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Fabrication of 3-D microstructures with a catalytic surface composed of an ion-implanted layer

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Abstract

A previously developed catalyst fabrication technique that uses ion implantation and surface etching (IISE technique) was applied to a microchemical system called a micrototal analysis system or (μ-TAS). μ-TAS is constructed from micrometer-sized chemical devices, i.e. inlets, watercourses, reactors, analyser and outlet, and has a total area of about 1 cm^2 % rev. The IISE technique uses the advantages of ion implantation, which are the ability to select and control the ion species and the specific area for fabrication, to support many types of catalysts on each device as the need arises. In this study, a catalyst was supported on two types of 3-D microstructures to simulate the reactor surfaces of the main components of μ-TAS: grooves to simulate watercourses and protrusions to simulate a roughened surface for increasing the reaction area. The IISE was applied to these structures by first implanting gold ions with 3.1 MeV into the grooves and protrusions on a silicon substrate, and then etching with potassium hydroxide solution. Results showed that gold nanoparticles could be supported on the grooves and protrusions. However, the shape of the grooves and protrusions was affected by the ion implantation process itself, although the distribution of the nanoparticles was not. Optimization of the ion implantation needs further study.

Keywords: Ion implantation; Chemical etching; Nanostructure; Gold; Silicon; Scanning electron microscopy (SEM)

1. Introduction

A nanoparticle catalyst fabrication technique, called the IISE technique, that uses ion implantation and a surface etching method was previously developed by Nakano et al. [1]. Advantages of this technique due to ion implantation include purity of the implanted ions, control of the quantity of ions by adjusting the ion dose, control of the depth distribution of the ions by adjusting the ion energy, ability to select a specific area for fabrication and variety of ion species. In the IISE technique, nanoparticles are fabricated during the etching process, which is easy to control, and the seeds of the nanoparticles are preserved inside the substrate and can be developed into nanoparticles by etching when needed. Though the IISE allows to develop nanoparticles just before use, thus using the flesh catalyst and increasing the life of the catalyst.

Micrototal analysis systems (μ-TAS) [2] and microchemical reactor systems such as ‘Lab on a chip’ [3,4] are being actively researched. Such microchemical systems have been combined with microelectromechanical system (MEMS) technology to make reactors, analytical instruments, watercourses and other micron-sized instruments whose total area is about 1 cm^2. Expected uses of such miniature chemical systems are on-site analysis during environmental field studies and bedside monitoring of the blood-sugar level of a patient. Although many types of sensors and microfluidic control technologies have been developed, chemical reaction systems are needed for “total analysis” systems. In μ-TAS, the catalyst is important as a reagent and for reaction of a testing sample.

In this study, the IISE technique was applied to μ-TAS to fabricate 3-D microstructures that have a catalytic surface. Nanoparticles were fabricated on models of two basic

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components of μ-TAS; namely, grooves that simulated a watercourse and protrusions that simulated a roughened surface for increasing the reaction area.

2. Experimental procedure

Fig. 1 schematically shows the IISE technique. For both types of structures (grooves and protrusions), (100) silicon wafers were used as the substrate, potassium hydroxide (KOH) was used for the etching after the patterning of the grooves and protrusions, and the nanoparticles were gold because it is a well-known redox catalyst [5,6].

The grooves were fabricated as follows. First, 1×10^{21} m^{-2} (1×10^{17} cm^{-2}) gold ions with 3.1 MeV energy were implanted into the entire surface of the silicon substrate at less than 130 K (Fig. 1A). Then, because the gold-implanted layer protected the silicon from KOH etching [7,8], a focused ion beam (FIB) was used to open a "window" into the silicon substrate for exposure to anisotropic etching [9,10] (Fig. 1B). Then, long, narrow grooves, each 10 μm wide and 250 μm long, were etched along the ⟨110⟩ direction of the substrate (Fig. 1C) by using KOH solution. The concentration of the solution was 7.5 mol/l, temperature was 345 K, and etch time was 10 min. Fig. 2(a) shows the "V" groove resulting from the etching by KOH. The depth of each groove was about 7 μm and the width was about 10 μm. Then, gold ions were implanted again into each V-groove as seeds for nanoparticles. The conditions of gold implantation were an energy of 3.1 MeV, dose of 1×10^{21} m^{-2} and substrate temperature of lower than 130 K. Finally, the grooves were etched by KOH (concentration of 7.5 mol/l, temperature of 345 K and etch time of 10 min) to fabricate the nanoparticles on the surface. The IISE conditions (implantation and etching) were the same of a previous study [1], yielded more than 800 particles/μm^2 on a flat surface. This second etching was to fabricate the gold nanoparticles on the surface, not to construct the shape of the microstructure. Both etchings were done using the conditions to construct the specific structure shape.

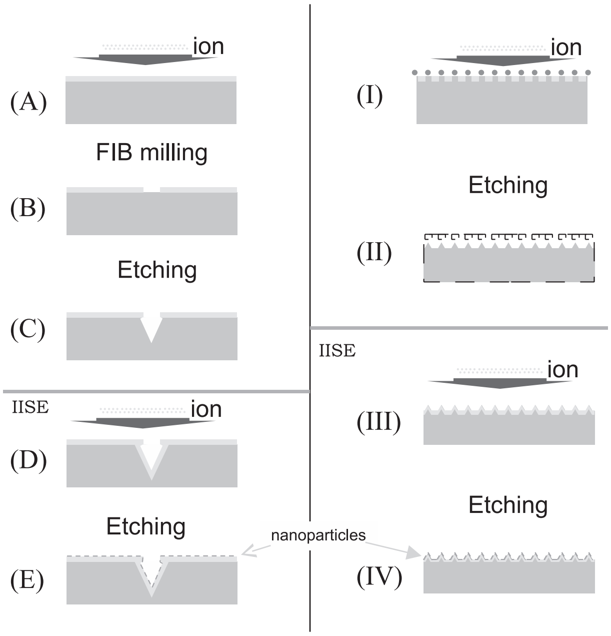

Fig. 1. Cross-sectional schematic of fabrication of gold nanoparticles on a silicon substrate with V-grooves (A–E) and protrusions (I–IV). (A) Gold ions implanted into a silicon substrate, (B) etching window opened by FIB, (C) V-groove structured on the substrate by anisotropic etching with KOH, (D) gold ions implanted as seeds for nanoparticles, (E) etching to fabricate nanoparticles on the structure surface. (I) Gold ions implanted into a silicon substrate with a mesh mask, (II) protrusions structured on the substrate by anisotropic etching with KOH, (III) gold ions implanted as seeds for nanoparticles, (IV) etching to fabricate nanoparticles on the structure surface.

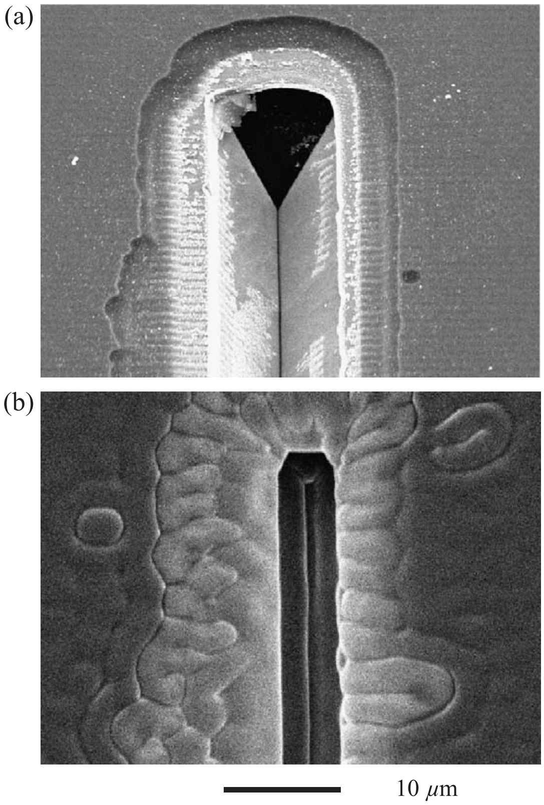

Fig. 2. 45° tilted SEM image of a V-groove. (a) Preliminary structure, (b) after gold ion implantation for IISE (3.1 MeV, 1×10^{21} ions/m^2). Structure shape was affected by the implantation.

The protrusions were fabricated as follows. First, a shadow mask was placed on a silicon substrate and then ions (1×10^{20} m^{-2}) were implanted into the substrate (Fig. 1I). The mask was a stainless steel mesh with a 63.5-μm period (400 meshes/in.). Then, the silicon surface was anisotropically etched by KOH solution (Fig. 1II). Due to the mask, different etch rates were achieved, thus bringing the silicon into relief as protrusions. The etching time was 40 min (30 min longer than that for the V-grooves). Fig.