Title : Development of an antenna coil type sensor device for hydrogen leakage detection

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1.Introduction

From a standpoint of environmental conservation, hydrogen energy system is highly expected because this system does not emit CO₂ gas substantially. Massive infrastructures composed of hydrogen energy system, such as electrolysis plant, liquid hydrogen tanker, large-scale storage tank, long pipeline and fuel cell power plant, are going to develop in the future. However, hydrogen is known as explosive material that has a large combustion range and small ignition energy. Therefore, reliable and low-cost hydrogen gas sensors that can detect leakage of hydrogen gas over a wide area are necessary for handling vast amount of hydrogen gas safely [1].

Until now, two types of hydrogen sensitive sensors, metal-oxide-semiconductor [2] and electrochemical [3] one, were developed and used practically. A high temperature operated oxide-semiconductor gas sensor has high sensitivity, reliability and maintenance-free nature. However, this sensor consumes large electric power for device heating. On the other hands, an electrochemical gas sensor consumes very little power, though electrolyte liquid within the cell has to be periodically replaced for the reliable sensing performance. In addition, these are zero-dimensional type sensors that measure hydrogen gas leakage only at a single point. Therefore, many sensor devices are needed for the leakage monitoring over wide area. Further improvement regarding to operation temperature, maintenance performance and cost are also

required.

The wireless sensor networks have been considered as one of the method that are effective in monitoring environment over wide area by distributing small sensors at many measuring points.

Wireless sensing is usually classified in active and passive sensing system. Active sensing system needs batteries with limited lifetime. Passive wireless sensors not only have the advantage of being wireless but can also work without batteries. For example, surface acoustic wave (SAW) is one of the passive devices that have been widely investigated and are commonly used for the detection of hazardous compounds in atmospheric environments with high resolution [4]. Q. Fu [5] developed an integrated passive impedance-loaded SAW H₂S sensor. F. JosseZ [6] investigated guided shear horizontal surface acoustic wave (guided SH-SAW) devices on LiTaO₃ substrates for high-sensitivity chemical and biochemical sensors in liquids. However, these sensor devices require dedicated operating and signal processing electric circuit. These characteristics lead to high cost of device manufacturing. Many other sensor devices also have similar problem.

Radio frequency identification devices(RFID) have simple structure with low cost. In the case of a passive RFID tag, they are only composed of memory microchip and an antenna coil. The antenna coil can be wirelessly transmitted and received information in the microchip at specific frequency. The cost of passive RFID tags that operate at 13.56 and 915 MHz has dropped from

\$ 0.5-0.7 in 2003, to \$ 0.04-0.4 in 2005, and to \$ 0.02-0.05 in 2006.[7][8] For having these merits, the RFID system has been used in various fields recently. In the supply chain and food industry, the shipping information has been managed with RFID tags [9]. RFID also has been used for chemical sensing. R. A. Potyrailo [10] demonstrated selective vapor sensors that involve the combination of organic electronic sensing materials and passive 13.56 MHz RFID device with multivariable signal transduction. They also applied these sensors to biopharmaceutical industry that required monitoring method of critical manufacturing parameters [11].

In this study, we tried to develop an antenna coil device which has hydrogen sensing function. In our previous studies, we had developed hydrogen sensitive film composed of platinum and tungsten trioxide (WO_3) by using so-gel method. It was found that the electrical properties of this film drastically changed in the presence of hydrogen gas. In addition, the film showed excellent selectivity and long-term stability [12]. Therefore, we coated sensing film onto antenna coil which has similar structure used in conventional RFID devices. It is supposed that simple and low-cost wireless hydrogen sensor device could be achieved without major design change of coil pattern. Therefore, this sensor will be easily applicable to RFID tag system. As shown in Fig.1, conventional RFID tags which are coated with the sensing film are allocated many points to monitor hydrogen leak sites. Then, RFID reader collects these data and sends

the information to host computer that issue an alert.

The hydrogen leakage detection capability of antenna coil device was evaluated by measuring the electrical properties at high frequency range for the wireless communication application.

2. Materials and methods

2.1 Sensor fabrication

Fig.2 (a)(b) shows a prototype antenna coil hydrogen sensing device coated with Pt/WO₃ film.

The platinum antenna coil with a size of 45 mm × 45 mm × 400 nm (10 coil turns) was fabricated on the quartz glass plate (800 × 800 mm, t = 1 mm) using the photolithography. The thickness of antenna coil, which was determined with surface roughness meter, was about 400 nm. The 50 nm titanium layer was deposited on the glass substrate as intermediate layer for enhancing adhesion strength of the platinum coil layer. The impedance characteristics of antenna coil portion was checked before and after deposition of hydrogen sensing film using a LCR meter (Agilent Co. Ltd., 4284A) at 1 MHz. The inductance and Q factor of Pt coil were 740 μ H and 0.10, respectively. After the sensing film was immobilized on Pt-coil, these values were almost unchanged. It indicates that sensing film would not affect resonant frequency of the sensor device.

The Pt/WO₃ film was coated on the platinum coil by spin coating method. The precursor

solution which is composed of tungstic acid and platinic acid was prepared. The detail composition of the solution was reported in our previous paper [12]. The solution was spread onto platinum coil device by spinner and formed a thin film. After that procedure, the film was dried 24 h and calcined at 773 K in air atmosphere for 1 h.

Due to this high temperature process, the quartz glass substrate and platinum coil which have good heat and chemical resistance were adopted as the prototype sensor materials. However, the selection and optimization regarding to sensor materials would be required for practical use.

2.2 Reaction mechanism

In the presence of hydrogen, following reduction reaction of tungsten trioxide takes place as a key reaction [13]

WO_3 is classified as oxide semiconductor with a band gap of about 3.2 eV. Its electrical resistance is very high due to wide band gap in oxidized state, but the resistance becomes low upon reduction due to generated free electrons [14]. This change in electrical property would

influence electric resonant behavior of the antenna coil device because the film resistance (R_A) and capacitance (C_A) of the gap between coil patterns are supposed to be changed considerably, as shown in Fig.2 (C). Therefore, it could be applied as sensing principle for wireless hydrogen leakage detection.

2.3 Experimental set up

Fig.3 (a)(b) shows schematic diagrams of experimental setup. The volume of air-tight gas chamber was 525 cm³. The room temperature was kept at 295±3K. The device was placed in the chamber and the wireless transmission evaluation was conducted at different conditions. In the case of response test, various concentration of hydrogen gases that were balanced with air or nitrogen gas, were fed to the chamber at constant flow rate of 2 L / min. In the case of recovery test, the test gas was replaced with dry air supplied from a gas cylinder. The measurement was performed by using a network analyzer (Agilent Co. Ltd., E5062A) in the frequency range from 300 kHz to 3GHz. In this study, the two kinds of parameters (S_{11} and S_{21}) were evaluated. S_{11} was defined as following formula.

$$S_{11} = 20 \log (b_1 / a_1) \quad -(2)$$

The a_1 is the transmitted signal from a network analyzer to the antenna coil device, b_1 is

reflection signal from sensor device (Fig3(a)).

$S21$ was defined as following formula

$$S21 = 20 \log (b_2/ a_1) \quad -(3)$$

The b_2 is the response signal of the receiver coil activated by antenna transmission from sensor device (Fig3(b)).

3 . Results and discussion

3.1 $S11$ of the sensor device

Fig.4 shows the frequency dependence of $S11$ in the presence or absence of hydrogen gas.

When the sensor device was exposed to 4 vol. % hydrogen balanced with nitrogen gas, three discriminative frequency regions were observed in the range from 0.3 MHz to 3000 MHz. This behavior results from the difference in electrical property change of hydrogen sensing films due to reduction reaction of tungsten trioxide, as given in formula (1). This reaction could induce the change of effective form of antenna coil.

In the region Aranging from 0.3 MHz to 10 MHz, the change in $S11$ before and after exposure to hydrogen gas was over 10 dB and showed almost no frequency dependence. This result

would indicate that film resistance of the gap between coil patterns (R_A) became low with reduction reaction of tungsten trioxide. Therefore, input current would flow thorough the shortest current pathway between beginning and ending of coil.

In the region Branging from 10 MHz to 500 MHz, it was seen that the S_{11} increases linearly with increasing the frequency (~ 80 MHz) under hydrogen containing atmosphere. It suggests that the gap resistance increased again by skin effect and therefore the current mainly pass through the coil pattern. The electric resonant frequency was measured at approximately 200 MHz in the air atmosphere with S_{11} of -12 dB. On the other hands, the S_{11} diminished at the same frequency in the presence of hydrogen gas. It is supposed that the quality-factor of electrical resonant circuit was influenced by the film resistance change. The quality-factor in the presence of hydrogen gas was quite lower than that in air condition. This result indicates that this considerably change in electrical resonant behavior could be available for hydrogen detection.

In the region C ranging from 500 MHz to 3000 MHz, some peaks are observed in both atmospheres. In this region, the electrical circuit of antenna coil device should be regarded as distributed constant circuit. Therefore, the many combinations of circuit element might result in complicated resonant behavior. Further investigation based on an equivalent circuit analysis would be required in order to clarify this behavior in detail. On the other hands, the resonant

peak shift with the exposure to hydrogen gas was observed. It is suggested that the inductance or capacitance of the sensor device would change in this frequency region. Although this peak shift could be also used as a sensor signal, the attenuation of peak in frequency region B was adopted as the signal in this study.

3.2 Response characteristics

The variation in SII at 188 MHz (frequency region B), which corresponds to sensor output, was measured. Fig.5 shows typical sensor response (ΔSII) when 4 vol. % H_2/N_2 gas was fed to the chamber. The response reached to the steady state within 6 seconds after the exposure to hydrogen gas. The 90% response time was approximately 3 seconds. Considering the experimental conditions, this response time was partially convoluted with the flow rate and the volume of the gas chamber, etc. It is supposed that the intrinsic response speed corresponding to surface chemical reaction rate of Pt/ WO_3 film and hydrogen gas is expected to be faster.

Fig.6 shows relationship between sensor output (SII at 190 MHz) and hydrogen volume concentration under N_2 and air atmosphere. The sensor outputs stayed at almost constant values in high concentration range under both atmospheric conditions. The sensitivity under N_2 atmosphere was more than four times greater than that under air atmosphere and it saturated even at 0.1 vol.%. The difference in sensitivity among atmospheric conditions would be due to

two competing reactions occurring simultaneously. The One is reductive reaction of WO_3 by hydrogen gas, the other is oxidation reaction of H_xWO_3 by oxygen gas as recovery process. This oxidation reaction inhibits hydrogen response reaction in the air atmosphere [13]. In these experimental conditions, it is found that the sensitivity is high enough to achieve a hydrogen leakage detection system. However, further improvement of sensitivity under air atmosphere would be needed for quantitative monitoring of hydrogen level.

3.3 Transmission characteristics

Fig.7 shows the evaluation result for the wireless communication. The distance between transmission and receiver coil was about 18 mm. The 1 vol % H_2 / N_2 hydrogen gas was fed to the chamber. In this frequency range from 100 MHz to 200 MHz, the resonant frequency was observed at approximately 110 MHz in the absence of hydrogen. When the hydrogen gas was fed to the chamber, the resonant frequency shifted with accompanying transmission loss. On the other hands, the new resonant peak appeared at 160 MHz in the presence of hydrogen gas. The decrease in S_{21} at this frequency was over 30 dB and it is highly expected for sensitive hydrogen detection. In addition, the reproducibility of these behaviors was within ± 0.1 dB. These results indicate that these sensor devices properly performed the wireless communication.

Fig.8 shows relationships between the sensitivity and the transmission distance. The sensitivity

was defined as the change in S_{21} at 110 MHz before and after the exposure to 4 vol.% hydrogen gas in the air atmosphere. Although the data was somewhat scattering (this data variability would result from stray capacitance of our measurement setup), the sensitivity almost linearly decreased with increasing of transmission distance. Accordingly this sensor device could send the information about hydrogen leakage within 100 mm from data receiver. Further investigation is underway for improving wireless transmission performances.

4. Conclusions

The sensor device that composed of platinum coil and hydrogen sensing film was fabricated and sensing characteristics were evaluated for applying to wireless hydrogen sensor. The device shows good hydrogen sensitivity in the frequency range from 100 MHz to 200 MHz. The obtained results demonstrated that the sensor device has promising potential of applying multipoint RFID tag sensor system for detection of hydrogen leakage point.

In terms of practical applications, enhancement of sensitivity to hydrogen in air atmosphere and development of long-distance wireless communication method would be required. Furthermore, optimizations of sensor system including multipoint sensor devices and data reader are also important. These studies are under investigation and the results will be reported in near future.

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Caption list

Fig.1 A schematic diagram of RFID system for hydrogen leakage monitoring.

Fig.2 Structure of an antenna coil type sensor device (a) ,
the sensor device coated with Pt/WO₃ thin film (b) and
schematic cross sectional view with the equivalent circuit model of gap between coil
patterns(c)

Fig.3 Experimental setup for evaluation of sensor response (a) and
S11 and *S21* measurements of sensor device by using network analyzer (b).

Fig.4 Frequency dependence of *S11* with or without hydrogen gas.

Fig.5 Typical response curve with the exposure to 0.1vol.% H₂/N₂ gas.

Fig.6 Calibration curves for hydrogen concentration under N₂ and air atmospheric conditions.

Fig.7 *S21* of the antenna coil type sensor device in the frequency range from 100 MHz to 200
MHz.

Fig.8 Plot of the sensitivity vs. the distance between antenna coil type sensor device and receiver
coil.

Biographies

Koya Tokutake obtained his Master degrees from Yokohama National University in 2010. His fields of interest are corrosion science and sensor engineering.

Shinji Okazaki received his BEng and MEng degrees from Yokohama National University in 1991 and 1993, respectively. He joined Yokohama National University as a research associate in 1997 and promoted to an associate professor in 2007. His major fields are electrochemistry and sensor engineering.

- The quartz glass plate
(800 mm × 800 mm × 1mm)
- The titanium layer (50 nm)

(a)

- Platinum coil
(45 mm × 45 mm × 400 nm, 10 coil turns)

Pt/WO₃ thin film

(b)

(c)

(a)

(b)

(c)