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Fabrication of AuNPs-Bridged Nanogap Electrodes for Chemosensitive Sensors

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***Abstract*—Simple fabricating methods of nanostructures are required for solving many kinds of problems in the field of electronic engineering. The fabrication of novel and functional nanostructures is a promising way toward innovations: low power consuming devices, sensors with higher sensitivity, selectivity, as well as other novel functions. However, various researches are limited in costly, complex and time-consuming methods. We demonstrated a simple way to obtain nanogap electrodes using ordinary photolithographic techniques and electromigration, and its application as chemoresistive gas sensor based on gold nanoparticles (AuNPs)-bridging.**

***Keywords*—nanogap electrodes, gold nanoparticles, electromigration, chemiresistors**

I. Introduction

The importance of fabricating for well-ordered electronic nanostructures is acknowledged, thus various kinds of researches have been investigated to obtain nanogap electrodes, employing electron beam lithography (EBL) [1], mechanical break junction [2], and shadow evaporation [3]. The commonly used technique of photolithography is very simple and not costly, but has not enough resolution limit to realize the nanogap formation. Then, we combined photolithography and current-induced break junction in order to form nanogaps, in the controlled configuration, and keep the procedure easy with low cost.

Chemical sensor is one of the expected application of electronic nanostructures based on nanogap electrodes. According to the well-known principle of chemical sensors, the materials of the sensing parts are preferred to be low-dimensional materials for high sensitivity. The low-dimensional materials such as thin films, nanowires, and nanoparticles possess high ratio of surface area to bulk volume, therefore those materials are considered to be more reflective to the changes near surface, compared to the bulk materials. There are some earlier studies about chemical sensors based on low-dimensional materials [4-10].

In this research, AuNPs were utilized as a functional material and a linker to molecule recognizing materials for fabricating AuNPs-bridged nanogap electrode, the AuNPs were deposited chemically between nanogap. The gap was made up with electrical-fused technique on the narrowed channel. Based on this simple fabricating procedure, high-functional chemoresistive sensor could be realized (Fig. 1). As shown in Fig. 1, it is expected that adsorption of target chemical to be detected would modify electrical properties of the AuNPs-bridged electrode.

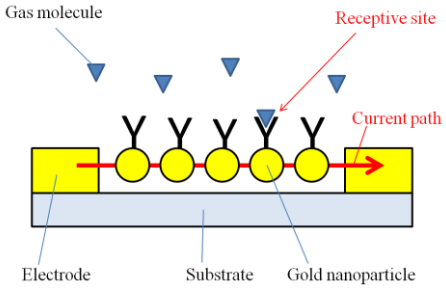

Figure 1. Conceptual scheme of the chemoresistive sensor based on AuNPs-bridged nanogap electrodes. It is considered to be high functional by introducing the receptive site.

II. Experimental

A. *Nanogap electrodes*

One of the purposes of the present research is to find the simple method to fabricate coplanar electrodes with a gap width in the order of nanometer. We combined the conventional photolithographic technique and electrical break-junction technique. Photolithography makes it possible to shape the electrodes into the intended configuration appropriate for sensor electrode, but its ordinal resolution limit is about 1 micrometer. If the configuration is arranged properly, by narrowing some specific part of a metallic channel, break-junction by applying electrical current is possible. When the current density is very high at the narrowed channel site, fusing of metal or electromigration occurs which causes the formation of a nanogap. The schematic configurations are shown in Fig.2.

At first, partially narrowed electrodes were made by photolithography, which is shown in Fig. 2 (a). Actual width of the narrowed channel is about 1 micrometer, which is fabricated on 200nm Au sputtered layer and 30nm Ti sputtered layer on a glass substrate. The current density is highest at the narrowed site of electrode, and the break of a channel will occur at that site (Fig. 2 (b)). Applying sudden voltage, about 1V, resulted in the formation of larger (*ca*. a few micrometers) gap. When the voltage is gradually raised from zero volt, nanogap electrode can be obtained. Once the break of the channel occurs, the current drops to almost zero ampere, and

no more electromigration proceeds (Fig. 3). In the figure, it is thought that the break occurs at about 0.5 V. Optical microscope image of the electrode and SEM image of nanogap is shown in Fig. 4. Fig. 4 (a) shows the broken site at the narrowed channel. Using this method, control of the positions of nanogaps, unlike when breaking nanowires electrically which has uniform thickness. SEM image of Fig. 4 (b) shows the width of the formed gap, which is estimated to be about 50 nm or below. Consequently, the formation of nanogap was successfully fabricated by using current-induced break junction method.

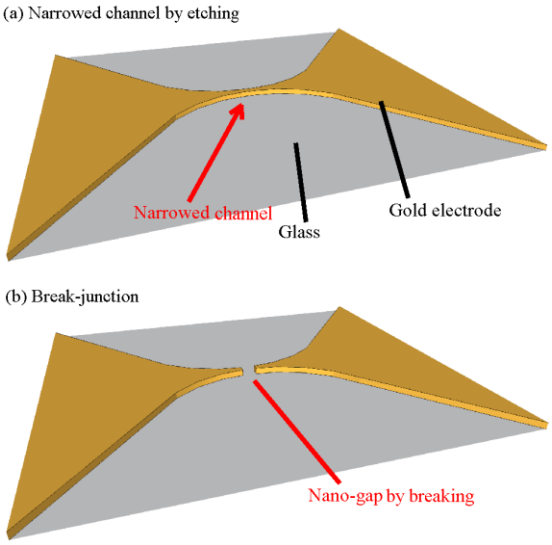

Figure 2. Schematic illustrations of an electrode configuration for electrical current-induced break-junction (a) and a nanogap formed by this way (b).

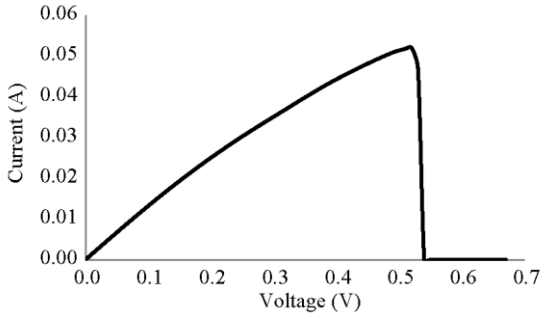

Figure 3. I-V curve of electrical current-induced break-junction.

B. *AuNPs-Bridging*

Coplanar nanogap electrodes are easy to be utilized for the study about mesoscopic phenomena or other electrical experiments. In this paper, for the application to chemoresistor, AuNPs-Bridged nanogap electrodes are fabricated. AuNPs are considered to have an ability of sensing chemical gases [7,8]. If the configuration of the nanostructure composed of AuNPs and nanogap electrodes is properly made, according to the low-dimension principle. In order to use the size effect of AuNPs, neighboring particles and electrodes should not be short-circuited entirely. For this reason, decanethiols and

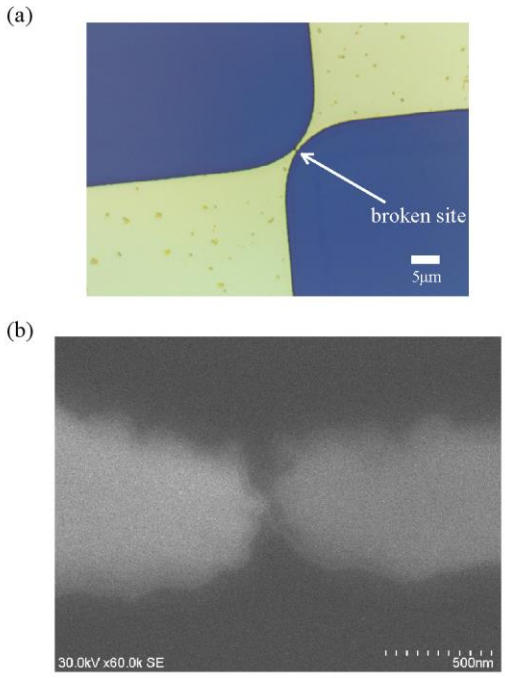

Figure 4. Optical microscopic image of a nanogap electrode (b), and SEM image of nanogap (c).

decadedithiols are employed to form the thin insulating layer. Thiol compounds have thiol functional groups, which have a role of anchoring the compounds to Au surface. One decane-thiol has one anchor, whereas one decanedithiol has two, which also has a role as a linker. Then, it being considered that the tunneling current flows between electrodes and AuNPs, the changes of the amount of current can be treated as the responses to the environmental changes such as gaseous concentration.

Two different procedures to obtain the AuNPs-bridged structures were conducted. Both of them adopted the wet process, in which the aqueous suspension of AuNPs and the ethanol solution of some kinds of organic materials were used. AuNPs were purchased from Sigma-Aldrich, and the sizes of AuNPs used in this study were 3.0-5.5nm. At first, AuNPs-adhesive layer was formed on the surface of electrodes, by treating the electrodes in the solution of decanedithiol for 12 hours. This layer also works as insulating layer, whose thickness is estimated at about 1nm (Fig. 5 (a)). Then, treating in the suspension of AuNPs for 12hours (Fig. 6 (a)), AuNPs-bridged structure could be obtained (Fig. 6 (b)). In another procedure, AuNPs-adhesive layer was formed on the glass surface between nanogap, by surface modification using the solution of (3-aminopropyl)tri-ethoxysilane (APTES). In order to avoid short-circuiting between AuNPs and electrodes, the insulating layer was formed by treating gold electrodes with decanethiols in advance (Fig. 5 (b)). Subsequently, by treating the nanogap electrode in suspension of AuNPs, bridging between the gap with AuNPs was performed (Fig. 6 (c)). After the above treatment, those electrodes were sonicated in water

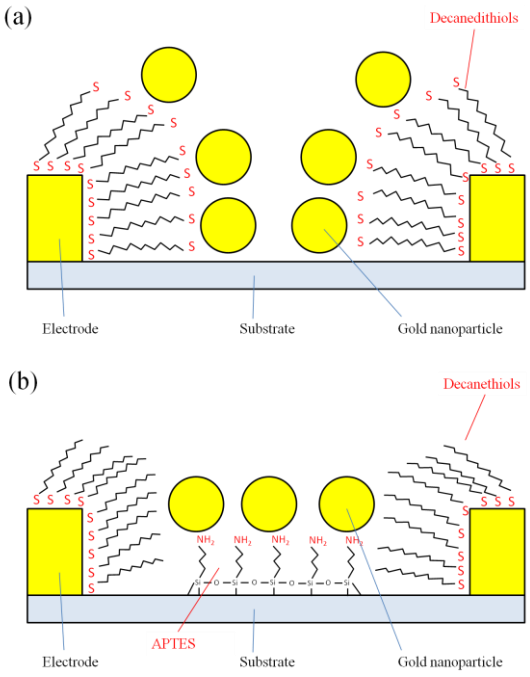

Figure 5. Schematic illustlation of the surface modification by the organic materials.

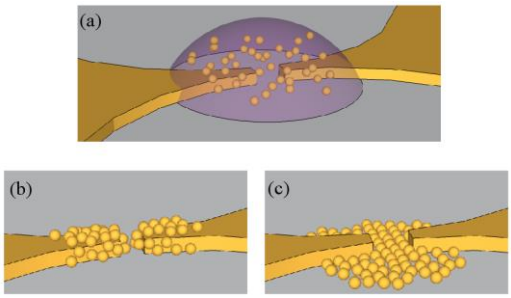

Figure 6. Schematic illustlation of the treating by the suspension of AuNPs (a), AuNPs-Bridged nanogap electrodes fabricated using dithiols (b), and using APTES and thiols (c).

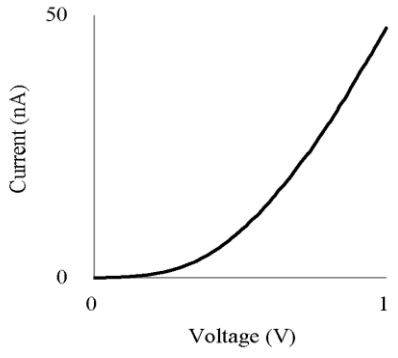

Figure 7. I-V curve of the AuNPs-bridged nanogap electrodes by the former way (Fig. 6 (b)). The current increased exponentially with the applied voltage, which implied the tunneling current was flowing. The result of the latter way (Fig. 6 (c)) shows a similar curve.

for 30 seconds, to remove aggregated AuNPs. In either AuNPs-bridged electrodes, tunneling current were observed (Fig. 7), which confirmed that bridging was succeeded. In the former way, although the possibility that AuNPs are not large enough to bridge over the gap width exists, AuNPs can be firmly stuck to the surface of electrodes owing to the existence of linker layer. Therefore, it is presumable that the electrodes with nanogaps whose gap width is smaller than 10nm could be fabricated, occasionally.

C. *Gas responses*

The prepared AuNPs-bridged nanogap electrodes were evaluated as chemoresistor for gas sensing. Applying the constant voltage, and exposing the sensor electrodes to some kinds of gaseous chemicals (ethanol, acetone, and toluene), the changes of current was observed. To consider the effect of AuNPs in the gap, the response of no-AuNPs-bridged nanogap electrodes, which exhibited small electrical conductance, to gases was also recorded. The result of the measurement is shown in Fig. 8.

Obvious difference between these responses is the difference in the sign of the current changes. The response of AuNPs-bridged one shows positive change, but the counterpart of not bridged one is negative. These results may imply that the response of AuNPs-bridged nanogap electrodes is caused by not only the changes in tunnel barrier, such as slow swelling process or changes in dielectric constant of the barrier [4], but also the reflection of the unique electronic property of nanomaterials such as AuNPs. Similar tendencies in the gas responses were observed in the response to acetone and toluene vapors.

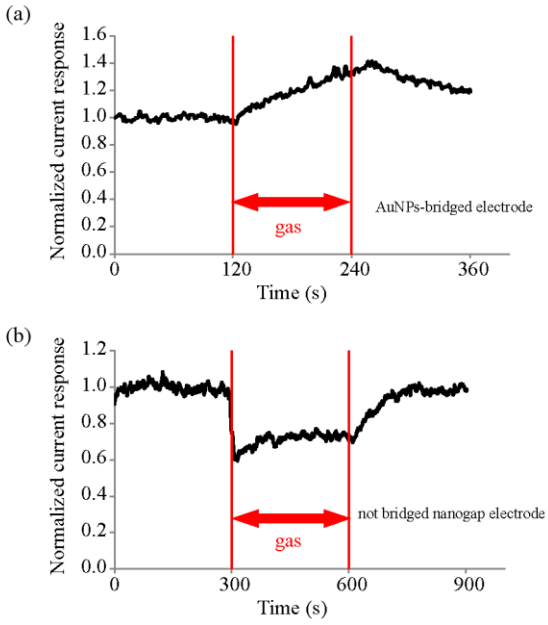

Figure 8. The response of AuNPs-bridged nanogap electrodes to the vapor of ethanol (a) and the response of not bridged electrodes (b). Current responses were normalized by initial electrical current value.

III. Conclusion

The simple methods of fabricating the coplanar nanogap electrodes and AuNPs-bridging were examined and demonstrated experimentally. The results of the measurements of the responses to gases of AuNPs-bridged nanogap electrodes as chemoresistors may suggest the reflection of the unique electronic properties of AuNPs in gas responses. However, since the actual structures of fabricated electrodes are not determined entirely, any other causes affecting electrical conduction may exist. More researches are necessary to reveal the mechanism of the responses of AuNPs-bridged nanogap electrodes, and to fabricate more functional chemical sensors by using molecule recognizing mechanism.

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