Three-Dimensional Self-Assembled Micro-Array Using Magnetic Force Interaction

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Abstract - We have demonstrated a fluidic technique for self-assembly of microfabricated parts onto substrate using patterned shapes of magnetic force self-assembled monolayers (SAMs). The metal particles and the array were fabricated using the micromachining technique. The metal particles were in a multilayer structure (Au, Ti, and Ni). Sidewalls of patterned Ni dots on the array were covered by thick negative photoresist (SU-8), and the array was magnetized. The array and the particles were mixed in buffer solution, and were arranged by magnetic force interaction. Binding direction of the metal particle onto Ni dots was controlled by multilayer structure and direction of magnetization. A quarter of total Ni dots were covered by the particles. The binding direction of the particles was controllable, and condition of particles was almost even with the Au surface on top. The particles were successfully arranged on the array.

Keywords: Self-assembly, Fluidic technique, Three-dimensions, MEMS, Magnetic force interaction

1. Introduction

In order to obtain 3D structures at the micro-scale, several methods such as the folding up of flat structures by a micro-probe have been proposed. However, these methods are very difficult to control and were therefore unsuitable. Self-assembly is a phenomenon in which basic units come together and form a structure spontaneously. We can see many self-assembling examples in the tiny natural world, like the self-reproduction of viruses and micellization.

It is expected that self-assembly will become an effective method in the future fabrication of microstructures. There are aspects to consider such as the gravity, the surface tension, the hydrophilic or hydrophobic interaction, the electrostatic force and the specific affinity of biomaterials etc., for construction of the system by using these methods [1~6].

In previous works, 100~500μm units were self-assembled using hydrophobic interaction as a bonding force [7~9]. At the micrometer-size, 3D self-assembly was realized using hydrophobic mono-layer films. One of the most important problems in micro self-assembly is to have a bonding force that is not only strong enough to bond units but that acts on the contact area only.

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The integrated type biosensor will be very useful, and it is expected to be applied in the various fields from now on. However, there is a problem in the integration of the sensor in sequential immobilization of a conventional biomaterial, and the measurement object is limited in a biosensor. In addition, there is the predicament that the selection width of the recognition element that uses the self-assembly of the particles is a simple target detection method and must select the recognition element suitable for use as the channel will become narrower.

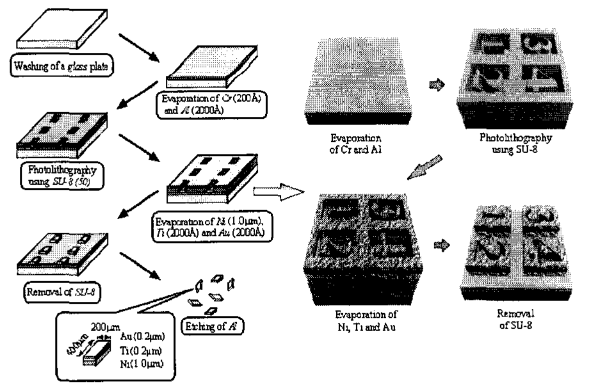
These biosensors [10-11] were fabricated using conventional techniques such as ink-jet printing, screen printing, photolithography, and photodeposition in which the sensing chemistries are applied directly to the sensor surface. Typically, multiple fabrication steps that are labor-intensive and subject to some degree of variability are required.

Thereupon, we have proposed a new construction method using an integrated type biosensor such as an enzyme chip, immunity chip, and DNA chip. If we use the self-assembly method to construct biosensors, there are many advantages such as low cost, simple processing and removal of labor-intensive activity. In particular, we think self-assembly using magnetic force interaction is an effective method in fabricating microstructures. This research is aiming at the development of the sensor array where the composite signal of light and electricity are able to be detected. The particles that immobilize a recognition element were fabricated with the metal in which electrochemical reaction and chemiluminescence's can be acquired. The self-assembly by magnetic force interaction for the arrangement of these particles onto the substrate were used. This research intended to integrate by using photolithography technology and the self-assembly method for integrated type biosensor construction. The significance to the development of the useful integrated type biosensor such as an enzyme chip, immunity chip and DNA chip is significant.

2. Experimental

2.1 Preparation of particles

Fig. 1 (a) indicates how to make the particles. Glass substrate was washed for 30 min each in the order of ultra pure water, IPA, acetone, IPA and ultra pure water with a supersonic wave washer. Cr (200Å) and Al (2000Å) were evaporated on this substrate. A resist pattern was made by using the negative resist SU-8. Ni (1μm), Ti (2000Å) and Au (2000Å) were evaporated on the substrate. The resist was peeled off by dipping the substrate in SU-8 REMOVER for 10 min at 80~85℃. The particles were obtained by Al etching. On the other hand, each particle is able to be recognized by marking a number on this with the process of Fig. 1 (b). The process is identical with Fig. 1 (a).

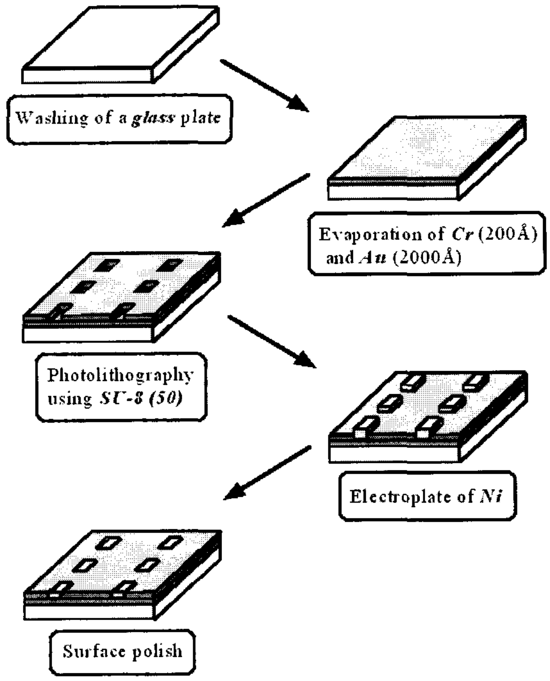


(a) Preparation of the particles (b) Marking with a number on the particles

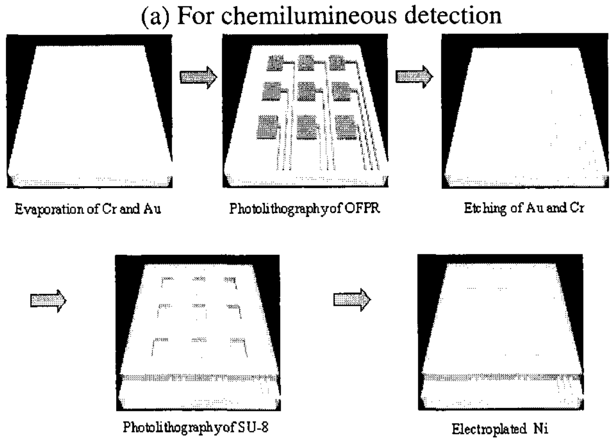
Fig. 1 Schematic representation of metal particles consisting of Ni, Ti and Au layers.

2.2 Preparation of the chip

The fabrication process of the chip is shown in Fig. 2 (a) for chemilumineous detection and (b) for electrochemical signal detection. In Fig. 2 (a), washing of the substrate, evaporation of Cr and Au for the electrode preparation and photolithography for the pattern preparation of the electroplating was carried out under conditions similar to the preparation of particles. Ni was electroplated, and the substrate was polished with sandpaper 2400 and ground with alumina as a finishing. The surface of the substrate was then smoothed. The chip for chemilumineous detection was fabricated. Ni-electroplating conditions are temperature: 50~60℃, current density: 3A/cm^2, pH: 4.0, and anode electrode: Ni anode. The deposition speed is 1.6μm/min.



(a) For chemilumineous detection



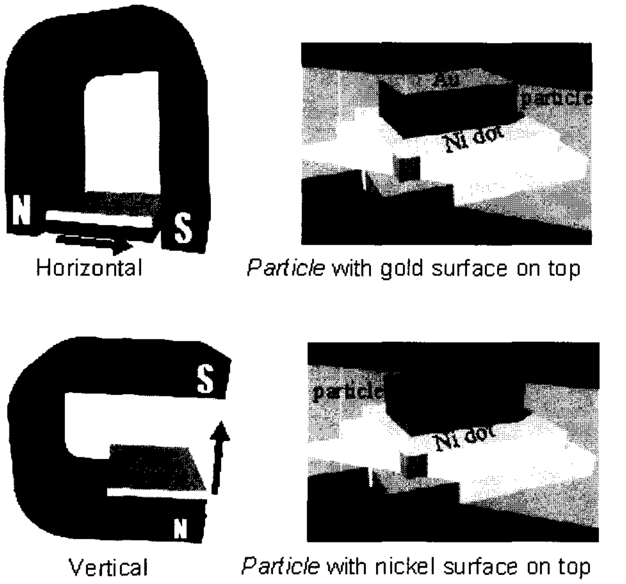
(b) For electrochemical signal detection

Fig. 2 Fabrication process of Ni dot arrays on a chip.

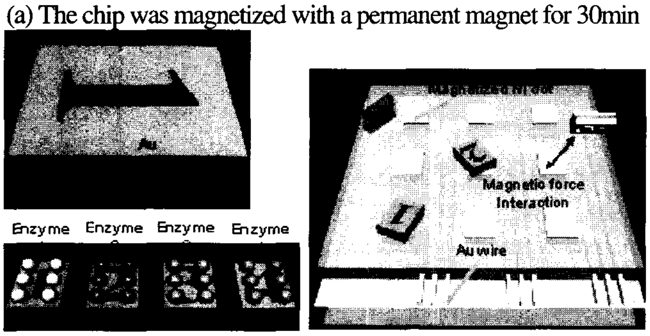
The fabrication process of the substrate for electrochemical signal detection is shown in Fig. 2 (b). The Cr and Au layer were etched by photolithography after Cr and Au were evaporated on the substrate and coated with OFPR of positive resist. SU-8 of negative resist was etched by photolithography after coating. Ni was electroplated, and the substrate was polished with sandpaper 2400 and ground with alumina as a finishing. The surface of the substrate was then smoothed. The chip for electrochemical signal detection was fabricated.

2.3 Arrangement of the particles on the chip

The matter whether the particles were arranged on the chip by the magnetic force was tested. An illustration of the experiment is shown in Fig. 3. The Ni pattern on the chip was magnetized by placing permanent magnets in the horizontal direction and vertical direction of the chip as shown in Fig. 3 (a). Next, the particles were inserted in the 1.5m*l* of sample tube containing the chip and water, and stirred for several minutes as shown in Fig. 3 (b). The chip was taken out from the sample tube and dried. This chip was observed with the digital microscope (KEYENCE) and the scanning electron microscope (SEM S-3500N Hitachi, Ltd.). Whether the particles can be arranged in the solution by magnetic force interaction, and whether the direction of the particles could be controlled were checked. Whether the particles can be arranged on the Ni pattern chip was examined by using the chip that was previously magnetized and the Ni particles that were not magnetizing. The particles having a thickness of 1.4μm and 200×400μm^2 were used. We considered the same method without magnetizing the particles and the chip as a control experiment. Furthermore, we examined whether the particles turn the Au layer to the outside if the particles are arranged on the Ni pattern of the chip by using the particles that are not magnetized and having two layer structures of Ni and Au and the chip that had the Ni pattern.



(a) The chip was magnetized with a permanent magnet for 30min



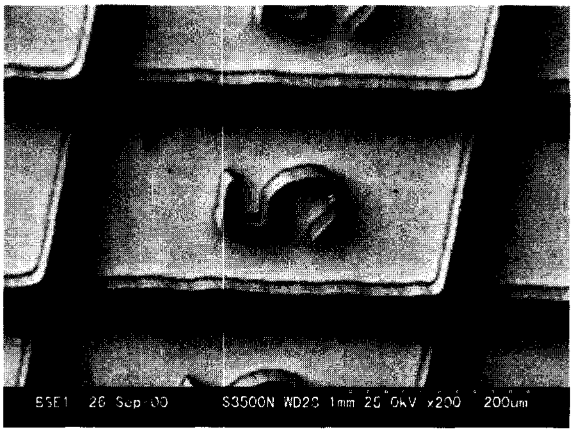
(b) After putting the chip, the particles and the water into a test tube, the tube was shaken for 2 min. The chip was taken out from the sample tube and dried in the air

Fig. 3 Schematic representation of the arrangement of particles on the chip.

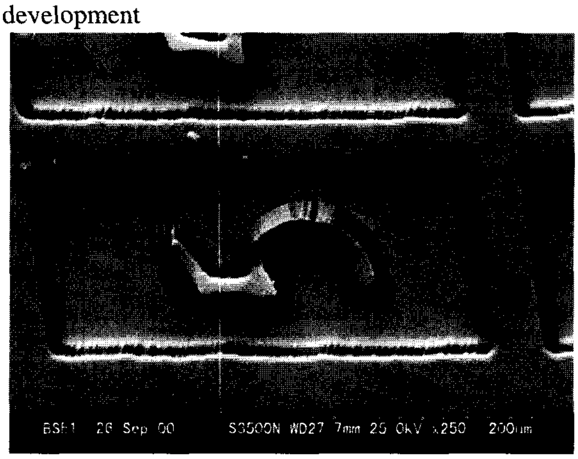
3. Results and Discussion

3.1 Preparation of the particles

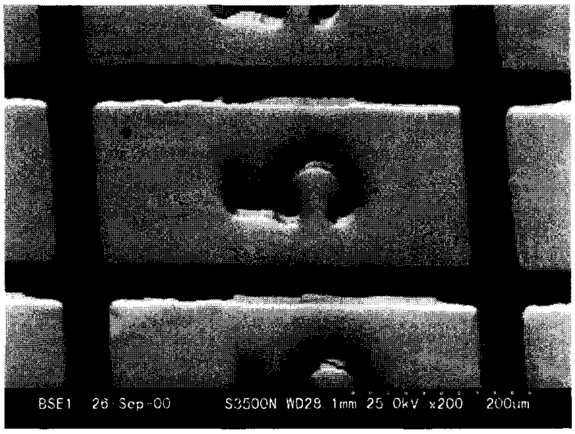
Fig. 4 shows the photograph of the particle taken with SEM. Fig. 4 (a) shows the particles that were evaporated Cr and Al on glass and spin-coated SU-8 and etched. Fig. 4 (b) indicates the particles after evaporation of Ni, Ti and Au layer on the substrate of (a). Finally, Fig. 4 (c) indicates the particles after removal of SU-8, Ni, Ti and Au layers from the substrate of (b). It is the number of Ni/Ti/Au layers and SU-8 that remain. The size of the particle was 200×400μm^2. The number was fabricated clearly from Fig. 4 (a), (b) and also (c). Various numbers, 5, 7, etc., were also fabricated.



(a) After SU-8 spin coating on glass/Cr/Al substrate and development



(b) After Ni/Ti/Au evaporation on glass/Cr/Al substrate



(c) After removal of SU-8 & Ni/Ti/Au layers

Fig. 4 SEM images of the particle for each fabrication process.

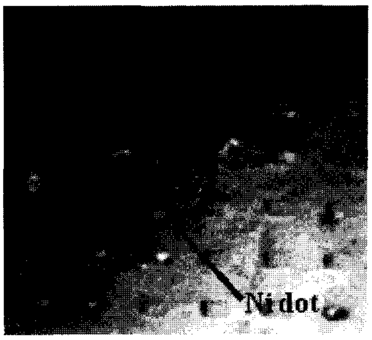
3.2 Preparation of the chip

Fig. 5 (a) shows the fabricated chip for chemilumineous detection. Magnetized Ni dots could be seen. 2,500 patterns of the thickness of 2µm and 200×400µm^2 have been formed on the chip. Fig. 5 (b) shows the fabricated chip for electrochemical detection. Magnetized Ni dots could be seen. Also, the fabricated Ni dot is shown in Fig. 5 (c). After Cr and Au evaporation on the glass, SU-8 was coated. And, the glass was etched by photolithography. Cr/Au/Ni layers were fabricated by electroplating Ni. By polishing the surface of Ni, flat Ni dots were obtained. The size of the Ni dot was 200×400µm.

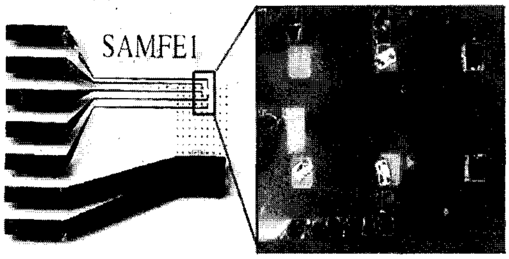
3.3 Arrangement of the particles on the chip

The chip was magnetized. Inserting the particles into the sample tube containing the chip and water, it was stirred for 2 min. Fig. 6 depicts the chip observed by a digital microscope after the chip was removed from the solution and dried. In Fig. 6, the thickness of the particle was 1.4µm and the size was 200×400µm^2. 2500 Ni patterns of thickness 1.2µm and 200×400µm^2 have been formed on the chip. The particles were arranging locally on the Ni pattern of the chip. 24 particles existed on other than Ni pattern and 249 particles were on the Ni pattern in an area of about 2mm^2. Therefore, approximately 91% of the particles were arranged on the Ni dots. We are able to distinguish each particle by each number. We performed the same experiment, without magnetizing the entire chip and the particles as the control experiment, to confirm that arrangement of these particles depend on magnetic force interaction. As a result, only several particles remained on the chip. From these results, it was conjectured that the particles were arranged on the chip by magnetic force interaction.

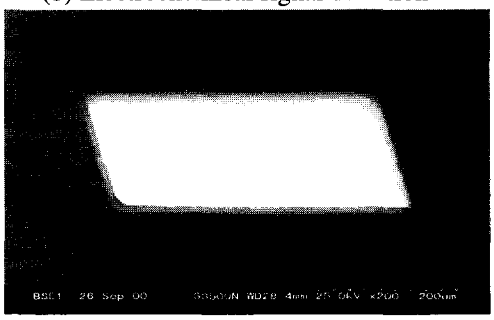
In the case magnetizing the Ni pattern of the chip by placing a permanent magnet in the horizontal direction and



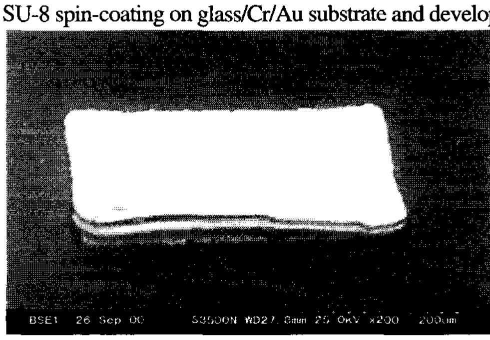
(a) Chemilumineous detection



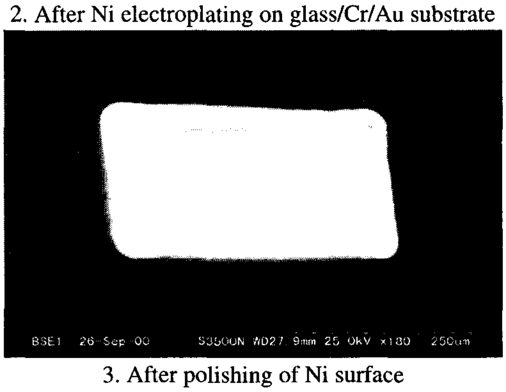
(b) Electrochemical signal detection



1. After SU-8 spin-coating on glass/Cr/Au substrate and development



2. After Ni electroplating on glass/Cr/Au substrate



3. After polishing of Ni surface

(c) SEM images

Fig. 5 Digital microscope and SEM images of the chip for each process.

vertical direction of the chip and arranging the particles, the proportion of Ni dots and Au face of the particles making contact are shown in Table 1. The total number of Ni dots on the chip was 2500 pieces. In Table 1, the number of particles contacting with Ni dots is 556 pieces and 56 pieces individually, and was considerably less in comparison with the Ni dot number of the chip. In the case that the chip was magnetized in a horizontal direction, the proportion that the Au face of the particles contact with Ni dots of the chip was more than in a vertical direction, by 22.2%. Also, the trend in which many particles arrange within the range of contact and be hardly arranging other than this was confirmed. The contacting position of the particles confirmed that it is not in the central area of the Ni dots on the chip, deviating somewhat to the part of an edge. We checked the magnetic field on the chip by using a magnetic flux, to verify these causes.

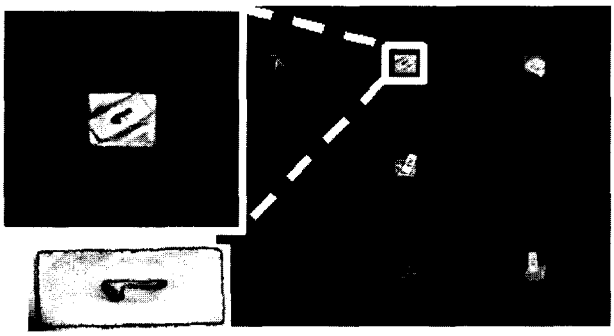


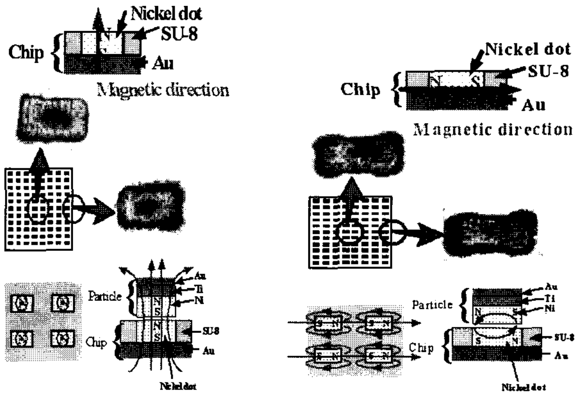
Fig. 6 Digital microscope image of sensor array. The particles arranged on the chip by magnetic force interaction. The chip had an Ni dot array of 400x200μm^2. The Ni particles of 400x200μm^2 were fabricated by evaporation. The chip was magnetized before mixing with particles.

Table 1 In the case magnetizing the Ni pattern of the chip by placing a permanent magnet in the horizontal and vertical directions of the chip, a proportion of Ni dots and Au face of particles make contact.

Condition of *particles* arranged on the chip		
Direction of magnetic flux	Horizontal	Vertical
Quantity of *particles* with:		
Gold surface on top	556 (22.2%)	56 (2.2%)
Nickel surface on top	47 (1.9%)	23 (0.9%)
Total number of nickel dots on the substrate is 2,500.		

The result of Fig. 7 (a) used the same chip as in Fig. 6. By placing a permanent magnet in the vertical direction of the Ni dot, the Ni pattern was magnetized. Marking Ni dots with a sigma marker for magnetic pattern observation, we observed this with the microscope. The black part is the magnetic pattern of the Ni dot in the perimeter portion of Fig. 7 (a). It is a magnetic flux. Because the magnetic flux was barely observed in the central part of Fig. 7 (a) and was observed in the part of the edge, we were able to confirm that all the Ni patterns are not magnetized, being magnetized only at one section of the perimeter of the entire pattern. Because of this, we understood that the number of the particles that contacted in Table 1 decreased.

Fig. 7 (b) was taken by using the same chip as in Fig. 6. By placing a permanent magnet in the horizontal direction of the Ni dot, the Ni pattern was magnetized. This chip was dried as is after applying the sigma marker on the Ni dots. The magnetic flux was formed on a portion of the Ni dot in this Fig. By magnetizing the Ni dot in a horizontal direction like this, we assumed that each Ni dot is able to magnetize.



(a) Magnetization for vertical direction (b) Magnetization for horizontal direction

Fig. 7 Microscopic images of magnetic fluidic arrangement on the Ni dot array of 400x200μm^2 in toluene solution.

It is expected that the magnetic field was produced unevenly by the direction in which the Ni pattern was magnetized from the aforementioned result, although it was thought that each Ni dot of the chip produced a magnetic field at the beginning. In Fig. 7, the equation of the mutual potential (U) [12] of a same size and parallel magnet is shown as follows:

$$U = \frac{1}{4\pi\mu_0}\frac{M\cos\theta}{r^2}[J/Wb]$$

where, M [Wb·m] is magnetic moment vector, μ_r [H/m] is permeability, r is distance between Ni dots, θ is the angle that is created to the direction of the magnet and the straight line that tied two magnets. From this equation, U is smallest and unstable at 90°. With this fact, we could understand that each Ni dot of the chip is able to be magnetized by magnetizing in the horizontal direction of the Ni dot.

4. Conclusions

We have proposed a new method to fabricate particles by MEMS and arrange this by self-assembly using magnetic force interaction on the chip. In this paper, we examined the fabrication of the particle for the enzyme immobilization in an integrated type biosensor construction and the chip, and its arrangement on the chip. The process number for the immobilization does not change even if the channel number of the sensor increases, when using this method to sensor construction. The biomaterials will be immobilized in parallel.

The arrangement on the chip of the particles was able to materialize by fabrication of the particles and the chip using the material of a strong magnetic substance and magnetizing the chip side. The arrangement by magnetic force interaction is a more active immobilization method than the interaction force such as gravity, surface tension, hydrophilic and hydrophobic interaction and electrostatic force. Also, even the confirmation of the type of sensor was possible by attaching a mark on these particles. It is conceivable that this method is extremely important as array technology for DNA and antibody chip fabrication. In the future, the self-assembly method using magnetic force interaction will be applied to construct biosensors.

Acknowledgements

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References

[1] Wilhelm T. S., Huck Joe Tien, and George M. Whitesides, "Three-Dimensional Mesoscale Self-Assembly", *J. Am. Chem. Soc.*, 120, 8267-8268 (1998).

[2] Andreas Terfort, Ned Bowden & George M. Whitesides, "Three-dimensional self-assembly of millimeter-scale components", *Nature*, 386, 162-164 (1997).

[3] Antony S. Dimitrov and Kuniaki Nagayama, "Continuous Convective Assembling of Fine Particles into Two-Dimensional Arrays on Solid Surfaces", *Langmuir*, 12, 1303-1311 (1996).

[4] Karri L. Michael, Laura C. Taylor, Sandra L. Schultz, and David R. Walt, "Randomly Ordered Addressable High-Density Optical Sensor Array", *Anal. Chem.*, 70, 1242-1248 (1998).

[5] John J. Lavigne, Steve Savoy, Marvin B. Clevenger, Jason E. Ritchie, Bridget McDoniel, Seung-Jin Yoo, Eric V. Anslyn, Jhon T. McDevitt, Jason B. Shear, and Dean Neikirk, "Solution-Based Analysis of Multiple Analyses by a Sensor Array: Toward the Development of an "Electronic Tongue"", *J. Am. Chem. Soc.*, 120, 6429-6430 (1998).

[6] David H. Gracias, Joe Tien, Tricia L. Breen, Carey Hsu, George M. Whitesides, "Forming Electrical Networks in Three Dimensions by Self-Assembly", *Science*, 289, 1170-1172 (2000).

[7] Yong-Sung Choi, Yamamura A., Murakami Y., Yokoyama K., Young-Soo Kwon and Tamiya E., "Fabrication of new DNA chip microarrays using hydrophobic interaction", Molecular Crystals and Liquid Crystals, 371, pp. 407~410 (2001).

[8] Yong-Sung Choi, Do-Kyun Kim and Young-Soo Kwon, "Highly Integrated DNA Chip Microarrays by Hydrophobic Interaction", KIEE International Transactions on Electro-Physical and Application, 11C-2, pp. 23-28 (2001).

[9] Y.S. Choi, D.K. Kim and Y.S. Kwon, "Development of a new DNA chip microarray by hydrophobic interaction", Colloid and Surfaces A: Physiochem. and Eng. Aspects, 201, pp. 261~264 (2002).

[10] A.V. Lemmo, J.T. Fisher, H.M. Geysen, D. J. Rose, "Characterization of an Inkjet Chemical Microdispenser for Combinatorial Library Synthesis", *Anal. Chem.*, 69, pp. 543-551 (1997).

[11] M. Chee, R. Yang, E. Hubbell, A. Bernon, X.C. Huang, D. Stern, J. Winkler, D.J. Lockheart, M.S. Morris, S.P.A. Fodor, "Accessing Genetic Information with High-Density DNA Arrays", *Science*, 274, pp. 610-614 (1996).

[12] H.J. Woo and W.J. Lee, *Electromagnetics*, Moon-WoonDang, p. 156 (1979).

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