

Enhanced wetting properties of silicon mesh microchannels coated with SiO₂/SnO₂ nanoparticles through layer-by-layer self assembly

Tao Zhang, Tianhong Cui*

Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA

ARTICLE INFO

Article history:

Received 18 December 2010
Received in revised form 25 February 2011
Accepted 25 April 2011
Available online 13 May 2011

Keywords:

Wetting property
Nanoparticle
Capillary
Layer-by-layer nano self assembly

ABSTRACT

The enhanced wetting property of silicon mesh microchannels coated with SiO₂/SnO₂ nanoparticles is presented in this paper. The SiO₂/SnO₂ bi-layers are prepared using layer-by-layer nano self assembly. It is found that the silicon mesh microchannels are super hydrophilic and demonstrated powerful capillary. The capillary rise rate is characterized by measuring the front location of liquid on the silicon mesh surface, laid on a 45° inclined platform. For a silicon mesh sample with an overall dimension of 25 mm × 25 mm, when the microchannel width is 0.5 mm, the liquid front can reach the top edge of the sample in approximately 30 s. The mesh silicon surface with a SiO₂/SnO₂ multilayer film presented in this paper has better wettability and higher capillary pressure than other hydrophilic surfaces reported. The results provide a new way to improve the capillary in microchannels with enhanced super hydrophilic surfaces in microchannels for variety of micro/nanofluidic applications.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The wetting of solid surfaces by a liquid (water in particular) is ubiquitous in daily life as well as industrial processes, and especially highly important to micro- and nano-fluidics. Super hydrophilic surfaces can promote cooling or heat spreading in heat exchanges. Wettability is one of the most important properties for a solid surface, and the wetting behavior is governed by two factors: the chemical composition and the roughness of solid surfaces [1]. Bico et al. [2] suggested that a surface geometry should be used to tune its wetting properties. Hashimoto et al. [3] stated that TiO₂ thin films exhibit an initial contact angle of several tens of degrees depending on the surface conditions, mainly the surface roughness. When Permpoon et al. [4] deposited a SiO₂/TiO₂ bi-layer from silica and titania sols, they found that SiO₂/TiO₂ bi-layer films exhibit a natural, persistent, and repeatable super-hydrophilicity without UV light irradiation. Ohsaki et al. [5] also explored the wettability of a SnO₂/TiO₂ bi-layer. They observed that the combination of TiO₂ and SnO₂ realized a long-term stability and more hydrophilic characteristics when thinner SnO₂ film is coated.

TiO₂, SiO₂/TiO₂ bi-layer, and SnO₂/TiO₂ bi-layer are all possible surface wetting materials, which can change the surface wetting properties from hydrophobic to hydrophilic. However, sometimes we not only need a super-hydrophilic surface, but also need a super

wettability, a property that is proportional to capillary pressure. The smaller the microchannel size, the higher the capillary pressure. However, it is a major challenge to make larger microchannels with a higher capillary pressure.

In this paper, a new and simple method of coating SiO₂/SnO₂ bi-layer using layer-by-layer nano self-assembly techniques is presented. The method can produce both a super hydrophilic surface and a higher capillary pressure in the silicon mesh microchannels with a feature size of 0.5 mm.

2. Experimental

The fabrication procedure of silicon mesh microchannels is described in the following. First, silicon wafers are cleaned using RCA standard cleaning process. (1) Standard cleaning solution consists of a mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂). Silicon wafers are boiled in 3:1 H₂SO₄:H₂O₂ solution for 10 min at 120 °C; (2) wafers are put in 1:1 H₂O:HF solution for 5 min at room temperature; (3) standard cleaning solution consists of a mixture of ammonium hydroxide (NH₄OH), hydrogen peroxide (H₂O₂), and DI water (H₂O). Wafers are boiled in 1:2:5 NH₄OH:H₂O₂:H₂O solution for 5 min at 80 °C; (4) standard cleaning solution consists of a mixture of hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), and DI water (H₂O). Wafers are boiled in 1:2:5 HCl:H₂O₂:H₂O solution for 5 min at 85 °C. There was an intermediate rinsing step using DI water and drying by nitrogen after every step. Second, silicon mesh microchannels are fabricated by photolithography and ICP dry etching. The depth of the mesh microchannels is approximately 50 μm.

* Corresponding author. Tel.: +1 612 626 1636.
E-mail address: tcui@me.umn.edu (T. Cui).

It is well known that the layer-by-layer (LbL) self-assembly technique offers an easy and inexpensive process for multilayer formation and allows a variety of materials to be incorporated within the film structure [6]. LbL self assembly is mainly conducted through electrostatic interaction. Alternation of the surface charges results in a continuous assembly between positively and negatively charged materials with a great freedom in layers and deposition sequence [7].

The sample with mesh microchannels is alternately immersed in aqueous poly (dimethylallyl ammonium chloride) (PDPA) and sodium poly (styrenesulfonate) (PSS) at a concentration of 10 mg/mL, in a sequence of [PDPA/PSS]₂. The subscript 2 designates the number of immersions. These polyion films enhance the subsequent nanoparticle adsorption [8]. Following the precursor layers, 10 nm SiO₂ (Aldrich®, nanopowder, 99.5%) and 15 nm SnO₂ (NYACOL®, SN15ES) nanoparticles are coated on the entire surface of the wafer in the sequence of [PDPA/SiO₂]₂ + [PDPA/SnO₂]₂.

To characterize the wettability, a contact angle meter (DATA-PHYSICS, OCA15plus) is used to test contact angles. The SiO₂/SnO₂ films are characterized by FTIR transmission spectroscopy in a range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹ using a Nicolet Series II Magna-IR System 750 spectrometer. Spectra corresponding to 100 scans are recorded in one atmosphere after purging the measurement chamber with dry air for 10 min. Surface analysis is performed by XPS from vacuum employing an Mg K_α source (1253.6 eV). The X-ray source is operated at 20 kV at a current of 80 mA. Scanning electron microscope (JEOL 6500) is used to take SEM images of microstructures and SiO₂/SnO₂ nanoparticles. MATLAB software image processing code is used to characterize the capillary rise rate defined by the front location for each video frame.

3. Results and discussion

A silicon mesh surface is fabricated with MEMS technology. This surface is coated with SiO₂/SnO₂ nanoparticles. As shown in Fig. 1, some patterned quadrangular prisms are patterned on a silicon wafer. W denotes the space between two quadrangular prisms, and H is the height of the prism.

When a liquid drops on the silicon mesh surface, the front edge curvature of the spreading liquid will reduce the liquid pressure along the front, creating a pressure gradient between the main liquid reservoir and the invasion front. It is this pressure gradient that drives the invasion front. The capillary pressure equation for the wetting of a rough surface is described by Hay et al. [9].

$$\Delta P_C = \gamma \left(\frac{(2H + W)\cos \theta - W \sin \theta}{WH} \right) \quad (1)$$

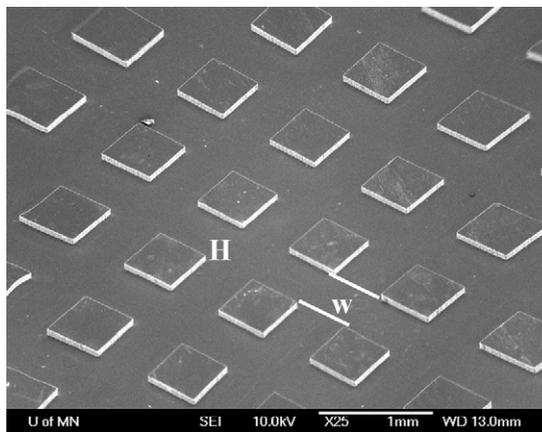


Fig. 1. SEM image of silicon mesh microchannels.

where ΔP_C is the pressure difference across the liquid–air interface caused by capillary forces, γ is the surface tension, and θ is the contact angle determined by the surface energies. It is obvious that the pressure will decrease as the prism space increases. With the increase of W , the capillary will decrease gradually, until it disappears from the mesh microstructures. When we need a super hydrophilic surface or high capillary forces in larger microchannels, the deposition of hydrophilic materials will be used to alter the chemical composition of the structures.

SiO₂ and SnO₂ nanoparticles were selected to coat silicon mesh microchannels. The wettability of silicon mesh microchannels was studied in ambient air at room temperature using a contact angle meter based on the sessile drop method. The mean contact angles were determined by averaging values measured at five different points on each sample. Fig. 2 shows the contact angle of a water drop (5 μ L) on a fresh silicon mesh surface (Fig. 2a), and also on a silicon mesh coated with SiO₂/SnO₂ (Fig. 2b). It was found that water completely wetted the coated mesh surface with a contact angle of 0°. Before coating, the contact angle was about 78°. This dramatic drop in contact angle indicates that the silicon mesh surface became super hydrophilic when coated with SiO₂/SnO₂. Similarly, the water contact angle of a planar silicon wafer coated with SiO₂/SnO₂ bi-layers is also 0°.

Wetting and its associated surface forces are responsible for other related phenomena, including capillary effects. This implies that the capillary rise rate and capillary pressure are important parameters indicative of wettability. The Young–Laplace equation asserts that capillary pressure is directly proportional to the height of a water front location because a greater capillary pressure forces liquid to rise higher on the substrate, the capillary rise rate can be

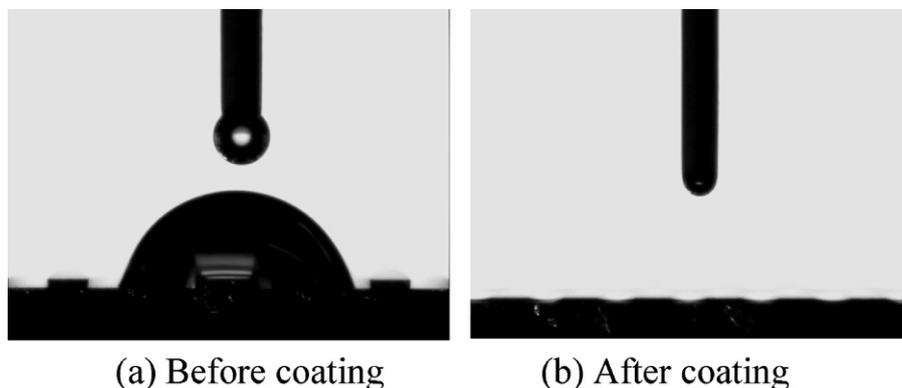


Fig. 2. Contact angle measurement.

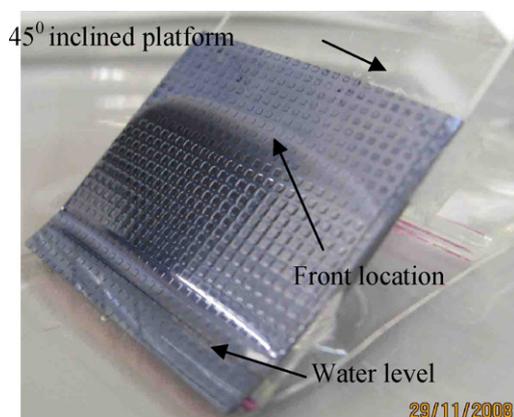


Fig. 3. Capillary flowrate testing.

used qualitatively to denote capillary pressure [10]. We can characterize the capillary rise rate by noting the location change of the water front on the silicon mesh surface at each instant. As shown in Fig. 3, the silicon mesh microchannels are set on at a test platform inclined at 45° . The base of the inclined platform is merged in a reservoir filled gradually with water. When liquid reaches the bottom edge of the silicon mesh surface, water climbs the inclined test platform. A video camera records the moving front of water, as it rises from the mesh base to the top edge. MATLAB image processing code is used to analyze the video and to determine the capillary rise rate by tracking the location of the water front at each frame. In contrast to the coated silicon mesh, no capillary rise phenomenon was observed when repeating the experiment with bare silicon mesh microchannels without a coating. Capillary forces are only evident in microchannels coated with $\text{SiO}_2/\text{SnO}_2$ nanoparticles.

Fig. 4a represents the capillary rise rate measured in microchannels of varying widths. It was found that the capillary rise rate decreases with increasing mesh width. When the space of prisms is 0.5 mm, the capillary rate is higher than 0.8 mm and 1.0 mm space, and the liquid front reaches the top edge of the sample in approximately 30 s. When the space of prisms is 1.0 mm, the capillary forces are much weaker. The results here are consistent with the capillary pressure theory for the wetting of a rough surface from Hay. As shown in Fig. 4b, when coating the silicon mesh surface with only SiO_2 , the capillary rise rate will increase slowly with the increasing concentration of a SiO_2 solution.

The difference of capillary performance is very different between microchannels ($W=0.5$ mm) coated with only SiO_2 and the one coated with both SiO_2 and SnO_2 , as shown in Fig. 5. It was found that the capillary rise rate of a sample coated with $\text{SiO}_2/\text{SnO}_2$ nanoparticles is faster than that of a sample coated with only SiO_2 . It was also discovered that the capillary rise rate decreases when using more than two layers of SnO_2 . For two layers of SnO_2 , as seen in Table 1, the weight percentage of tin is 5.13%, and the atomic percentage is about 1.05%.

Why does the capillary rise rate decreases when the number of the SnO_2 layers or the concentration of SnO_2 increases? It is possible that when depositing SnO_2 nanoparticles over pre-existing SiO_2 nanoparticles, a dense composite material is formed [11]. As shown in Fig. 6c, the composite film has a foam structure, which

Table 1
The content of Sn.

	$\text{SiO}_2/(\text{SnO}_2)_1$	$\text{SiO}_2/(\text{SnO}_2)_2$	$\text{SiO}_2/(\text{SnO}_2)_3$
Wt.%	3.27	5.13	7.77
At.%	0.66	1.05	1.56

The subscripts 1–3 outside bracket designate the layers of SnO_2 .

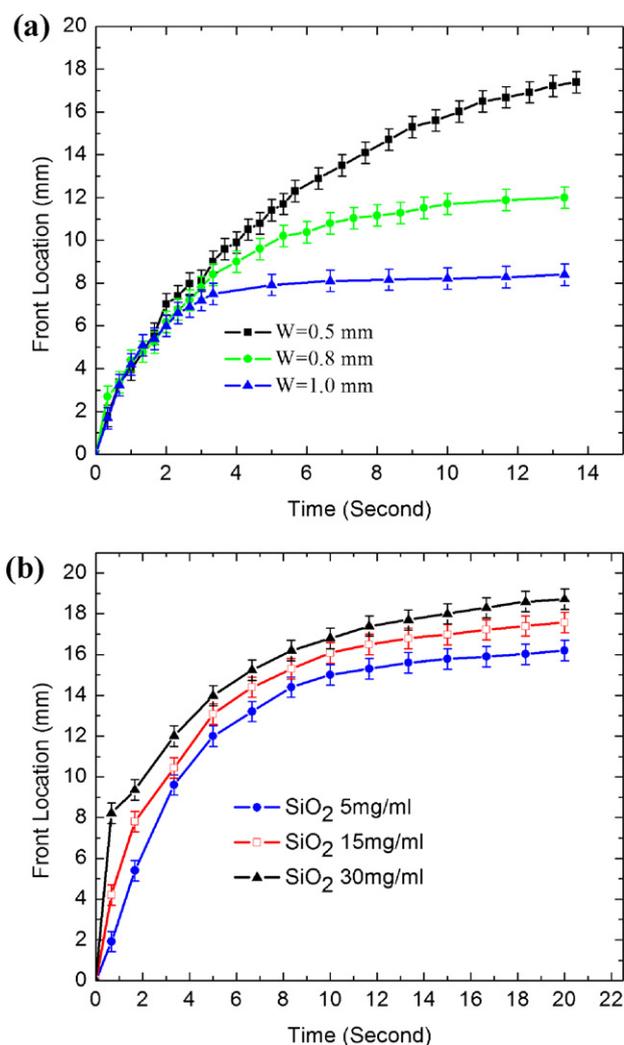


Fig. 4. (a) Capillary rise rate in different mesh microchannels, (b) capillary rise rate in the different concentrations of SiO_2 .

helps to soak liquid and enhances the surface wettability. As shown in Fig. 6a, the coating of only SiO_2 nanoparticles may close some porous space. SnO_2 can open or connect the pore space after coating SnO_2 , as shown in Fig. 6b. However, excessive SnO_2 particles

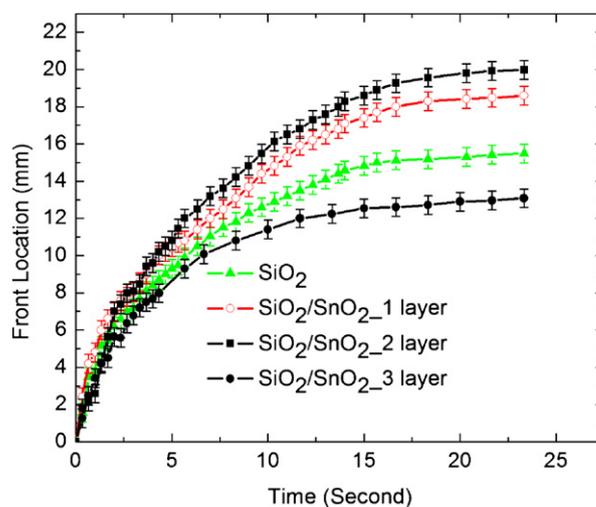


Fig. 5. Capillary rise rate with different layers of SnO_2 in multi-layer $\text{SiO}_2/\text{SnO}_2$ film.

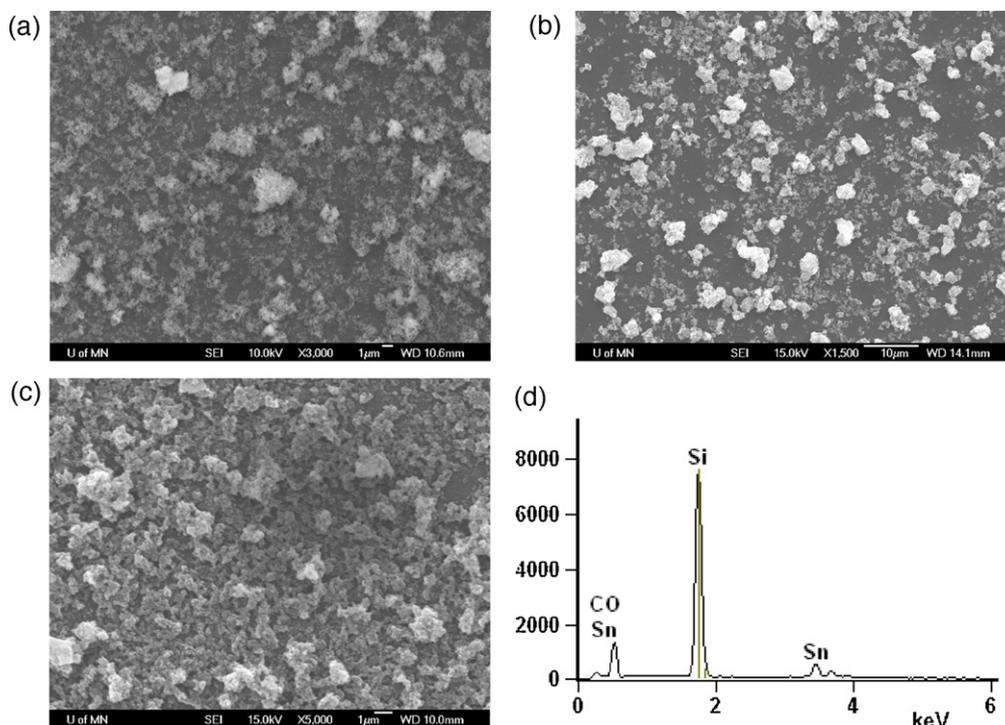


Fig. 6. SEM image of SiO₂ monolayer film (a), SEM images of SiO₂/SnO₂ film in different concentration of SnO₂: (b) 100 mg/mL, (c) 1000 mg/mL, (d) EDS analysis of SiO₂/SnO₂ bi-layers film.

may clog open pores, as shown in Fig. 6c, which would prevent the structure from soaking more water.

Because the OH groups have a strong effect on the film hydrophilicity [12], we performed other studies using FTIR and XPS spectroscopy to explain the reason why the capillary rise rate of a sample coated with SiO₂/SnO₂ nanoparticles is faster than that of a sample coated with only SiO₂ and why the capillary rise rate decreases when using more than two layers of SnO₂. However, moisture in atmospheric ambient may change the interpretation of OH absorption bonds from the substrate. Therefore to minimize water adsorption, the measurement chamber was purged with a dry air for 10 min before collecting FTIR data.

FTIR absorption spectra in the hydroxyl region (3800–3200 cm⁻¹) are illustrated in Fig. 7, and the following observations are implemented on freshly deposited films. A large component with an absorption maximum is centered about

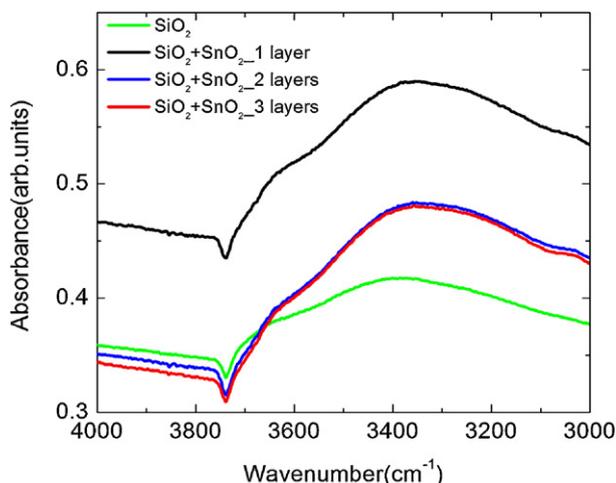


Fig. 7. FTIR spectra in the hydroxyl region for SiO₂ and SiO₂/SnO₂ bi-layer film.

3400 cm⁻¹, commonly associated with absorbed water to form Si–OH or Sn–OH groups linked to water molecule through hydrogen bonds. An intermediary region about 3650 cm⁻¹, where pairs of OH linked through hydrogen bonds are depicted [4], with a high wave number peak or shoulder at about 3745 cm⁻¹, corresponding to isolated surface OH groups. The OH bond on SiO₂ and SiO₂/SnO₂ indicates the presence of water. When the sample is coated with one layer SnO₂ particles, it has the highest amount of OH groups on the surface than other coating conditions.

XPS is also used to study the surface chemistry properties, to provide insights in surface wetting mechanisms yielding a super hydrophilic surface. In this paper, XPS was used to investigate the freshly deposited SiO₂ and SiO₂/SnO₂ bi-layer films, about 12 h after the film deposition. Because the hydrophilic properties of SiO₂ and SiO₂/SnO₂ surfaces rely on the presence of OH groups on the coatings, the corresponding peaks are located at about 533 and 531 eV, respectively. Basically, the O 1s peak can be decomposed into two components, one at 531 eV for bulk oxide (O²⁻) and the other at 533 eV for hydroxyl (OH) species. Fig. 9 is the high resolution XPS spectra of O 1s of SiO₂ and SiO₂/SnO₂ films. It can be seen that the O 1s BE is observed at 531.36 eV for the O²⁻ group and at 533.04 eV for the OH group. When the sample was coated with SiO₂ and one layer of SnO₂ particles, it has the highest OH binding energy than that only coated with SiO₂ particles (Fig. 8a). On the other hand, the hydroxyl binding energy decreases with increasing layers of SnO₂ (Fig. 8b).

As shown in Table 2, the atomic concentration peak at 533.04 eV is 71.384, and the one at 530.36 eV is 28.616 when coating with

Table 2
The atomic concentration of peak OH⁻¹ and O²⁻.

	SiO ₂ /(SnO ₂) ₁	SiO ₂ /(SnO ₂) ₂	SiO ₂ /(SnO ₂) ₃
OH ⁻¹	45.49	71.384	37.499
O ²⁻	54.51	28.616	62.501

The subscripts 1–3 outside bracket designate the layers of SnO₂.

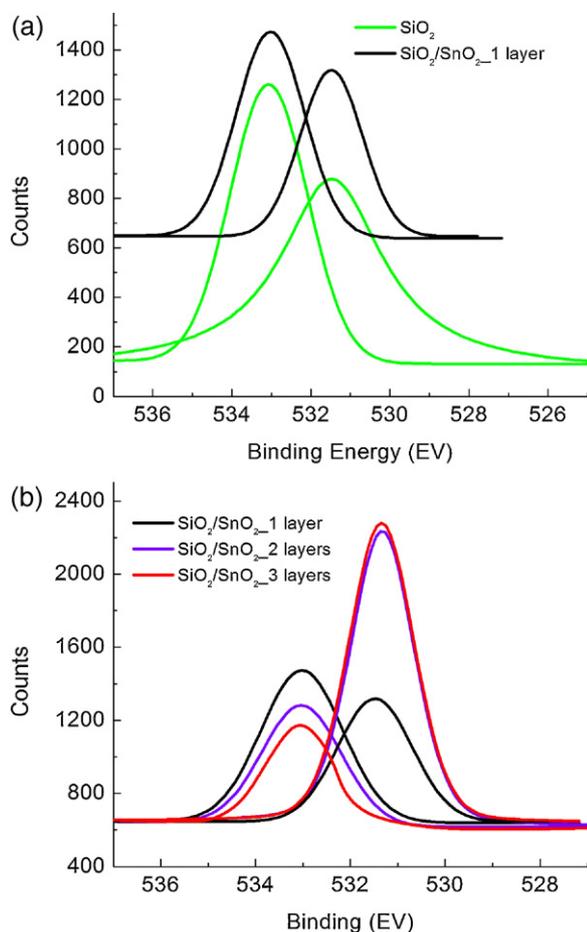


Fig. 8. High resolution XPS spectra of O 1s: (a) monolayer SiO_2 film and one layer of $\text{SiO}_2/\text{SnO}_2$ film, (b) one layer, two layers and three layers of $\text{SiO}_2/\text{SnO}_2$ film.

only one layer of SnO_2 . It can be seen that the film coated with SiO_2 and one layer of SnO_2 particles has the highest atomic peak of OH group. The data illustrated in FTIR and XPS spectra confirm that the capillary rise rate of a $\text{SiO}_2/\text{SnO}_2$ film is faster than that of a SiO_2 film, and the capillary rise rate decreases when using more than two layers of SnO_2 .

Fig. 9a illustrates the capillary rise rate with respect to different concentrations of SnO_2 . It is found that the capillary rise rate increases when the concentration of SnO_2 rises from 10 mg/mL to 100 mg/mL. However, when the concentration is 1000 mg/mL, the capillary rise rate is smaller than that at a concentration of 100 mg/mL.

Fig. 9b demonstrates the change of a capillary rise rate when samples were exposed to air. It was found that when the samples were exposed to an ambient air for 5 days, both the SiO_2 monolayer film and the $\text{SiO}_2/\text{SnO}_2$ bi-layer film degraded, and no longer performed well as the initial test. The capillary rise rate of $\text{SiO}_2/\text{SnO}_2$ bi-layer films is still greater than that of SiO_2 monolayer films after the exposure. The possible reason of the wettability and capillary degradation is that the coating may get contaminated with organic or inorganic residuals after exposure to an ambient air.

Durability testing of $\text{TiO}_2/\text{SnO}_2$ multilayers has also been investigated in Ref. [5]. The film can keep hydrophilicity after storing in a dark box 5 days, even if there is a little change of water contact angle. However, our research, $\text{SiO}_2/\text{SnO}_2$ multilayer film in silicon mesh microchannels still keep capillary pressure after storing in air 5 days and the water contact angle still keep zero. Therefore the mesh silicon surface with

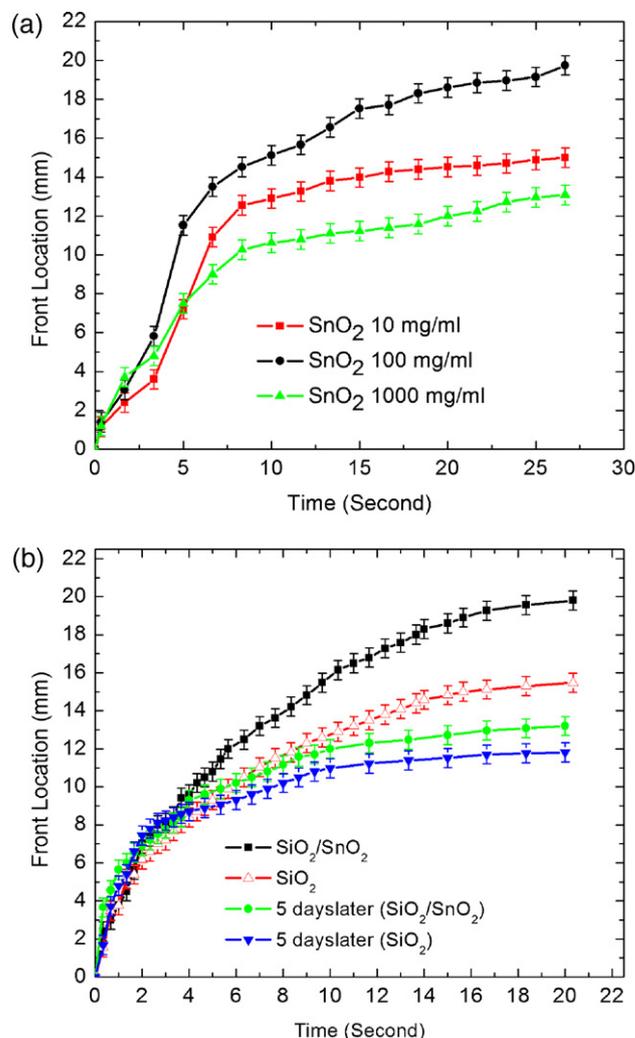


Fig. 9. (a) Capillary rise rate in different concentration of SnO_2 , (b) durability testing of capillary rise rate.

$\text{SiO}_2/\text{SnO}_2$ multilayer film presented in this paper has better wettability and stringer capillary pressure than other hydrophilic surfaces.

4. Conclusions

The wetting property of silicon mesh microchannels coated with $\text{SiO}_2/\text{SnO}_2$ nanoparticles was investigated. The silicon chip with mesh microchannels is 25 mm \times 25 mm, with a mesh space of 0.5 mm. The silicon mesh microchannels are super hydrophilic, and demonstrated strong capillary forces after being coated with a $\text{SiO}_2/\text{SnO}_2$ bi-layer film. The liquid front rises from the chip base to the top edge in approximately 30 s. In addition, the silicon mesh microchannels coated with a $\text{SiO}_2/\text{SnO}_2$ bi-layer film have better wettability than those only coated with a SiO_2 monolayer. The mesh silicon surface with $\text{SiO}_2/\text{SnO}_2$ multilayer film presented in this paper has better wettability and stronger capillary pressure than other hydrophilic surfaces reported.

The results in this paper provide a new way to achieve super hydrophilic surfaces and to improve the capillary pressure in microchannels for variety of micro/nanofluidic applications.

Acknowledgement

We are grateful to the Nanofabrication Center and Characterization Facility at the University of Minnesota for their help with fabrication and characterization.

References

- [1] Y.J. Sheng, S.Y. Jiang, H.K. Tsao, Effects of geometrical characteristics of surface roughness on droplet wetting, *J. Chem. Phys.* 127 (2007) 1–7.
- [2] J. Bico, C. Tordeux, D. Quéré, Rough wetting, *Europhys. Lett.* 55 (2001) 214–220.
- [3] K. Hashimoto, H.S. Irie, F. Akira, TiO₂ photocatalysis: a historical overview and future prospects, *J. Appl. Phys.* 44 (2005) 8269–8285.
- [4] S. Permpoon, M. Houmard, D. Riassetto, L. Rapenne, G. Berthome, B. Baroux, J.C. Joud, M. Langlet, Natural and persistent superhydrophilicity of SiO₂/TiO₂ and TiO₂/SiO₂ bi-layer films, *Thin Solid Films* 516 (2008) 957–966.
- [5] H. Ohsaki, N. Kanai, Y. Fukunaga, M. Suzuki, T. Watanabe, K.H. Ashimoto, Photocatalytic properties of SnO₂/TiO₂ multilayers, *Thin Solid Films* 502 (2006) 138–142.
- [6] K. Ariga, J.P. Hill, Q.M. Ji, Layer-by-Layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application, *Phys. Chem. Chem. Phys.* 9 (2007) 2319–2340.
- [7] W. Xue, T. Cui, Characterization of layer-by-layer self-assembled carbon nanotube multilayer thin films, *Nanotechnology* 18 (2007) 1–7.
- [8] T. Cui, F. Hua, FET fabricated by layer-by-layer nano assembly, in: *Transducers'04 Conference*, March, 2004, pp. 503–506.
- [9] K.M. Hay, M.I. Dragila, J. Liburdy, Theoretical model for the wetting of a rough surface, *J. Colloid Interface Sci.* 325 (2008) 472–477.
- [10] W.K. Chan, C. Yang, Surface-tension-driven liquid–liquid displacement in a capillary, *J. Micromech. Microeng.* 15 (2005) 1722–1728.
- [11] C. Hall, W.D. Hoff, *Water Transport in Brick, Stone and Concrete*, Spon Press of Taylor & Francis, London, 2002.

- [12] M. Nakamura, L. Sirghi, T. Aoki, Y. Hatanaka, Study on hydrophilic property of hydro-oxygenated amorphous TiO_x: OH thin films, *Surf. Sci.* 507–510 (2002) 778–782.

Biographies



Tao Zhang He received his Ph.D. degree in mechanical engineering from Chinese Academy of Sciences, China, in 2007. He joined Prof. Tianhong Cui's group at the University of Minnesota in 2008. Currently, he works as a post-doctoral associate in the Department of Mechanical Engineering at the University of Minnesota. His research interest includes micro/nanofabrication, microfluidics, and surface modification.



Tianhong Cui received his B.S. degree from Nanjing University of Aeronautics and Astronautics in 1991, and Ph.D. degree from the Chinese Academy of Sciences in 1995. He is currently a Professor of Mechanical Engineering at the University of Minnesota. From 1999 to 2003, he was an assistant professor of electrical engineering at Louisiana Technical University. Prior to that, he was a STA fellow at the National Laboratory of Metrology, and served as a postdoctoral research associate at the University of Minnesota and Tsinghua University. He received research awards including the Nelson Endowed Chair Professorship from the University of Minnesota, the Research Foundation Award from Louisiana Tech University, the Alexander von Humboldt Award in Germany, and the STA & NEDO fellowships in Japan. His current research interests include MEMS/NEMS, nanotechnology, and polymer electronics.