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BUBBLE BASED MICRO/NANO FABRICATION METHOD

Xiao-Dan Bai and Jing Liu*

P. O. Box 2711, Technical Institute of Physics and Chemistry,
Chinese Academy of Sciences, Beijing 100080, P. R. China
(*E-mail address: jliu@cl.cryo.ac.cn; Tel: +86-10-82543765; Fax: +86-10-82543767)

ABSTRACT

Micro/nano structures, especially those in one dimensional, such as nano wires, are commonly used building blocks for the bottom-up assembly of electronic, photonic or mechanical devices. However, their fabrications are generally limited to the expensive equipments and methods capable of only working in an extremely small space. A big challenge facing the current scientific society is to overcome this barrier and build up a bridge between the macroscopic manipulation/observation and the fabrication in small world. Here, we proposed a new conceptual fabrication method, which can easily be implemented to synthesize, etch and construct micro or nano structures through manipulating the large scale bubbles composed of specific chemical compounds. The core of the method lies in the chemical reaction occurring at the interfaces between two or more soap bubbles. A surprisingly unique virtue of the bubble is that it can have a rather large diameter however an extremely small membrane thickness, whose smallest size even reaches nano scale. Therefore, the chemical reaction and synthesis occurred in the common boundary of such contacting bubbles would lead to products with very small size. Most important of all, all these were achieved via a much easy and straightforward way. To better understand the physical picture of the new method, the principle and mechanism for the bubble based fabrication process were interpreted. Several fundamental equations for characterizing the bubbles were proposed and preliminarily discussed. As the first trial to demonstrate the new concept, several typical micro structures were successfully fabricated in our lab. Particularly, a micro wire which can be used as tiny temperature sensor was made and tested. Being flexible, easily controllable and observable, environmentally friend and extremely low in cost, the present method is expected to be a significant technical route for making micro/nano structures in the near future. It also indicated for the first time that blowing soap bubbles means not just funny but also opens a new world for micro/nano fabrication.

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 nanostructures from being easily available via an 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 necessary prerequisite and have to rely heavily on the expensive and complex processes of lithography or other fabrication methods. Up to now, only rather limited techniques were ever developed to fabricate micro/nano structures through a much simple approach [5].

Aiming to establish a highly flexible and straight forward cheap way to fabricate the micro/nano objects, we proposed here to synthesis and etch the structures by introducing for the first time the easily available bubble interfaces as the working site for the micro/nano chemical reactions. The basic principle and typical applications for the new method will be illustrated as follows.

PRINCIPLE OF BUBBLE BASED FABRICATION

The core of the present method starts from the chemical reaction occurring at the interfaces of the two or more contacting soap bubbles. A surprisingly unique property of a bubble lies in that it can have a rather large diameter such as one meter long however an extremely small membrane thickness. The smallest size of a bubble membrane thickness has been found to be even in several nano meters [15, 16]. Therefore, chemical reaction and synthesis in the boundary site of the bubbles would easily lead to structures much smaller than that. This provides a natural way to bridge the macroscopic manipulation/observation and the fabrication in small space.

Without any doubt, people are familiar with the soap bubbles because of their daily roles in dish washing and room cleaning. We even always ignore the existences of the bubbles. However, as an important object for scientific investigation, soap bubble keeps arousing attentions among scientists over multidisciplinary fields [15-22]. In fact, the formation nature of the soap bubble and its corresponding applications had ever been studied for centuries. When dissolving the surfactant in a solvent, the gas, solvent and surfactant would often form a 3-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 very large, say even in several meters. Therefore, in some acrobatics performances, magician even blows a tremendously large soap bubble to embrace a person inside, which makes the demonstration rather fascinating. Meanwhile, its components such as membrane thickness can be extremely small, for example, to nano meter 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.

Many recent researches on the bubbles are related to foam drainage with an emphasis on the effects of interfacial rheology [17, 18]. Except for the free-floating bubbles, the membranes of the bubble have to be supported by certain frames, bulk surfaces or other films. When bubbles meet with each other or contact to some other external solid surfaces, it is spontaneous to define the thin liquid films as lamellae and the tubes of liquid at the junctions of the lamellae as plateau border, which serves to separate and support the films [19].

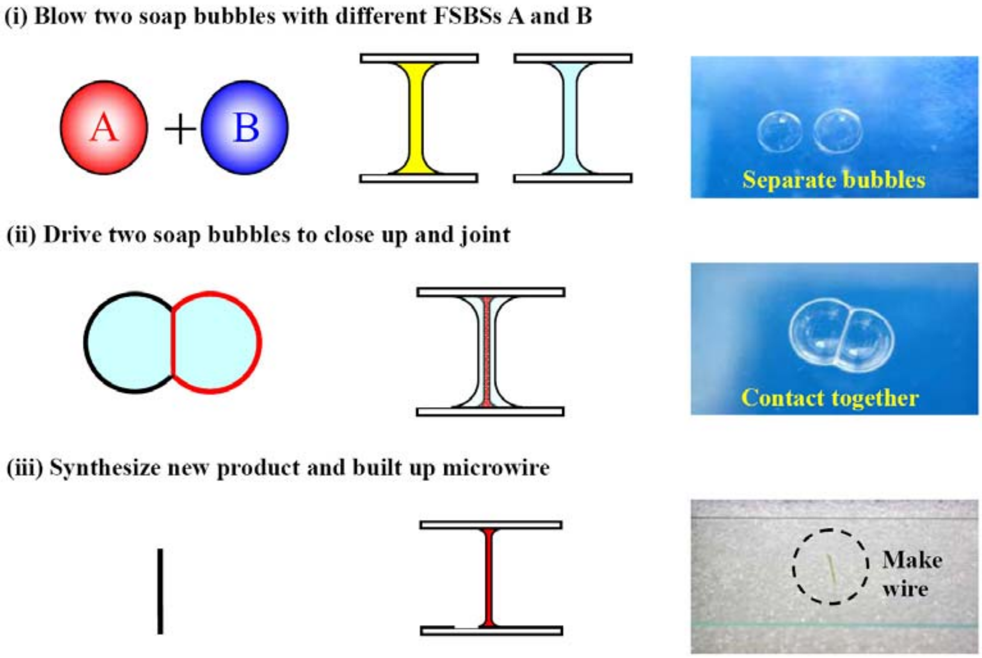


Fig. 1 Procedures for synthesis and assembly of a micro wire in the confined plateau borders at the junction of two bubbles A and B: (i) Blow two bubbles with different FSBSs A and B; (ii) Drive two bubbles to contact; (iii) Synthesize a wire through chemical reaction confined in the junction of bubbles A and B. The left picture is for illustrating the principle of bubble based micro-fabrication; the right one gives the real photos actually taken, which is corresponding to the fabricated output following the left procedure.

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. On the contrary, a single soap bubble and its membrane thickness can also be very small. For example, the size of the plateau borders generally has a magnitude of several micro meters, and the lamellae can be especially as small as the size realized by the current advanced nanotechnology [16]. In addition, the lamellae could still become much thinner when subject to foam drainage, which as a result will allow the bubble to have a nano scale membrane. As reported before [15, 16], an ultimate thickness of the lamellae with sodium stearate in solution as an instance is about 5-15 nano meters. Such liquid membrane can no longer be able to support the pressure of the gas inside the bubble space beyond the limit. Clearly, the bubble could have a large sized sphere and is thus easy for manipulation and observation. Meanwhile, it also contains micro or nano scale membrane elements, which would serve as the perfect working site for the micro/nano chemical reactions. All these unique characters of the bubbles favour us to fabricate the micro or nano structures via a much easy and straightforward way.

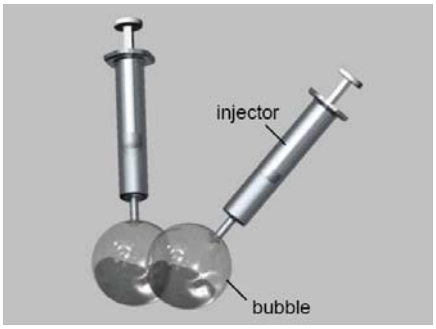
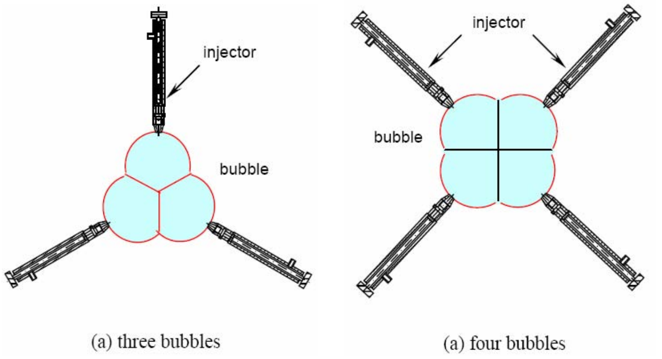


Fig. 2 Sketch for using two injectors to blow bubbles and drive them to contact to each other for the micro fabrication.

Basically, the present method for making the micro or nano structure is realized through contacting two or more soap bubbles together which would subsequently lead to chemical reactions in the bubble interfaces (Fig.1). Before the fabrication, one needs to prepare two kinds of soluble reagents A and B, which could react and synthesize to another compound C that should be insoluble or behave as an etchant operating on the substrate. This reaction process can be expressed as $A+B\rightarrow C$. Through mixing with soluble surfactant and water, two kinds of functional soap bubble solution (abbreviated as FSBS) were prepared in advance. Afterwards, each FSBS with an appropriate volume was taken with care by an injector to blow a soap bubble, respectively (Fig. 2). Then the two bubbles were transferred to the experimental wafer. The two different reagents were contained in their solution confined by the lamellae of the isolated soap bubbles, respectively. With the drainage of the foam, the solvent film would gradually become thin in response to the gravity, the local pressure gradient and the surface tension. The reagent was concentrated in the liquid rings close to the wafer, although there is still a small volume in the lamellae. Finally, a synthesis happened in the interface between the two soap bubbles and the wafer by driving these two soap bubbles together to a junction.

When the two soap bubbles contacted to each other, their interfacial zone and the substrate would form a common liquid channel called plateau border (Fig. 1). The chemical reaction or the etching process will thus most probably occur in these areas. Then the micro or nano structure can be formed with the advancement of the chemical reaction in the plateau border, which appears as a one-dimensional confined space and has a size scale of microns or nano meters. Afterwards, a micro or even nano wire with component C was left on the wafer or a micro channel has been dug out there, which was etched through the reaction between the active reagent C and the wafer itself after the unwanted surfactant and solvent was cleaned away.

Overall, as explained in Fig. 1, the whole procedures for synthesis and assembly of a micro/nano wire in the confined plateau borders at the junction of two bubbles A and B can generally be classified as four steps: (i) Preparation of the functional soap bubble solutions; (ii) Blow two bubbles with different FSBSs A and B; (iii) Drive two bubbles to contact to each other; (iv) Synthesize new product and build a wire through chemical reaction confined in the micro/nano scale bubble junctions. Clearly, additional combinations of multiple bubbles can still help realize different micro/nano structures. For such purpose, one needs to blow multiple bubbles with different sizes and drive them to contact via certain specific spatial configurations. As an example, Fig. 3 presented two of such technical approaches which would find practical applications in integrating more complex micro/nano devices and systems.



(a) three bubbles (a) four bubbles

Fig. 3 Technical approaches for making complex structures through flexibly manipulating multiple bubbles to join together.

Further, to illustrate the separation process of the two reagents due to isolated soap bubbles, we provided in Fig. 4 to show the reaction of two chemicals in red and green colour. It explains in details the fundamental mechanisms for latter synthesis and assembly in confined micro or nano scale bubble membrane, which would directly form the micro or nano wires through reactions or acting as an etchant to dig out micro channels on the wafer.

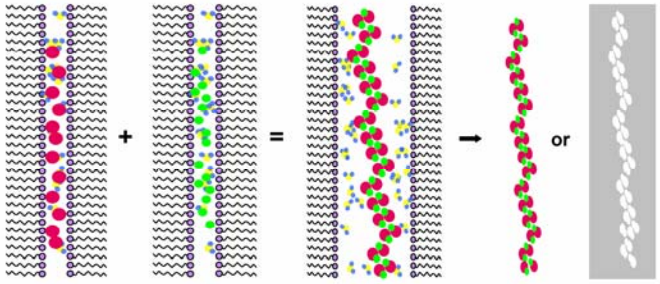


Fig. 4 Separation and reaction of two reagents in red and green colors due to contact of isolated bubbles. Products from the reactions directly formed micro wires, which can subsequently act as an etchant to dig out micro channels on the wafer. The mechanism was illustrated by the schematic combinations between the red balls and the green balls representing two different reagents in the figures, respectively.

SIZE CONTROL OF BUBBLE PLATEAU BORDERS

It is worth noting that, the size of the lamellae and plateau border plays a critical role in the synthesis and final fabrication output. Therefore adjusting this size is of significant practical value. Various thicknesses of soap bubble lamellae and extent of plateau border can be obtained through controlling the FSBS dosage and the volume of a soap bubble. When the bubble is in a freely floating state and the lamellae is assumed as uniform by ignoring the effect of gravity, the thickness of lamellae was mainly dominated by the radius of the soap bubble and the bulk solution due to mass conservation. Then one can write out a simple equation to describe the thickness of the lamellae as

$$V = 4\pi R^2 \cdot h \tag{1}$$

where, V, R, and h are respectively the volume of FSBS, radius of soap bubble and thickness of the lamellae. The radius of the bubbles depends on the pressure difference between the interior and the external atmosphere of the soap bubble as well as the surface tension of the liquid membrane. The equation relating the pressure difference across these lamellae of the two similar bubbles can be described by the classical Young-Laplace equation [16, 21], i.e.

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{2}$$

here, R_1 and R_2 are respectively the inner and outer radius of the bubble, γ the surface tension of the liquid membrane.

Considering that the thickness of the lamellae is so small that the curvatures of their outer and inner surfaces could be approximately regarded as the same, one gets the following equation:

$$\Delta P = \frac{2\gamma}{R} \tag{3}$$

which leads to

$$R = \frac{2\gamma}{\Delta P} \tag{4}$$

Sketch for the cross-section of the formed bubbles, the plateau border and its connection with lamellae and solid surface can be illustrated in Fig. 5(a). The force balance at the junction between the plateau border and the lamellae requires a finite contact angle, which is typically small, ranging from somewhat less than 1 degree to a few degrees [20, 21]. Here, one basic hypothesis can be reasonably made as that the characteristic width l of the plateau border is much larger than the characteristic thickness h of the lamellae. Then we can simplify the mathematical expression of the cross section of the plateau border based on the assumption that the interface between the liquid and the gas has a constant curvature r^{-1}, which is tangent with the lamellae for a very small contact angle at one side, and connected to the solid base with certain contact angle θ depending on the surface tension γ at the other side. Then the volume dosage for the used FSBS can be expressed as

$$V = 2\pi R \cdot r^2\left[2\cos\theta - \cos\theta\sin\theta - \pi/2 + \theta\right] + 2\pi R^2 \cdot h \tag{5}$$

The width of the plateau border comes from the geometrical relationship, i.e.

$$l = r\left(1 - \sin\theta\right) \tag{6}$$

then one gets

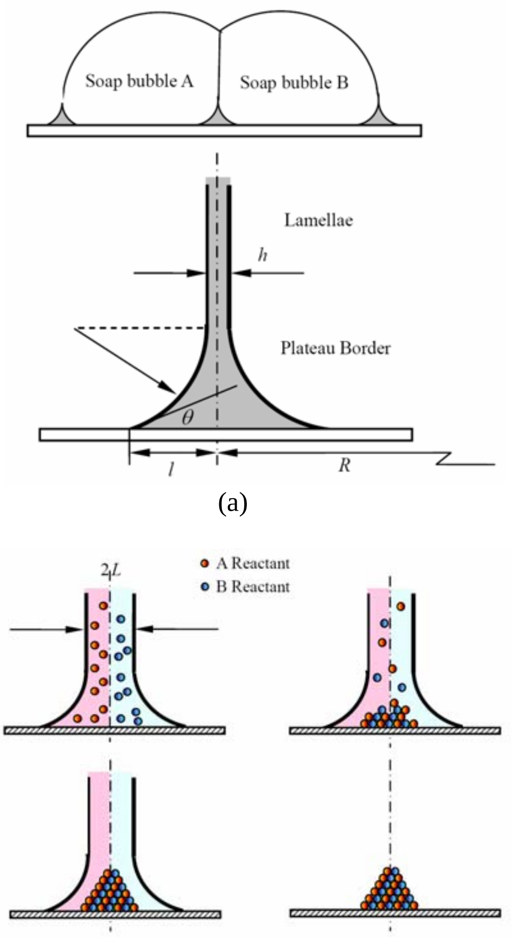
$$l = \left(1 - \sin\theta\right) \cdot \left(V - 2\pi R^2 \cdot h\right)^{\frac{1}{2}} \cdot \left[2\pi R\left(2\cos\theta - \cos\theta\sin\theta - \pi/2 + \theta\right)\right]^{-\frac{1}{2}} \tag{7}$$

where the contact angle can be obtained from the following relation

$$\cos\theta = \frac{\gamma_{s-g} - \gamma_{l-s}}{\gamma_{l-g}} \tag{8}$$

here, the subscripts, s, l and g denoted different mediums at the contact surface as solid, liquid and gas, respectively. Calculations on the above equations predict that the smallest membrane thickness can fall in the micro or even nano scale. Some of such predictions on the width of the plateau borders between the two soap bubbles can be found in the Appendix 1. And a diffusion-reaction model for interpreting the mechanisms of the synthesis reactions occurring in the plateau borders has also been given in Appendix 2. Readers are referred there fore more details.

With the drainage of the foam, the size of the lamellae can be reduced accordingly. When the lamellae become stable or appears as a metastable black membrane, the size scale of the confined space may eventually be in depth of several molecules [15, 16]. Then the reactions of these particles are compelled to arrange in a given order and the product of the synthesis is totally different as that occurs in the free space. Therefore what one got will only be a structure in micro or nano scale.



(a)

(b)

Fig. 5 Quantification of the bubble structure and chemical reactions inside. (a) Sketch for the cross-section of the formed bubbles, the plateau border and its connection with lamellae and solid surface; (b) Illustrations for the sequential diffusion-reaction process.

Still, one can find that the fabricated micro / nano structure could be smaller since such synthesis and etching did not in fact react through out the entire domain of the lamellae and the plateau border. It should be noted that most micro flows and drainage flow through these canals and films in the soap bubbles are in laminar state, because Reynolds number here is generally smaller than one in all physical situations [17, 22]. Therefore the reactions indeed occurred at the interface between the laminar flows within the lamellae and the plateau border. It is well known that quite a few methods are already capable of controlling the delivery of reagents in a laminar flow at low Reynolds number and have been fully exploited before [7, 23]. Adoption of such strategies in the near future may make the present fabrication rather convenient in operation. To better understand the chemical reaction process in the micro bubble membrane, we provided a schematic picture in Fig. 5(b) for illustrating the diffusion development in the laminar flow of the bubble interface. A detailed physical process can be predicted via the theoretical models as given in the Appendix 2.

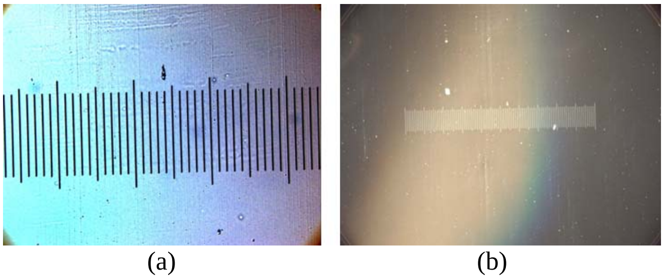
Further, it should be pointed out that, although the information displayed by Fig. 5 and Fig. 1 appears a little different, what has been presented in both pictures is consistent. They represent two cross sections from different view directions, respectively. For example, Fig. 1 is for the bottom view while Fig. 5 is depicted from the front site. Both pictures reflected the formation of a solution sheet at the common interface of the two bubbles during the synthesis process. Fig. 1 gives a more generalized illustration on the fabrication principle while Fig.5 is provided here particularly to reveal a much detailed physical picture at the base. In reality, contact of two bubbles with different chemical compounds will often give rise to a sheet at their common interface during the early developmental stage. However, due to gravity and the drainage occurred at the base between the two bubbles and the substrates, this sheet will have an irregular cross section with a slim layer at its upper part and a much thicker layer at the bottom. Besides, it can only hold for a short period of time. After a few time's reaction, the upper part of the sheet will disappear with the collapse of the bubbles. Only the dense part drained to the base channel will be left, which later gives rise to the final curve. Unless certain innovative way can be proposed in the future to maintain the whole sheet structure, fabrication of the micro/nano sheet from the present method is still not possible at the present stage. Therefore, although one does can see from Fig. 1 that a sheet has been formed at the interface of the two bubbles, only the most densely formed layer at the base will be finally generated. This is just the case reflected by the picture actually taken at the right hand side of the Fig. 1. From another view direction, Fig. 5 is provided to show the detail of the reaction occurred at the interface of the two bubbles staying on the wafer surface. For such purpose, one can blow and confine the two bubbles into a rectangular box specifically designed. Then the common interface of the two bubbles can be manipulated to form a stable enough planar surface. An intact sheet structure can thus possibly be made via this way. But if contacting between two bubbles can not guarantee the stable formation of an intact layer, more specific administration should be adopted. For example, one can blow and deposit a bubble to the surface of a solid substrate. Then after certain duration time's reaction, a sheet of the product will be left in the substrate. Further, one can even deposit the bubble to the surface of certain solution with specific components, then a thin intact layer can also possibly be formed there. But a detailed investigation on making such layer is beyond the scope of the present paper. Here, attentions will be mainly paid to demonstrate the most basic feature of the new method.

DEMONSTRATION EXPERIMENTS

To demonstrate the capability of the bubble based method for fabricating micro structures, a series of conceptual experiments were carried out in this paper. Aiming to realize a micro wire with specific metal compound, we had prepared two kinds of FSBSs which were made of solutions of Ferric Chloride and Sodium Carbonate, respectively before the synthesis (Fig. 6). 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 (SDS) 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 0.1mol/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 within 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 generally be characterized using Auger spectroscopy or other measurement [24]. Over this process, injectors were used to blow the soap bubbles and a suitable bit of FSBS was sucked into its head before the air was breathed into the soap bubbles via an appropriate volume. 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 a smallest scale of 10 μm as given in Fig. 7 was used.

Fig.6 Regents and injector prepared for bubble fabrication.

What have been depicted in Fig. 8 are some typical optical microscope images for the micro wires fabricated by following the above experimental procedures. As indicated by the inserted bar, the left photo is for a micro wire with about 500 microns in width and nearly 10 mm in length. The right one is for a micro wire with about 5 mm in length and average 80 microns in width. Here, the compound of the fabricated micro wire is ferric oxide. The difference between these two experiments lies in that the air injected into the bubble is only one fourth of the injector volume for the former case, while the whole air in the injector has been completely injected to blow the bubble during the second experiment. Therefore, one can realize a very different bubble and thus micro wire size. Clearly, blowing with different air volume will help set up a flexible way to control the final output. Here, contact of the two bubbles has led to a micro wire with an irregular cross section, approximating to a semi-elliptical or rectangular shape. Reasons for this phenomenon can be attributed to that, chemical reaction in fact occurred in a small channel formed at the interfaces between two bubbles. When two bubbles contact together, the forces generated by their surface tensions and the molecule attractions will drain the solution within the interface to form a liquid channel, which then serves as the site for the chemical reaction and subsequently leads to the formation of a micro wire. One such photo actually taken in a real fabrication process has been given in the right picture of Fig. 1, where a curve can be found to form between the two bubbles. However, if the bubble junction can be deformed via the externally applied air flow or other physical effects, more complex micro wires with certain specific shape can also possibly be fabricated. In this sense, the wire will not just be a linear rod but may appear as certain three-dimensional structures. A complete investigation on this interesting issue is beyond the scope of the present paper. Tremendous works are worth of pursuing in the near future.



(a) (b)

Fig. 7 A standard micro ruler in optical photo from microscope. The width between two short scales in the ruler is 10μm. (a) The photo was magnified to 400 times larger than its original size; (b) The photo was magnified to 100 times larger than its original size.

To test the effects of different solution concentrations to the fabricated structures, additional conceptual experiments were performed. Results presented in Fig. 9 represented the microscope image for two micro wires fabricated using different concentrations of FSBSs. Here, FSBSs with various reactant concentrations were obtained through diluting the original solution by a magnitude of 100%, 50% or more, respectively. Clearly, different micro wires had been made in the experiments. From the left to the right picture, the solvent crystallization surrounding the micro wire appears as rather different, which can be attributed to the effects of the varied recant concentrations. Therefore, justification of the original solution concentration may provide a flexible way to control the detailed structure of the final output. Using a standard micro ruler as mentioned above, the detail of the micro wires in the optical photos can be displayed in Fig. 10(a). As indicated by the inserted bars, the minimal width of the fabricated micro wire falls in several microns here. In order to better display the sharp end of the micro wires, an additional image as shown in Fig. 10(b) 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 microns in width, 20 microns in height and nearly 1000 microns 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 for some traditional fabrication method [1-4].

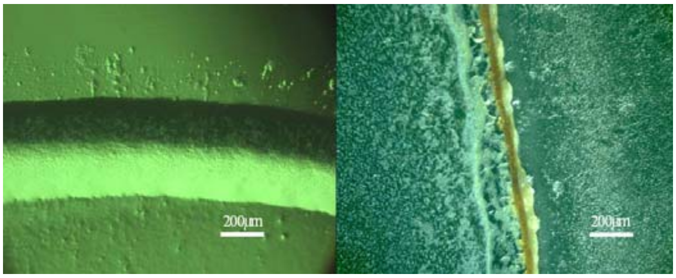


Fig. 8 Optical microscope images for the micro wires fabricated by the present method. The left photo indicates a micro wire with about 500 microns in width and nearly 10 mm in length; the right one is for a micro wire with about 5 mm length and average 80 microns width. The component of the micro wire is ferric oxide.

The present method is rather versatile in fabricating various structures. As illustrated above, a basic element obtained in this way is the micro wire. Such wire can serve as a temperature sensitive resistance, which could find very practical value in the bioengineering or other fields where temperature measurement in small space was strongly requested. For this purpose, 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 excrescent 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 still subject to oxidizing when exposed to the atmospheric environment. In this way, a copper wire resistance with an average size of about 40 microns in width, 30 microns in height and nearly 1200 microns in length was successfully fabricated. Previously, obtaining such extremely thin wires had to rely on expensive equipment or complex procedures [25]. This trouble was successfully resolved in a large extent by the present bubble based fabrication method. Further, to test the thermal performance of the temperature sensitive resistance thus made, additional measurements were made in this study. The corresponding resistance response to the temperature were obtained and presented in Fig. 11. This nearly linear correlation between resistance and temperature is very beneficial for the temperature measurement of a thermal sensor. Clearly, such a tiny temperature sensor can be directly fabricated in a specific substrate as requested. This would find significant applications in many situations such as in a biochemical reactor or biological chip etc.

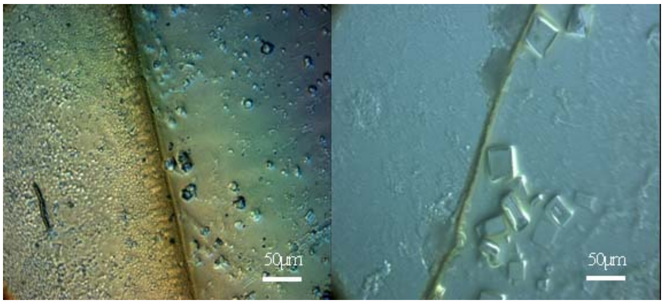
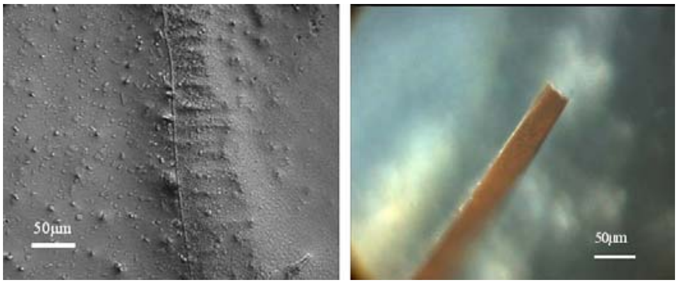
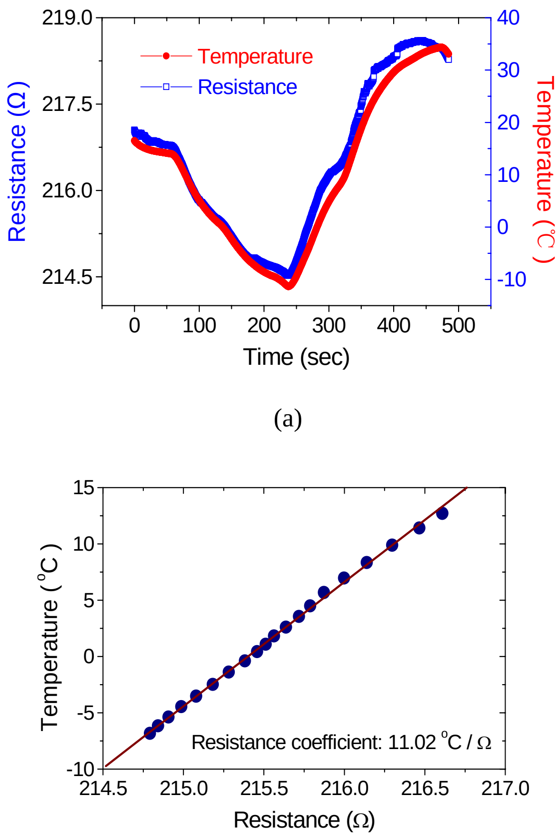


Fig. 9 Optical microscope images of the micro wires fabricated by the present method. Inserted bar, 50 microns. Under various concentrations (from left to right: the original solution diluted by the magnitude of 100%, 50% respectively, were used) of FSBSs, different micro wires were made. From left to right, the solvent crystallization surrounding the micro wire appears different. The component of micro wire is ferric oxide.



(a) (b)

Fig. 10 (a) Optical microscope images of micro wires fabricated by the present method. The minimal width of micro wire is several microns. (b) Optical microscope images of the fabricated micro wires cut and detached from the wafer. The micro wire has an average size of about 30 microns in width, 20 microns in height and 1000 microns in length with a rectangular section. In both figures, the component of micro wire is ferric oxide.



(a)

(b)

Fig. 11 Micro metal 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°C to 40°C; (b) Temperature dependent resistance of the fabricated micro wire within temperature range of -6°C to 12°C.

DISCUSSION AND CONCLUSION

Additional studies still indicate that, the way to manipulate the soap bubbles could affect the final output of micro/nano structures. When two bubbles contact to each other, two statuses can possibly occur. One is that the two soap bubbles may form a complex with common plateau border and stay in a stable or metastable state. In this case, the synthesis reaction at the plateau border has long enough time to finish building the target structure. However, the final rupture of the soap bubbles sometimes may cause disturbance to the fabrication process. The other one is that two soap bubbles will join together to combine into a single new soap bubble as soon as the complex was formed. The reaction for the product and formation of the micro structure thus takes a shorter time and the reaction may be incomplete. The micro wire in this case could therefore be much thinner than that in the former case. For such case, there is no rupture of soap bubble, which will help protect the structure of the product from evident damage. One interesting phenomenon as observed in the experiment still lies in that, when the contacting process occurs, the unstable joint plateau border will be rapidly stretched at its two opposite directions by the new soap bubble. The fabricated micro wire can even reach nano scale in the plateau border.

Further, the location for the bubbles to contact also plays an important role in the fabrication since foam drainage may drive the solution to flow from the plateau border, due to gravity and pressure gradient. If placing the soap bubbles upside down on the lower surface of a wafer, gravity may drain the soap bubble solution from lamellae to the plateau border. Therefore, taking full use of such behaviour can help planning well for the fabrication of various specific micro/nano structures.

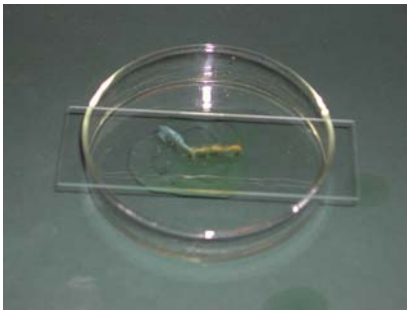


Fig. 12 An optical image for two connected wires with different components. The junction represents a thermal couple.

More approaches to integrate micro/ nano structures are still very possible to be carried out following the present procedure. We have extended it to manufacture a thermocouple with size in microns. For this purpose, three solutions such as that of Copper Chloride, Ferric Chloride and Sodium Carbonate should be prepared in advance. Then three soap bubbles were blown on the wafer surface and patterned as a figure of "Y", just as shown in Fig. 3(a). Then 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. As a result, a set of thermocouples in micro scale were fabricated. Presented in Fig. 12 is an optical image for two connected wires with different components. Such "Y" structure represents a thermal couple. The above effort indicates that, using a couple of soap bubbles with different chemical compounds can produce various complex micro structures, not just a single wire. For the experiments as described in the paper, we had recorded several simple movies to display the whole manipulation process of the present fabrication method. And three such movies have been available, which were to reflect the fabrication process by three soap bubbles, two soap bubbles, and that the bubbles were combined into a single new one after joining together, respectively. These supplementary materials can be supplied upon requests.

Clearly, realization of the micro and nanofabrication within a confined space of soap bubbles promises a new method for material synthesis and etching. Such fabrication can be done by a person without any particular training, which may allow its wide adoption in the near future. Besides, the fabrication is relatively clean and produces little pollution to the environment. In contrast, many existing methods such as photolithography have to rely heavily on complex apparatus. For example, a mask with micro/nano sized structures embedded inside is often a prerequisite for carrying out photolithography, which however needs to be prepared in advance via a much expensive way. Therefore, with the present macro manipulation enabled by bubble as a realistic strategy for the construction of valuable structures in small scale, the new method is expected to play an important role in the field of micro/nano technologies. Efforts made in this paper demonstrated that macro operations can handle and manufacture micro and nanostructures in a rather straightforward strategy. This concept can be possibly extended to more wide area of MEMS, nanotechnology and biotechnology (e.g. regarding plateau borders as micro fluidic channels in micro systems and fabrication of other nanostructures as membranes and particles.). For example, it is possible to manufacture semiconductor nano wires by adjusting components of the reactants. Besides, micro fluidic systems can also be etched by the bubbles via a much cheaper and convenient way. For this purpose, by blowing two bubbles composed with specific etchants to the substrate, they would etch the substrate at the confined plateau borders between the junction of two bubbles and the substrate. Then a micro channel can possibly be formed there. Except for the investigations as mentioned above where soap bubble stands on a wafer, two bubbles freely flowing in the air can also be driven to collide together to batch fabricate micro or nano structures. In that case, effect of the plateau due to drainage or surface tension of the wafer can be significantly decreased. Such fabrication can also be tried at the external space far from the earth so that the gravity effects can be largely weakened. The outcome (shape and size) of the fabricated structure will mainly depend on the size, the duration time for contact and the component of the lamellae.

Overall, it should be pointed out that, the present work is still at its first stage as proof-of-concept to initiate a new fabrication method. Tremendous efforts are strongly needed to better understand and implement the method. Establishment of the bubble fabrication opens many possibilities for integration with other technologies. For example, the concept of the bubble reaction can be implemented as an important tool to flexibly control and manipulate a complex biochemical reaction, which would find significant applications in micro/nano fluidics and thus lead to innovation of the traditional devices. Interesting enough, origination of the life may also find certain clues from the bubble reaction. For example, in the early stage of the life evolution, two single-cell objects could possibly contact with each other, which as a result formed a much complex multicellular body. In this sense, reactions occurred at the interfaces of two cells may finally lead to evolution from simple structure to an advanced life. Except for the above description, the role of the bubble fabrication appears rather versatile as mentioned in the paper. If taking chemistry as an example, multiple bubbles can be driven together by an automatically controlled mechanical or fluidics device to react simultaneously or just manipulated to contact with each other one by one. After this process, various three-dimensional micro/nano structures can be formed as desired. By directly fabricating a specific structure in a wafer, this will help make important sensors or structures for the application in biotechnology, chemistry, or micro machine etc. In electronics industry, the bubbles with specific solutions could be used as a micro etching tool to fabrication certain chip or device surface, so as to construct a specific small structure with requested compounds. In optics, the bubble fabrication may possibly help synthesis certain polymer fiber, through carefully administrating the bubble parameters such as reactant compound, number, size, shape, and spatial and temporal configuration etc.

Clearly, a complete understanding and implementation of the new method is beyond the scope of this research. Efforts made in the present paper warrant future investigations in this area.

ACKNOWLEDGMENTS

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REFERENCES

[1] Huang, Y., Duan, X., Wei, Q., and Lieber, C. M., 2001, “Directed assembly of one-dimensional nanostructures into functional networks,” Science, **291**, pp. 630-633.

[2] Heath, J. R., Kuekes, P. J., Snider, G. S., and Williams, R. S., 1998, “A defect tolerant computer architecture: Opportunities for nanotechnology,” Science, **280**, pp. 1716-1721.

[3] Boal, A., Ilhan, F., DeRouchey, J., Thurn-Albrecht, T., Russell, T., and Rotello, V., 2000, “Self-assembly of nanoparticles into giant spherical arrays,” Nature, **404**, pp. 746-749.

[4] Hayward, R. C., Saville, D. A., and Askay, I. A., 2000, “Electrophoretic assembly of colloidal crystals with optically tunable micropatterns,” Nature, **404**, pp. 56-59.

[5] Steinhart, M., Wendorff, J. H., Greiner, A., Wehrspohn, R. B., Nielsch, K., Schilling, J., Choi, J., and Go¬sele, U., 2002, “Polymer nanotubes by wetting of ordered porous templates,” Science, **296**, pp. 1997.

[6] Postma, H. W. C., Teepen, T. F., Yao, Z., Grifoni, M., and Dekker, C., 2001, “Carbon nanotubes single-electron transistors at room temperature,” Science, **293**, pp. 76–79.

[7] Tans, S. J., Verschueren, A.R.M., Dekker, C., 1998, “Room-temperature transistor based on a single carbon nanotube,”

Nature, **393**, pp. 49-52.

[8] Bachtold, A., Hadley, P., Nakanishi, T., and Dekker, C., 2001, “Logic circuits with carbon nanotube transistors,” Science, **294**, pp. 1317-1320.

[9] White, C. T., and Todorov, T. N., 1998, “Carbon nanotubes as long ballistic conductors,” Nature, **393**, pp. 240-242.

[10] Javey, A., Wang, Q., Ural, A., Li, Y., and Dai, H., 2002, “Carbon nanotube transistor arrays for multistage complementary logic and ring oscillators,” Nano Letters, **2**, pp. 929-932.

[11] Smith, P. A., Nordquist, C. D., Jackson, T. N., Mayer, T. S., Martin, B. R., Mbindyo, J., Mallouk, T. E., 2000, “Electric-field assisted assembly and alignment of metallic nanowires,” Appl. Phys. Lett., **77**, pp. 1399-1401.

[12] Tanase, M., Bauer, L. A., Hultgren, A., Silevitch, D. M., Sun, L., Reich, D. H., Searson, P. C., Meyer, G. J., 2001, “Magnetic alignment of florescent nanowires,” Nano Letters, **1**, pp. 155-158.

[13] Salalha, W., and Zussman, E., 2004, “Nanowires assembly using microfluidic: an experimental investigation,” XXI ICTAM 2004, Warsaw, Poland.

[14] Kenis, P. J. A., Ismagilov, R. F., and Whitesides, G. M., 1999, “Microfabrication inside capillaries using multiphase laminar flow patterning,” Science, **285**, pp. 83-85.

[15] Lyklema, J., and Mysels, K. J., 1965, “A study of double layer repulsion and van der Waals attraction in soap films,” J. Am. Chem. Soc., **87**, pp. 2539-2546.

[16] Myers, D.: Surfaces, Interfaces, and Colloids (Second Edition), Chapter 12: Foams, 295-316 (John Wiley & Sons, Inc, New York, 1999).

[17] Durand, M., and Langevin, D., 2002, “Physicochemical approach to the theory of foam drainage,” Eur. Phys. J. E, **7**, pp. 35-44.

[18] Astone, H., Akoehler, S., Hilgenfeldt, S., and Durand, M., 2003, “Perspectives on foam drainage and the influence of interfacial rheology,” J. Phys.: Condens. Matter, **15**, pp. S283–S290 PII: S0953-8984(03)55155-4.

[19] Breward, C. J. W., and Howell, P. D., 2002, “The drainage of a foam lamellae,” Journal of Fluid Mechanics, **458**, pp. 379-406.

[20] Kornev, K., and Shugai, G., 1998, “Thermodynamic and hydrodynamic peculiarities of a foam lamellae confined in a cylindrical pore,” Phys. Rev. E, **58**, pp. 7606-7619.

[21] Exerowa, D., and Kruglyakov, P. M., 1998, Foam and Foam Films (Elsevier, Amsterdam).

[22] Carrier, V., Destouesse, S., and Colin, A., 2002, “Foam drainage: a film contribution,” Phys. Rev. E, **65**, 061404.

[23] Kenis, P. J., Ismagilov, R. F., Takayama, S., Whitesides, G.M., Li, S., and White H.S., 2000, “Fabrication inside microchannels using fluid flow,” Accounts Chem. Res., **33**, pp. 841-847.

[24] Betz, G., Wehner, G. K., and Toth, L., 1974, “Composition-vs-depth profiles obtained with Auger electron spectroscopy of air-oxidized stainless-steel surface,” Journal of Applied Physics, **45**, pp. 5312-5316.

[25] Ho, J.-R., Chen, C.-C., and Wang, C.-H., 2004, “Thin film thermal sensor for real time measurement of contact temperature during ultrasonic wire bonding process,” Sensors and Actuators, A: Physical, **111**, pp. 188-195.

ANNEX A

PREDICTING THE WIDTH OF PLATEAU BORDERS OF TWO SOAP BUBBLES

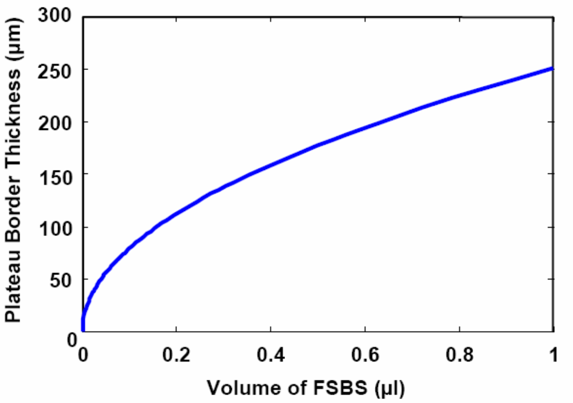

Fig. A1 Thickness of plateau border versus volume of FSBS to form soap bubble.

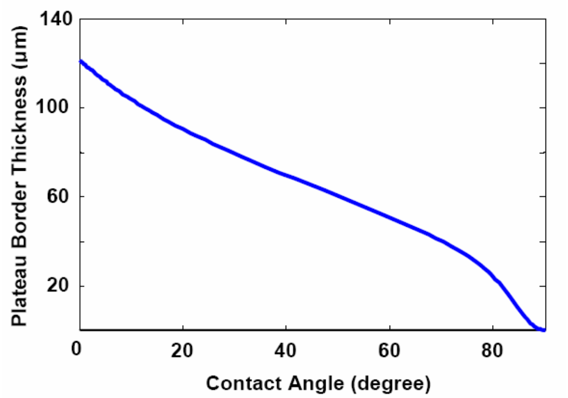

Fig. A2 Thickness of plateau border versus contact angle between the plateau borders of the soap bubble and the solid surface.

Since foam is composed of gas pockets surrounded by thin films, knowing the film properties is very necessary for a target fabrication. The films between the bubbles are called lamellae. Using the equations established in the text for characterizing the pressure difference across these lamellae, Fig. A1-A3 presented some calculated trend of the thickness of the plateau border by varying the volume of FSBS, the contact angle between bubble and the solid surfaces, as well as the bubble radius. Compared with the plateau border, the membrane thickness of the soap bubble can be several orders smaller. The smallest thickness of soap bubble has been found before as around 5-15 nm [15, 16]. Therefore, chemical reaction occurred in such scale will directly lead to extremely small objects.

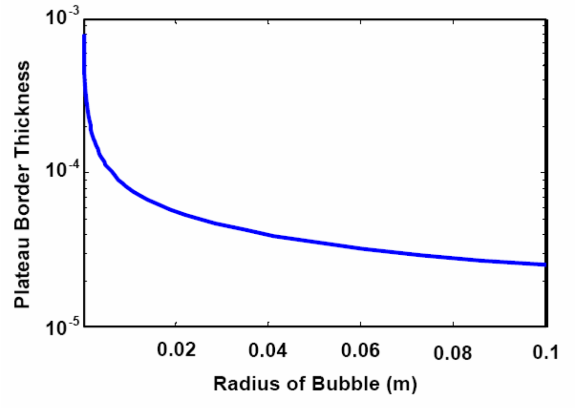

Fig. A3 Thickness of plateau border versus radius of soap bubble.

ANNEX B

DIFFUSION-REACTION MODEL FOR SYNTHESIS REACTIONS IN PLATEAU BORDERS

To characterize the fabrication process, a simple diffusion-reaction model can be established as follows. Several assumptions can reasonably be made such that the thickness of lamellae is large enough to maintain a diffusion progress and meanwhile thin enough to insure that it is a flat, compared with the wider plateau border zone.

The reactions only obeyed diffusion across the boundary of FSBS streams. The diffusion equation for the chemical compounds in the bubble membrane can then be established as follows:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - k \cdot C_A C_B = \frac{\partial C_A}{\partial t} \qquad -L < x < L \qquad \text{(A1)}$$

$$D_B \frac{\partial^2 C_B}{\partial x^2} - k \cdot C_B C_A = \frac{\partial C_B}{\partial t} \qquad -L < x < L \qquad \text{(A2)}$$

with initial conditions

$$C_A = \begin{cases} c_A & -L < x < 0 \\ 0 & 0 < x < L \end{cases} \qquad t = 0 \qquad \text{(A3)}$$

$$C_B = \begin{cases} 0 & -L < x < 0 \\ c_B & 0 < x < L \end{cases} \qquad t = 0 \qquad \text{(A4)}$$

and boundary conditions

$$\frac{dC_{A,B}}{dx} = 0 \qquad x = -L\,, x = L \qquad \text{(A5)}$$

where, D, C and c_A, c_B are respectively the diffusion coefficient, instantaneous concentration and initial concentration of FSBS, respectively; k the rate constant and L the half width of the reaction zone, while t is diffusion-reaction time. Subscripts A and B refer to two kinds of FSBSs.

Calculation on the above model will help interpret the spatial and transient reaction details of the bubble fabrication.