主 論 文 の 要 約

論文題目　Three-dimensional Cu-based microfabrication using femtosecond laser-induced reduction of CuO nanoparticles
(CuO ナノ粒子のフェムト秒レーザ還元を用いた三次元 Cu 微細構造体の作製)

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論 文 内 容 の 要 約

In this thesis, two-dimensional (2D) and three-dimensional (3D) Cu-based microfabrication using femtosecond laser-induced reduction of CuO nanoparticles (NPs) was demonstrated. The Cu-based microfabrication technique was utilized to produce microdevices such as hot-film and calorimetric flow sensors. This thesis is composed of 6 chapters.

In Chapter 1, background and purpose of this thesis was introduced. Various types of electronic sensors and actuators consist of 3D microstructures. For example, microbridge structures are used as heaters in flow, gas, and acceleration sensors. Cavities underneath microbridge heaters serve to thermally isolate the substrates, thereby improving the thermal response and power consumption of the sensors due to lower thermal energy transfer to their substrates. These 3D microstructures are generally fabricated using 3D microelectromechanical systems (MEMS) technology. Although this technique is suitable for mass-production, it involves multiple processes, such as sputtering, lift-off, and etching method.

Alternatively, one resorts to a number of direct writing technologies, which are maskless methods that enable the creation of complex 2D and 3D structures from a variety of materials by a simple process. In particular, electron-beam melting (EBM) and selective laser sintering (SLS) are suitable fabrication techniques for 3D bulk metal structures. However, these techniques are not suitable for fabricating 3D microstructures as raw metal powders are easily oxidized when downsized.

Conversely, 2D micropatterning using laser reduction of metal oxide (CuO, Cu_2O, and NiO) nanoparticles (NPs) has been reported to successfully produce 2D Cu and Ni micropatterns. In this method, an oxide nanoparticle solution is prepared by mixing metal oxide NPs, a reducing agent, and poly(vinyl pyrrolidone). Reduction, agglomeration, and sintering of metal oxide nanoparticles are simultaneously induced by irradiation with a continuous wave or nanosecond lasers in ambient conditions; this is in contrast to the inert atmospheres (such as vacuum, argon, or nitrogen atmospheres) used in EBM and SLS.

It is expected that lower thermal diffusion in femtosecond laser helps to convey thermal energy in depth efficiently, enabling fabrication of thicker micropatterns in the process of laser-induced reduction of CuO NPs. This is advantageous for creation of high aspect 3D structures in layer-by-layer lamination processes. Another expectation is that it is easy to control the degree of reduction of Cu-based microstructures easily with local heating by controlling femtosecond laser conditions.

In Chapter 2, experimental methods are described. Fabrication process of Cu microfabrication using femtosecond laser-induced reduction of CuO NPs is as follows. First, the CuO NP solution was spin- or dispensing-coated onto the substrate. Next, Cu-based micropatterns were directly fabricated by femtosecond laser irradiation. Then, the CuO NP solution was dispensing-coated onto the first layer. The dispensing coating and laser irradiation processes were repeated until the micropatterns at final layer was formed. Finally, 3D Cu-based microstructures were obtained by removing away the nonreduced areas of the CuO NP solution with ethanol.

Two types of laser-writing systems were used in this process, one is for micropatterning with piezo electric stages and the other is for fast patterning with mechanical stages. A femtosecond fiber laser (Toptica Photonics FemtoFiber pro) operating with a pulse duration of 120 fs, a wavelength of 780 nm, and a repetition frequency of 80 MHz was utilized.

In Chapter 3, fabrication and characteristics of 2D micropatterns are demonstrated. First, the conditions of concentration ratios of CuO NP solution and spin-coating were evaluated. When the concentration of CuO NPs of 60 wt% and spin-coating rate of 7000 rpm, the thin uniform CuO NP solution film was obtained.

Then, micropatterns were produced by laser-writing system for micropatterning. Degree of reduction of the Cu-based micropatterns was evaluated under various scanning speeds using X-ray micro-diffractometer. A pulse energy was 1.2 nJ in this measurement. It was found that Cu-rich and Cu_2O-rich micropatterns were selectively fabricated at scanning speeds of 500 µm/s and 1000 µm/s, respectively. The Cu-rich and Cu_2O-rich micropatterns respectively exhibited metal- and semiconductor-like temperature coefficient of resistance (TCR).

Next, micropatterns were formed with laser-writing system for fast patterning. The effect of solvents, such as EG, 2-propanol, and glycerol on the micropatterns was investigated. The most conductive Cu-rich micropattern was achieved using CuO NP solution, containing EG and glycerol. The Cu-rich and Cu_2O-rich micropatterns were also selectively fabricated using this solution, and a microtemperature detector composed of Cu-rich electrodes and a Cu_2O-rich detector was formed. The microtemperature detector exhibited high temperature sensitivity (TCR: -1×10^{-2}/°C) with a small error (hysteresis: 6.3% F.S.).

In Chapter 4, 3D microstructures were fabricated using a combined process of dispensing coating and femtosecond laser irradiation. First, fabrication properties, such as dispensing coating and laser irradiation in the 2D micropatterns were investigated to obtain most Cu-rich micropatterns. A dispensing pressure of 20 kPa and a raster scan pitch of 350 µm were used to create 3D microstructures to obtain the thin uniform CuO NP solution films.

Characteristics of the 3D microstructures were estimated. Each layer of the Cu microstructure was electrically connected, resulting in a decrease in resistance by increasing layer number. In contrast to the decrease in resistance, the resistivity slightly increased with increasing number of layers due to the decrease in the I_{Cu}/I_{CuO} intensity ratio, which indicate the ratios of the Cu(111) peak intensity to the CuO(111). When the second and above layers were fabricated on previously formed 2D Cu micropatterns, thermal energy transfer to the underlying layer increased due to a larger thermal conductivity than that of the glass substrate. As a result, the thermal energy used for the reduction of the CuO NPs decreased with increasing number of layers. To evaluate the degree of reduction above the 4^{th} layer, the I_{Cu}/I_{CuO} intensity ratios for the 10^{th} Cu micropattern layer and for a single layer pattern on a bulk Cu specimen (thickness ≈ 1 mm) were measured. Even though this intensity ratio should be lower for the single layer pattern on the bulk Cu specimen (due to the large thermal energy transfer to the underlying bulk) actually it was found that the value with approximately as low for the 10^{th} micropattern layer was Cu-rich one. This result indicates that Cu-rich patterns can be obtained in many-layered microstructures.

Then, the 3D pyramidal structure with 10 layers was created by this method. The total height of the pyramidal structure was approximately 250 µm.

In Chapter 5, 3D Cu-based microfabrication technique was applied to microdevices. First, the microbridge heater was produced by four layer-by-layer lamination, and its characteristics were evaluated. Owing to the thermal insulating space underneath the bridge component, the microbridge heater generated heat at only the 4^{th} layer of the microbridge part by applying a voltage.

The single Cu-rich microbridge heater was used for a hot-film flow sensor with a constant temperature circuit. The Cu-rich microbridge structure composed of 1^{st}–4^{th} layer electrodes and fourth layer microbridge heater. The space underneath the microbridge heater which was expected to work as the thermal isolation from the substrate was observed. Owing to this thermally insulating space, the application of a voltage only generated heat at the fourth layer of the microbridge heater. The relationship between the flow rate and sensor output was fitted to King's law model. The Cu-rich flow sensor enabled us to measure in a wide range of 0–450 cc/min due to its dynamical measurement.

A hot-film flow sensor with Cu_2O-rich microbridge single heater was tried to fabricate following a procedure similar to that used for the fabrication of the Cu-rich microbridge single heater. However, when the single Cu_2O-rich microbridge heater was operated as a hot-film flow sensor, the sensor output was not stable because the sensor was easily influenced by the ambient temperature because of its higher TCR. In contrast, the low thermal conductivity of the Cu_2O microstructures is advantageous for heaters, enabling efficient conversion of electrical energy to thermal energy with lower driven power. Furthermore, the higher temperature sensitivity of the Cu_2O microstructures was effective for temperature detection. Therefore, the calorimetric flow sensor composed of a Cu_2O-rich microbridge heater and temperature detectors was demonstrated with a circuit for measurement of temperature difference. Although the measurement range was smaller than that used for the Cu-rich flow sensor, the Cu_2O-rich flow sensor could detect bi-directional flows and its output error was small.

In Chapter 6, conclusions and future works of this thesis were mentioned. To fabricate 3D microstructures such as microbridge heater by MEMS technology requires multiple processes (e.g. sputtering, lift-off, and etching). Moreover, some of these processes must be conducted in a vacuum chamber. Therefore, the direct writing process of 2D and 3D metal and semiconductor microstructures in ambient conditions not relying on the conventional complicated methods demonstrated in this study is useful for the fabrication of prototype devices.