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Highly sensitive trace moisture ball SAW sensor using SiOx film

SiOx 膜を用いた高感度微量水分ボール SAW センサ

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1. Introduction

In highly pure semiconductoer-related gases, it is neccesary to measure trace moisture less than 1 μmol/mol (frost point -76 ℃). A chilled mirror hygrometer and capasitive hygrometer are used for this purpose, but they are not sensitive nor fast enough [1]. A surface acoustic wave (SAW) sensor using metal-organic framework film achieved to measure 0.28 μmol/mol (frost point -85℃), but the sensitivity and response time are still not sufficient. On the other hand, a ball SAW sensor [3], developed by our group, achieved the measurement of 1 μmol/mol in 15 s using a delay time response [4]. However, the response mechanism was not clear and the repeatability in production was nor established. In this study, we aim to develop highly reproducible fabrication technique of sensitive and fast ball SAW trace moisture sensor.

2. Origin of response in quartz sensor without sensitive film

There were sensitive sensors (SA) and insensitive ones (SB) in the quartz ball SAW sensors. **Fig.1** shows the observation by laser microscope topography after etching with buffered hydrofluoric (BHF) acid. Many pits and grooves emerged in SA (**Fig.1 (a)**), where the profiles of a groove were irregular, suggesting a low crystallinity. On the other hand, smooth surface with a few pits was observed in SB, where the profiles of a pit were linear, indicating high crystallinity. Since quartz could be damaged by lapping to form amorphous silica layer (**Fig.2**), the result of **Fig.1** suggests such a damaged layer.

Furthermore, since amorphous silica can be hydrated as

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{H_2O} \leftrightarrow 2\mathrm{Si(OH)_2} \cdots (1),$$

the concentration of hydroxyl group is expressed by

$$[\mathrm{OH}] = \sqrt{K p_{\mathrm{H_2O}}} \cdots (2),$$

where K and $p_{\mathrm{H_2O}}$ are an equilibrium constant and a partial pressure of water vapor, respectively. [OH] is proportional to the square root of $p_{\mathrm{H_2O}}$, which could explain the concentration dependence of the delay time response [4].

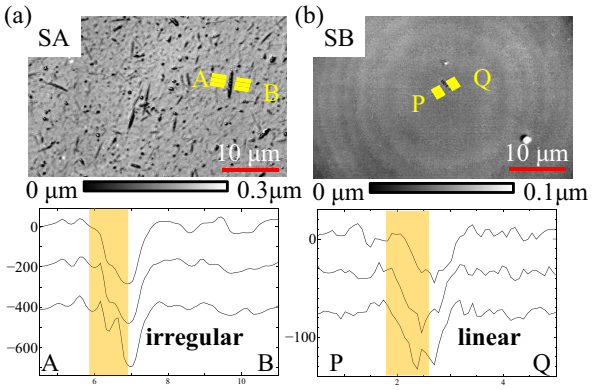

Fig.1 Laser microscope topographiy of quartz ball SAW sensor after BHF etching. (a) SA and (b) SB.

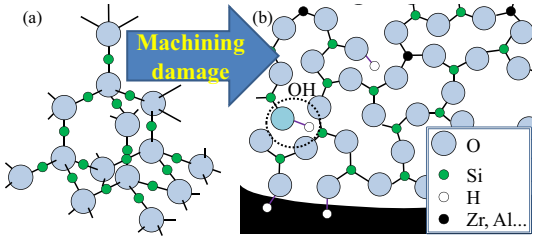

Fig.2 Structural change of quartz by lapping damage. (a) quartz and (b) amorphous silica.

3. Experimental procedure

3.1 Fabrication of sensor with SiOx film

The reproducible fabrication of the damaged layer is difficult. However, amorphous silica layer can be formed by another method. Thus we developed the sensor with sol-gel silica (SiOx) film using the fabrication process reported in Ref. 5. First, tetraethoxysilane was hydrolyzed and polymerized with an acid as a catalyst to obtain SiOx. Next, it was diluted with isopropanol and adjusted to 0.5 wt% solution. Finally, it was coated

to harmonic ball SAW sensor [6] (quartz, ϕ3.3 mm, 80 MHz, 240 MHz) that can compensate temperature drift accurately.

3.2 Measurement by wavelet analysis

Fig.3 (a) shows a waveform at the 4th turn, and **Fig.3 (b)** and **(c)** show real part of the wavelet transform (solid line) and intensity (dash line) of 80 MHz and 240 MHz, respectively. To measure the delay time precisely, a zero cross time was calculated with a precision of 10 fs by bisection method. The amplitude was determined by the value shifted at -1/4 period from the zero cross time. The sensor response was measured every 5 s.

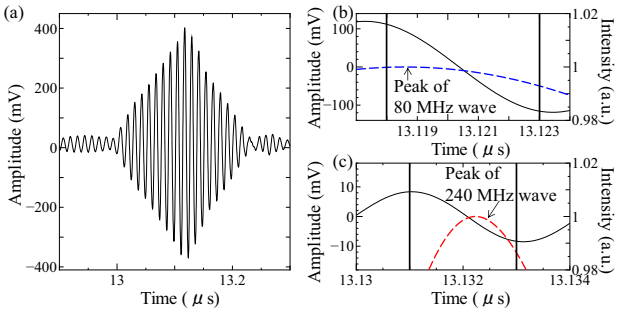

Fig.3 Wavelet analysis (a) waveform at 4th turn, an analysis result and initial values (vertical solid lines) for bisection method (b) 80 MHz and (c) 240 MHz

4. Measurement of trace moisture

Fig.4 shows the delay time response to N_2 gas (flow rate 0.1 L/min) at frost point from -65℃ to -90℃ generated by diffusion tube method [4]. The temperature drift observed in each frequency (**Fig.4 (a)**) was eliminated by subtracting 80 MHz from 240 MHz. (**Fig.4 (b)**). Negative delay time change indicates an increase of elastic moduli on the propagation route (elastic loading). The magnitude of the response was proportional to the square root of the concentration similar to quartz sensor (SA) [4].

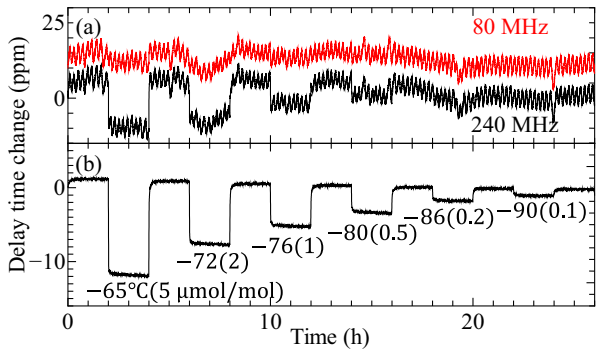

Fig.4 Delay time response to N_2 gas at frost point from -65℃ to -90℃ (a) 80 and 240 MHz (b) subtraction.

Fig.5 (a) shows the amplitude response at 240 MHz to N_2 gas (flow rate 2 L/min) at the frost point from 0℃ to -95℃ without a temperature drift. As the gas was dried from the frost point of 0℃, the amplitude increased monotonically. Thus, the frost point can be determined from the amplitude value.

Fig.5 (b) shows the delay time response. Negative shift was observed from 0℃ to -40℃, and positive shift was observed from -40℃ to -95℃. Switching from the negative to positive shifts can be explained by the mass loading dominant in high concentration range, and the elastic loading dominant in low concentration range. Moreover, the delay time at -80℃ at 8 h was equal to the initial value at 0 h, demonstrating the long-term stability.

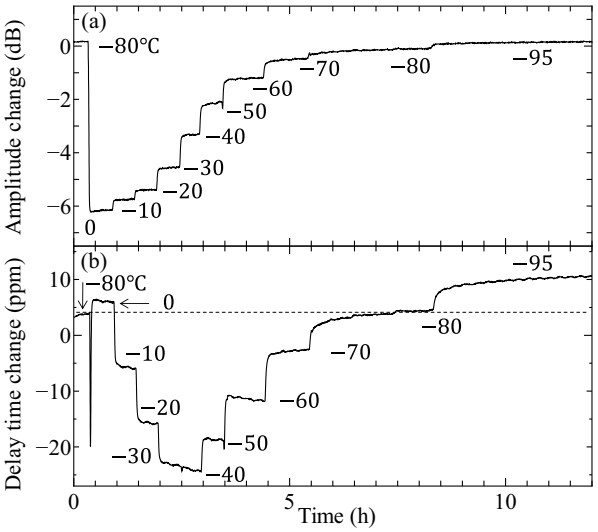

Fig.5 Response of wet gas from frost point 0 to -95℃ (a) amplitude change of 240 MHz (b) subtracted delay time change

5. Conclusion

It was found that the sensitivity of quartz sensor without sensitive film to trace moisture was caused by a damaged layer of amorphous silica. By simulating the damaged layer by a sol-gel SiOx film, it was demonstrated that a highly sensitive sensor with long-term stability could be developed.

6. References

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