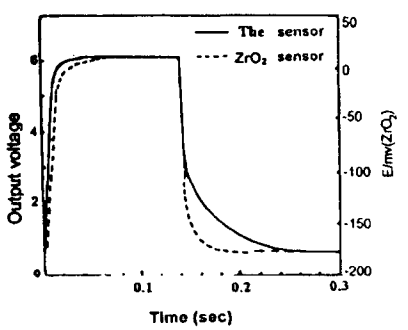

Fig.7. Comparison between the response time for the sensor and that for ZrO_2 oxygen sensor at 600°C when λ changes from 0.9 to 1.1 and vice versa.

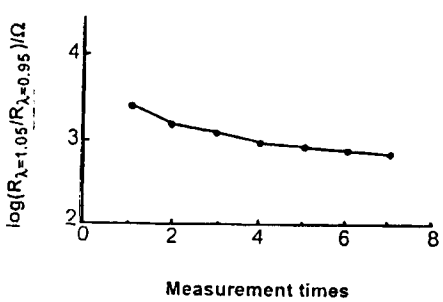

Fig.8. The resistance jump at the stoichiometric point in the characteristic curves which changes with the measurement time.

3.5 Stability

Equation(1) shows that the lower the activation energy, the lower the TCR(temperature coefficient of resistance) for oxygen-sensitive film. That is, the higher the thermostability for the oxygen-sensitive device. Figure 8 shows the stability of the λ-sensor. Initially the λ-sensor presented a high sensitivity which then decreased slightly as the time for measuring increased, and it became stable after seven measurements were taken. Therefore, to carry out the aging process, the stable response characteristic of the sensors must be obtained.

4. Conclusion

A new automotive air/fuel sensor based on Pt- and TiO_2-doped Nb_2O_5 thin film was developed using the IBED technique and planar microsystem technology. The sensor performed well, exhibiting such factors as high sensitivity and good stability, as well as the possibility of cost-effective production. However, further studies are needed to produce a λ-sensor with optimum performance that can be applied to automotives. For example, it is necessary to place a protective layer on the surface of oxygen-sensitive films to reduce the adverse effects, specifically those due to the poison action of lead, sulfur and phosphorus.

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