論文の内容の要旨

Development of localized surface plasmon resonance sensors

aiming for monitoring H_2S and SO_2 in volcanic gases

（火山ガスのH_2SとSO_2のモニタリングを目指した局在表面プラズモン共鳴センサの開発）

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1. Introduction

Volcanic gases are composed of H_2O, CO_2, SO_2, H_2S, HCl, HF, H_2, CO, S_2, N_2, CH_4, SiF_4 etc., and their chemical compositions and emission amount are important indicators of volcanic activity. In addition, volcanic gases are one of the major factors that cause volcanic disasters. Among volcanic gases, SO_2 and H_2S have been vigorously observed because they are highly toxic and are the most common volcanic gas species after H_2O and CO_2. Volcanic gases are conventionally observed by direct sampling and spectroscopic methods. Direct sampling methods allow for detailed analysis, but it is dangerous to directly collect gas samples from fumaroles. In addition, rapid assessment of volcanic activity is difficult because sample preparation and analysis in a laboratory are complex and time-consuming. Spectroscopic methods enable continuous measurement at a safe distance from active craters. However, they have limitations such as the need for an appropriate light source, the complexity of data analysis, the difficulty in autonomous operation, and the high cost of purchasing instrument. Recently, methods using small and low-cost electrochemical sensors have been developed for remote and real-time monitoring of volcanic gases. However, there are still some problems with the sensors, such as sensor stability, cross-sensitivities, uncertainties of gas ratios caused by

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differences in response time.

In recent years, localized surface plasmon resonance (LSPR) has been applied to sensing of various gases including H_2S, except for SO_2. LSPR is a phenomenon in which light induces collective vibration of electrons on a metal surface. LSPR sensing is conventionally carried out by measuring the peak shift of an LSPR absorption spectrum caused by refractive index change when target gas is flowed on metal nanostructures. In principle, LSPR sensors can respond quickly by change in refractive index and have robustness against corrosive gases using durable materials. By coating LSPR nanomaterials with appropriate adsorbents and applying chemical modification, high sensitivity and selectivity can be obtained, and multivariate analysis using multiple LSPR sensors makes it possible to distinguish multiple gases. Therefore, LSPR sensing can be a promising candidate for monitoring volcanic gases. In this study, I have developed LSPR chips for sensing H_2S and SO_2 by investigating chemical modification and adsorbents to enhance the sensitivity and selectivity.

2.   Fabrication of LSPR chips

The finite-difference time-domain simulation revealed that the optimal diameter and pitch of a Au nanopattern for the gas detection were 400 nm and 800 nm, respectively. At first, the simulated Au nanopattern was fabricated using electron beam lithography (EBL) to confirm the agreement of its LSPR spectrum with the simulated one. The process of UV nanoimprint lithography (UV NIL) was established to produce LSPR chips more easily and quickly than EBL and thermal NIL. To improve an LSPR spectrum, the annealing temperature of Au nanopattern was optimized to 450 °C.

3.   Mesoporous-silica-coated LSPR chips

The mesoporous silica layers on the Au-nanopatterned chips were modified with amine silane coupling reagents, 3-aminopropyltrimethoxysilane (APTMS) or (*N,N*-dimethylaminopropyl) trimethoxysilane (DAPTMS), by chemical vapor deposition. The amine-modified chips were able to detect 20 ppm of SO_2 in 10 min under a dry condition. The DAPTMS-modified chip showed the higher sensitivity than the APTMS-modified one and enabled to detect 0.6 ppm of SO_2. The enhancement of the sensitivities can be attributed to the high porosity and superficial hydroxyl groups of mesoporous silica, and the strong interaction between the amino or amine group and SO_2. On the other hand, the APTMS-modified chip showed the higher sensitivity to H_2S than the DAPTMS-modified one. The

sensitivities of both chips to H_2S were lower than those to SO_2, indicating the selectivity to SO_2. Furthermore, the sensitivity to SO_2 was enhanced under a humid condition. However, the spectra greatly shifted with changes in relative humidity (RH) because H_2O is absorbed by the mesoporous silica layer. This result suggests that it is difficult to detect subtle changes in absorbance induced by the target gases without a water absorbent or dehumidifier.

4. ZnO-deposited LSPR chips

The Au-nanopatterned chips deposited with ZnO layer showed the high sensitivity and rapid response to H_2S and SO_2, enabling to detect 0.1 to 20 ppm of H_2S in 0.5 min at 70 % RH. The sensitivity to SO_2 was higher than that to H_2S. A correlation between the H_2S concentration and absorbance change was observed at 0.5 min after exposure to H_2S, but no correlation was observed above 0.5 min after exposure. As the thickness of ZnO increased, the peak wavelength of LSPR upshifted and the peak width broadened. The sensitivity increased up to a ZnO thickness of 20 nm and remained almost constant in the range of 20–30 nm. Therefore, a ZnO thickness of 20–30 nm was sufficient to detect the target gas with high sensitivity. However, heating the ZnO-deposited chips in air could not regenerate the chips exposed to H_2S because of the grain growth of ZnO.

5. ZIF-8-coated LSPR chips

By coating ZIF-8 on a Au nanopattern as a benchmark metal organic framework (MOF), the sensitivity to SO_2 and H_2S increased with increasing RH, resulting in the detection of 0.1–10 ppm H_2S and 0.1–20 ppm SO_2 within 5 min at 70 % RH. The ZIF-8-coated chip was more sensitive to SO_2, while at 0 % RH it was less sensitive. Even higher concentrations of SO_2 would have been detected without the limitations of the gas generation system. By heating the chip coated with ZIF-8 at 200 °C in air, the sensitivity and LSPR spectrum could be regenerated about a dozen times. Moreover, the amount of humidity-induced shift in the LSPR spectra was much smaller than that of a DAPTMS-modified mesoporous-silica-coated chip. This will enable to measure the concentration of SO_2 and H_2S in volcanic gases without the use of a water absorbent or dehumidifier.

6. Conclusions

The LSPR chips coated with amine-modified mesoporous silica, ZnO, and ZIF-8 were developed

for sensitive detection of SO_2 and H_2S from sub-ppm to ppm. In particular, the ZIF-8-coated chips demonstrated the high sensitivity, some selectivity and regeneration ability under high humidity, indicating the possibility of detecting typical concentrations of H_2S and SO_2 in volcanic gases. In practical, the developed chips can be used to measure integrated concentrations of H_2S and SO_2 for a certain period because the absorbance remained almost constant after the exposure to the gases was stopped. Furthermore, an observation system with multiple LSPR sensors coated with various adsorbents can be small, inexpensive and has the potential to measure all volcanic gas components. Thus, this study showed the future potential of LSPR sensing to measure volcanic gases.