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To cite this article: Pengfei Song et al 2018 Nanotechnology 29 415501

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Nanotechnology 29 (2018) 415501 (9pp)

# Rolled-up SiO<sub>x</sub>/SiN<sub>x</sub> microtubes with an enhanced quality factor for sensitive solvent sensing

### Pengfei Song<sup>1,2</sup>, Cheng Chen<sup>3</sup><sup>®</sup>, Juntian Qu<sup>1,2</sup><sup>®</sup>, Pengfei Ou<sup>3</sup>, M H T Dastjerdi<sup>4,5</sup>, Zetian Mi<sup>4,6</sup>, Jun Song<sup>3</sup> and Xinyu Liu<sup>1</sup><sup>®</sup>

<sup>1</sup> Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, M5S 3G8, Canada

<sup>2</sup> Department of Mechanical Engineering, McGill University, 817 Sherbrooke Street West, Montreal, Quebec, H3A 0C3, Canada

<sup>3</sup> Department of Mining and Materials Engineering, McGill University, 3610 Rue University, Montreal, Quebec, H3A 0C5, Canada

<sup>4</sup> Department of Electrical and Computer Engineering, McGill University, 3480 Rue University, Montreal, H3A 0E9, Canada

<sup>5</sup> Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States of America

<sup>6</sup> Department Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI 48109, United States of America

E-mail: xyliu@mie.utoronto.ca

Received 16 April 2018, revised 26 June 2018 Accepted for publication 3 July 2018 Published 3 August 2018



#### Abstract

The microtubes made through rolling-up of strain-engineered nanomembranes have received growing research attention after their first invention due to the technology's high flexibility, integrability, and versatility. These rolled-up microtubes have been used for a variety of device applications including sensors, batteries and transistors, among others. This paper reports the development of highly sensitive whispering-gallery mode (WGM) chemical sensors based on rolled-up microtube optical microcavities (RUM-OCs). For the first time, such microcavities were batch fabricated through rolling-up of plasma-enhanced chemical vapor deposition (PECVD)-synthesized SiO<sub>x</sub>/SiN<sub>x</sub> bilayer nanomembranes, which have better optical properties than the conventional electron-beam-deposited SiO/SiO<sub>2</sub> bilayers. Benefiting from the high refractive index (RI) of PECVD-deposited SiN<sub>x</sub>, our RUM-OC shows an enhanced quality factor of 880 that is much higher than that (50) of a SiO/SiO<sub>2</sub> RUM-OC with the same dimensions. The developed RUM-OC is used for sensitive WGM solvent sensing, and demonstrate a limit of detection of  $10^{-4}$  refractive index unit (RIU), which is 10 times lower than that ( $10^{-3}$  RIU) of a SiO/SiO<sub>2</sub> RUM-OC.

Supplementary material for this article is available online

Keywords: rolled-up microtube, plasma-enhanced chemical vapor deposition, optical cavity, whispering-gallery mode, chemical and biosensors

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Recently, microtube-based optical cavities fabricated through rolled-up nanotechnology have gained accumulated research interests thanks to their unique advantages including the nanometer-sized, subwavelength wall thickness of the microtube, excellent compatibility with on-chip integration and mass production, good material versatility and fabrication tunability [1-6]. The rolled-up nanotechnology is characterized by batch fabrication of self-assembled microtubes through release of pre-strained multi-layer nanomembranes from their mother substrate. This technology has enabled both fundamental studies and practical applications of these rolled-up microtubes [7–10]. These microtubes can serve as high-performance whispering-gallery-mode (WGM) optical resonators, and their optical resonance originates from the constructive interference of light guided within the thin wall of a microtube by total internal reflection. This phenomenon has led to a variety of applications including chemical and biosensing [6, 11–14]. Particularly, the nanometer-sized, subwavelength wall thickness of the rolled-up microtubes permits a large fraction of the WGM evanescent wave penetrating into the external environment, thereby enabling a higher sensitivity to change of the external refractive index and making it suitable for sensing applications [12, 15].

The pioneering work of developing rolled-up microtubebased optical cavities (RUM-OCs) for WGM solvent sensing was reported by Huang et al [12]. The authors fabricated the RUM-OC from a bilayer of electron-beam (e-beam) evaporated SiO/SiO<sub>2</sub> nanomembranes, and demonstrated a much higher sensitivity of 425 nm/refractive index unit (RIU) than that (typically <100 nm/RIU) of conventional WGM sensing platforms (e.g., the glass capillary). The enhanced sensitivity could be attributed to the subwavelength wall thickness (less than 100 nm) of the rolled-up microtube; however, the ultrathin wall also significantly reduces the level of light confinement. This pronounced light loss in turn shortens the photon lifetimes and broadens the resonance modes of the RUM-OC, resulting in a low quality factor (Q-factor; <100) and thus a low limit of detection (LOD) of the developed sensor [12].

Significant research efforts have been dedicated to enhancing the light confinement in rolled-up microtubes and thus improving the LOD of the optical resonance sensor [16–19]. The existing methods for improving the Q-factor of the RUM-OC are primarily based on the adjustment of the microtube structure or material composition. Among these methods, coating the inner and outer wall surfaces of the microtube with a high-refractive index material (e.g., HfO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) has been demonstrated to provide the maximum enhancement of the Q-factor of the RUM-OC. The Q-factor enhancement is mainly due to the coating of high-refractive index materials onto the microtube surfaces that improves the light confinement capability of the microtube [20]. RUM-OCs made from SiO/SiO<sub>2</sub> have been coated with HfO<sub>2</sub> through atomic layer deposition (ALD), and reported to have a Q-factor of up to 660 [12]. However, the employment of ALD increases the complexity and cost of microtube fabrication, and thus, to some extent, hinders the wide adoption of this method.

RUM-OCs with axial light confinement microstructures have been fabricated from high-refractive index  $Y_2O_3/ZrO_2$ bilayer, and proved to possess a *Q*-factor as high as 1600 [12, 17]. Despite the high *Q*-factor achieved by the  $Y_2O_3/ZrO_2$ RUM-OC, the  $Y_2O_3$  material is toxic for human skins and model cells and is also soluble in an alcoholic environment [21], making it not suitable for certain types of biological and chemical sensing applications. In addition,  $Y_2O_3$  absorbs light of <700 nm and thus limits the further improvement of *Q*-factor of the RUM-OC, as RUM-OC sensors were usually operated in the visible range (400–700 nm) [22]. Therefore, it is still necessary to seek other alternative materials, which have high-refractive indexes, good biocompatibility, and easy synthesis/fabrication processes, for batch construction of RUM-OCs with high *Q*factors.

Silicon nitride  $(SiN_x)$  is non-toxic and biocompatible, and has a high-refractive index [23]; it has been widely used for constructing optical cavities and waveguides [24, 25]. Although  $SiN_x$  microtubes have been previously utilized to study neuron cells or act as inductors [26, 27], there has been no study on fabricating  $SiN_x$ -based RUM-OCs for sensing applications. It has been shown that  $SiN_x$  has a higher refractive index than that of  $SiO_x$ , promising a better light confinement capability of  $SiN_x$ -based RUM-OCs [28]. In addition,  $SiN_x$  only absorbs light at a wavelength of below 300 nm, and thereby does not lead to undesired light absorption in RUM-OCs operating in the visible wavelength range. Finally,  $SiN_x$  films can be deposited using chemical vapor deposition (CVD) techniques, which are facile and cost-effective.

In this paper, we report the fabrication, testing, and chemical sensing application of RUM-OCs made from a bilayer of  $SiO_r/SiN_r$  nanomembranes. The  $SiN_r$  layer provides a high-reflective index and thus improves the light confinement of the RUM-OCs, and the  $SiO_x$  layer provides a proper level of strain mismatch with the  $SiN_x$  layer to drive the rolling-up process. The focus of this paper is to illustrate the role of the high-reflective-index  $SiN_x$  layer in enhancing the Q-factor of the RUM-OCs; thus, we opt not to use other Q-factor improvement techniques such as ALD coating and axial light confinement structures. We demonstrate the precise control of the RUM-OC diameter by adjusting the nanomembrane thickness, providing high flexibility of the microtube fabrication. The developed RUM-OC reveals an enhanced Q-factor of up to 880, which is much higher than that of the conventional SiO/SiO<sub>2</sub> RUM-OC and comparable to that (660) of the previously reported HfO<sub>2</sub>-coated SiO/SiO<sub>2</sub> RUM-OC. We applied our RUM-OC to solvent sensing, and achieved a LOD of  $10^{-4}$  RIU. This result is ten times lower than that  $(10^{-3} \text{ RIU})$  of the SiO/SiO<sub>2</sub> RUM-OC.

#### 2. Microtube fabrication

The  $SiO_x/SiN_x$  microtubes were fabricated through controlled release of strain-engineered bilayer  $SiO_x/SiN_x$  nanomembranes. The strain difference between the  $SiO_x$  and  $SiN_x$  layers is the driving force for the self-rolling of the nanomembranes. The value of the strain difference needs to be above a certain threshold to roll the bilayer nanomembranes into a tubular microstructure rather than forming non-tubular substrates such as wrinkles or buckles [29]. Therefore, the prerequisite of microtube rolling-up is to determine a suitable strain difference value between the  $SiO_x$  and  $SiN_x$  layers. As the  $SiN_x$  film was the major layer we investigated, we directly used the standard recipe provided by our microfabrication facility for  $SiO_x$  deposition (see details below), and only tuned the deposition parameters for  $SiN_r$  to achieve two objectives: (1) to determine the optimal strain difference between the  $SiO_x$  and  $SiN_x$  layers and obtain the highest yield of microtube rolling-up, (2) to maintain a high-refractive index of  $SiN_x$  (as the reflective index of  $SiN_x$  is also affected by the deposition parameters).

There are several parameters to tune for the  $SiN_x$  deposition, including the deposition power, frequency, temperature, and the SiH<sub>4</sub>/NH<sub>3</sub> gas ratio. These parameters all could affect the built-in stress and the refractive index of the deposited  $SiN_x$ film. In order to simplify the experiment, we only tuned the  $SiH_4/NH_3$  gas ratio with other parameters fixed (70 W, 13.56 MHz, and 300 °C). We chose to only tune the  $SiH_4/NH_3$ gas ratio because it is the most commonly adjusted parameter during PECVD deposition of  $SiN_x$  films and has been extensively studied [23, 25, 30]. It was commonly observed that, with the increase of SiH<sub>4</sub>/NH<sub>3</sub> gas ratio, the refractive index of deposited  $SiN_x$  film became higher (which yielded better light confinement of the optical cavity) while the built-in tensile stress of the film became smaller (which compromised the rolling-up process) [23, 30, 31]. This result could be explained by that the higher  $SiN_x$  flow leads to the larger Si-incorporation in the deposited film, creating the so-called 'Si-rich' film and thereby the higher refractive index and lower tensile stress. Fourier-transform infrared spectroscopy (FTIR) measurements shows the increase of Si-H bonds and the decrease of N–H bonds [23], which supports this explanation. Therefore, a balanced SiH<sub>4</sub>/NH<sub>3</sub> gas ratio needs to be experimentally determined. Maintaining the NH<sub>3</sub> flow rate at a common level of 10 standard cubic centimeter per minute (sccm), we used three typical  $SiH_4/NH_3$  volume ratios (1, 2, and 3) to deposit the  $SiN_x$  films, and examined the rolling-up yield of the  $SiO_x/SiN_x$  bilayer nanomembranes with the same in-plane pattern. We achieved the highest rolling-up yield of 99% (n = 300) at the gas ratio of 1, and thereby the flow rate of 10 sccm for both SiH<sub>4</sub> and NH<sub>3</sub> was used in the following experiments.

As shown in figure 1(A-i), the fabrication process started from e-beam deposition (equipment: BJD 1800, Temescal) of an aluminum (Al) sacrificial layer (50 nm) on a pre-cleaned three-inch silicon wafer. We chose Al as the sacrificial layer because of its highly selective wet etching over  $SiO_x/SiN_x$ and its low surface roughness (<1.25 nm) [32]. The  $SiO_x/SiN_x$  (bottom/top) bilayer nanomembranes were then deposited by PECVD (equipment: Plasmalab System100, Oxford Instruments). The following gas flow parameters of PECVD were used: (i) 8.5 sccm of SiH<sub>4</sub> and 710 sccm of N<sub>2</sub>O for SiO<sub>2</sub> deposition, and (ii) 10 sccm of SiH<sub>4</sub> and 10 sccm of NH<sub>3</sub> for SiN<sub>x</sub> deposition. These parameters ensured the suitable stress difference for driving the rolling-up of microtubes (see details in the section of 'analysis of microtube diameter tunability'). The deposition temperature, power, and frequency were maintained at 300 °C, 70 W, and 13.56 MHz for deposition of both SiO<sub>x</sub> and SiN<sub>x</sub> layers.

The  $SiO_x/SiN_x$  bilayers were then patterned into a U-shape (figure 1(A-ii)) through standard photolithography (etch mask: 1.4  $\mu$ m thick S1813, and SiO<sub>x</sub>/SiN<sub>x</sub> etchant: 4.9% hydrofluoric acid). After that, rectangular photoresist strips were patterned to cover the legs of the U-shaped  $SiO_x/SiN_x$  nanomembranes (figure 1(A-iii)), which anchored rolled-up microtubes to the substrate during the releasing process. The  $SiO_x/SiN_x$  nanomembranes were released from their substrate using an aluminum etchant (type-A, Transene Inc.) at 60 °C, during which the  $SiO_x/SiN_x$  bilayers self-rolled once the sacrificial Al layer was etched off (figure 1(A-iv)). Once the rolling-up process was completed, the anchoring photoresist strips were removed. The sample wafer was immersed in DI water, and then in 200-proof isopropyl alcohol (IPA) three times with 20 min immersion for each time. Finally, the sample wafer was dried in a CO<sub>2</sub> critical point dryer (Autosamdri<sup>®</sup>-815, Tousimis). Figure 1(B) shows an array of rolled-up microtubes with the anchor photoresist removed. The final fabrication yield was determined to be 99% (n = 300).

#### 3. Analysis of microtube diameter tunability

In addition to the high rolling-up yield of the microtubes, the tunability of the microtube diameter is also critical for optimizing the sensor performance as it determines the light-path length of the WGM resonance cycle. The good tunability and reproducibility of the microtube diameter are highly desired. To gain insights about the deterministic factors of the microtube diameter, the rolling-up process of the microtube was first theoretically analyzed within the framework of continuum mechanics [33]. Compared to the conventional analytical model of the microtube rolling-up [33], we developed a new model that considers, for the first time, the effects of the longitudinal and transverse mismatch strains simultaneously. The new model can be used to more accurately calculate the curvature  $\kappa$  of a thin-film bilayer with mismatched strains  $\varepsilon_0$  and  $\eta \varepsilon_0$  along the longitudinal and transverse directions respectively. The details of the model derivation can be found in a separate paper [34]. Briefly, this model was derived from the Von-Karman plate theory [35, 36] and Rayleigh–Ritz model [35, 37, 38], and accounts for the anisotropic lattice mismatch coefficient  $\eta$ . Note that, in the particular case of  $\eta = 0$ , equation (1) below simplifies to the Timoshenko formula [39] which was employed by previous studies to predict the roll-up curvature [40, 41]. In our calculations, the mechanical properties of  $SiO_x/SiN_x$  were taken as  $(E_b, E_t) = (72.2, 175)$  GPa, v = 0.25 [42]. Here, we provide the final derived equation of the microtube curvature

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**Figure 1.** (A) Schematic views of the rolled-up microtube fabrication process. (B) SEM image of a rolled-up microtube array and zoomed-in views of a single microtube. (C) Schematic setup for photoluminescence measurement on a rolled-up microtube.

(the reciprocal of the microtube radius):

$$\kappa$$

$$=\frac{6 \cdot \varepsilon_0 \cdot E_b \cdot E_t \cdot h_b \cdot h_t (h_b + h_t)(1 + \eta \nu)}{E_b^2 h_t^4 + 4h_b \cdot h_t \left(h_b^2 + \frac{3}{2}h_t \cdot h_b + h_t^2\right) E_b \cdot E_t + E_t^2 h_t^4},$$

where the bottom and top layers are respectively of Young's moduli ( $E_b$ ,  $E_t$ ), thicknesses ( $h_b$ ,  $h_t$ ), and the same Poisson ratio v. The most straightforward way of tuning the microtube diameter is to adjust the thicknesses ( $h_b$ ,  $h_t$ ) of the two nanomembrane layers because the Young's moduli and Poisson ratio are independent of the film thickness [43].

We also experimentally demonstrated that the built-in stresses ( $\varepsilon_0$  and  $\eta \varepsilon_0$ ) of the SiO<sub>x</sub> and SiN<sub>x</sub> nanomembranes are also independent of the nanomembrane thicknesses. We measured the built-in stresses of SiO<sub>x</sub> and SiN<sub>x</sub> nanomembranes using a film stress measurement system (Flexus 5200, Tencor). The results showed repeatable built-in stresses of – 831.5 ± 21.4 MPa (n = 20; compressive stress) for SiO<sub>x</sub> films of four different thicknesses (15, 25, 35 and 45 nm; five measurements for each thickness) and 221.5 ± 12.1 MPa (n = 15; tensile stress) for SiN<sub>x</sub> films of three different thicknesses (10, 20 and 30 nm; five measurements for each

thickness). Thus, by adjusting the nanomembrane thicknesses, we fabricated microtubes with diameters of  $3.9-16.1 \mu$ m. A scanning electron microscope (SEM, FEI 50) was used to measure the microtube diameter. Figure 2 shows the theoretically predicted (through equation (1)) and experimentally measured microtube diameters as functions of the top (SiN<sub>x</sub>) and bottom (SiO<sub>x</sub>) layer thicknesses. One can see that our developed model accurately predicts the microtube diameter based on the different combination of the nanomembrane thicknesses, and thus can be used for guiding future microtube designs. In addition, the measured microtube diameter for each combination of nanomembrane thicknesses shows a small variation (<0.5  $\mu$ m; n = 10), confirming that the microtube diameter can be well-controlled with high reproducibility.

#### 4. Photoluminescence characterization of microtube

The WGM resonance performance of the fabricated RUM-OC was characterized at room temperature using a photoluminescence (PL) microscope (InVia 3000, Renishaw). An



**Figure 2.** The microtube diameter as a function of (A)  $SiN_x$  and (B)  $SiO_x$  thicknesses (with the thickness of another layer fixed). The theoretically predicated diameters (red lines) are in good agreement with the experimentally measured values (black dots; n = 10).

excitation line at 514 nm was used and the emission spectrum was collected through a 50× objective (numerical aperture: 0.55). The *Q*-factor of a resonance mode is calculated as  $Q = \lambda/\Delta\lambda$ , where the  $\lambda$  is the mode position and  $\Delta\lambda$  is the full width at half maximum of the mode [12].

As shown in figure 3(A), the PL spectrum collected from the center spot of a RUM-OC (6.8  $\mu$ m diameter, 10 nm SiO<sub>x</sub> and 35 nm SiN<sub>x</sub>) showed a broad emission band, which was due to the emission from defect centers inside the SiO<sub>x</sub>/SiN<sub>x</sub> layers [5]. The modulation of the PL intensity by the tubular structure was also clearly observed, which was contributed by the WGM resonance in the tubular structure of the RUM-OC. The WGM resonance modes were polarized in parallel with the microtube axis, corresponding to the transverse magnetic (TM) modes. No clear transverse electric polarization was observed in the PL spectrum due to the lack of axial optical confinement structure in our microtube design [44].

To analyze the observed resonance modes, the azimuthal mode number *M* was calculated by  $M = n_{eff} \frac{d}{\lambda}$ , where  $n_{eff}$  is the effective refractive index of the microtube wall material

and the surrounding medium penetrated by the evanescent field of the guided light, d is the microtube diameter, and  $\lambda$  is the wavelength of the mode. The effective refractive index  $n_{eff}$ can be calculated using  $n_{eff} = x \cdot n_{SiO_x} + (1 - x) \cdot n_{SiN_x}$ where x is the filling ratio of each material for constructing the microtube. For our RUM-OC,  $n_{eff}$  was calculated to be 1.86. The Q-factor was then calculated for each mode by extracting the value of  $\Delta\lambda$  using Lorenz fitting, and the highest Q-factor was determined to be 880 at mode 39. This Q-factor is much higher than the reported value ( $\sim 100$ ) of non-HfO<sub>2</sub>-coated  $SiO/SiO_2$  RUM-OCs [44], and is comparable to that (660) of HfO<sub>2</sub>-coated SiO/SiO<sub>2</sub> RUM-OCs [12]. We also fabricated SiO/SiO<sub>2</sub> RUM-OCs using e-beam evaporation (without HfO<sub>2</sub> coating) with the same microtube diameter (6.8  $\mu$ m) and the same total microtube wall thickness (45 nm; 10 nm for SiO and 35 nm for SiO<sub>2</sub>), and compared their Q-factor with that of our  $SiO_x/SiN_x$  RUM-OC. Figure 3(B) shows a typical PL spectrum measured on a SiO/SiO<sub>2</sub> RUM-OC. The highest Q-factor of the SiO/SiO<sub>2</sub> RUM-OC was measured to be 50, which is much lower than that of our  $SiO_x/SiN_x$ RUM-OC.

The enhanced *Q*-factor of our  $\text{SiO}_x/\text{SiN}_x$  RUM-OC is mainly due to the higher refractive index of the  $\text{SiN}_x$  film in the visible range over that of the  $\text{SiO}_2$  film, which was confirmed by our ellipsometry measurement results shown in figures 3(C) and (D). One can see that the refractive index of  $\text{SiN}_x$  was measured to be ~66.7% higher than that of the  $\text{SiO}_x$ . Although the *Q*-factor is still lower than the previously reported value of  $\text{Y}_2\text{O}_3/\text{ZrO}_2$  RUM-OC [17], the low light absorption of our  $\text{SiO}_x/\text{SiN}_x$  RUM-OC promises further improvement of its *Q*-factor by using various techniques such as ALD HfO<sub>2</sub> coating [12] and axial light confinement structures [19].

#### 5. Solvent sensing experiments

As a proof-of-concept demonstration, we used the developed  $SiO_x/SiN_x$  RUM-OC for solvent sensing. During optical resonance in the RUM-OC, the WGM evanescent wave penetrates the RUM-OC wall and interacts with its surrounding medium. Once the optical property of the external environment changes, the altered interaction between the WGM evanescent wave and the surrounding medium leads to a detectable change of WGM resonance spectrum; thus, the detection of the surrounding medium of the RUM-OC makes it particularly suitable for medium sensing applications, as the large fraction of the WGM evanescent interacts with the external medium, and thereby promises an enhanced sensitivity.

In the sensing experiments, we measured the PL spectra of the RUM-OC in two different solvents: DI water and ethanol, and compared the measured spectra with the back-ground spectrum of the RUM-OC measured in air (relatively humidity: 40%). The RUM-OCs used in the experiments have a diameter of 6.8  $\mu$ m and a wall thickness of 45 nm (10 nm for SiO<sub>x</sub> and 35 nm for SiN<sub>x</sub>). The PL spectra were collected



**Figure 3.** (A), (B) Photoluminescence (PL) spectra of (A) a SiO<sub>x</sub>/SiN<sub>x</sub> RUM-OC made by PECVD and (B) a SiO/SiO<sub>2</sub> RUM-OC made by e-beam deposition. The intensity of each spectrum is normalized against its strongest mode. (C), (D) Ellipsometry measurement results of the complex refractive indices of (C) SiN<sub>x</sub> and (D) SiO<sub>2</sub> thin-films.  $k(\lambda)$  and  $n(\lambda)$  are the absorption coefficient and refractive index, respectively.

at room temperature using the same 50× objective and excitation line at 514 nm. Figure 4(A) shows the PL spectra of the RUM-OCs in DI water, ethanol, and air. The WGM resonance was observed in the spectra measured in all the three different environments, but with clear differences. Specifically, a red shift of the spectrum occurred once the RUM-OC was immersed into a solvent due to the higher refractive index of the new medium than air. This observation can be explained by this simplified equation:  $2\pi R \cdot n_{eff} \approx M \cdot \lambda$ . For the same mode number *M*, the  $\lambda$  increases with  $n_{eff}$  (the effective reflective index of the microtube wall and the surrounding medium).

To quantify the sensing performance of the developed RUM-OC, the analytical mode positions (based on the mature analytical method [12]) were calculated. The resonant TM modes of an optical cavity can be analyzed by the following

equation with waveguide approximation [12]:

$$\tan\left(\gamma h\right) = \frac{2\delta/\gamma}{1 - (\delta/\gamma)^2},\tag{2}$$

where  $\delta = \sqrt{(2m/d)^2 - \varepsilon_2(2\pi/\lambda_0)^2}$ ,  $\gamma = \sqrt{\varepsilon_1(2\pi/\lambda_0)^2 - (2m/d)^2}$ , *h* and *d* are the tube thickness and diameter respectively, *m* is the azimuthal mode number, and  $\varepsilon_1$  and  $\varepsilon_2$  are the dielectric constants of the microtube wall and surrounding medium respectively. In our calculations, due to the centrosymmetric tube structure, the rolled-up microtube was treated as a slab and no surface curvature effects and notches at the rolling edge of the tube were considered. This treatment simplified it into a twodimensional problem. The effective thickness *h* and the dielectric constant  $\varepsilon_1$  of the microtube wall were obtained by combining the thickness and dielectric constant of the SiO<sub>x</sub> and SiN<sub>x</sub> layers (which constitute the microtube wall), respectively,



**Figure 4.** (A) PL spectra of rolled-up microtubes in different solvents. (B) Peak position of the TM mode as a function of refractive index of surrounding medium. The solid lines are predicted values, and the black, blue, and red triangles represent experimental mode positions in air, water, and ethanol solution, respectively.

using the method derived in [12]. The detailed calculations can be found in the supplementary material available online at stacks.iop.org/NANO/29/415501/mmedia.

The theoretically calculated position shifts and experimental data were shown in figure 4(B). It can be seen that the calculated position shifts agree well with the measured data. The sensitivity of the RUM-OC can thereby be determined by

$$S = \frac{\lambda_{M,ethanol} - \lambda_{M,water}}{n_{ethonal} - n_{water}},$$
(3)

where  $\lambda_{M,ethanol}$  and  $\lambda_{M,water}$  represent the TM mode positions for the same azimuthal number M in ethanol and water, respectively. The  $n_{ethonal} = 1.36$  and  $n_{water} = 1.33$  are the refractive indices of ethanol and water, respectively. The highest sensitivity was determined to be 510 nm/RIU at mode 3. This result is consistent with the analytical calculation showing that a smaller azimuthal number mode possesses a higher sensitivity.

The LOD is another important parameter of the RUM-OC sensor, and can be estimated by

$$LOD = \frac{3\sigma}{S},$$
 (4)

where  $\sigma$  is the standard deviation of the system noise and *S* is the value of the sensitivity. The system noise  $\sigma$  of the RUM-OC was primarily contributed by statistical distributions of the peak position measurements, and could be approximated by  $\sigma = \Delta \lambda / 50$ , where the  $\Delta \lambda$  is the line width [12]. We chose the PL peak at 660 nm (M = 39), with  $\Delta \lambda = 0.75$  nm, as it provided the highest *Q*-factor and thereby the best LOD among all the WGM supporting modes in our RUM-OC. The obtained LOD of our RUM-OC is in the order of 10<sup>-4</sup> RIU, which is 10 times lower than that (10<sup>-3</sup> RIU) of the HfO<sub>2</sub>-coated SiO/SiO<sub>2</sub> RUM-OC [12]. The improved LOD was contributed by the high *Q*-factor of the WGM supporting mode at M = 39. The LOD improvement could be explained by that the light loss during the WGM resonance within the ultrathin wall was reduced by the

high-refractive index of  $SiN_x$ . The enhanced light confinement of the microtube wall prolonged the photon lifetimes, and thereby increased the quality factor, resulting in the improved LOD of the developed sensors.

#### 6. Conclusion

By adopting a new material combination of  $SiO_x$  and  $SiN_x$ , we successfully fabricated RUM-OCs with an enhanced Qfactor and applied them to sensitive solvent sensing. The  $SiN_x$ material featured high-refractive index and zero light absorption in the visible range, and thus provided good light confinement capability for the  $SiO_x/SiN_x$  RUM-OC. The PECVD technique used for synthesizing  $SiO_x$  and  $SiN_x$ allowed facile tuning of the thicknesses and build-in stresses of the  $SiO_x/SiN_x$  bilayers, thus leading to precise and reproducible control of the RUM-OC diameter. Benefiting from the good light confinement capability of  $SiN_x$ , our RUM-OC provided a Q-factor of up to 880, which is comparable to that (660) of the previously reported HfO<sub>2</sub>-coated  $SiO/SiO_2$  RUM-OC and much higher than that (50) of the non-coated SiO/SiO<sub>2</sub> RUM-OC. For solvent sensing, our  $SiO_r/SiN_r$  RUM-OC revealed a sensitivity of 510 nm/RIU and a LOD in the order of  $10^{-4}$  RIU. The LOD of our  $SiO_x/SiN_x$  RUM-OC is 10 times lower than that (10<sup>-3</sup> RIU) of the HfO<sub>2</sub>-coated SiO/SiO<sub>2</sub> RUM-OC.

#### Acknowledgments

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (grant numbers: STPGP/463182-2014, RGPIN-06374-2017, and RGPAS-507980-2017). The authors also acknowledge the financial support from the Canada Research Chairs Program

(grant no. 237293) to X Liu, from the Chinese Scholarship Council to P Song and C Chen, and from CMC Microsystems (for device microfabrication) to P Song. The authors also thank Dr Sasa Ristic at the McGill Nanotools Microfab Facility and Dr Di Han from Fudan University, China for their discussions.

#### **ORCID** iDs

Cheng Chen **b** https://orcid.org/0000-0003-3062-9048 Juntian Qu **b** https://orcid.org/0000-0002-1799-5847 Xinyu Liu **b** https://orcid.org/0000-0001-5705-9765

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