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Capacitive porous silicon sensors for measurement of low alcohol gas concentration at room temperature

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Abstract Capacitive alcohol gas sensors using a porous silicon (PS) layer were fabricated and investigated for the measurement of breath alcohol concentration. Since the PS layer shows high adsorption against ethanol along with a large internal surface area, detecting low alcohol gas concentrations without any heating may be realized in comparison with metal oxide sensors. In this work, we measured the capacitance for the range of 0–0.5% alcohol concentrations using the proposed sensors, and observed how illumination of UV light affected the sensitivity. In addition, the effect of CO_2 and N_2 gases involved commonly in exhaling breath was estimated, and the same experiment for methanol gas was executed to compare qualitatively with ethanol gas.

Key words Porous silicon · Alcohol sensor · UV light · Capacitance

Introduction

Measurements of alcohol concentration in the body, especially blood, are becoming prevalent in order to attempt to prevent traffic accidents. Generally, if the alcohol concentration in a driver's blood exceeds 0.05%, the driver may be punished for the violation of drinking and driving regulations. At present, there are several types of sensing devices available for electronic breath alcohol measurement. One of typical alcohol sensors is the fuel cell-type utilizing a catalytic platinum electrode, which is often used for official alcohol measurements owing to accuracy. However, these sensors have the disadvantages of high prices and high power consumption to drive the amplification circuits because of quite small signal generation [1]. On the other hand, there are metal oxide alcohol sensors based on ZnO and SnO_2 that respond primarily to oxidizable gases such as CH_4 and CO. They have the benefits of low cost, small size and process compatibility with integrated circuit technology [2]. However, they are used only for self-testing because of insufficient accuracy, and furthermore they have the problem that they must be heated to 200–500 °C to increase the sensitivity, resulting in high power consumption. Therefore there has been a need for more convenient sensors along with accuracy and low power consumption for measurements even at room temperature.

Currently, there is much interest in the use of a porous silicon (PS) layer in a applications to gas sensors owing to a large internal surface area, as well as electroluminescent devices from the original discovery [3]. The first example was the humidity sensor [4, 5], and the alcohol sensor was introduced later [6]. The original alcohol sensor was a resistance type where it was possible to measure at room temperature, but there was a detection limit of approximately 3000 ppm for alcohol gas which was beyond the ordinary range of breath alcohol measurement.

In this paper, capacitive alcohol gas sensors using a PS layer were fabricated, the capacitance was measured at room temperature for low alcohol concentration without any heating, and the effect of UV light on the capacitance properties of the sensors was investigated.

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Experimental

Heavily doped p^+-type (100) silicon wafers with 0.02 Ω cm resistivity were used as substrates. First, an n-epi-layer of 10^{15} cm^{-3} was grown on the wafers with auto doping from the substrate, in which the thickness of the grown epi-layer was shown to be about 4 μm throughout the spread resistance profile (SRP). Then the wafers were implanted with boron at a dose of 10^{15} cm^{-2} over the patterned area to be converted to the PS layer during the anodic reaction later. Anodization to form a PS layer was done in a double cell made with Teflon in 25% HF solution mixed with ethanol at a constant current density of 13 mA/cm^2 for 120 s. During this process the n-region was protected by a photoresist film for the selective anodization. After anodization, a nitride layer was deposited by chemical vapor deposition, and then the PS region was oxidized partially by wet oxidation and etched to set up the bottom electrodes. Formation of contact holes followed, and a Cr/Au film with 30 nm thickness was formed by sputtering and lift-off processes to serve as the alcohol permeable electrode. Finally, samples were completed by the process of Al metallization, die cutting and wire bonding. Figure 1a shows a cross section of the realized device, Fig. 1b a top view, and Fig. 1c a photograph of the completed sensor with a sensitive area of 2.3 × 2.3 mm^2.

All capacitance measurements were carried out with a LCR meter at ambient pressure and room temperature as shown in Fig. 2. To remain as close as possible to the conditions of the air expelled by breathing, the sample was fed with vapors carried by N_2 and CO_2 gases via alcohol-water solutions, where the temperature of the solutions was kept at 35 °C, close to the human body temperature. The capacitance was measured 30 s after exposure to the gases at the two frequencies of 120 Hz and 10 kHz.

Results and discussion

The operating principle of capacitive sensors employs the dependence of the capacitance on the dielectric constant. A PS layer can be regarded as a complicated dielectric material, where dielectric properties will be dependent on various polarizations from the PS, water vapor, and organic gases. A scanning electron micrograph photograph of the PS layer taken from the completed sensor is shown in Fig. 3. The PS layer consists of long voids that are obtained typically from heavily doped silicon [7]. The thickness was observed to be about 4 μm, a little thicker than the epi-layer, and the porosity is evaluated to be about 35% by weight measurements.

At low frequency the relative permittivity, ε, of the PS layer is much influenced by the orientational polarization which usually occurs in liquids or gases composed of molecules with permanent or induced dipole moments, and it is determined by the relaxation time of permanent dipole moments whose response is relatively slow, and can be described by Debye's equations as follows:

$$\varepsilon = \varepsilon_\infty + \frac{(\varepsilon_r - \varepsilon_\infty)}{1 + w^2\tau^2} \quad (1)$$

$$\tau = \frac{A}{kT} \quad (2)$$

where ε_r is the static dielectric constant, ε_∞ the high-frequency dielectric constant, τ the characteristic relaxation time for dipoles, and A a constant related to the viscous lag of the molecule. From these equations we can know that it decays with τ, and decreases with increasing frequency and decreasing temperature. Generally the capacitance of the sensors will increase with the vapor pressure of the alcohol in the flask, whose static dielectric constant is 25. Alcohol is very volatile, so even the human body's temperature of 35–37 °C can cause high vapor pressure. The relation of the vapor pressure of the solution to the temperature can be expressed theoretically by the Clausius-Clapeyron equation as follows:

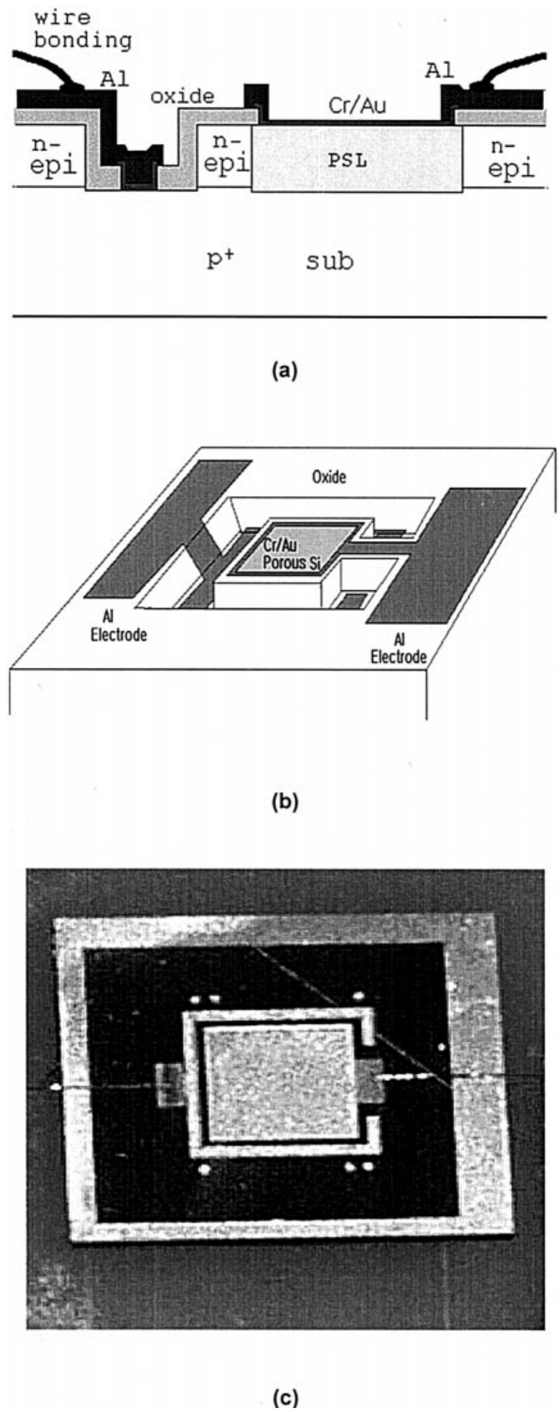

Fig. 1 **a** The cross section, **b** the top view, and **c** a photograph of the fabricated sensor

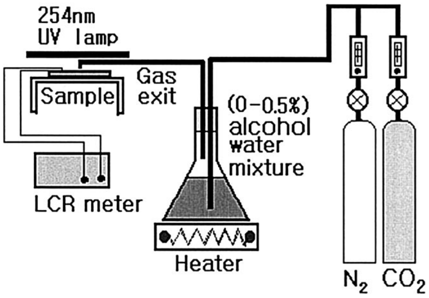

Fig. 2 The set of equipment to measure the capacitance of sensors

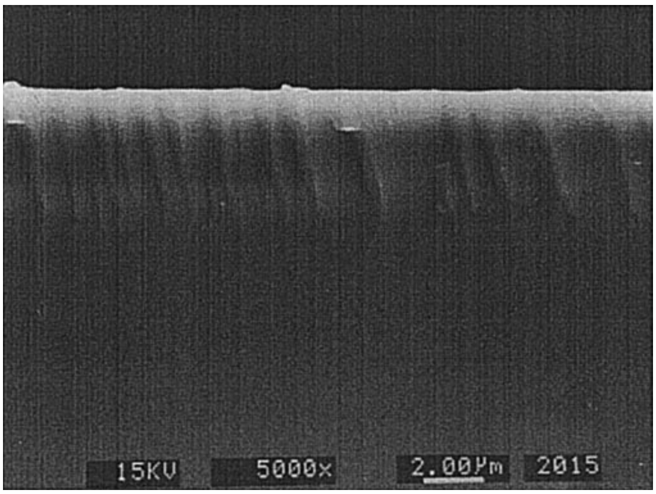

Fig. 3 A SEM photograph of the PS layer taken from the completed device

$$\log_{10}\frac{P_2}{P_1} = \frac{\Delta H_v}{2.30R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \tag{3}$$

where R is the gas constant, T the absolute temperature, P the vapor pressure, and ΔH_v, the molar heat of vaporization. As ΔH_v of alcohol and water at their boiling points are 9.3 and 9.7 kcal/mol, respectively, the vapor pressure of alcohol becomes usually much higher than that of water. Therefore the variation of the capacitance is determined by the alcohol vapor evaporated from the solution. Figure 4 shows the capacitance characteristics when the alcohol-water mixture is kept at a temperature of 35 °C. Under no UV light the slope of the capacitance curve measured at 120 Hz indicates an increase of 2.5% capacitance per 0.1% alcohol solution concentration, while the slope at 10 kHz was observed to be less owing to the effect of dielectric dispersion. By the way, when UV light with 254 nm wavelength is irradiated over the surface of the sensors, there was a definite increase in the slope and the initial values of the capacitance curves. While the slope measured at 120 Hz without UV light indicated the increase of 2.5% capacitance per 0.1% alcohol solution concentration, the slope under UV light increased to 4%. At 10 kHz the capacitance response showed the slope increased to 1.2% in comparison with

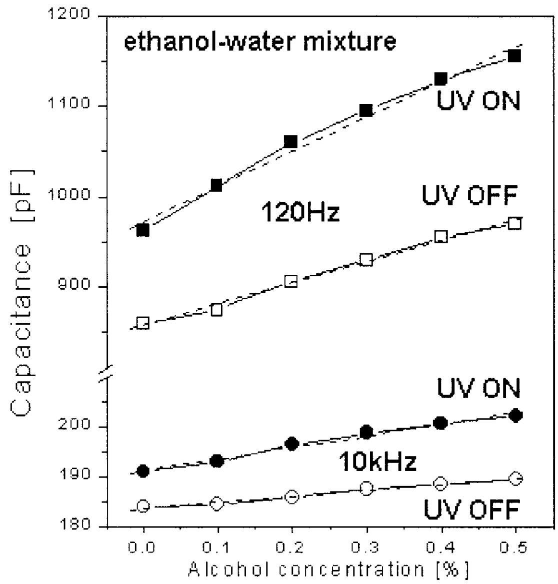

Fig. 4 Dependence of the capacitance on ethanol volume percent concentration for ethanol-water mixtures

0.6% under no UV light. Such an increase in the capacitance by UV light is supposed to be due to the reason that the photonic energy supplied by the UV light activates the viscous lag of the orientational polarization for the AC field, and then it reduces the relaxation time. However, the effect by UV light in detail must be discussed further.

We examined the effect by a normal human's exhaling gases composed typically of N_2, CO_2, and water vapor without alcohol gas, as shown in Fig. 5. The capacitance was measured for the range of 0–100 volume percent concentration of CO_2 gas, controlled by mixing with N_2 gas via the pure water. The capacitance remained unchanged independently of these gas concentrations because the static dielectric constant of N_2 and CO_2 gases is close to 1, similar to air, and the effect of UV light was also found to be independent of the concentration except for the initial increase of the capacitance.

In addition, we measured the variation of the capacitance by methanol gas according to the same experimental procedure as executed for alcohol to compare the capacitance responses. Methanol is more volatile than alcohol. It has a high dielectric constant of 33, a low boiling point of 65 °C, and a low vaporization heat at its boiling point of 8.4 kcal/mol (in comparison with alcohol). However, as shown in Fig. 6, the measured capacitance was low in spite of the high dielectric constant and high vapor pressure. That is, while the slope of the capacitance curve at 120 Hz was observed to increase at 1.6% under no UV light, the slope even under UV light increased hardly any more. Therefore it is obvious that there are other factors affecting to the capacitance responses besides the dielectric constant and the concentration of the gases. Here, the result of the low capacitance for methanol gas is caused by the

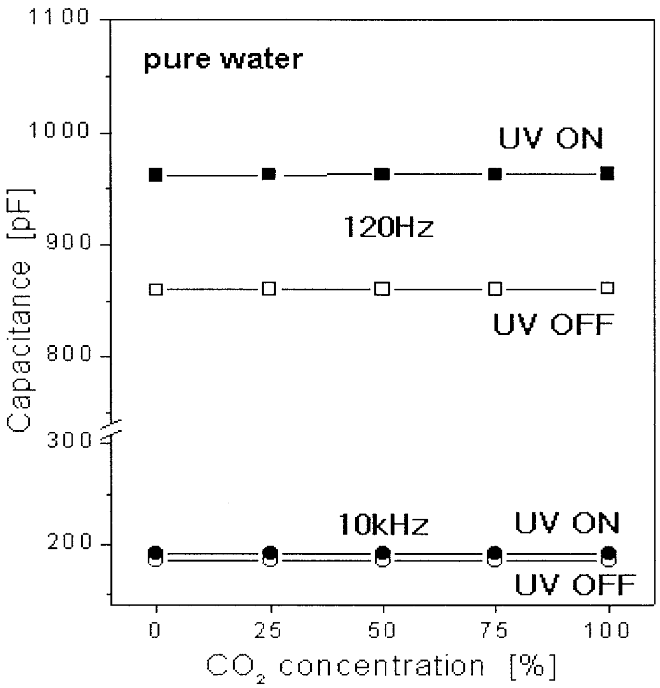

Fig. 5 Dependence of the capacitance on CO_2/N_2 gas volume percent concentration for pure water

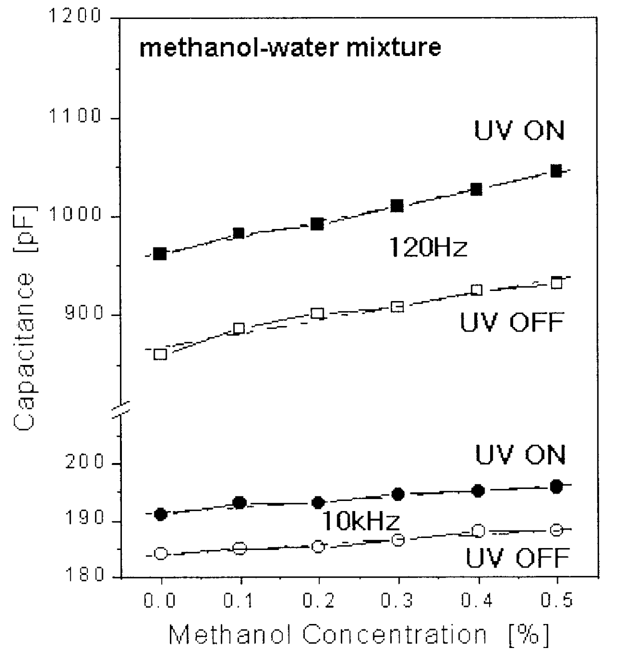

Fig. 6 Dependence of the capacitance on methanol volume percent concentration for methanol-water mixtures

difference of the amount of adsorbed gases. Generally, alcohol has been known to be very permeable into the silicon wafer, so it has been often used to help chemical reactions when silicon wafers are treated in aqueous solutions. Therefore, the physical adsorption should be considered when we choose a sensitive layer in the sensor.

Conclusions

For breath alcohol measurements, sensors should have the capability to detect low alcohol concentrations. In this work, we fabricated capacitance-type alcohol sensors using a PS layer, and their capacitance responses were investigated for the range of 0–0.5% alcohol concentrations at room temperature. The capacitance characteristics exhibited a slope of 2.5% against the alcohol concentration increment of 0.1% at 120 Hz under ambient conditions, and further showed improved sensitivity with the slope increasing to 4.0% when UV light was irradiated on the surface of the sensitive layer. The results show the possibility of PS alcohol sensors having considerable sensitivity even at low alcohol concentrations. In addition, it was observed that CO_2 and N_2 gas concentrations included in exhaling breath had little effect on the capacitance responses, and through a comparison experiment with methanol gas it was proved that the PS layer is an excellent sensitive layer for alcohol gas as it has a very large physical adsorption for alcohol.

Finally, it is concluded that the capacitance type is more flexible in respect that there is the possibility of improving the sensitivity and the selectivity by affecting the relaxation time of the dielectric polarization by the applied electromagnetic wave.

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