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Possibility for sub-ppm hydrogen detection with the ball SAW sensor

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ABSTRACT

For efficient control of fuel cells, highly sensitive measurement of the concentration of hydrogen gas (H_2) under high humidity is required. In this study, we fabricated the ball SAW sensor with sputtered Pt-coated Zno film as a sensitive film and evaluated the response to H_2 of the concentration in the range of 200 ppm to 20 ppm. The thicknesses of ZnO and Pt films are 200 nm and 5 nm, respectively. The sensor succeeded in detecting 20 ppm H_2 by the amplitude change of -0.79 dB. After the sensor was wetted by water, the response was measured again. As a result, 20 ppm H2 was detected by 0.4 dB. We calculated the detection limit (DL) defined as the concentration corresponding to the signal to noise ratio of 3. Since DLs before and after wetted was 0.47 ppm and 0.27 ppm, respectively, the sensitive film was not deteriorated by wetting. In conclusion, it was shown that the ball SAW sensor with Pt-coated ZnO film was useful for humidity-proof H2 sensor with sub-ppm DL.

INTRODUCTION

For efficient control of fuel cells, highly sensitive measurement of the concentration of hydrogen gas (H_2) under high humidity is required. We succeeded in detecting H_2 of 10 ppm by the ball surface acoustic wave (SAW) sensor with a sensitive film of Pd-Ni hydrogen absorbing alloy [1], where highly sensitive measurement is realized using ultramultiple roundtrip propagation of SAW (more than 100 turns). However, the deterioration of the sensitive film by humidity was a problem. In this situation, although the planer SAW sensor with Pt-coated ZnO film was reported as a humidity-proof H_2 sensor [2], the possibility of detecting 10ppm H_2 was not clear. In this study, we aimed to evaluate the response of the ball SAW sensor with sputtered Pt-coated ZnO film to low concentration hydrogen gas.

PRINCIPLE OF BALL SAW SENSOR

Figure 1 shows the principle of the ball SAW sensor [1]. The ball SAW sensor is made of a piezoelectric crystal sphere such as quartz and langasite by the fabrication of an interdigital transducer (IDT) with an aperture $a = \sqrt{\lambda D}$ on the z-axis cylinder, where λ is a wavelength and D is a diameter of the sphere. When the IDT is excited by an RF pulse signal, naturally collomated SAW propagates along the equator without diffraction, realizing multiple roundtrip propagation. Since Pt-coated ZnO film deposited on propagation route reacts with H_2 and changes the conductivity, the delay time and amplitude of the roundtrip wave are changed. Although those in one turn are small, they are proportionally accumulated as a function of the number of turns. Thus, high sensitivity is realized by multiple-roundtrip propagation of SAW.

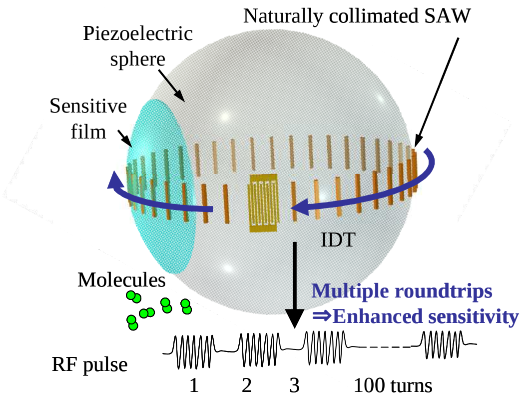

Figure 1 Principle of ball SAW sensor

EXPERIMENTAL SETUP

Deposition of Pt-coated ZnO film

We deposited Pt-coated ZnO film as the sensitve film on the langasite ball SAW device with a diameter of 3.3 mm by RF magnetron sputtering. Table 1 shows the sputtering condition. ZnO film with a thickness of 200 nm was deposited and subsequently Pt film with a thickness of 5 nm was deposited over the ZnO film as a catalyst. Using a stencil mask, the sensitive film was deposited on one third of total propagation route. Figure 2 shows the ball SAW sensor after the deposition.

Table 1 Sputtering conditions

Target	ZnO	Pt
Base pressure (Pa)	4.0E-6	4.0E-6
Ar pressure (Pa)	0.67	067
Power (W)	50	50
Deposition time (min)	90	1
Thickness (nm)	200	5

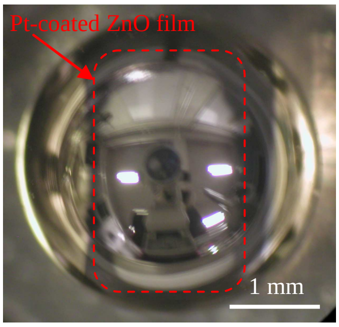

Figure 2 Ball SAW sensor with Pt-coated ZnO film

Measurement apparatus

Figure 3 shows a schematic diagram of the measurement apparatus. The concentration of a sample gas is controlled by two mass flow controllers (MFCs), where 0.1%H_2-N_2 and N_2 are mixed on the condition that total flow rate becomes 100 ml/min. The sequence of the measurement was consisted of the repetition of the exposure of the sample gas for 8 minutes and the purge of the carrier gas for 20 minutes. The sample gas flows into into a flow cell with a dead volume of 57.4 mm^3 and is measured by the ball SAW sensor. The temperature of the flow cell is controlled by an oven of a gas chromatograph.

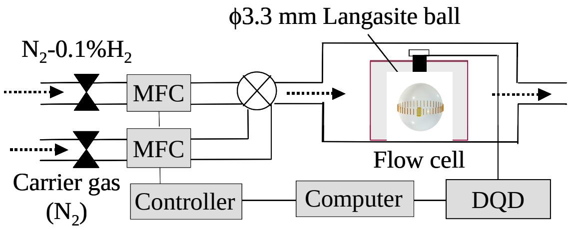

Figure 3 Measurement aparatus

A digital quadrature detecter (DQD) was used for the transmission and reception of SAW, as shown in Fig. 4 [3], where the excitation frequency and the intermediate frequency are 150 MHz and 10 MHz, respectively. By virtue of the high-speed digital signal processing in the field-programable gate array (FPGA), the phase and the amplitude can be calculated with an interval of 1 ms. Here, the data were output with an interval of 0.256 s because of averaging over 256 times. The delay time t and the amplitude V are caluculated by

$$t = \frac{n_{counter}}{f_s} - \frac{\phi / 360}{f}, \quad (1)$$

$$V = \sqrt{\cos^2 \phi + \sin^2 \phi}, \quad (2)$$

where n_{counter} and f_s are the number of a counter and the system clock frequency in the FPGA and f is the excitation frequency.

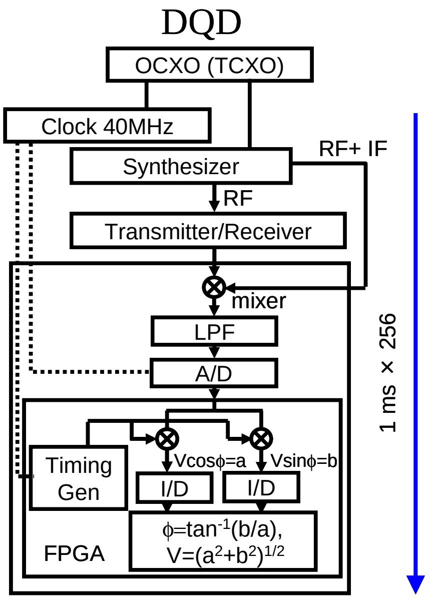

Figure 4 Block diagram of DQD

MEASUREMENT RESULTS

Waveform of ball SAW sensor

A multiple roundtrip waveform of the sensor with sensitive film was measured by the impulse signal of an ultrasonic flaw detector, as shown in Fig. 5. Figure 5 (b) is the waveform at the 50th turn, where the amplitude of 10 mV was obtained.

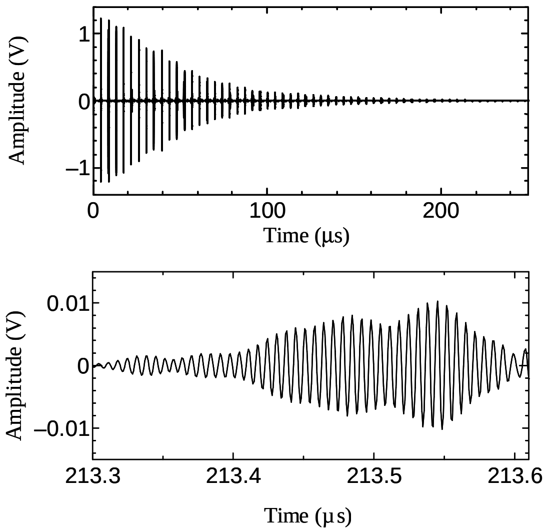

Figure 5 waveform of ball SAW sensor
(a) multiple roundtrip, (b) 50 turns

Attenuation change by sensitive film

The attenuation coefficient was calculated from the change of the amplitude of the multiple-roundtrip waveform [4]. Figure 6 shows multiple-roundtrip waveforms of the sensor with (a) no sensitive film and (b) Pt-coated ZnO film, where the vertical axis is logarithmic scale.We calculate the attenuation coefficient by fitting the linear function to the peak amplitudes of each roudtrip waveform shown by open circles. As a result, the attenuation change due to the deposition was 39.6 dB/m, since the attenuation coefficients of (a) and (b) were 39.4 dB/m and 79.0 dB/m, respectively.

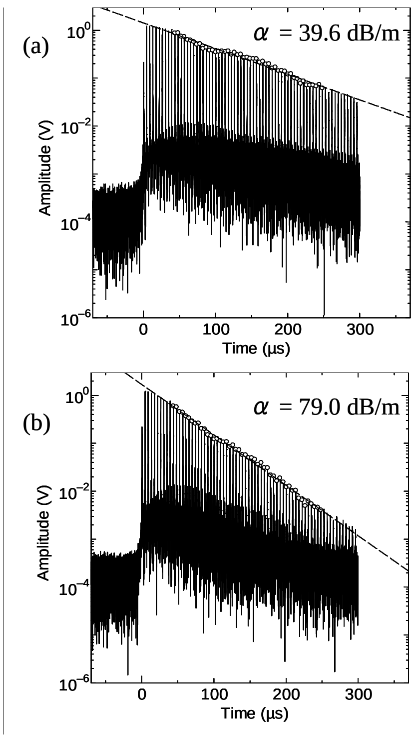

Figure 6 Roundtrip waveform of Ball SAW sensor (a) no sensitive film, (b) ZnO/Pt sensitive film

Measurement of hydrogen gas

Figure 7 shows the response of the sensor to H2 with the concentration of 200, 100, 50, and 20 ppm at 80℃. The bottom figure represents the change of H_2 concentration. The top and middle figures represent the delay time and amplitude changes, respectively. Although the both responses detected all concentrations of sample gases, the amplitude response is clearer than the delay time response with regard to the recovery to a baseline during purge period. As a result, 20 ppm was measured by the amlitude change of -0.79 dB. The mechanisum of the decrease of the amplitude by H_2 is considered as follows; first, hydrogen molecules are adsorbed, dissociated and ionized on Pt surface. Then, the conductivity of ZnO film of n-type semiconductor increases because a depletion layer of ZnO decreases [5]. Therefore, the energy of SAW that is converted to electrical energy is dissipated by Joule effect.

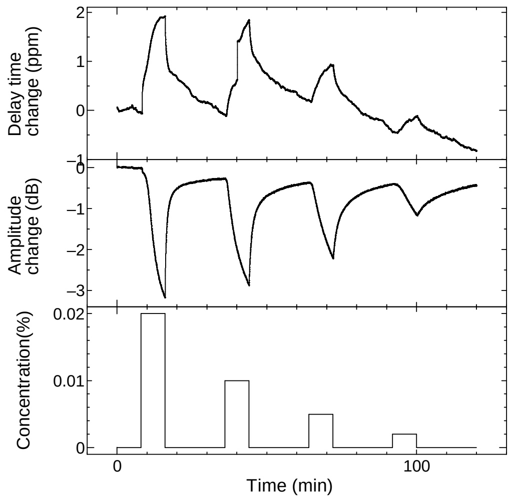

Figure 7 Response of Ball SAW sensor toward hydrogen gas of 200-20 ppm

After the sensor was wetted by water and dried, the response was measured again. Figure 8 shows the measurement result. The responses similar to the shape of fig. 7 were obtained and the amplitude change for 20 ppm was -0.48 dB. It was shown that the sensor was water-proof, therefore, it was estimated that the sensor was humidity-proof..

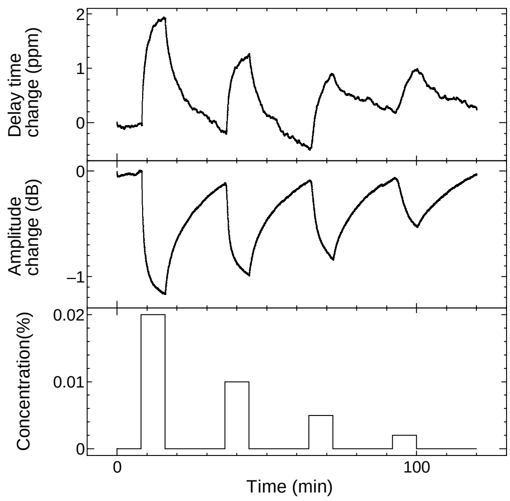

Figure 8 Response of Ball SAW sensor after wetted and dried

EVALUATION OF DETECTION LIMIT

Evaluation of relative noise

To evaluate the detection limit (DL), the relative noise of the amplitude chage was measured [6]. Figure 9 (a) shows the amplitude change measured in carrier gas. This waveform is filtered by FFT in the range of 0.0333-1.67 Hz because of the significance to the sensor response, resulting in Fig. 9(b). The relative noise is obtained from the root mean square (RMS) of the amplitude of this waveform. The relative noises before and after wetted were 0.0063 dB and 0.0022 dB, respectively.

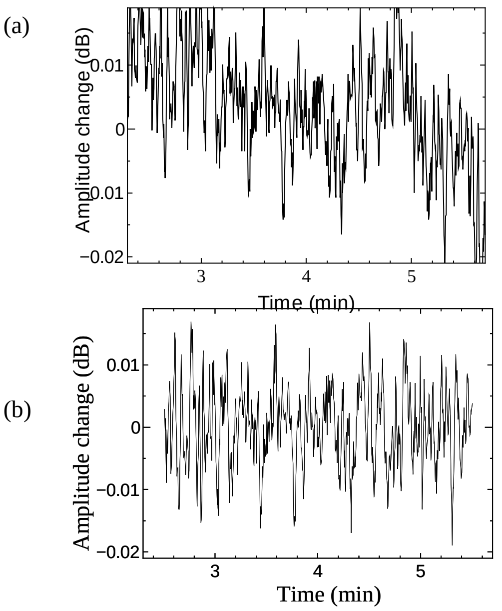

Figure 9 Evaluation of noise
(a) raw data (b)FFT-filtered data

Calculation of DL

DL is defined as the concentration corresponding to the signal to noise ratio of 3. Figure 10 shows the relation between H_2 concentrations and the amplitude changes measured in Fig. 7, where the range of the order of magnitude in vertical axis is the same as that in horizontal axis. The solid line with a slope of 45^o represents the proportional relation between concentrations and amplitude changes in the case of 20 ppm data. Result showed that the sensitivity increased as the concentreation decreased. Two broken lines represent the relative noise σ and the three times of this value (3σ) respectively. Since DL is given by the concentration at the intersection of the solid line and the broken line of 3 σ , DL was 0.47 ppm in this case.

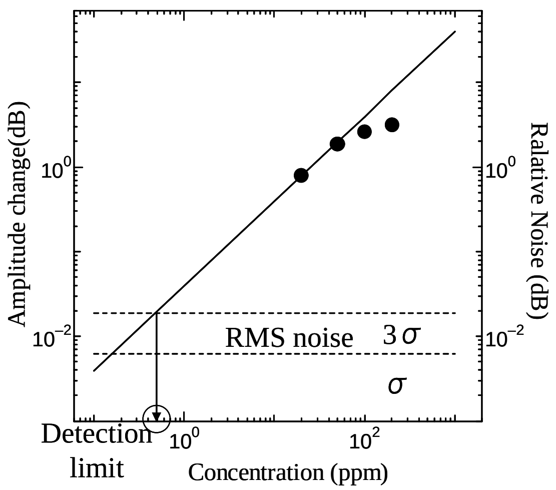

Figure 10 Evaluation of DL

Tempreature dependence of DL

Figure 11 shows the relation between the DLs and the temperature. Solid circle represents DL before wetted and open circles and open triangles represent DLs after wetted. At 80^oC, DLs before and after wetted was 0.47 ppm and 0.27 ppm respectively. Therefore, the degradation of DL was not observed. Sub-ppm DLs are obtained at all temperatures and these values were improved as the temperature increased.

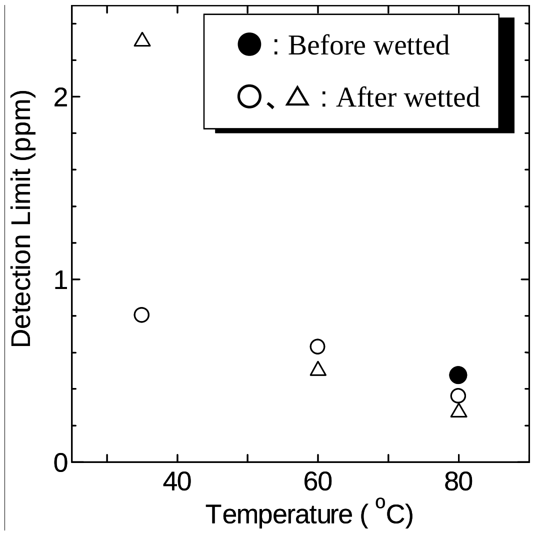

Figure 11 Relation between detection limit and temperature

CONCLUSION

H_2 was measured by the ball SAW sensor with Pt-coated ZnO sensitive film. H_2 of 20 ppm was detected by the sensor before and after wetted, then DLs were calculated. Sub-ppm DLs were attained in the temperature of 35 ℃ to 80℃ and the degradation of DL by wetting was not observed. Therefore, it was shown that the ball SAW sensor with Pt-coated ZnO film was useful for humidity-proof H_2 sensor with sub-ppm DL.

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