

Ball SAW gas chromatograph for detection of mixed VOC and FC gases

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ABSTRACT

In order to realize on-site monitoring of mixed gases of volatile organic compounds (VOCs) and fuel cell (FC) gases, we propose a ball surface acoustic wave (SAW) gas chromatograph (GC) that operates at room temperature, using ball SAW sensors and micro-electro mechanical systems (MEMS) columns. The ball SAW GC can rapidly analyze mixed gases including wide range of molecular weights by switching two combinations of column sensor pairs from series to parallel. As the component suitable for portable GC, we developed metal MEMS column to improve the robustness and reduce the cost of previous silicon MEMS columns. A prototype of the ball SAW GC was assembled and the performance was evaluated by the analysis of a model VOC gas and a model town gas. As a result, it was verified that this system can separate and detect each component of these mixed gases. Moreover, we succeeded in fabricating active-carbon-packed metal MEMS column for FC gas including H₂. Therefore, the ball SAW GC will realize on-site monitoring of VOC and FC gases to be used at cars, home and smart grids.

INTRODUCTION

We discovered the naturally collimated beam of surface acoustic wave (SAW) on balls and developed ball SAW sensor that has a unique advantage of ultra-multiple roundtrips more than 100 turns [1]. We achieved for the first time, sensing range of hydrogen from 10ppm (0.001%) to 100% with a single sensor element, essential for hydrogen stations and fuel cell (FC) cars. However, on-site monitoring of mixed gases of volatile organic compounds (VOCs) and the FC gases (H₂, N₂, water vapor, and hydrocarbons) has not been realized. In this study, we propose small portable gas chromatograph (GC) (ball SAW GC) using the ball SAW sensor and the micro-electro mechanical systems (MEMS) columns [2,3] to realize this goal.

PRINCIPLE

Ball SAW GC

Figure 1 shows the principle of ball SAW GC [4]. Carrier gas always flows through a gas line. When a sample of mixed gases is injected, it flows into a separation column. Mixed gases are separated into each gas component in time domain due to the difference of the solubility to the stationary phase of the separation column. The separated gas is measured by the ball SAW sensor where the SAW is excited by an interdigital transducer (IDT) and the delay time and the amplitude, after multiple roundtrip propagation, are measured by the digital quadrature demodulation [5]. The origins of the

changes of these parameters differ with the sensitive films (described in the section Ball SAW sensor). Finally, the chromatograms are displayed by plotting temporal change of these parameters.

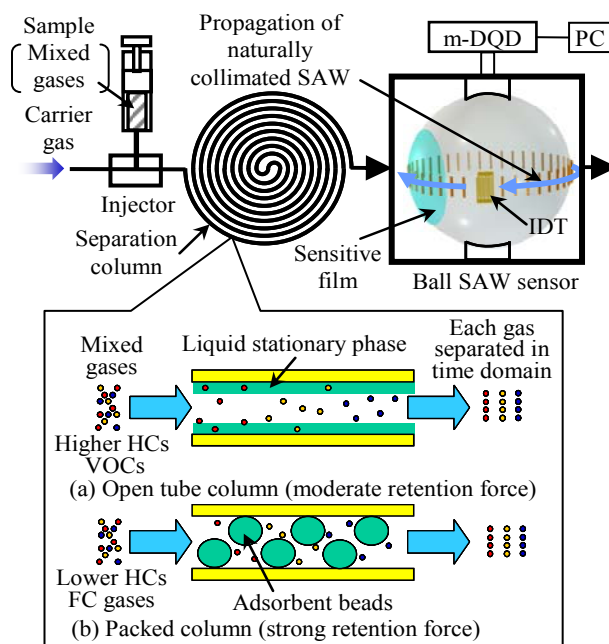


Figure 1 Principle of ball SAW GC.

Forward-flush method

For the separation of low molecular weight (MW) gases such as H₂ and CH₄, the column with strong retention force is required. However, it takes too long for such column to separate high MW gases such as higher hydrocarbons (HCs) and VOCs at room temperature. We shorten the analysis time of mixed gases including wide range of MW, by switching two combinations of column sensor pairs from series to parallel (forward-flush method), as shown in Fig. 2 [4,6].

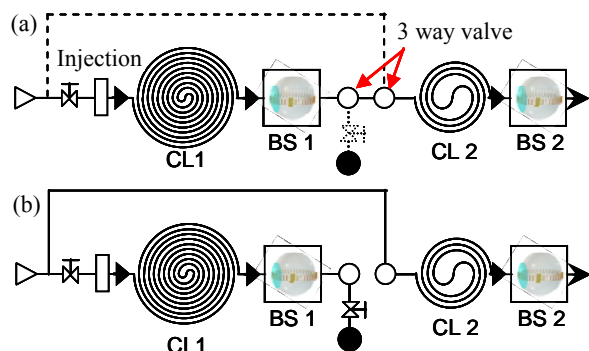


Figure 2 Schematic diagram of forward-flush method (a) series connection (b) parallel connection.

CL1 and CL2 represent the columns with moderate and strong retention forces, respectively, and BS1 and BS2 represent the ball SAW sensors with suitable sensitive films. The sample is injected and the output of BS1 is monitored in the connection shown in Fig. 2(a). When the output indicates the passage of low MW gases, not separated by CL1, three-way valves are switched into the connection shown in Fig. 2(b). As a result, we can rapidly analyze mixed gases including wide range of MW at room temperature.

EXPERIMENT

MEMS column

We developed miniature columns suitable for portable GC with MEMS technology, as shown in Fig. 3. The specifications are shown in Table 1. For separation of mixed gas, two types of silicon MEMS columns were fabricated; open tube (OT) MEMS column with moderate retention force for VOCs, shown in Fig. 3(a) [2], and packed MEMS column with strong retention force for FC gases, shown in Fig. 3(b) [3]. Here, we protected the column from destruction by the internal pressure (4 MPa) by using a jacket to load compressive stress while packing the beads. Moreover, metal packed MEMS column was developed using diffusion bonding of stainless steel plates to improve the robustness and reduce the cost of previous silicon MEMS columns, as shown in Fig. 3(c). It was packed either with styrenedivinylbenzene (SDB) copolymer beads for humid FC gas or with active carbon (AC) powder for H₂. The packing pressures of SDB and AC were 4 MPa and 2 MPa, respectively.

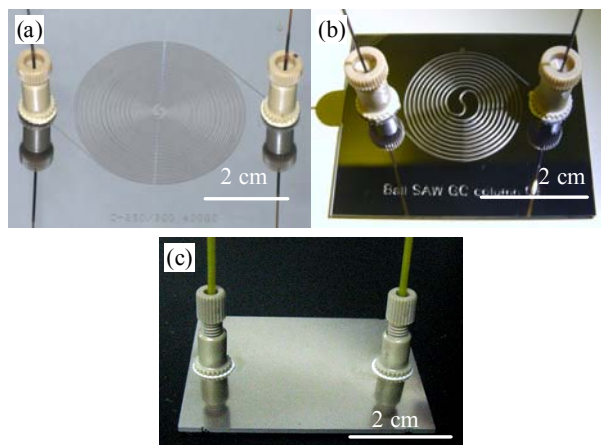


Figure 3 MEMS columns (a) open tube and (b) packed silicon MEMS columns and (c) packed metal MEMS column

Table 1 Specifications of MEMS columns

MEMS column	Open tube silicon	Packed silicon	Packed metal	
Channel	Length (m)	2.8	0.52	0.52
	Width (mm)	0.15	0.44	0.55
	Depth (mm)	0.24	0.50	0.40
Wall width (mm)	0.06	0.50	0.445	
Stationary phase	5%phenyl-PDMS*	SDB** beads	SDB beads or AC*** powder	

* poly(dimethylsiloxane), ** styrenedivinylbenzene copolymer, ***active carbon

Ball SAW sensor

The ball SAW sensors, operating at 150 MHz with a diameter of 3.3 mm, were made by the fabrication of the IDT on the z-axis cylinder of a langasite crystal ball, as shown in Fig. 4. They were coated either by polymer films such as PDMS for VOCs using the off-axis spin coating [7] or by Pt-coated ZnO sputtered film for FC gases. The delay time change and the amplitude change in the case of the polymer films are dominated by the mass-loading effect and the viscoelastic change, respectively [8]. Those in the Pt-coated ZnO sputtered film are dominated by the change of the conductivity due to the adsorption and dissociation of H₂ [9]. In the case of no film, the amplitude change is caused by the leaky-loss [10].

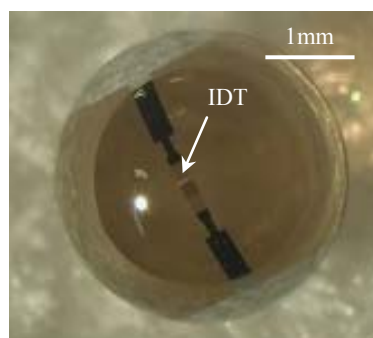


Figure 4 Ball SAW sensor (ϕ 3.3mmLGS, 150MHz)

Ball SAW GC

We assembled the above components to form the ball SAW GC system operating at room temperature [4,6], together with

a carrier gas bomb (He), an injection inlet, and a digital quadrature detector (DQD) [5], as shown in Fig. 5.

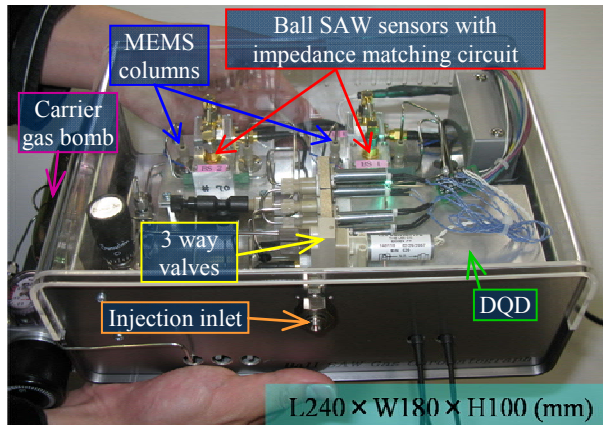


Figure 5 Ball SAW GC

We used the OT silicon MEMS column and the packed silicon MEMS column as CL1 and CL2, respectively, and the PDMS-coated sensor and the no film sensor as BS1 and BS2, respectively. As flow paths, 1/16 inch stainless-steel tubes of 0.25 mm inner diameter were used. We assembled a pair of three-way valves to form the flow-path-switching valve. The composition of the sample gases and the measurement condition are shown in Tables 2 and 3, respectively.

Table 2 Composition of sample gases (mol% under atmospheric pressure)

Model VOC gas				
CO ₂	C ₂ H ₆	C ₃ H ₈	benzene	toluene
32.8	32.8	32.8	0.7	0.7
Model town gas (standard gas of 13A)				
CH ₄	C ₂ H ₆	C ₃ H ₈	C ₇ H ₁₆	C ₈ H ₁₈
88.5	5	5	0.75	0.75

Table 3 Measurement condition

Sample gas	VOC	Town gas
Carrier gas pressure (MPa)	0.2	0.2
Flow rate (ml/min)	Series connection	1.1
	Parallel connection	0.85
Sample volume (ml)	CL1	2.02
	CL2	1.40
		1.14
	0.3	0.3

RESULTS

Waveform of ball SAW sensor

Typical waveform of the ball SAW sensor is shown in Fig. 6 [7]. Fig. 6(a) shows the multiple roundtrip signal of the sensor with no film, measured by an impulse signal of an ultrasonic flaw detector. Figure 6(b) shows the signal at the 50th turn. Although the propagation length attained 518 mm, the signal was measured with sufficiently high S/N. When the DQD was applied to this sensor, the noise, defined by RMS of the fluctuation of the delay time, was as small as 1 ps at the 50th turn, leading to the relative noise 1 ps / 218μs = 0.005 ppm. This is comparable to the lowest relative noise (stability of 1 Hz in 100 MHz oscillator) of planar SAW sensors [7].

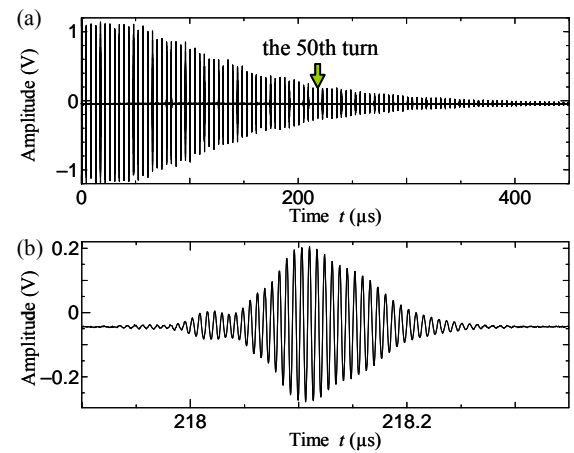


Figure 6 Typical waveform of ball SAW sensor (a) multiple roundtrip waveform (b) waveform at the 50th turn

Analysis of model VOC gas

Chromatograms of the model VOC gas, used to simulate “sick house” gases, are shown in Fig. 7, where the dotted arrows show the valve-switching time. Figure 7(a) shows chromatograms of the delay time change (top) and the amplitude change (bottom) for the gases detected by BS1. Peaks of benzene and toluene were separated from the overlapping peak of CO₂+C₂H₆+C₃H₈. At the same time, the overlapping peak, which was not separated by CL1, was separated by CL2 and detected by the amplitude change of BS2, as shown in Fig. 7(b). Therefore, we verified that mixed VOC (CO₂, C₂H₆, C₃H₈, benzene, and toluene) was separated into each component within 10 minutes at room temperature.

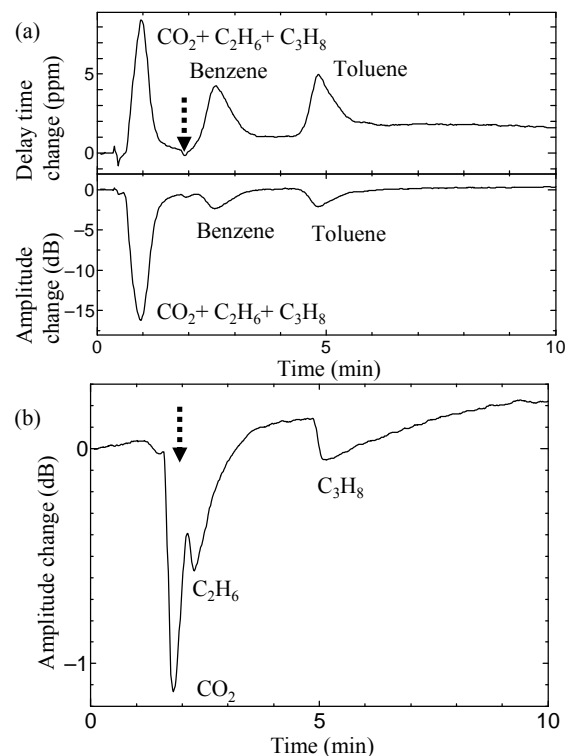


Figure 7 Chromatogram of a model VOC gas (a) Delay time change and amplitude change of BS1 coated by PDMS film (b) amplitude change by BS2 without sensitive film.

Analysis of model town gas

Figures 8 show chromatograms of the model town gas (standard of 13A) that may be used as a source of H_2 production for FC. Similar to Figs. 7, Figs. 8(a) and 8(b) represent the results of BS1 and BS2, respectively. Peaks of C_7H_{16} and C_8H_{18} were separated from the overlapping peak of $CH_4+C_2H_6+C_3H_8$ (Fig. 8(a)). At the same time, the overlapping peak, which was not separated by CL1, was separated by CL2 into the major component of CH_4 and minor components of C_2H_6 and C_3H_8 , which were detected by BS2 (Fig. 8(b)). This result shows that the ball SAW GC is potentially useful for the process monitoring of natural gas.

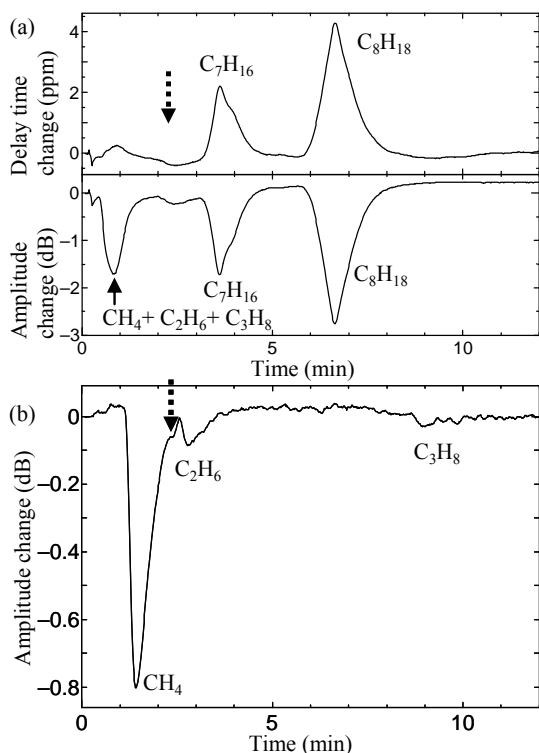


Figure 8 Chromatogram of a model town gas (a) Delay time change and amplitude change of BS1 coated by PDMS film (b) amplitude change by BS2 without sensitive film.

Separation of FC gas

The AC-packed metal MEMS column was evaluated using a thermal conductivity detector (TCD) operating at $200^\circ C$. Figure 9 shows the chromatogram of $3\%H_2-N_2$. The measurement condition is described in the figure. Although the condition of packing AC powder was not probably optimized, we succeeded in separating H_2 and N_2 using the packed MEMS column, for the first time.

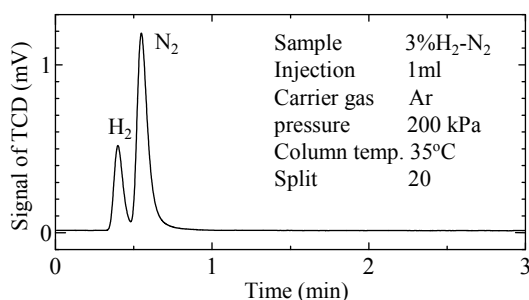


Figure 9 Chromatogram of $3\%H_2-N_2$ by TCD

CONCLUSIONS

We presented the ball SAW GC that can rapidly analyze the mixed gases including wide range of MW at room temperature. As the component suitable for portable GC, we developed metal MEMS column to improve the robustness and reduce the cost of previous silicon MEMS columns. A prototype of the ball SAW GC was evaluated by the analysis of a model VOC gas and a model town gas. As a result, it was verified that this system can separate and detect each component of these mixed gases. Moreover, we succeeded in fabricating active-carbon-packed metal MEMS column for the FC gas including H_2 . Therefore, the ball SAW GC will realize on-site monitoring of VOC and FC gases to be used at cars, home and smart grids.

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