

Multi-ion sensing in solutions by a terahertz chemical microscopy

K. Akimune, Y. Okawa, T. Hagiwara, K. Sakai, T. Kiwa, K. Tsukada*

Graduate School of Natural Science and Technology, Okayama University,
3-1-1 Tsushimanaka, Kitaku, Okayama 700-8530, Japan, en422403@s.okayama-u.ac.jp

Abstract

A terahertz chemical microscopy (TCM) has been proposed and developed in order to visualize the chemical potential changes in the water solution. In this paper, ion sensing in solutions, as an application of terahertz chemical microscopy, are introduced, and we observed the variation of amplitude of THz wave. In TCM, we detect the change in the amplitude of radiated THz wave from a THz sensing plate. The sensing plate is that the amplitude of radiated THz wave changes when chemical reactions are undergo on the THz sensing plate.

We immobilized ion sensitive membranes, which can take the certain ion, on the surface of SiO₂ side of THz sensing plate. We dropped the sodium solution of 10⁻⁴ M and 10⁻¹ M. The amplitude of radiated THz wave as the concentration of 10⁻¹ M was large in magnitude than the concentration of 10⁻⁴ M where the ion sensitive membrane was immobilized. We can also visualize the concentration of ions to get image. From these results, we can detect ions in solution using TCM.

1. Introduction

There are various ions, such as sodium (Na⁺) ion and potassium (K⁺) ion, in our body and these kinds of ions are well-balanced to maintain our life system. Loss of ion balances lead to be serious diseases. Therefore the sensing systems for ions are required in the medical diagnoses. Conventionally, some ion sensing systems or devices is available. An ion chromatography is widely used in medical diagnosis. Ion chromatography is the method of leading solutions into the column which has the ion exchange resin [1]. Holding time in the ion exchange resin is different in the ions which have electron affinities or ionic valences or ionic radiuses to the ion exchange resin, so ions in solutions can be separated. However, this type of system could not separate ions that have similar magnitude of polarities. There is also method such as an ion selective electrode. Electrode which responses certain ions and reference electrode are soaked in the solution to measure a potential difference between electrodes [2]. The ion selective electrode can realize real-time detection of ions; however, a lot of electrodes are required in order to achieve multi-ion sensing.

In this work, multi-ion detection using terahertz chemical microscopy (TCM) has been proposed and demonstrated.

2. Experimental

Fig. 1 (a) shows the photograph of the TCM we developed. The size is 630 mm times 380 mm times 275 mm. The TCM utilize THz sensing plates to detect the chemical reactions. The THz sensing plate consisted of a three-layers of Sapphire/Si/SiO₂ with the thickness of each layers is 600 μm, 150 nm and 275 nm, respectively [3-5].

Fig. 1 (b) shows the schematic band diagram of THz sensing plate. By irradiating femtosecond laser pulses from the sapphire side of the THz sensing plate, photo-excited carriers are generated in Si layer and accelerated by the depletion field near the boundary of the SiO₂ and Si layers. This modulation of carriers could be the instantaneous current and the current lead to the THz wave generation that can be expressed by Eq. (1). Where $J(t)$ is the instantaneous current density, $n(t)$ is the density of the excited carrier, and $v(t)$ is the accelerated speed of excited carrier, respectively.

$$E_{THz} \propto \frac{\partial J(t)}{\partial t} = e \frac{\partial n(t)}{\partial t} + e \frac{\partial v(t)}{\partial t} \quad (1)$$

When the chemical or electric potential shift at the surface of the SiO₂ film, the magnitude of depletion field shift, which result in the change in the amplitude of radiated THz wave. Because the radiated THz wave has the information exactly where the laser hits, the distribution of the potential across the sensing plate surface could be visualized by scanning the laser. Note that the spatial resolution of this type of laser-excited technique is generally determined by the wavelength of the laser and not by the wavelength of THz wave and the current spatial resolution of our system is approximatly 50 μm.

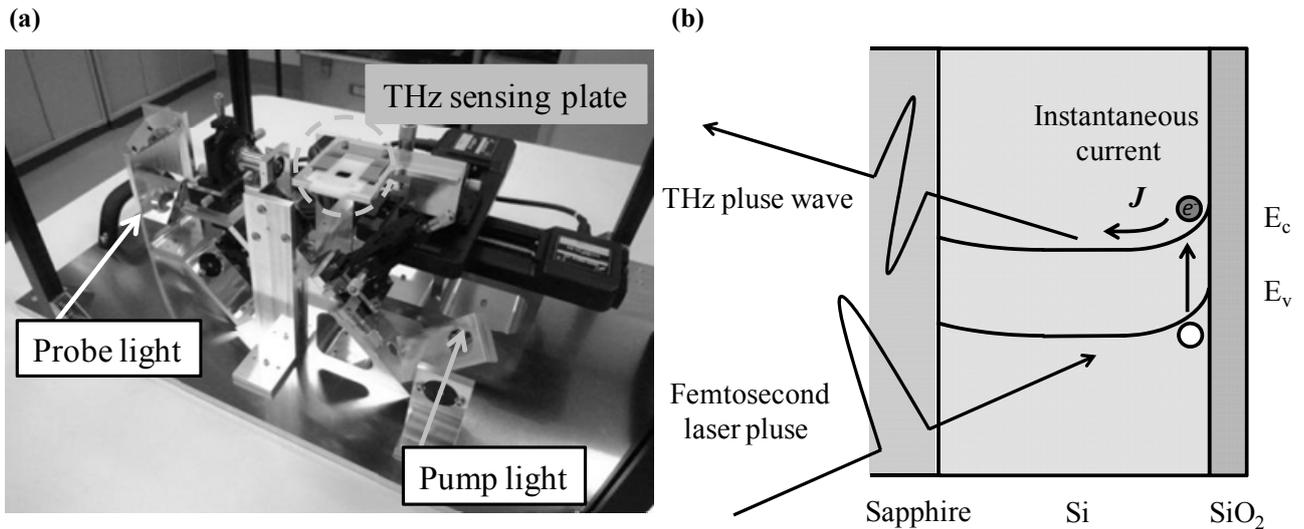


Fig. 1 (a) Photograph of TCM and, (b) Schematic band diagram of THz sensing plate

In order to detect ions in the solutions, ion sensitive membranes were immobilized on the sensing plate surface. Fig. 2 shows the schematic diagram of the sensing plate used in experiments. The ion sensitive membrane, which can take the certain ion, is immobilized on the surface of SiO_2 side of THz sensing plate. The ion sensitive membrane is made of base material (Polyvinyl Chloride), the plasticizer (Dioctyl adipate) and the ionophores (ETH2120 for sodium ions or Valinomycin for potassium ions), the anion excluder (Sodium Tetrphenylborate: NaTPB or Potassium Tetrphenylborate: KTPB for sodium or potassium ions, respectively). The ionophore was infected to absorb specific ions into the membrane. Fabricating process of the ion sensitive membrane was as follows. First, all chemicals were resolved and mixed by adding the Tetrahydrofuran. Then, the solution was dropped on the flat plate and vaporized to form the membrane. After that, the prepared ion sensitive membrane is peeled off from flat plate, and cut to the round shape. Finally, membranes were immobilized on the surface of SiO_2 . When the sample solution is dropped on the ion sensitive membrane, ions are taken into the ion sensitive membrane, then the exchanges of ions reach to the thermal equilibrium state. If the ion concentration is changed, the thermal equilibrium state shift which result in the change in the electric potential at the surface of the THz sensing plate. As the result, depletion field changes, and simultaneously, the amplitude of the radiated THz wave changes.

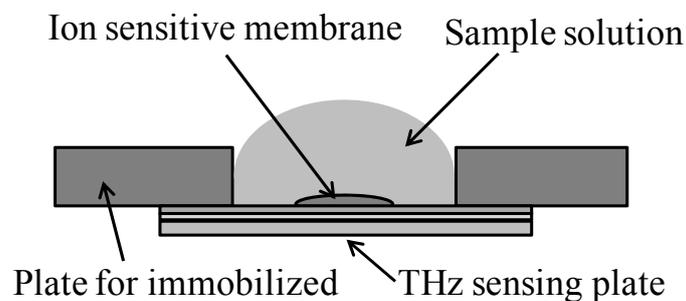


Fig. 2 Sample used in experiment

Fig. 3 (a) shows the immobilized membrane on the sensing plate. The diameters of the membranes were 2 mm, 3 mm, 4 mm and 5 mm in diameter. Fig. 3 (b) is the THz amplitude shift when the sodium concentration of the solution was change from 10^{-4} M to 10^{-1} M. One can see that the amplitude of THz was enhanced at where the ion selective membrane was immobilized. This result indicates that the TCM can used to detect the ion concentration of the solutions. In the presentation, multi-ion detection by arraying the different sizes of sensing membrane on a single chip will be demonstrated.

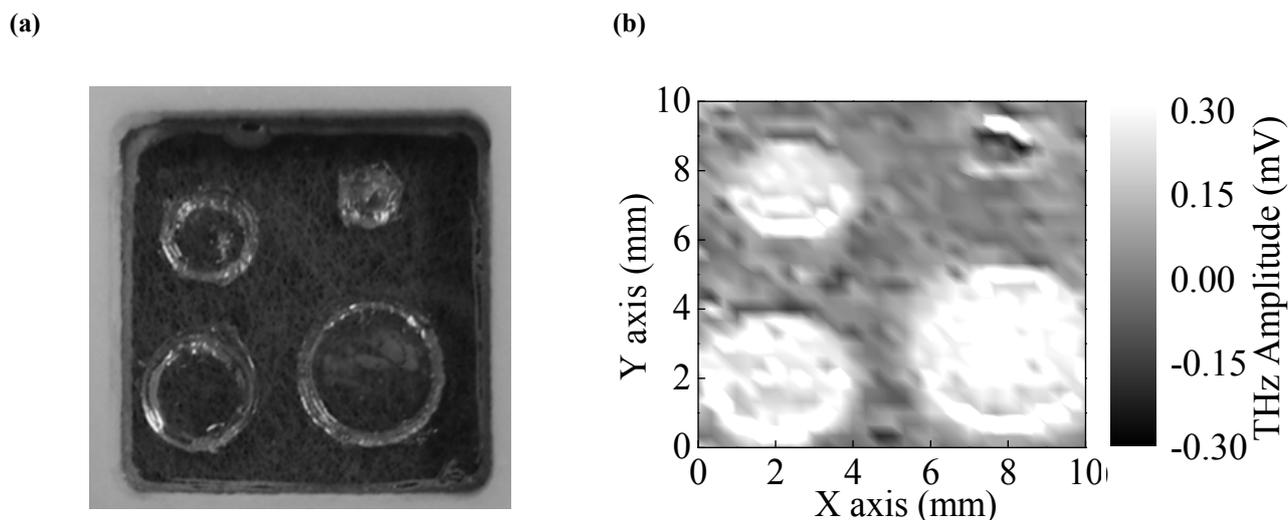


Fig. 3 (a) Photograph of sensing plate and (b) TCM image when the concentration of sodium ions was changed.

3. Summary

The TCM was developed and the ion detection in the solution was demonstrated. The TCM image when the concentration of the sodium ions was changed from 10^{-4} M to 10^{-1} M was clearly visualized. This result indicates that the ion detection using TCM is possible.

4. Acknowledgements

This study was partially supported by the Industry-Academia Collaborative R&D of the Japan Science and Technology Agency (JST).

5. References

1. Bing-Sheng Yu, Li-Hua, Shou-Zhuo Yao: "Ion chromatographic study of sodium, potassium and ammonium in human body fluids with bulk acoustic wave detection," *Journal of Chromatography B*, 693 43-49(1997)
2. T. Komori, T. Yamamoto, K. Oda, K. Sakai, T. Kiwa, K. Tsukada: "Characterization of New Structural Ion Sensor for Sodium Ion", *IEEJ Transactions on Sensors and Micromachines* Vol.133 No.7, 309-313
3. T. Kiwa, J. Kondo, S. Oka, I. Kawayama, H. Yamada, M. Tonouchi, and K. Tsukada: "Chemical sensing plate with a laser-terahertz monitoring system," *Appl.Opt.*,47,18, pp. 3324-3327 (2008)
4. T. Kiwa, S. Oka, J. Kondo, I. Kawayama, H. Yamada, M. Tonouchi, and K. Tsukada: "A Terahertz Chemical Microscope to Visualize Chemical Concentration in Microfluidic Chips," *Jpn. J. Appl. Phys.*, 46, pp. 1052-1054 (2007)
5. T. Kiwa, S. Oka, Y. Minami, I.Kawayama, M. Tonouchi, and K. Tsukada: "Measurement of pH in Fluidic Chip Using a Terahertz Chemical Microscope," *IEEJ Trans. Sens. Micromachines*, 129, 7, pp. 221-224 (2009)