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DETECTION OF HYDROGEN IN AMBIENT AIR USING A COATED PIEZOELECTRIC CRYSTAL

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A gas sensor using a piezoelectric quartz crystal coated with thin Pd layers was found to have a high sensitivity and selectivity to hydrogen gas. At a room temperature, the frequency shift showed a linear relation with the partial pressure of hydrogen and response times were about 2 min.

Recently, as hydrogen have become a popular material and the fuel in industries, a number of hydrogen gas sensors have been reported; a Pd-gate MOS transistor by Lundström and coworkers,[1-4] a Pd-CdS Schottky barrier diode by Steele and MacIver,[5] a Pd-TiO_2 Schottky diode by Tsubomura et al,[6] and a semiconductor hydrogen sensor using silver-added tin dioxide by Seiyama and coworkers.[7]

In recent years, coated piezoelectric crystal detectors have become of increasing interest for detection of traces of toxic atmosphere pollutants, not only as highly sensitive and selective detectors, but also as simple, inexpensive and portable devices. Since King have developed a coated crystal analyzer sensitive to water,[8] many workers have proposed their use in a static system for the detection of trace of toxic atmosphere pollutants; the detection of sulfur dioxide by Frechette and Fasching [9] and sensitive and selective detectors for organophosphorus pesticides, sulfur dioxide, ammonia, nitrogen dioxide, hydrogen chloride, hydrogen sulfide, explosives and toluene in the atmosphere by Guilbault and coworkers.[10-17]

In this letter, we have developed a hydrogen sensitive piezoelectric crystal by using a palladium film as the coating material which adsorbs hydrogen specifically. This letter describes an evalution of a palladium for the detection of hydrogen and discusses the physical-chemical mechanics.

The principle of detection by a piezoelectric crystal is that the frequency of vibration of an oscillating crystal is decreased by the increase of mass of a coating material on its surface. The gas is selectively adsorbed by a coating on the crystal surface which is specific for the gas, thereby increasing the mass on the crystal and decreasing the frequency.

Adsorption and desorption were monitored by using the piezoelectric crystal detector with evaporated Pd film on both sides. The crystals used are 6-MHz AT cut quartz crystals supplied by Kinseki Mfg. Co. with electrodes of 17 mm in diameter. The instrumentation consists of a transistor oscillator powered by a regulated power supply (the transistor oscillator and the power supply were made by authors using an electrical circuit supplied by Kinseki Mfg. Co.). The output frequency from the oscillator was measured by a frequency counter with a resolution of 0.1 Hz (FC-8841 Iwatsu Electric Co. Ltd.).

When the sample gas of hydrogen was introduced into the piezoelectric crystal cell, adsorption occurred and caused an increase in frequency of the crystal. Figure 1 shows a typical curve of the adsorption-desorption vs. time. This experiment shows that the frequency of vibration of the crystal detector increases in the presence of hydrogen and decreases when the hydrogen is removed. This phenomenon is reverse of the principle of the detector; however, this event suggests that the mass on the crystal decreased due to removal of the other heavy molecule on Pd surface by introduction of hydrogen and thereby, the frequency of the detector increased. This event is mentioned later in connection with chemical reaction which occurs on the surface. The change of frequency, ΔF is usually defined as the frequency difference between the base line and the steady state which occurs when the saturation of hydrogen adsorption on Pd is achieved. The response time and the recovery time are defined as the time which is required until the response approaches to

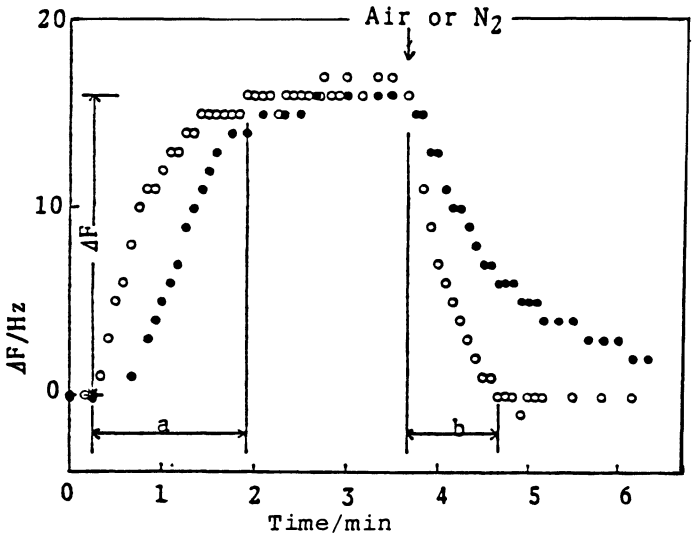

Fig.1. Adsorption-desorption curve
5120 ppm H_2 in N_2;flow rate 266 ml/min
carrier gas ○;air : ●;N_2.

the steady state, and the time which is required until the saturation state returns to the original base line, respectively, which are shown as ' a ' and ' b ' in Fig.1.

Generally, it is needed for a sensor that the coating should adsorb the sample gas selectively and sensitively, and the interaction of the coating with the gas should be reversible. On this study, a complete reversibility was obtained in less than 2 min, depending on the concentration of sample. The response time was about 1 min. No interference was observed at 1000 ppm (V/V) of CH_4, C_2H_6, and C_3H_8 at 100 ppm of NO_2, at 1000 ppm and 5000 ppm of CO_2 and at 10000 ppm of SO_2. This sensor shows very high selectivity to hydrogen.

The gas sensitivity is usually dependent on temperature. The effect of the cell temperature on the sensitivity, response time and recovery time was studied by changing temperature from 10 °C up to 35 °C. As temperature increased, a decrease in sensitivity, response time and recovery time was observed. Decrease in sensitivity is due to the shift of the adsorption-desorption equilibrium by the exothermic reaction of the hydrogen adsorption on Pd surface. Since the sensitivity, response time and recovery time gave slightly poor reproducibility at 15 °C, a higher temperature than 15 °C is better for sensitivity, response time and recovery time.

Figure 2 shows the dependence of the change of frequency, ΔF on H_2 concentration at a cell temperature of 20 °C. For hydrogen in air, ΔF showed a linear relation with the partial pressure of hydrogen (open circles), at hydrogen-concentration from 0 to 1%. The regression line was shown in Fig.2. The relative standard deviation is about 9%. But in an atmosphere of nitrogen, ΔF had larger values than those of air under a low level of partial pressure of hydrogen (filled circles). We think that this difference of ΔF is due to the influence of the shift of the adsorption-desorption equilibrium of oxygen on Pd surface which was caused by the change of the partial pressure of oxygen.

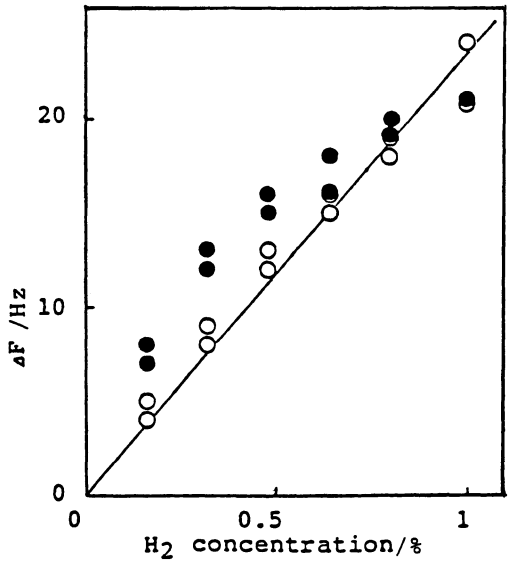

Fig.2. The dependences of ΔF on H_2 concentration (○;H_2 in air: ●;H_2 in N_2) at room temp.

On a reaction mechanism of H_2 and O_2 on Pd, it is reported that Pd surface preadsorbs oxygen when exposed to air [18] and that the reaction between hydrogen and oxygen on the Pd surface at 273 K goes to completion, producing desorbable water. [19,20] Lundström and coworkers explained the reaction mechanism on a Pd-gate MOS transistor that hydrogen alone is adsorbed on the surface of Pd and then the adsorbed hydrogen reacts with oxygen molecule in air, producing desorbable water. However, on this work, frequency of the crystal increased by introducing H_2 (ΔF is positive value in Fig.1) and when nitrogen and air were used on H_2 removal, oxygen enhanced H_2 removal and thereby the recovery time became greatly short (Fig.1). Therefore, preadsørbed oxygen plays an important role in the reaction between hydrogen and Pd. When nitrogen was introduced, the frequency decreased more slowly than oxygen and did not return to the original value. This phenomenon suggests the nitrogen adsorption on Pd surface, but there is still some possibility that nitrogen was contaminated by the air. From these results, we believe that the working mechanism of this sensor is due to the reaction between hydrogen and preadsorbed oxygen leading to the removal of oxygen from the Pd surface as water. Therefore, the weight of Pd surface decreased by above reactions and thereby, the frequency of the detector increased. Thus piezoelectric crystal detector with Pd film can be used for hydrogen in air and in nitrogen with reasonable response time at room temperature.

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