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Notes

Double Schottky Diode-Type Gas Sensor for Discriminative Detection of Phosphine and Hydrogen

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In semiconductor industries, such dry processes as chemical vapor deposition, diffusion and dry etching are becoming more important than wet processes to improve the quality of products. In this trend, a number of hazardous (flammable, explosive, toxic or corrosive) gases are used in large quantities. Hydrogen, which is used as a carrier or diluent, has a danger of explosion due to an electrostatic spark when its atmospheric concentration reaches 4%(v/v) or higher. Phosphine, often used to dope phosphorus atoms and to prepare insulator films (*e.g.*, phosphosilicate glass), is very toxic with a threshold level value (TLV) of 0.3 ppm (v/v). Accordingly, a relatively large leak of hydrogen and an extremely slight leak of phosphine must be detected simultaneously and discriminated between each other in semiconductor industries.

Sintered semiconductor gas sensors using ferrite oxide, tin oxide or a ferrite-based mixed oxide are not sensitive enough to detect phosphine in its TLV.[1] On the other hand, Schottky diode-type gas sensors are rather sensitive to various reductive gases.[2-6] Some characteristics of such sensors separately composed of a gold or a palladium film were reported in a preceding paper.[6]

In this work, an attempt was made to obtain a single semiconductor to hold both Au and Pd films in parallel on it in the hope of detecting hydrogen and phosphine. We propose here a new sensor structure called a "double Schottky diode-type gas sensor", which is available for wider applications.

Experimental

The sensor was integrated on a silicon chip of 0.4×7×7 mm, as shown in Fig. 1. The sensor was constructed in two parts: one is the gas sensitive area and the other a temperature-control area. The former consists of two noble metal films (Au and Pd) deposited on titanium oxide. The latter is made up of a nickel-chrome heater and a nickel thermo-sensor having a positive thermal coefficient.

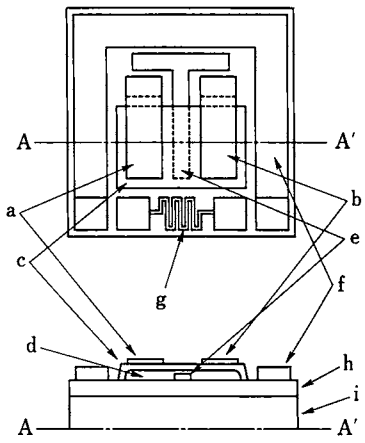

Fig. 1 Structure of the sensor chip. (a) Au film, (b) Pd film, (c) titanium oxide, (d) Ti, (e) common electrode, (f) heater, (g) thermo-sensor, (h) silicon oxide, (i) silicon substrate.

The heater, thermo-sensor and bonding pads were prepared by means of RF sputtering and photolithography on a silicon substrate, as described elsewhere.[6] On the substrate, a Ti film was deposited and its surface was oxidized at 500°C for 70 min in an oxygen stream. Au and Pd thin films were then deposited separately on the titanium oxide by means of evaporation.

Test gases of various concentrations were prepared by diluting standard gases with air by the help of mass flow controllers, and were allowed to flow into a chamber where the gas sensor was placed. The relative humidity of test gases was set at 65% by using a silica-gel dryer and a thermo-controlled water bubbler. The sensor responses were measured using an electric circuit. The outgoing gas was exhausted after bubbling through a KOH solution to absorb toxic gases.

Results and Discussion

It is important to prepare noble-metal films with an appropriate thickness in order to construct a sensor which is sensitive to reductive gases. We therefore prepared Au and Pd films having different thickness. When these metal films were thicker than 30 nm, the base line was increased due to an increase in the diode leak current; the difference in the current in the presence and absence of the reductive gas of interest was small. This was probably due to the adsorption of atmospheric oxygen on the metal films. With an increase in the film thickness, the oxygen concentration in the interior of the film may become lower than that on the surface. This may be responsible for changing the work function at the boundary between the metal film and the semiconductor.

Appropriate bias potentials were applied between each of the noble metals and the common electrode. Each connection showed an I – V characteristic of diode, thus yielding the formation of two Schottky diodes. The current was extremely small below the diode's threshold voltage, and increased steeply when the applied voltage went up above the threshold voltage. The threshold voltage was lowered by introducing reductive gases. Namely, the same level of voltage was supplied continuously to each connection, the resulting current increased along with the concentration of the reductive gases.

Figure 2 shows response transients of the sensor to hydrogen and phosphine. For hydrogen, the Pd-side unit exhibits a response which is dependent on the gas concentration, while the Au-side unit does not show any response below hundreds of ppm; at 1500 ppm, the response of the Au-side unit gives only a slight response. On the other hand, for phosphine, the Au-side unit exhibits an extremely high sensitivity, while the Pd-side unit shows only a small response, even at 20 ppm, which is seventy-times as high as TLV for this gas. Therefore, the present sensor can discriminately detect hydrogen before it reaches the explosion limit and phosphine in its TLV.

In the field of chemical sensors, an accumulation of constituent sensing elements and intellectuality of sensors have become more and more important from practical points of view. Several attempts have been reported, including those based on a sensitivity difference depending on the kind of additional materials.[7-9] The sensor elements, however, are not sufficiently discriminative to distinguish between the components of gases, and complex electric logic interfaces are necessary to discriminate the components.

The present sensor elements can be easily accumulated on a single substrate by separate depositions of noble-metal films, and the sensing properties of each sensor element for the individual gas is not lost due to accumulation. The Schottky diode-type gas sensor is therefore more appropriate and effective than other semiconductor-type gas sensors for accumulation. Also, it can easily discriminate gases without an electric logical treatment. The present Schottky diode-type gas sensor can be extended to a triple or even higher stage.

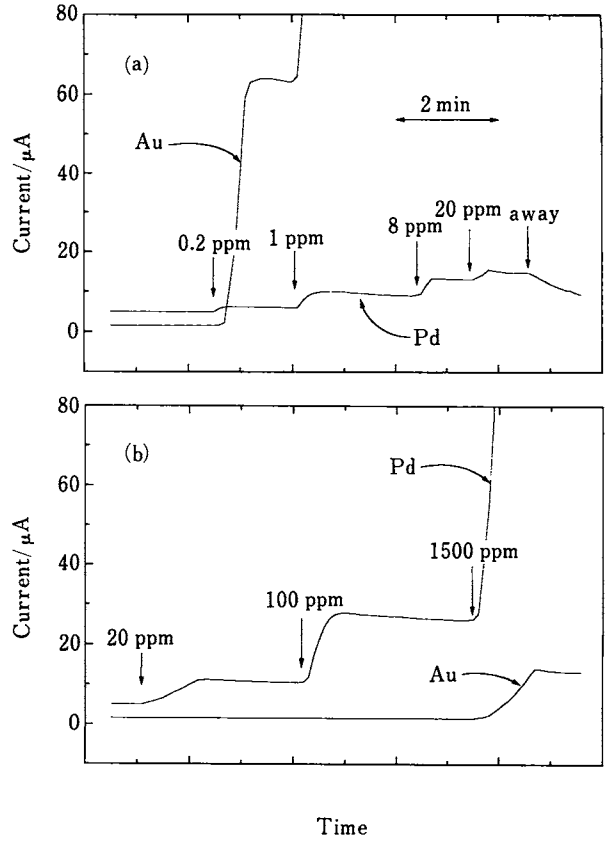

Fig. 2 Response of the double Schottky diode-type gas sensor to phosphine (a) and hydrogen (b). Temperature of sensor, 200°C; applied voltage, 150 mV; relative humudity, 65% (20°C).

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