Terpene sensor array with bridge-type resistors by CMOS technology

Sung Pil Lee[1]

Department of Electronic Engineering, Kyungnam University, Kyungnam, Changwon 631-701, Korea

E-mail: sensors@kyungnam.ac.kr

Abstract. The interaction of terpene gas with the sensing element in the sensor array can cause changes in electrical properties because of a charge transfer and the polymer chain structure. Resistive type interdigited electrode sensor arrays covered with a mixture of molecularly imprinted polymer (MIP)/ conductive polymer (CP) were designed and fabricated to detect terpene gases. MIP coated on CP (MOC) type showed markedly higher sensitivity compared to mixture of MIP and CP (MMC) type. The gas detection patterns by PCA were used to get higher selectivity of multicomponent chemical media.

1. Introduction

Terpene is an oxygenated hydrocarbon, and is beneficial to humans in diverse ways including stabilization of people and ozone removal. A few types of terpene with such benefits are being utilized as commercial air fresheners. While terpene possesses unique scent based on its types, research is being delayed because there are many terpene types with similar characteristics. The major terpene detection methods that have been mainly researched involve high performance liquid chromatography (HPLC) [1], gas chromatography mass spectrometry (GC/MS) [2], and quartz crystal microbalance (QCM) [3, 4]. In addition, studies that use molecular imprinted polymers (MIP) to fabricate QCM or resistant terpene sensors are being actively performed. With high selectivity and superior molecular imprinting capacity, MIP [5, 6] is being widely applied in various fields. MIP is formed of cross-linker, functional monomers, and template, and functional monomers around the template are arranged at the binding site in advance for binding. To maintain the arrangement of the template bound function monomers, the cross-linker and polymerization initiator are added for polymerization. By removing the template from the polymers in the next step, 3-dimensional MIP with special pores in accordance to the template is synthesized. Template removed-MIP is utilized as a detection substance of sensors using the characteristic of simple rebinding between templates.

A conductive polymer (CP), which has π-conjugated electrons spread along the polymer backbone and has a delocalized electron structure after doping, is the solution to reducing the electrical resistance in resistive-type sensors [7]. The conductivity increases with increasing polyaniline content in the range 20 – 60 %. Polyaniline is classified based on its oxidation state, leucoemeraldine, emeraldine, or pernigraniline [8]. y=1 is called leucoemeraldine base, y=0.5 is emeraldine base, and

[1] Address for correspondence: Sung Pil Lee, Department of Electronic Engineering, Kyungnam University, Kyungnam, Changwon 631-701, Korea. Tel.: 82-55-2492642; Email: sensors@kyungnam.ac.kr.

y=0 is pernigraniline, respectively. Unlike most other polyaromatics, the polyaniline in the fully oxidized state is not conductive. Polyaniline becomes conducting when the moderately oxidized states, in particular emeraldine base, are protonated and charge carriers are generated. It is this process, generally called protonic acid doping, which makes polyaniline unique. The conduction mechanism is believed to involve polarons. In the case of protonated emeraldine, a delocalized poly (semiquinone radical cation) is the polaronic carrier. For intellectualization of the gas sensors or ion sensors, multi-functionality and miniaturization is essential. The purpose of fabricating sensor arrays in gas sensors or ion sensor system is for simultaneous detection of target substances of various types. In this study, the sensitivity of sensors was compared according to the fabrication method of resistant terpene sensors using conductive polymers and MIP.

2. Experimental

For the sensor array, a terpene sensor, temperature sensor, and analytical elements were designed within the same package [9]. Figure 1 shows the layout and sensing areas of the sensor array. A conductive polymer was coated on top of three resistance areas to create a bridge-type, and the substance that detects terpene was coated only on the top of an element used as a sensor. Four bridge resistance sensors were arranged to allow respond to each terpene. A general p-n junction was employed for the diode temperature sensor. The CMOS 0.5 μm rule was applied using the Cadence and Autocad with 30 bonding pads. To create a diode temperature sensor, a P-N junction was formed via ion implant and photolithography processes. After formation of the electrode pattern with poly silicon, a hole was connected with gold electrodes and bonded to the pad with aluminum.

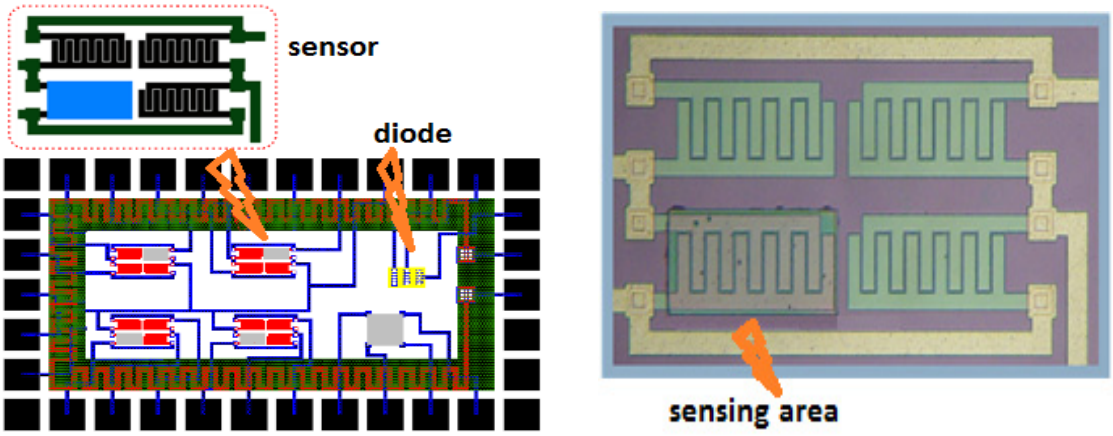

Figure 1. Terpene sensor module with resistive bridge; (a) layout of sensor array and (b) photograph of sensing area.

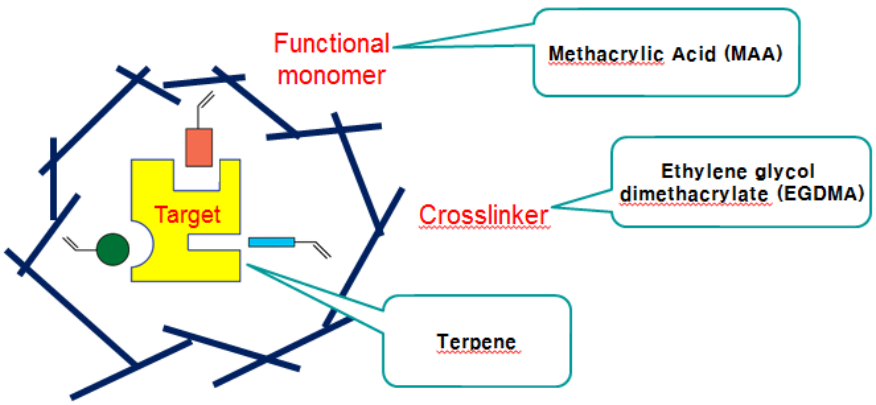

Figure 2. Formation of molecular imprinted polymers.

The methacrylic acid (MAA) as the functional monomer was positioned spatially around the template and their positions were fixed by copolymerization with cross-linking (ethylene glycol dimethacrylate, EGDMA). 2, 2'-azobisisobutyronitrile (AIBN) was selected as the polymerization initiator as shown in figure 2 [4]. The solution was purged with nitrogen gas for 10 minutes to remove any oxygen content as previously reported [10].

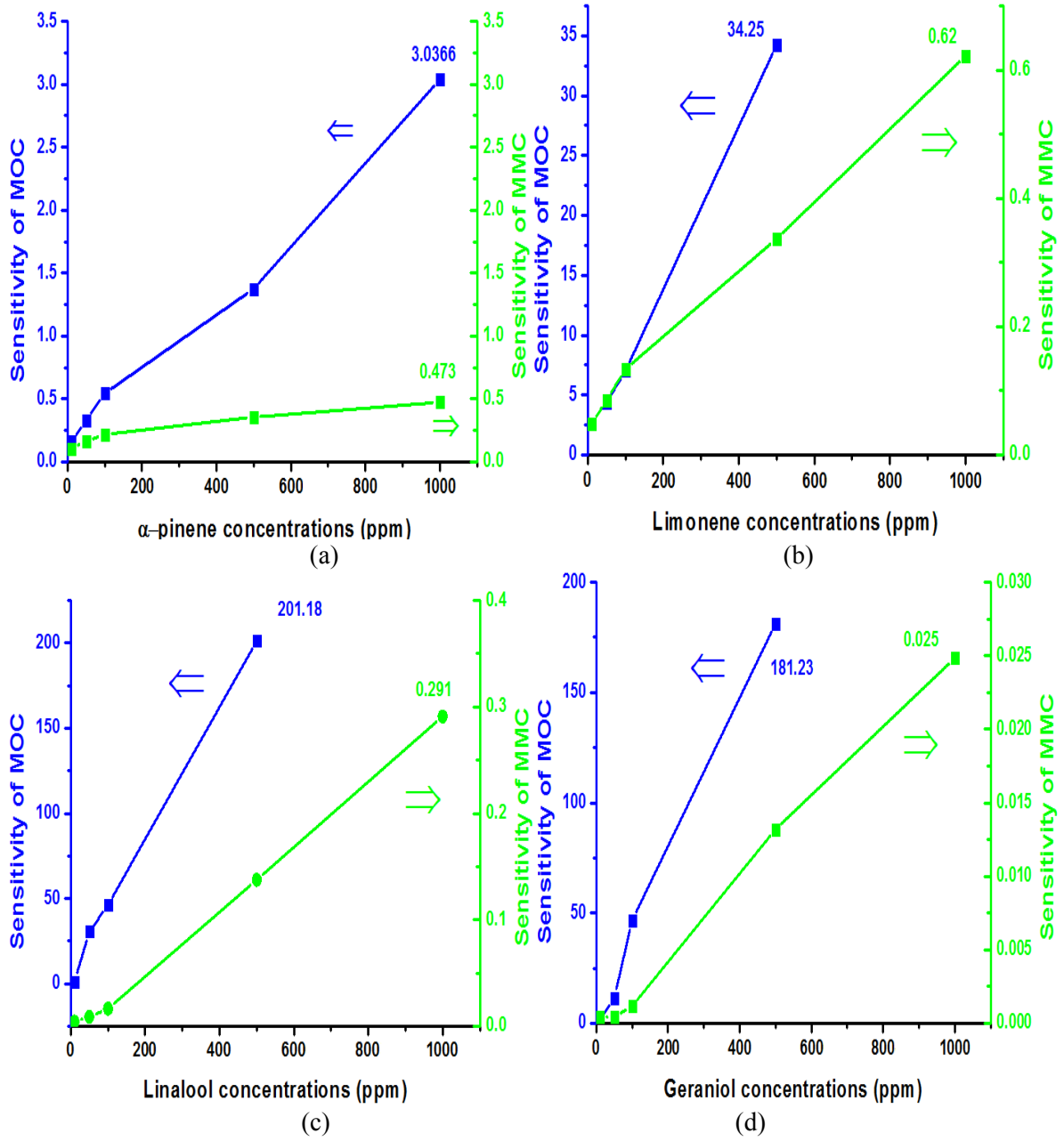

Figure 3. Sensitivity comparison of MOC sensor and MMC sensor for (a) α-pinene, (b) limonene, (c) linalool and (d) geraniol gas.

3. Results and discussion

Figure 3 shows a comparison of the characteristics of sensitivity to α-pinene and limonene in sensor arrays formed by MMC and MOC. The MMC sensor exhibited 0.473 sensitivity at the α-pinene concentration of 1000 ppm, whereas the MOC sensor showed much higher sensitivity (3.04). Regarding the response to limonene as presented, the MMC sensor exhibited sensitivity of 0.62 at

1000 ppm, while MOC sensor showed a much higher sensitivity of 34.25, even at 500 ppm. The sensor sensitivity is defined as the difference between electrical resistance before terpene gas injection and sensor resistance after gas adsorption. As for the response to linalool demonstrated in figure 3(c), the MMC sensor showed sensitivity of 0.29 at 1000 ppm, whereas the MOC sensor revealed a much higher sensitivity of 201.18, even at 500 ppm. Similarly, in response to geraniol (figure 3(d)), the MMC sensor showed the lowest sensitivity of 0.025 at 1000 ppm, but the MOC sensor exhibited a relatively high sensitivity of 181.23 at 500 ppm.

There are two possible conduction mechanisms of terpene sensors using MIP and conductive polymers. In the first, a charge transfer is induced between the cavity and the template through terpene gas adsorption, and in the second, the electrical characteristics are altered through the change of the polymer chain structure. Ryu et al. [8] reported that charge carrier mobility, parallel to the polyaniline chain, is a major causative factor of increases in electrical conductivity. In other words, the parallel conductivity ($\sigma_{\parallel}$) dramatically changes with the increase of the draw ratio, while the vertical structural conductivity ($\sigma_{\perp}$) hardly changes. Here, the parallel direction is the direction in which the film stretches, and the vertical direction is the direction perpendicular to the direction the film stretches. The MIP is synthesized via copolymerization of functional monomers in the presence of template molecules. After polymerization, monomers are separated from the template molecules. Template molecules are divided after monomer polymerization. Template molecule extraction from the completely formed polymer-nets creates a cavity that forms an arrangement in its functional group size, shape, and spatial arrangement.

Figure 4 demonstrates the selectivity for each terpene exhibited by the MOC-type sensor arrays. Sensor array was individually exposed to different terpene gases at the same concentration, and were normalized for inter-comparison according to the sensitivity of each sensor. Terpene is a substance that is biosynthesized from isoprene (molecular structure C_5H_8), and its basic structure retains $(C_5H_8)n$, a multi-structure of (C_5H_8). Limonene is monoterpene like α-pinene, but generally has a higher sensitivity for the same concentration. This is because limonene is monocyclic while α-pinene is bicyclic. With similar structures, the $C_{10}H_{16}$ group of limonene and α-pinene share similar structures and relatively low selectivity.

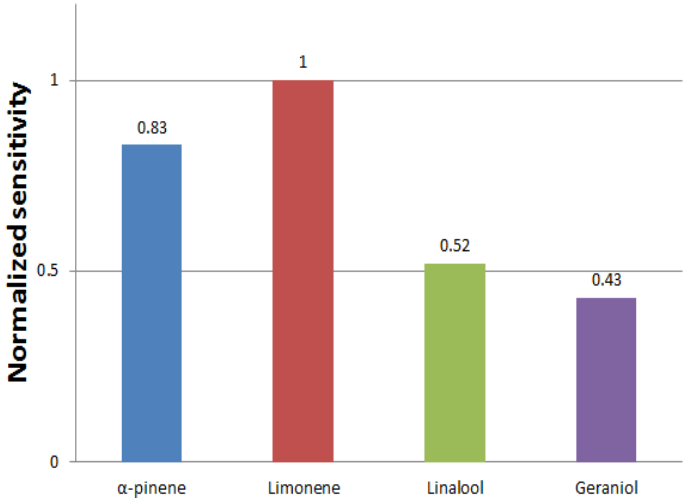

Figure 4. Selectivity of MOC type sensor array for limonene gas.

4. Conclusions

Using MIP molecular imprinting characteristics and conductive polymer, MIP mixed- or coated-resistant terpene sensor arrays were fabricated. The MOC-type sensor showed markedly higher sensitivity compared to the MMC-type sensor. At the terpene concentration of 500 ppm, the MOC sensor exhibited about 6.5 and 100-times higher sensitivity for α-pinene and limonene, respectively, compared to the MMC sensor. In the investigation of selectivity for each terpene using the sensor

array, limonene and α-pinene possess identical chemical formulas with similar structures. We need to investigate to get the sensitivity and selectivity for more terpene gases.

Acknowledgment
The author wishes to acknowledge the financial support of Kyungnam University made in the program year of 2013.

References
[1] Onyeike E, Ikewuchi J, Ikewuchi C and Uwakwe A 2010 *The Pacific Journal of Science and Technology* **11** 480-2
[2] Yermakov A, Khlaifat A, Qutob H, Abramovich R and Khomyakov Y 2010 *Chemical Sciences Journal* **7** 1-10
[3] Tsuru N, Kikuchi M, Kawaguchi H and Shiratori S 2006 *Thin Solid Films* **499** 380-5
[4] Kikuchi M, Tsuru N and Shiratori S 2006 *Science and Technology of Advanced Materials* **7** 156-61
[5] Vasapollo G, Sole R, Mergola L, Lazzoi M, Scardino A, Scorrano S and Mele G 2011 *Int. J. Mol. Sci.***12** 5908-45
[6] Yan H and Row K 2006 *Int. J. Mol. Sci.***7** 155-78
[7] Skotheim T 1986 *Handbook of Conducting Polymers* (Dekker New York)
[8] Ryu K, Chang S, Kang S, Oh E and Yo C 1999 *Bull. Korean Chem. Soc*. **20** 333-6
[9] Lee S 2010 *Electronic Materials Letter* **6** 1-5
[10] Jung J and Lee S 2012 *Journal of Sensor Science and Technology* **21** 345−51