SELF-POWERED GAS SENSOR USING THIN-FILM PHOTOVOLTAIC CELL AND MICROSTRUCTURED COLORIMETRIC FILM

Kyungnam Kang[1], Kwangmin Na[2], Donguk Kwon[1], Jung-Yong Lee[2] and Inkyu Park[1]
[1]Department of Mechanical Engineering, KAIST, Daejeon, KOREA and
[2]Graduate school of EEWS, KAIST, Daejeon, KOREA

ABSTRACT

We have developed a self-powered gas sensor operating without external power under a light source, unlike a sensor that requires an external power source, such as a chemiresistive gas sensor or an electrochemical gas sensor. The sensor consists of a colorimetric film and an organic solar cell. The sensor uses a color change caused by the reaction of the N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPD) with NO_2 gas. The color change caused by the redox reaction of the colorimetric material does not require a separate light source and photodetector, unlike the conventional colorimetric sensor, because it directly changes the output of the solar cell by changing the transmittance of the film. Using this sensor, 1, 5, 10, 20ppm NO_2 gas was detected without external power source, and the performance of the gas sensor could be improved by using microstructure. This work is the first demonstration of self-powered gas sensor based on the combination of photovoltaic cell and microstructured colorimetric film.

KEYWORDS

Gas Sensor, Colorimetric, Nitrogen Dioxide, Solar Cell, Self-Powered

INTRODUCTION

Air pollution and gas leaks in the workplace can cause serious illness to an individual's health. Therefore, it is becoming important to check the existence of toxic gas for individual health. There are many kinds of instruments that can measure gas (optical type, mass spectroscopy, chemiresistive type, electrochemical type etc.). Among them, metal oxide based chemiresistive sensors and electrochemical sensors are widely used as portable sensors because of their compact size and low cost process than optical or mass analysis based gas sensors [1, 2]. But they consume high heating power for gas sensing. As an alternative for lower power consumption, colorimetric sensors have been developed [3]. Many colorimetric gas sensors using color change of materials have utilized light emitting diodes (LED) and photodetectors [4]. This type of sensors still consumes electrical power for detection and it is difficult to make compact size gas sensor due to LED and photo detectors.

In this paper, we introduce a novel gas sensor by combining photovoltaic cell and colorimetric structure for self-powered and simple gas sensor system. The colorimetric material formed on the surface of the transparent film reacted with the target gas to change the transmittance in the visible light region and it was possible to fabricate a NO_2 sensor that operates without external power consumption while directly causing current output change of the solar cell [5]. In addition, it has been confirmed that the performance of the gas sensor is improved by forming the micro post array that can widen the surface area on the surface of the sensing film.

EXPERIMENTAL METHODS

Self-powered gas sensor system

As shown in Figure 1, the self-powered gas sensor system consists of a sensing film covering one side of the solar cell and a light source on top. A source meter was used to measure the current value from the solar cell in real time.

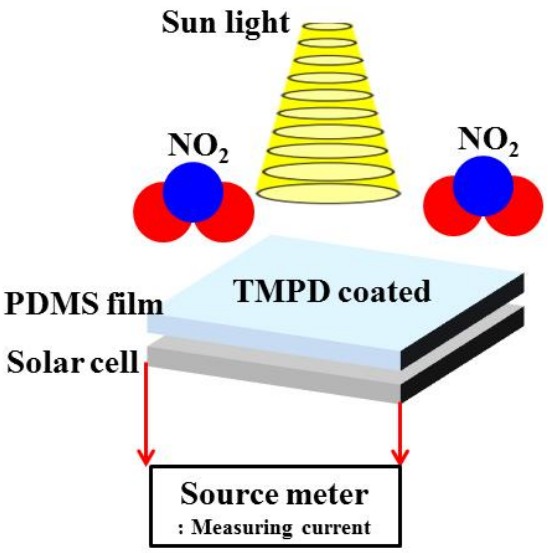

Figure 1: Schematic of self-powered NO_2 gas sensor combining TMPD coated PDMS film and photovoltaic cell.

Fabrication of solar cell

The film layer of zinc oxide (ZnO) and poly-3-hexylthiophene-2,5-diyl (P3HT) : phenyl-C61-butyric acid methyl ester (PCBM) mixture was formed on a glass substrate coated with indium tin oxide (ITO) by spin coating method. P3HT:PCBM is a photoactive layer and ZnO is an electron transport layer. Finally, molybdenum oxide (MoO_3), which is a hole transport layer, and silver layer used as an electrode were formed by thermal evaporation.

Formation of colorimetric film

In order to make a sensor combined with a solar cell, the sensing film must be transparent because film should not block the light entering the solar cell. For this reason, the polydimethylsiloxane (PDMS) material was used as the film. In the case of the plain film, it was molded using a no patterned Si wafer.

The film with the micro-post array was fabricated in the same method as Figure 2 (b). First, Su8-50 photoresist is spin-coated on a Si substrate, and then a micro-post array is formed using a photolithography and a lift-off process. Then, a micro-post array pattern was molded using PDMS. The surface of the PDMS film was spray coated with isopropyl alcohol (IPA) - TMPD solution to coat the sensing material for gas detection.

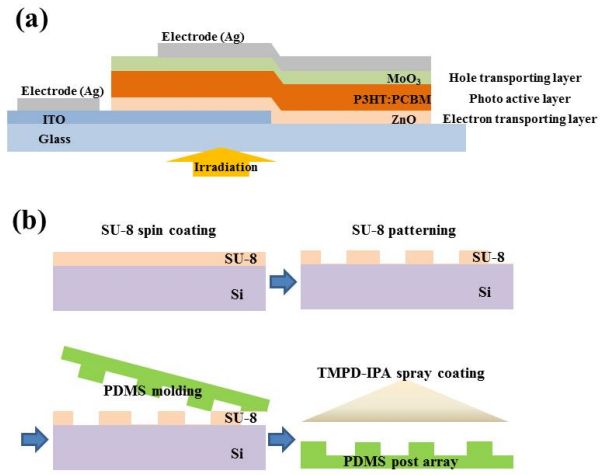

Figure 2: (a) Solar cell structure fabricated by spin coating and thermal evaporation on ITO coated glass, (b) Fabrication process of TMPD coated PDMS film for NO_2 sensing.

Uv-vis spectroscopy of sensing film

The transmittance of the plain film and the film with the micro-post array in the visible region was measured with an Uv-vis spectroscopy. In order to observe changes in the reaction of TMPD with NO_2, transmittance was measured before and after reaction with 20 ppm of NO_2 and sensing film.

NO_2 gas test

For the gas test, the sensor system was placed in a chamber and a transparent cover was used to allow light to enter. The target gas and air were injected using mass flow controller (MFC), and the output change of the solar cell was measured by source meter in real time.

RESULTS AND DISCUSSION

Uv-vis spectroscopy

Figure 3 (a) shows the transmittance of non-coated PDMS films. As there is no material that reacts with the gas, even if exposed to NO_2 for 30 min, the transmittance in the visible region is maintained at 90%. There was no difference in light transmittance between the micro post array film and plain PDMS film. The PDMS film coated with TMPD has a change in light transmittance when NO_2 gas is exposed. The TMPD is oxidized by the oxidation-reduction reaction of NO_2 gas, and color change occurs. The transmittance of the film was decreased in the region of 550 to 660nm due to color change. In the case of a plain film, the transmittance is reduced to 80% in that region, and to 70% in the case of a film with micro-post array. Due to the presence of the micro-post array, it can be assumed that the area in which the gas can react is widened, resulting in more color change.

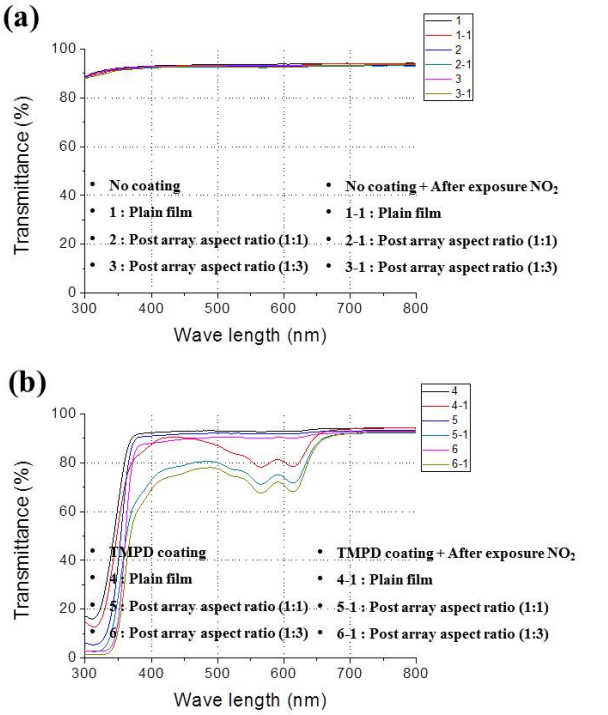

Figure 3: Uv-vis spectroscopy of PDMS film before and after NO_2 (20 ppm, 30 minutes) exposure. (a) Original PDMS film, (b) TMPD coated PDMS film.

About poly(3-hexylthiophène-2,5-diyl) (P3HT), poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th), and polythieno[3,4-b]-thiophene-co-benzodithiophene (PTB7) which are used for photo active layer, the absorption rate and the current change of the solar cell were calculated (Figure 4). First, the absorption of the thin film was calculated by transfer matrix formalism (TMF) -based optical simulation for each material [6], and the change in the current of the solar cell was calculated by using the transmittance change of the plain film produced by the reaction with NO_2 in Figure 3 (b). As a result, the change rate of P3HT was the largest as shown in Figure 4 (b). This means that P3HT, the photoactive layer used in this study, can exhibit the greatest sensitivity as a gas sensor among the three materials mentioned above.

Gas test with plain film and microstructured film

After confirming that the TMPD coated film reacts with NO_2 to change color and change its transmittance, we conducted actual self-powered gas sensor test was conducted. In Figure 5 (b) - (c), there are two types of micro-post array films, and NO_2 gas tests were performed under the light source with three kinds of detection films including plain films without any external power consumption. The current change is observed only in the 1: 3 aspect ratio micro-post array film at the 1 ppm concentration. At other concentrations, the current change of the solar cell is also increasing as the gas concentration increases in all three types of sensors (Figure 5 (a)).

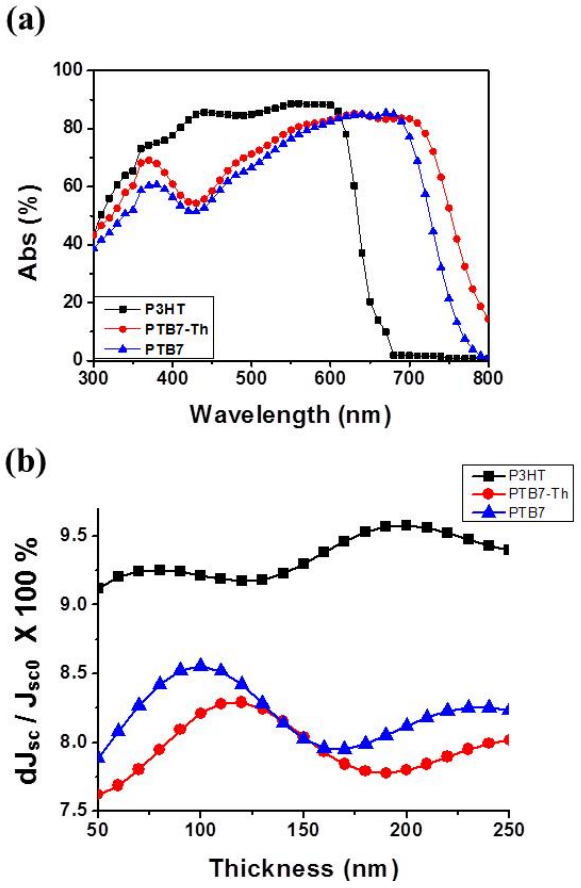

Figure 4: (a) Active layer light absorption spectrum in solar cell of P3HT, PTB7-Th and PTB7, (b) expected current change rate of each material.

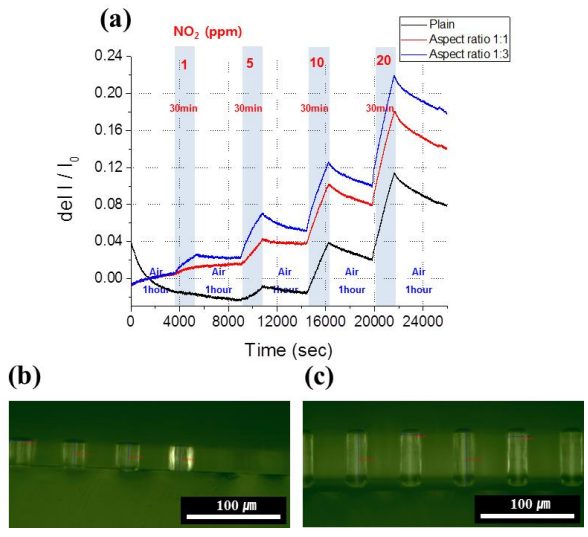

Figure 5: (a) Real time NO_2 gas sensing graph of plain and micro post array structure coated with TMPD and optical images of PDMS micro post array : Aspect ratio (a) 1:1, (b) 1:3.

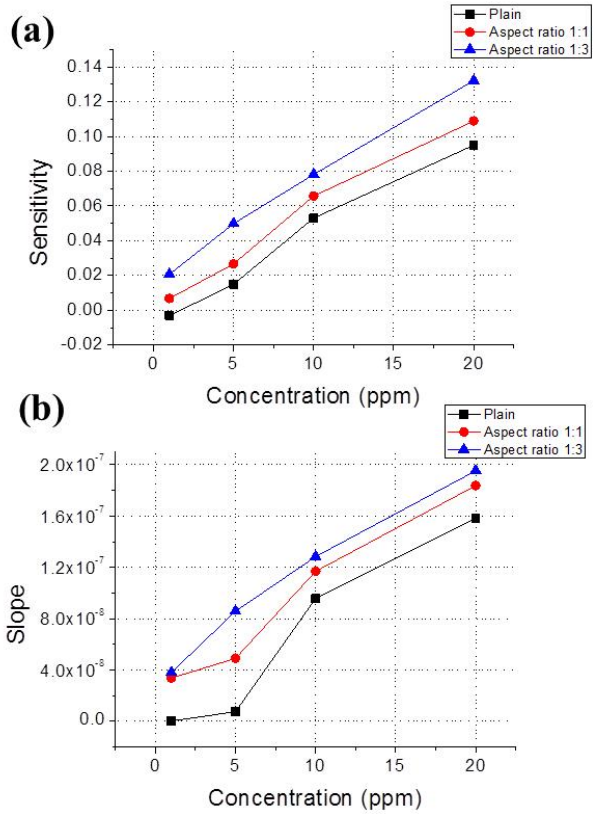

Figure 6: Gas sensing performance to NO_2. (a) Sensitivity ($\Delta I / I_0$, ΔI : current change of solar cell, I_0 : the current value before gas exposure) and (b) slope (current change for 300 seconds after gas exposure).

The performance of the three types of gas sensors was compared in terms of sensitivity ($\Delta I / I_0$, ΔI : current change of solar cell, I_0 : the current value before gas exposure) and slope (current change for 300 seconds after gas exposure) (Figure 6). Overall, films with micro-post arrays exhibited better sensor performance than plain films, and films with larger aspect ratios performed better. This can be seen as a result of NO_2 gas reacting with more TMPD due to the increased surface area due to the micro-post array. At the lowest concentration of 1 ppm, the sensitivity of plain film is close to zero, 0.0067 for aspect ratio 1: 1 and 0.021 for aspect ratio 1: 3 film. At the highest concentration of 20 ppm, the sensitivity was 0.095, 0.11, and 0.13, respectively, and the sensitivity increased by 36.8%. The slope was also 2.67E-10, 3.37E-8 and 3.81E-8 at 1 ppm and 1.58E-7, 1.84E-7 and 1.95E-7 at 20 ppm, respectively. The slope increase due to micro-post array structure at 20 ppm of NO_2 was 23.4%.

CONCLUSION

We have developed a self-powered NO_2 gas sensor by combining a solar cell and a colorimetric material. The photoactive layer of the solar cell uses P3HT, which is the material with the largest output change due to NO_2 reaction, based on the optical simulation. A transparent PDMS film coated with TMPD was used as a sensing film. A TMPD, a colorimetric material, was changed in color by NO_2 gas, which directly caused a current change in the output of the solar cell. As a result, under the light source, the gas sensor was able to detect NO_2 gas at concentrations of 1, 5, 10,

and 20 ppm without external power consumption. In addition, the performance of the sensor has been improved by forming a micro-post array on the surface of the sensing film to widen the surface area through photolithography process. The gas detection system using the light source is expected to be more convenient for the user because the power consumption is not required.

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CONTACT

*I. Park, tel: +82-42-350-3240; inkyu@kaist.ac.kr