

Formation of micro/nano structures out of soap bubbles

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Abstract

We proposed to synthesize, etch and construct micro/nano structures through manipulating the large-scale bubbles composed of specific chemical compounds. The core of the method lies in the chemical reaction occurred at the interfaces between two or more soap bubbles. A unique virtue of the bubble is that it can have a rather large diameter however an extremely small membrane thickness, whose smallest size could reach nano scale. Therefore, the chemical reaction and synthesis occurred in the common interface of such contacting bubbles would lead to products with very small size. Several typical micro structures were fabricated to demonstrate the feasibility of the new method. Being flexible, easily controllable and environment friendly, the present concept may open a straightforward low-cost way for making micro/nano structures.

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1. Introduction

The micro/nano structures are often required as building blocks to be assembled as devices or sensors used in a variety of scientific areas such as electronics, photonics and bioengineering [1–5]. For example, individual nano wires with semi-conducting properties have been shown as possible units to work as field-effect transistors [6–8], photo detectors and bio/chemical sensors [4]. Researchers also reported some sophisticated logic devices formed from the nano wires or nano tubes [9,10]. Among these practices, high cost encountered in the conventional lithography-based fabrication is often a big barrier to prevent the micro or nano structures from being easily available via a much economic way [5]. The attempts ever made before to fabricate the micro or nano size structures can generally be classified as two categories, such as by imposing external physical fields or assembly through making use of the internal properties of the materials. In this side, electric [11] and magnetic [12] fields have been adopted to manipulate and fabricate nano wires in liquid. Meanwhile, fluidics-

based methods for aligning nano wires were also reported for assembly of nano devices [13,14]. However, among many existing technical routes, the ready-made micro-channels are often a prerequisite and have to rely heavily on the expensive and complex processes of lithography or other fabrication methods. Up to now, few techniques were available to fabricate micro/nano structures through a much simple approach. Here, we show a flexible and straightforward cheap way to synthesize and etch the micro/nano structures by introducing for the first time the easily available bubble interfaces as the fabrication sites.

2. Fabrication principle and demonstration experiment

The core of the new method is based on the chemical reaction occurring at the interfaces of the two or more contacting soap bubbles. The soap bubbles are familiar to every one of us because of their daily roles in dish washing and room cleaning. As an important scientific topic, soap bubble keeps arousing attention among scientists over multidisciplinary fields. In fact, it has been a long history for investigating the formation mechanisms of the soap bubble and their corresponding applications. When

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dissolving the surfactant in a solvent, the gas, solvent and surfactant would often form a three-dimensional pattern, which is just the so-called soap bubble and structured by a solvent membrane covered by two molecular mono-layers of the surfactant [15,16]. Handling of the bubble is rather easy since its overall configuration is in macro scale, spanning from millimeters to even several meters in diameter. A small agglomerate of foam can contain a large number of soap bubbles. Trace amount of water with surfactant would be enough to blow a giant bubble. In some acrobatics performances, magician even blows a tremendously large soap bubble to contain a person inside, which makes the demonstration rather fascinating. A unique virtue of the bubble lies in that its components such as membrane thickness can be extremely small, for example, to nanometer scale in many situations [15,16]. It is this distinctive feature of the bubbles that enables a brand new and highly flexible method for fabricating the micro/nano structures.

Presented in Fig. 1 are several typical optical microscope images for the micro wires fabricated using the present bubble method. As indicated by the inserted bar, Fig. 1(a) is for a micro wire with about 500 μm in width and nearly 10 mm in length, which has realized an extremely large length-to-diameter ratio. Here, the compound of the fabricated micro wire is ferric oxide. As shown by Fig. 1(b), the minimal width of another fabricated micro wire falls in several micrometers. In order to better display the sharp end of the micro wires, an additional image as shown in Fig. 1(c) was provided to reflect the situation where the wire was cut and detached from the wafer. It was found that the micro wire could have an average size of about 30 μm in width, 20 μm in height and nearly 1000 μm in length. All these pictures demonstrate that the micro wires have been successfully fabricated from the reactions of the soap bubbles via a rather convenient and economic way. In addition, a very different aspect ratio for the wire can easily be obtained by controlling the bubble contacting area and configurations, which however has long been a rather difficult task by some traditional fabrication method [1–4].

A generalized procedure for the bubble fabrication method can be illustrated by Fig. 2. Specifically, the following steps have been taken for realizing the micro wires as given in Fig. 1. Before the synthesis, we prepared two kinds of functional soap bubble solution (FSBS) which were made of solutions of ferric chloride and sodium carbonate, respectively. Each FSBS is mixed by two parts such as surfactant solution and reactant solution with a volume ratio 2:1. Here, the surfactant is made in advance through mixing sodium lauryl sulphate with glycerine via a volume ratio of 4:1. After that, its solution is diluted as a 10% mixture by adding deionized water. The concentration of the reactant solution is carefully prepared as 0.1 mol/l. Later, we adopted two syringe injectors to carefully take each FSBS to blow two soap bubbles, respectively. The two bubbles were subsequently transferred to the experimental glass wafer and driven to contact to each other. And a small liquid ring immediately close to the wafer surface will be formed in the interface of the two bubbles. As a result, the two reagents of ferric chloride and sodium carbonate drained to this site began to gradually react. After a few time, a ferric oxide micro wire was synthesized with the advancement of the micro chemical reaction. In this way, a micro wire for ferric oxide was left on the wafer after the unwanted surfactant and solvent was cleaned away. The composition of the product can be characterized using Auger spectroscopy or other measurement [17]. It should be pointed out that, justification of the dosage of FSBSs and the air volume coming into the soap bubbles will lead to structures with different scales. To measure the size of the fabricated wires, a microscope Leica DM IRB (Germany) was used in this study to get the optical images. To quantify the size of the fabricated micro wires, a standard micro ruler with its smallest scale of 10 μm has been used. Clearly, the experimental results as presented in Fig. 1 successfully demonstrate the feasibility of using bubble interface as the chemical reaction site for micro fabrication.

In the above cases, the obtained basic element is a ferric oxide micro wire. In fact, the present method is rather versatile in fabricating objects with various materials.

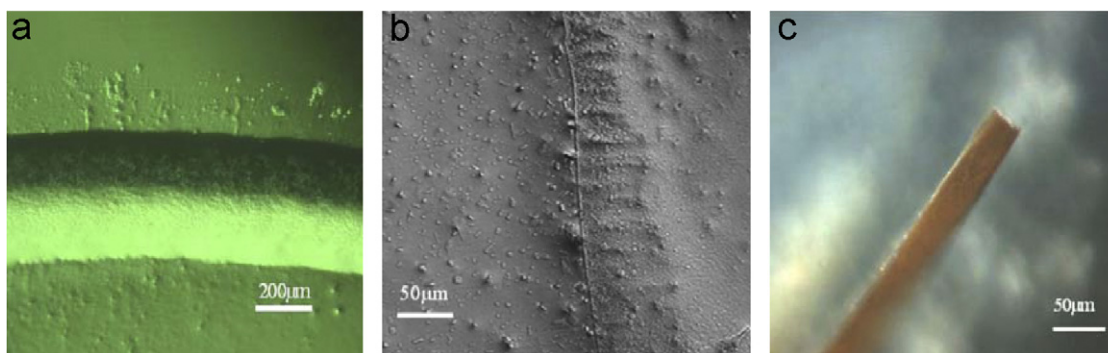
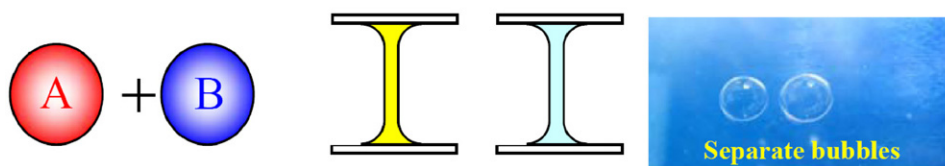
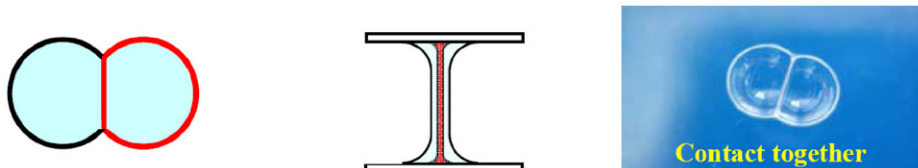


Fig. 1. Optical microscope images for the micro wires fabricated by the present method. (a) Micro wire with 500 μm in width and nearly 10 mm in length. (b) Micro wire whose minimal width is several micrometers. (c) Micro wire cut and detached from the wafer, which has an average size of 30 μm in width, 20 μm in height and 1000 μm in length with a rectangular section. In these figures, the component of micro wire is ferric oxide.

i Blow two soap bubbles with different FSBSs A and B



ii Drive two soap bubbles to close up and joint



iii Synthesize new product and built up microwire

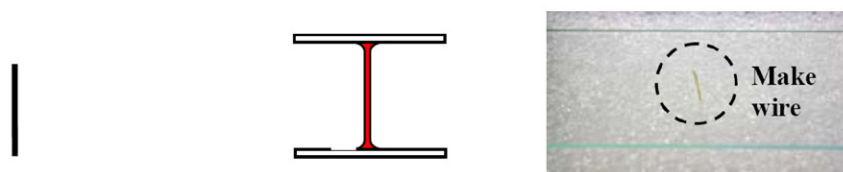


Fig. 2. Procedures for synthesis and assembly of a micro wire in the confined plateau borders at the junction of two bubbles A and B: (i) blow two bubbles with different FSBSs A and B; (ii) drive two bubbles to contact; (iii) synthesize a wire through chemical reaction confined in the junction of bubbles A and B. The left picture is for illustrating the principle of bubble-based micro-fabrication; the right one just gives the real photos actually taken, which is corresponding to the fabricated output following the left procedure.

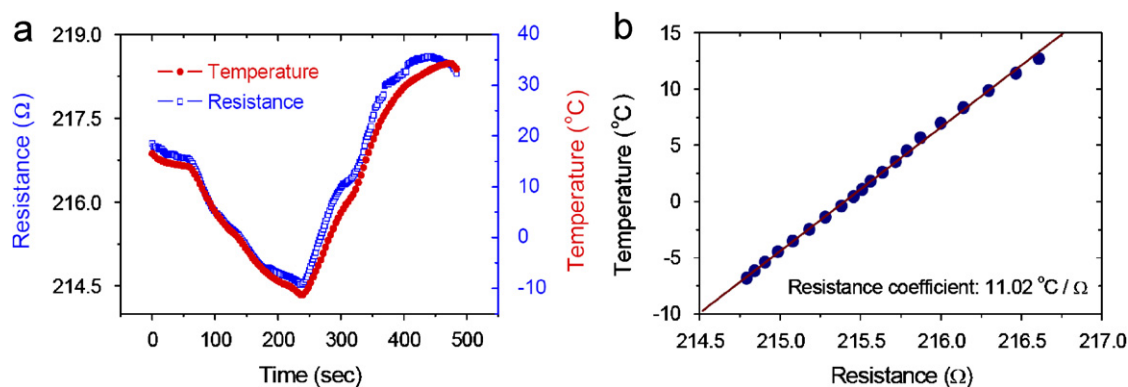


Fig. 3. Micro copper wire used as a tiny temperature sensor. (a) Transient resistance and temperature of the sensor when subjected to temperature change within a range of -15 to 40 $^{\circ}\text{C}$. (b) Temperature-dependent resistance of the fabricated micro wire within temperature range of -6 to 12 $^{\circ}\text{C}$.

As an illustration, more results were given as follows for the fabrication of a wire-like temperature-sensitive resistance, which could find very important application in the bioengineering or other fields where temperature measurement in small space was strongly requested. For such fabrication, two solutions as copper chloride and sodium carbonate were prepared in advance. The soap bubbles thus formed, respectively, contained different kinds of such solutes. After they were blown on the experimental wafer, the synthesis was initiated at the bubble interface. The product, which is copper hydroxide, was then assembled as a micro wire due to chemical reaction. After cleaning excess surfactant and solution by continuously blowing hydrogen to the product, we could deoxidize the wire of the

metal oxide to a pure metal wire, although it may be still subject to oxidizing when exposed to the atmospheric environment. In this way, a copper wire resistance with an average size of about 40 μm in width, 30 μm in height and nearly 1200 μm in length was successfully fabricated. Previously, obtaining such extremely thin resistance wires generally had to rely on expensive equipment or complex procedures. This difficulty was successfully resolved in a large extent by the present bubble-based fabrication method. To test the thermal performance of the temperature sensitive resistance thus made, additional measurements were also made. The corresponding resistance response to the temperature was obtained and presented in Fig. 3. This nearly linear correlation between resistance

and temperature is beneficial for the temperature measurement of a thermal sensor. If needed, such tiny temperature sensor can be directly fabricated in a specific substrate as requested. This would find valuable applications in many situations such as in a biochemical reactor or biological chip, etc.

Further, the present method has also been extended for more complex manufacturing such as realizing a thermocouple with size in micrometers. For this purpose, three solutions such as that of copper chloride, ferric chloride and sodium carbonate were prepared in advance. Then, three soap bubbles were blown on the wafer surface and patterned as a figure of “Y”. The synthesis began to occur within the three branches of the lamellas. Subsequently, three compounds were assembled as three micro wires due to chemical reaction. Their terminals were connected together by one common wire. By blowing hydrogen or adding other reducer, the wires of metal oxide could be deoxidized to pure metal wires. In this way, a set of thermocouples in micro scale were fabricated. These efforts indicate that, using a couple of soap bubbles with different chemical compounds can produce various complex micro structures, not just a single wire.

3. Future outlook

Micro and nano fabrication within the confined space of soap bubbles opens a new way for material synthesis and etching. Such fabrication can be conducted by a person without particular training, which may allow its wide adoption in the near future. Besides, the fabrication is clean and produces little pollution to the environment. In contrast, many existing methods such as photolithography have to rely heavily on complex apparatus. And a mask with micro/nano sized structures embedded inside is often a pre-requisite for carrying out photolithography, which however needs to be prepared in advance via a much expensive way. The present efforts demonstrated that macro operations can handle and manufacture micro and nano structures in a rather straightforward way. The method can easily be extended to more practical situations by carefully administrating the bubble parameters such as reactant compound, number, size, shape, and spatial and temporal configurations, etc. For example, it is possible to manufacture semiconductor nano wires or particles by

adjusting components of the reactants. Besides, multiple bubbles can be driven together by certain automatically controlled mechanical or fluidics device to react simultaneously or manipulated to contact with each other one by one. After that, various three-dimensional micro/nano structures can be formed as desired. Except for the trials as performed in this study where soap bubble stands on a wafer, bubbles freely flowing in the air can also be driven to collide to each other to batch fabricate micro or nano structures. Finally, it should be pointed out that, the present work is still at its first stage as proof-of-concept. Tremendous efforts are needed to better understand and implement the method. This study guarantees further research in this area.

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