Proceedings of Symposium on Ultrasonic Electronics, Vol. 34 (2013) pp. 155-156
20-22 November, 2013

Fast and sensitive ball SAW hydrogen sensor with porous Pd-Pt alloy film

多孔性 Pd-Pt 合金膜を用いた高速かつ高感度な
ボール SAW 水素センサ

Toshihiro Tsuji[1†], Satoshi Hagihara[1], Toru Oizumi[1], Nobuo Takeda[1], Tsuneo Ohgi[2], Takayuki Yanagisawa[2], Shingo Akao[2,1], Noritaka Nakaso[2], and Kazushi Yamanaka[1]
([1]Tohoku Univ.; [2]Toppan Printing Co. Ltd.)
辻俊宏 [1†], 萩原啓 [1], 大泉透 [1], 竹田宣生 [1], 大木恒郎 [2], 柳沢恭行 [2], 赤尾慎吾 [2,1], 中曽教尊 [2], 山中一司 [1]([1] 東北大, [2] 凸版印刷)

1. Introduction

To use H_2 gas as common energy source, fast and sensitive sensor is required for early detection of the leakage. For monitoring use, sensors working at room temperature (RT) were studied and developed, based on resistive and surface acoustic wave (SAW) sensors[1-4]. In this situation, a ball SAW sensor, that enhances the sensitivity by multiple-roundtrip propagation of collimated SAW beam, realized the widest detection range (10 ppm to 100%) [5] with Pd-Ni alloy film [6]. However, their response time at low concentration were not still sufficiently short, typically ～100 s to 100 ppm H_2.

To shorten the response time, both the dissociation and diffusion of hydrogen atoms into the sensitive film should be promoted. They may be enhanced by increasing surface area such as porous structure and by alloying catalytic element such as Pt [7]. In addition, Pt alloying Pd was proof against the phase transition [7]. Thus, although porous Pd-Pt alloy film is promising for H_2 gas sensing, it has not been applied to the ball SAW sensor. In this study, we develop the ball SAW sensor with porous Pd-Pt alloy film for realizing fast and sensitive hydrogen sensor working at RT.

2. Measurement implementation

Typical sputterd-film structure with respect to a substrate temperature and an Ar pressure was reported in reference 8. Based on it, we deposited porous Pd-Pt film at RT and 2.7 Pa using an rf magnetron sputrtering. Pt-alloying was performed by co-sputtering of Pd (50W) and Pt (20W). As a result, Pd-20%Pt alloy film was fabricated on a langasite ball SAW device (ϕ3.3 mm, 150 MHz) with a thickness of 40 nm.

A schematic diagram of an apparatus is shown in Fig. 1. In order to adjust H_2 concentration, H_2-N_2 mixed standard gas was diluted with N_2 gas (G1 grade), using the digital mass flow controllers (MFCs) so as to be total flow rate of 50 ccm. The sensor was set in a sensor cell with a dead volume of 0.005 cm^3 and the temperature kept constant at 35℃. An amplitude at the 10th turn were measured using a digital quadrature detector (DQD) [9].

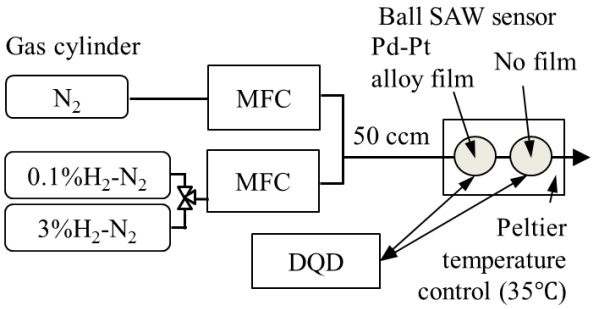

Fig. 1 Schematics of measurement apparatus

3. Result

A result of H_2 measurement is shown in Fig. 2. Clear amplitude response was observed from 1000 ppm to 20 ppm. S/N of the response to 20 ppm H_2 was 7.6, comparable to the best result of the ball SAW sensor with Pd-30%Ni alloy film [5]. Moreover, the response time from 10% to 90% at 1000 ppm was 4.1 s as shown in Fig. 3.

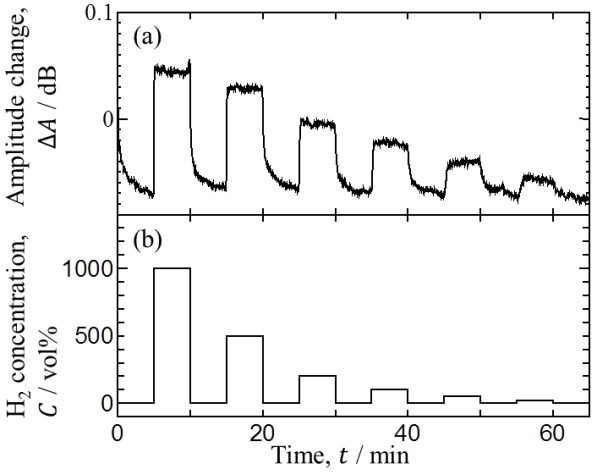

Fig. 2 Measurement of H_2 (a) amplitude change at the 10th turn. (b) H_2 concentration in N_2.

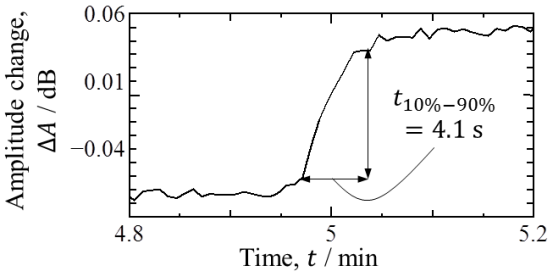

Fig. 3 Response to 1000 ppm H_2.

Fig. 4 shows the concentration dependence of an amplitude change, plotted with log-log scales. The amplitude response is expressed by the function of the square root of the concentration. The reason may be explained by Sievelts's law, where the solubility of a diatomic gas in metal is proportional to the square root of the partial pressure [7]. Although similar dependence were reported in sensitive resistive sensor [1], it was for the first time in SAW sensor. The detection limit at S/N of 3 was 3.7 ppm.

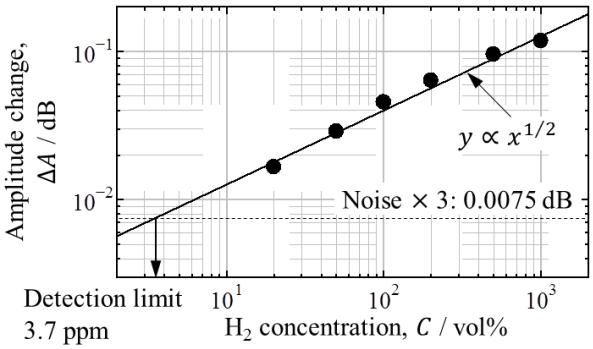

Fig. 4 Evaluation of detection limit. Symbols represent experimental results. Solid and dotted lines represent the fitting of square root function and triple value of rms noise, respectively.

4. Discussion

We compare the concentration dependence of the response time with those of pioneering studies, as shown in Fig. 5. Solid circle (●) represents the result of this study. Upper triangle (△)[2], square (□)[3], and lower triangle (▽)[4] represent the results of planar SAW sensors. Cross (×)[1] represents that of resistive sensor. The response time of the ball SAW sensor was 5 times shorter than the best value of planar SAW sensor and resistive sensor. This result may be explained by improving a permeation of H_2 gas into the film due to porous structure, shorting an equilibrium time due to tens nm thickness, and promoting dissociation of H_2 molecule due to Pt alloying.

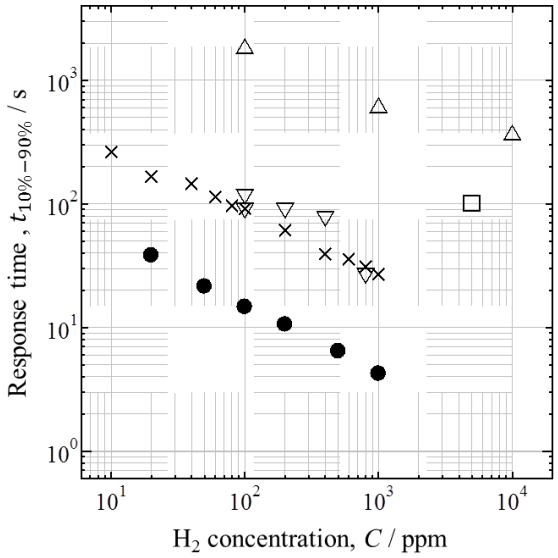

Fig. 5 Comparison of H_2 concentration dependence of 10%-90% response time with pioneering studies. ● represents this study. △, □, and ▽ represent planar SAW sensors with Pd film [2], Pd-Cu phthalocyanine composite film [3], and InOx film covered with thin Pt layer [4], respectively. × represents resistive sensor with carbon nanotube with Pd nano-particles [1].

5. Conclusion

It was shown that the fastest and most sensitive H_2 sensor working at room temperature could be realized using the ball SAW sensor with porous Pd-Pt alloy film.

References

1. S. Ju, J. M. Lee, Y. Jung, E. Lee, W. Lee, S. Kim: Sens. Actuators B **146** (2010) 122.
2. A. D'Amico, A. Palma, E. Verona: Proc. IEEE Ultrason. Symp. (1982) 308.
3. W. P. Jakubik, M. W. Urban´czyk, S. Kochowski, J. Bodzenta: Sens. Actuators B **82** (2002) 265.
4. C. Wang, Y. Wang, S. Zhang, L. Fan, X. Shui: Sens. Actuators B **173** (2012) 710.
5. K. Yamanaka, S. Ishikawa, N. Nakaso, N. Takeda, D. Y. Sim, T. Mihara, A. Mizukami, I. Satoh, S. Akao, and Y. Tsukahara: IEEE Trans. Ultrason. Ferroerectr. Freq. Control **53** (2006) 793.
6. R. C. Hughes and W. K. Schubert.: J. Appl. Phys. **71**, 542 (1992).
7. F. A. Lewis: *The Palladium Hydrogen System* (Academic Press, New York, 1967) p. 84.
8. J. A. hornton: J. Vac. Sci. Technol. **11** (1974) 666.
9. T. Abe, N. Iwata, T. Tsuji, T. Mihara, S. Akao, K. Noguchi, N. Nakaso, D. Sim, Y. Ebi, T. Fukiura, H. Tanaka, and K. Yamanaka: Jpn. J. Appl. Phys. **46** (2007) 4726.