Mechanical sensors

Piezoresistive Nanomechanical Humidity Sensors Using Internal Stress In-Plane of Si-Polymer Composite Membranes

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Abstract—This article presents the design and fabrication process of a highly miniaturized nanomechanical Si-polymer composite membrane-type internal-stress sensor (MIS) with piezoresistive elements for humidity detection. The 500-μm^2 area dimension sensor consists of a thin Si-polymer composite membrane supported by two piezoresistive Si beams. The composite membrane is fabricated as follows: First, 1-μm-wide width Si slits with 1 μm separation gaps are formed by using photolithography and deep reactive-ion etching, and then, the Si slits are filled with a functional polymer (methyl methacrylate based acrylate resin: OLESTER™Q155). This composite device acts as an absorber of vapor molecules and, consequently, generates stress. The fabricated sensor in a humidity-controlled chamber shows a relative resistance change $\Delta R/R_{\text{device}} = 0.6\%$ for 58% relative humidity (RH) change and a highly linear steady response of 5.2 mV/%RH up to 70% RH change with sensing resolution of 0.5% humidity. The measured polymer expansion ratio of $\epsilon_p = 2.4 \times 10^{-3}$ is consistent with the theoretical estimation using the weight fraction of water adsorbed in the polymer.

Index Terms—Mechanical sensors, piezoresistive sensor, polymer swelling, Si-polymer composite membrane.

I. INTRODUCTION

Cantilever-based nanomechanical sensors are increasingly attracting interest as tools for advanced detection of molecules in various fields. Their notable advantages are fast response and highly sensitive real-time and label-free detection ability [1]–[6]. A wide range of applications has been demonstrated using nanomechanical sensors, including process monitoring, disposable medical diagnostic biosensing, and sensing for gases and solvent vapors [7]–[10]. The most of the studies are devoted to the nanomechanical sensors, which employ cantilevers coated with functional polymers or molecular films as the main active layers. The latter devices take advantage of the bending of the cantilever beam due to stress caused by the adsorption of molecules on the functional layer, and the bending is monitored by optical detection methods. Although these sensors can detect target materials in a picogram range, the practical applications are limited by the bulky size of the optical measurement system and the necessity to align a laser toward each cantilever [11]–[13]. A promising alternative that may overcome these problems is a self-sensing method based on a piezoresistive strain sensor. We demonstrate that it can be applied to develop portable sensing devices for the detection of gaseous analytes in medical diagnosis.

Composite blocks made of two different building materials such as organic and inorganic materials are promising systems for many micro- and nanodevice applications because composites show often excellent synergistic properties [14]. Polymers exhibit high coefficients of thermal expansion, low elastic stress, and, consequently, are characterized by a slow recovery from elastic deformations. On the contrary, inorganic materials such as silicon are highly elastic. Consequently, silicon can recover its initial state quickly after the removal of the force causing deformation. One potential approach to obtain faster recovery response, i.e., the response to instantaneous change of gas molecule concentrations, is to use a composite membrane made of Si and polymer as gas or vapor absorber. Considering the fundamental and practical viewpoints, the Si-polymer membrane can yield higher strength and better elastic modulus compared to a monolayer polymer membrane.

Many cantilever- and membrane-type sensors with absorbers have been reported as piezoresistive strain sensors [3], [7]. These devices detect the surface stress changes caused by swelling effects of the absorbers with the bending of absorber and Si membrane. Such surface stress measurement based on the bending might not be effective because of the energy loss for bending in the vertical direction and for slipping in the lateral direction due to the low bonding strengths at the interface between the Si surface and absorber material [15]. In addition, the vertical swelling of one-side free film causes an extra low Young's modulus of absorber during swelling and results in lower surface stress changes applied to sensors [16]. In order to more efficiently transduce the swelling effect of the absorber to strain in the piezoresistive element and, therefore, achieve higher sensitivity, we embed the absorber in the sensor. The sensing principle is based on the internal stress change caused by the absorber swelling. In this study, a highly sensitive and simple Si-polymer membrane-type internal-stress sensor (MIS) with piezoresistive elements for humidity detection is designed, fabricated and evaluated as a prospective gaseous molecule detector.
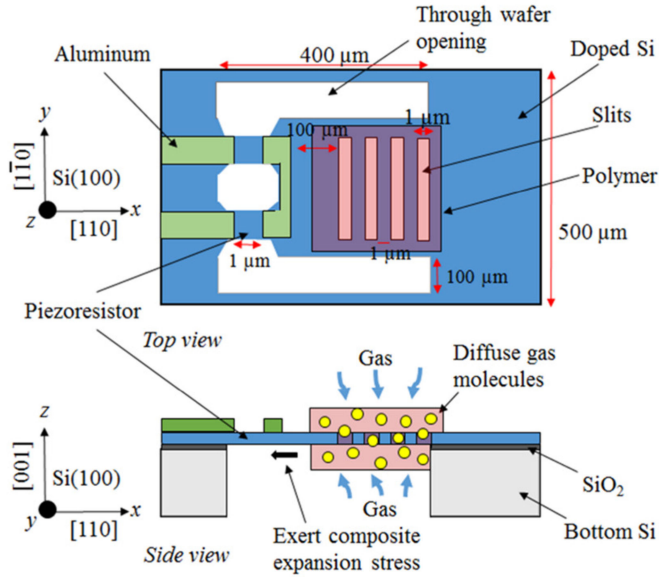
Fig. 1. Schematic design diagram of a Si-polymer MIS with piezoresistive elements and working principles based on stress on the Si-polymer composite membrane due to water-vapor containing gas adsorption into the membrane.

Table 1. Device Design Parameters for Estimating Structural Sensitivity.

Device design parameters	
Slit width	1 μm
Piezoresistor size	$1 \times 11 \times 5$ μm^3
Young's modulus of polymer	2.0 GPa
Expansion ratio of polymer	0.01*

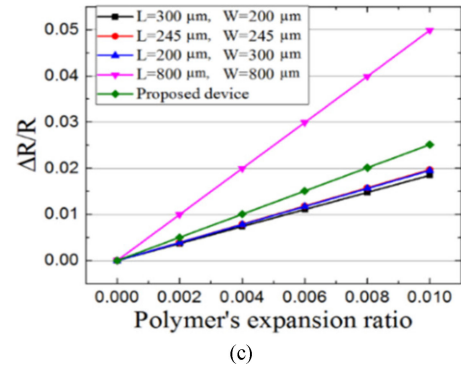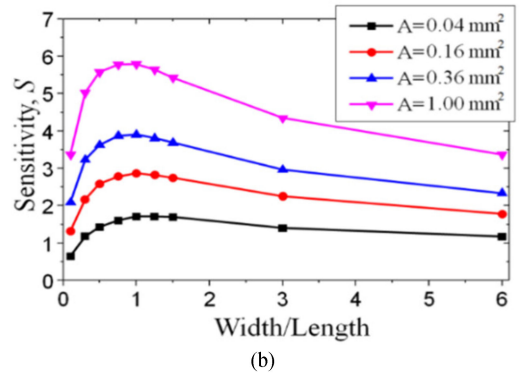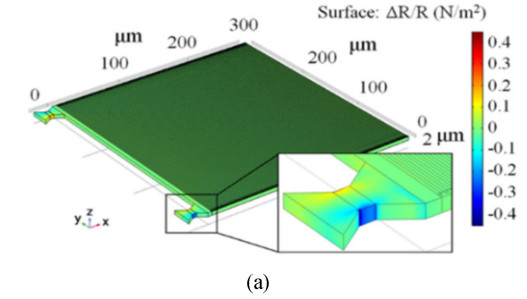*The possible value of expansion ratio of polymer as absorber.

(a)

(b)

(c)

Fig. 2. (a) Distribution of the expansion ratio in Si-polymer MIS structure. (b) Membrane size dependence on the sensitivity S. (c) Piezoresistance changes plotted as a function of polymer's expansion ratios for various membrane sizes.

II. DEVICE PRINCIPLE AND DESIGN CONSIDERATIONS

Fig. 1 shows the proposed schematic design of MIS along the [110] direction of the p-type Si (100) wafer. A functional Si-polymer composite membrane is formed by embedding polymer into silicon slits. The membrane is supported by two narrow piezoresistive sensing silicon beams. The composite membrane acts as an absorber of vapor molecules. The gaseous water analytes absorbed on the functional membrane diffuse into the polymer and expand the composite membrane. Consequently, a longitudinal nanomechanical stress acts into the silicon piezoresistors, which is detected as a piezoresistance change by comparing with a reference Si resistor. The relative piezoresistance change ratio of [110] direction for longitudinal configuration $\Delta R/R$ is calculated as [17]

$$\Delta R/R = (^1/_2) \times (\pi_{11} + \pi_{12} + \pi_{44})\sigma_x \tag{1}$$

assuming for plain stress, i.e., $\sigma_y = \sigma_z = 0$.

For a p-type Si with a 7.8 Ω·cm resistivity indicating $\sim 10^{15}$ atoms/cm^3 of B dopants, the piezoresistive coefficient values are $\pi_{11} = 6.6 \times 10^{-11}$ Pa^{-1}, $\pi_{12} = -1.1 \times 10^{-11}$ Pa^{-1}, $\pi_{44} = 138.1 \times 10^{-11}$ Pa^{-1}, respectively [18]. The stress induced on the piezoresistor along the [110] direction of Si crystal is denoted by σ_x. For compressive force caused by the swelling Si-polymer membrane, the stress σ_x takes negative values.

The structural sensitivity of the sensor is simulated by the finite element analysis using COMSOL Multiphysics under assumption that the polymer expansion ratio is 0.01. The parameters used in calculations are summarized in Table 1. The typical example of distribution of the polymer expansion ratio in the structure is shown in Fig. 2(a). The averaged force is used in the estimation of piezoresistivity because at the edges of piezoresistors both compressive and tensile force components are found. The averaged structural sensitivity S of the rectangular part of the piezoresistor increases with the area of the Si-polymer membrane a, and the maximum sensitivity S is observed for the width to length ratio of approximately 1 [see Fig. 2(b)]. Moreover,

the sensor response is linear with respect to polymer expansion ratio, as shown in Fig. 2(c). Therefore, the structural sensitivity S can be defined as

$$S \cong \frac{\Delta R}{R}/\epsilon_p \tag{2}$$

where $\Delta R/R$ is the relative resistance change of the sensing piezoresistor, and ϵ_p is the linear expansion ratio of polymer. On the basis of the analysis and fabrication capability, the following Si-polymer MIS design is finally adopted: The Si-Polymer membrane size is $300 \times 288 \times 5$ μm^3 (Slit-bar: $1 \times 298 \times 5$ μm^3; slit gap: 1 μm),

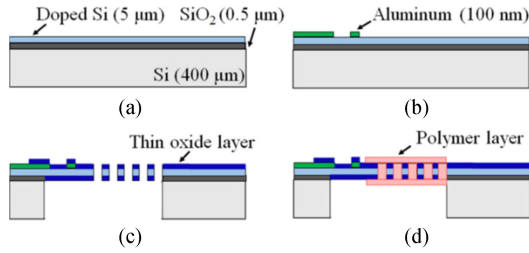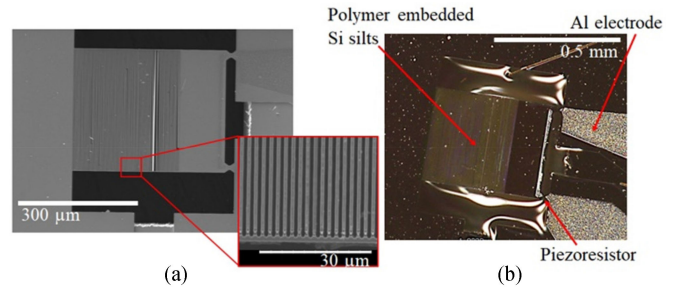Fig. 3. Fabrication process of the sensor device.

Fig. 4. (a) SEM image of the fabricated device structure and (inset) Si slits membrane. (b) Optical image of the fabricated device with embedded polymer.

whereas the piezoresistor part size is $1 \times 11 \times 5\ \mu m^3$ so that the overall dimension of the sensor chip size remains within $500\ \mu m^2$. The structural sensitivity S of our proposed Si-polymer MIS is estimated at about 2.5.

III. FABRICATION PROCESS

The proposed Si-polymer MIS was fabricated on a silicon-on-insulator (SOI) wafer with a p-type (100)-oriented device layer with a thickness of 5 μm, and a 0.5-μm-thick buried oxide layer, as shown in Fig. 3. In order to form piezoresistor using boron doping into silicon, a spin-on dopants diffusion method was employed. The wafer was annealed by rapid thermal annealing at 900 °C for 1–3 min [see Fig. 3(a)]. The device structures were formed by etching using deep reactive-ion etching process followed by the release process from the buried oxide layer by vapor HF etching. Afterward, a 20-nm-thick Al_2O_3 layer was deposited by atomic layer deposition as a passivation layer. Contact windows for metal electrodes were opened by ion beam milling and Al contact pads were formed [see Fig. 3(b) and (c)]. Then, Al electrodes were sintered at 400 °C. Finally, polymer (methyl methacrylate based acrylate resin, OLESTER^{TM}Q155, Mitsui Chemical, Inc., Japan, Mw = 25000) was embedded in the fabricated structure simply by dipping process [see Fig. 3(d)].

IV. RESULT AND DISCUSSION

The sheet resistance of the SOI sample wafers has been measured before and after the diffusion of the boron atoms in the Si layer using the four-point probe measurement method. The sheet resistance of the sample device layer is found to be around 195 Ω/sq, which is ~30 times lower than that of the nondoped Si layer. Considering that the distance diffused by boron atoms at 900 °C within few minutes is about 100 nm, the resistivity is estimated to be <0.002 $\Omega\cdot$cm indicating 10^{20} atoms/cm^3. Since the piezoresistance coefficient of π_{44} decreases from ~140×10^{-11} to ~60×10^{-11} Pa^{-1} at the doping concentration from 10^{16} to 10^{20} atoms/cm^3, the measured resistance change of the fabricated sensor is about half that of the expected value [18].

The fabricated devices before and after polymer embedment are shown in Fig. 4(a) and (b), respectively. The overall device structure area is 500 μm^2. To investigate the performance, the response of the sensor to humidity is investigated in a humidity-controlled chamber. The fabricated Si-polymer MIS device with the embedded functional polymer shows the sharp response to a dynamic humidity change, as shown in Fig. 5. The relative humidity (RH) was monitored by a commercial humidity sensor (SHT-31, SENSIRION). The temperature inside of the chamber shows the stable signal against to gas switching while a slow drift of 0.01 °C/min exists. The response time (t90) of 2.7 ± 0.3 min has been observed as the average of three times switching
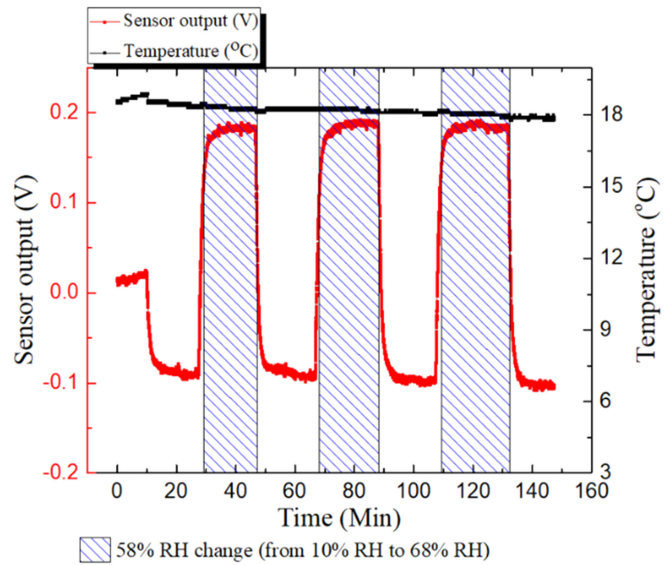

Fig. 5. Si-polymer MIS sensor with Q155 polymer shows a quick instantaneous response to dynamic humidity change when the inside temperature of the humidity-controlled chamber is almost constant, around of 18 °C with ± 0.1 °C fluctuation.

responses. During the operation, the sensor shows a relative resistance change $\Delta R/R_{device} = 0.6\%$ for 58% RH change, from 10% RH to 68% RH at temperature of 18 °C. Since the structural sensitivity is $S = 2.5$ for the used sensor, the polymer expansion ratio of $\epsilon_p = 2.4 \times 10^{-3}$ is estimated using (2).

This expansion ratio is consistent with the roughly estimated polymer expansion coefficient of around 1.0×10^{-3}, which is estimated from the weight fraction of water adsorbed on the device (3.1×10^{-3} at 58% RH). The volume changes of the sensing polymer layer are assumed to be similar to the analogous changes caused by the water penetrating polymer films. Moreover, the weight and volume changes are treated equivalently because of the similar densities of liquid water and polymers. On the basis of the measured weight fraction of adsorbed water ($w = 3.1 \times 10^{-3}$ at 58% RH), and the known water partial pressure $p = 1.8 \times 10^3$ Pa at room temperature, an apparent Henry's constant H of the resin in the sensing layer (5.9×10^5 Pa) can be estimated using Henry equation $p = Hw$ [19]. On the other hand, using the estimated expansion ratio theoretically, the expected $\Delta R/R_{device}$ is 2.6×10^{-2}, which is 2.3 times higher than the measured resistance change. The reason for the response lower than the theoretical one could be the undesirable coating condition of the sensor with polymer. Since the swollen polymer fills also other open spaces on the device, swelling may degrade the output signal.
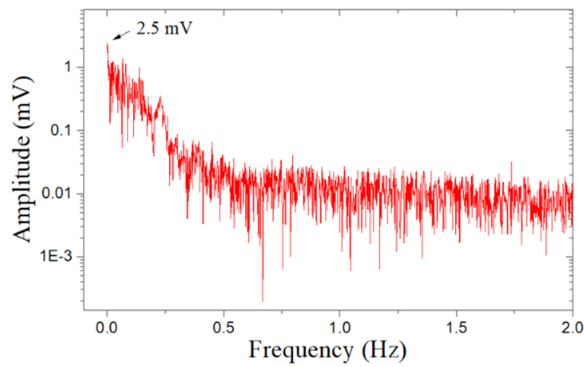
Fig. 6. FFT analysis results of noise resolution of the Si-polymer MIS device operating under constant humidity (60% RH) condition at the temperature of 18 °C. The 0.5% of resolution is calculated using 5.2 mV/%RH obtained from Fig. 7.
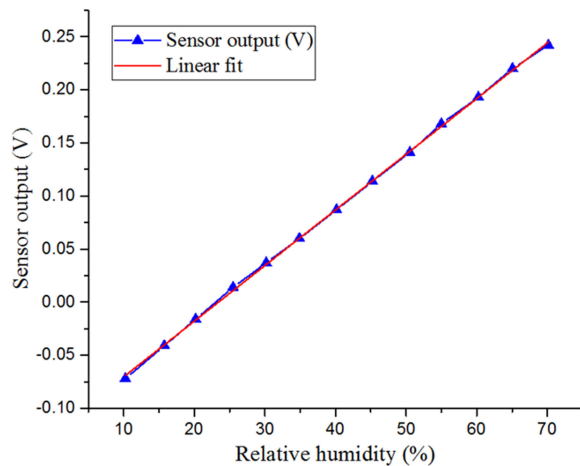

Fig. 7. Sensor device shows a linear static response to humidity at 19.5 °C.

The noise resolution of the Si-polymer MIS device is characterized by the FFT analysis when the sensor device is operating under constant humidity (60% RH) condition at the temperature of 18 °C. Fig. 6 shows the FFT noise analysis. Using the FFT analysis method on the sensor response, it is found that the fabricated Si-polymer MIS device shows a resolution of 2.5 mV/$\sqrt{Hz}$ as an ideal response of humidity using a low-pass filter.

Moreover, it has been found that the static response of the Si-polymer MIS device is observed within humidity range from 10% to 70%, as shown in Fig. 7, when the temperature of the sensor environment is room temperature (around 19.5 °C). The device shows a good linear response to humidity of 5.2 mV/%RH with negligible deviations from linearity, which is consistent with the calculated result, as shown in Fig. 2(c). Using the sensitivity of the sensor for humidity, the 0.5% of resolution is calculated.

V. CONCLUSION

In summary, a new portable piezoresistive humidity sensor, which consists of a Si-polymer composite functional membrane has been proposed and fabricated. The new design shows a linear static response in the measured range within 10% and 70% of RH with sensing resolution of 0.5% humidity. A set of the proposed device structures, i.e., a sensor array, with the proper selection of the absorbent functional polymers could be a potential detector of various gas analytes in human breath and/or in atmosphere.

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