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Fabrication of thermoelectric gas sensors on micro-hotplates☆

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ABSTRACT

We present a series of fabrication processes of high-performance thermoelectric gas sensor micro-devices including a membrane–releasing process in KOH for the mass production of hot-plate type membrane devices. The fabricated devices are hydrogen gas sensors based on the thermoelectric detection of the catalytic hydrogen combustion. The KOH wet etching membrane–releasing process, using protective wax or polymer coating shows fabrication yields of over 70% and 80%. Most sensors detect wide range hydrogen concentration from several part-per-million, ppm, to percent in air demonstrating robust sensor process. As the device working principle of the Seebeck effect is linear phenomena, a good linear relationship between voltage signal and hydrogen concentration can be achieved, 1 mV = 1000 ppm, down to 50 ppm hydrogen in air. The test method for a large number of sensor devices has been developed, and the validation study for mass production of gas sensors is carried out.

1. Introduction

The development of hydrogen sensor is accelerated by the global reason to use hydrogen as new energy carrier [1]. Not only for this, but also for the monitoring of the human breath, hydrogen sensor is necessary, such as the evaluation of colonic flora [2]. Many of these activities need portable and cheap sensor to monitor the hydrogen in the very low concentration selectively. Furthermore, the sensor devices, which can be produced in mass and require less amplification electronics and less power consumption are also desirable, such as the micro-hotplate type gas sensors [3–4]. The gas sensitive area is located on the membrane, where a cavity is etched through the whole substrate to release the membrane.

A membrane–releasing process using KOH wet etching is adopted for the fabrication of a high-performance thermoelectric gas sensor device using micro-hotplates for the hydrogen gas sensing. The fabricated devices are micro-Thermoelectric Hydrogen Sensors (μ-THS) which use the thermoelectric detection of the catalytic hydrogen combustion [5]. However, the drawbacks of this sensor fabrication are low process yield of wet etching process, especially in the case that the membrane is larger than a millimeter, and difficulties to reduce the deviation of the performance. The similar disadvantage of the micro gas sensors using the metal oxide sensing materials is also a lack of reproducibility, which is often handled by means of post production selection of the devices of good and stable performance, by preliminary functional characterization [6].

We have developed a mass production process of μ-THS using 100 and 150 mm diameter wafer process and new surface-coating polymer layer in the wet etching process. This report describes the process of this device in detail and reports if the gas sensing performance is changed by different process and or by scale-up process of large wafer. Furthermore, the same device process has been outsourced, and carried out with a 150 mm wafer for the feasibility study of mass production.

For gas sensors, to evaluate the device performance, especially the gas sensing performance, is important industrial technology. In this report, a method of sensor test for the series of device set of 20 sensor chips is proposed and demonstrated, using the sensors obtained from the 100 mm wafer process fabricated in this study.

2. Sensor fabrication and test method

Fig. 1(a) shows a snap of the micro-fabricated μ-THS device which is composed of a catalyst of circle shape, a thermoelectric SiGe line, Pt micro-heater meander patterns, contact electrodes and the thin dielectric membranes are made of silicon nitride–silicon oxide multi layer. The unique feature of the sensor in this study is that both thermoelectric and catalytic parts on a single membrane, hot-plates. This new design has a platinum resistor line pattern on the chip to read atmosphere temperature (the narrow lines patterned on the Si rim shown over the membrane).

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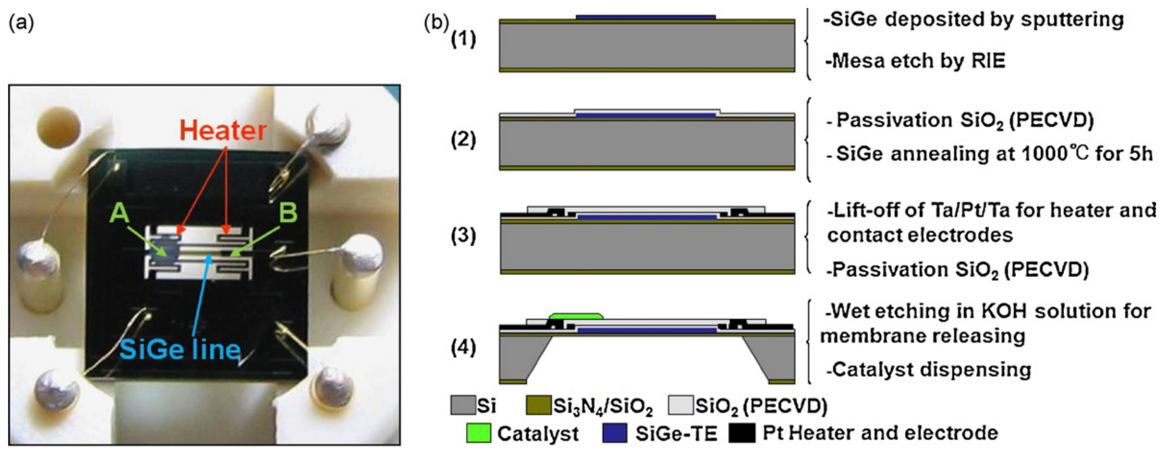

Fig. 1. Schema of the thermoelectric gas sensors and process. (a) The catalyst on the left side of heater, A, meander triggers the combustion of the hydrogen that produces heat and a temperature gradient, $\Delta T_{A\text{-}B}$, (right side meander is B) appears between the hot point A and the cold point B of the thermocouple, (b) The fabrication process flow of the μ-THS device.

The catalyst of ceramic Pt/alumina was deposited on the hot junction of the thermocouple and heated up to 100 °C by the Pt-heater. The combustion of the hydrogen on this catalyst produces heat and a temperature gradient appears between the hot point A and the cold point B, and then thermoelectric voltage is established between the hot and the cold point.

Fig. 1(b) shows the process flow of the μ-THS device chips developed in this study. The sensor is fabricated on a 100 mm diameter, 350 μm thick, double side polished (1 0 0) silicon wafer. The wafer was thermally oxidized to form an insulating SiO_2 layer and then nitride film was deposited by low-pressure chemical vapor deposition (LPCVD) to form 250 nm Si_3N_4/80 nm SiO_2 multi layers on both the front and back surfaces. To study the process feasibility, the same device process has been carried out with a 150 mm wafer, 550 μm thick, wafer with a 1080 nm thick multi layer of silicon nitride–silicon oxide on both sides. The multi layer structure and SiGe process of 150 mm wafer are different from those of 100 mm, depending on the outsourcing foundry condition. Boron-doped thermoelectric $Si_{0.8}Ge_{0.2}$ layer is deposited by RF magnetron sputtering for 100 mm wafer process and by LPCVD for 150 mm wafer process.

To monitor these processes, film deposition and etching processes, a test pattern is designed into the chip and wafer. Fig. 2 shows the test pattern layout prepared to observe the multi layer cross-section of the wafer after the process ends, in the process of 100 mm wafer. The cross-section in the test pattern line can be observed by SEM after the process, cutting the device across the test pattern line.

The SiGe thermoelectric pattern is formed by RIE process, and the front side of the wafer is covered by a 300 nm thick-PECVD-SiO_2 layer. After this the film is crystallized by thermal annealing. Thermal annealing temperature was 1050 °C for 100 mm wafer and 850 °C for 150 mm wafer process for 5 h. The lower temperature condition is decided considering the stress of silica layer of 150 mm process. The micro-heater is composed of a 10 nm-thick Ta layer, a 200 nm-thick Pt layer, and a second 10 nm-thick Ta layer, deposited by sputtering. A 300 nm thick-PECVD SiO_2 layer is used before and after the micro-heater patterning to insure a good insulation between the heater and the thermoelectric film, the second and third SiO_2 as shown in Fig. 2.

Backside patterning is then carried out to make KOH etching cavities aligned to the front side patterns. The front-side of the wafer was then covered by a protective layer, black wax (Skywax, Nikka Seiko) [5] and polymer of ProTEK (B1, Brewer Science, which was used for other wet etching process [7]) and left for around 6 h (over 10 h for 0.55 mm wafer) in a KOH bath to release the membrane. We have chosen the KOH concentration of 60% in water and the etching temperature 78 °C, and the singulation of device chip is carried out by breaking along the grooving cut-line, which is etched out in this wet etching process

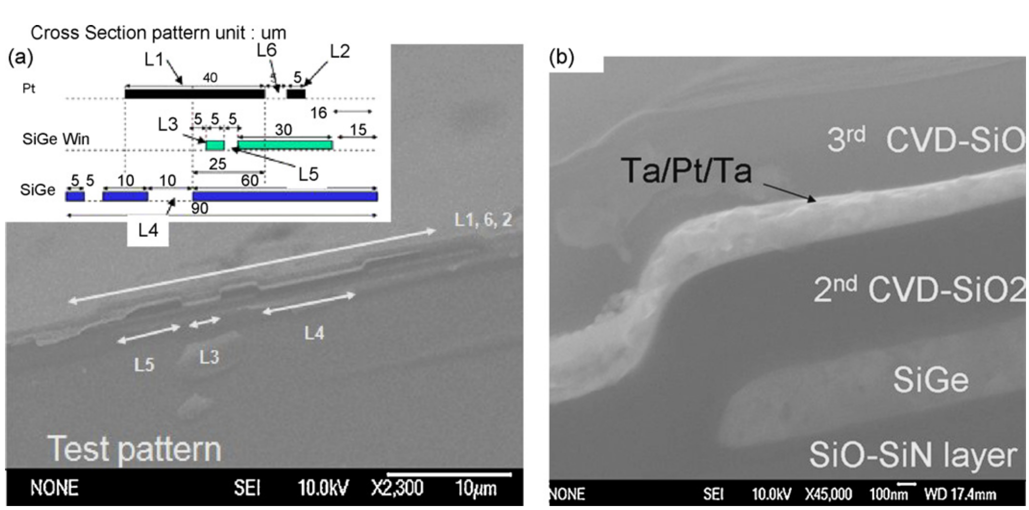

Fig. 2. Cross-sectional process monitoring by SEM.