Confined optical modes and amplified spontaneous emission from a microtube cavity formed by vacuum assisted filtration

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The authors demonstrate a new route to the fabrication of individual aluminosilicate microtubes that can act as micron-scale optical cylindrical resonators. The microtubes were prepared using a simple vacuum assisted wetting and filtration through a microchannel glass matrix. Microphotoluminescence spectra of the microtube cavity show sharp resonant modes with quality factors up to 3200. A strong reduction of the emission decay time at high excitation power confirms the occurrence of amplified spontaneous emission from a single microtube. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356691]

Optical emitters with cylindrical or microcapillary dielectric resonators which support whispering gallery modes (WGMs) have gained much interest due to their microscopic size, high quality factor Q, and the possibility of achieving low threshold lasing.[1–3] The resonantly enhanced optical response and material compatibility with telecommunications optical fiber make these high-Q microcavities attractive as novel building blocks for photonic devices. The cylindrical cavity format is also compatible with a large variety of sensing modalities such as immunoassay and molecular diagnostic assay.[4,5]

Experimentally, the most widely studied configuration of thin-wall microtube cavities is the microcapillary filled with a highly luminescent dye solution.[2,3] The diameter (typically 50–200 μm) and wall thickness of these microcapillaries can be controlled by the etching of commercially available glass samples in a HF-water solution. The short-distance evanescence field in these microcavities and the limited photostability of dye molecules may limit potential applications. In the small-size regime (diameter <10 μm), semiconductor microdisks of finite height or micropillars have been widely used as tools to control spontaneous emission and confine photons in three dimensions.[1] The evanescent field in these photonic structures extends a couple of micrometres into the surroundings providing the possibility for efficient coupling to an external photonic device. However, fabrication of small (<10 μm diameter) high-Q cylindrical microcavities generally involves complex and expensive processes.[1,6]

In this letter, we describe a simple method for fabricating highly luminescent small aluminosilicate microtubes (MTs) of $\sim 7-8$ μm outer diameter using sol-gel processing and a microchannel glass membrane as a template. The most important advantage of these hollow MT cavities, as compared to bulk microcylinders or microcapillary filled with dye solution, is the controlled arrangement and placement of the light-emitting dipoles close to the surface of the microcavity. The sharp periodic structure observed in the emission spectra originates from strong light confinement of WGMs in the MT cavity. We also report on the modification of spontaneous emission rate under varying optical excitation which indicates that we have achieved amplification of spontaneous emission (ASE) in the MT.

In our fabrication approach, we took advantage of the well developed sol-gel technique[7,8] combined with the versatility of ordered porous membranes as templates. The $Si(OC_2H_5)_4$ (tetraethylorthosilicate) was first hydrolyzed for 1 h at room temperature with a solution of H_2O, C_2H_5OH, and HCl in the molar ratio 1:1:0.0027 per mole of $Si(OC_2H_5)_4$, respectively. Then $Al(OC_4H_9^{sec})_3$ was added to this solution and the mixture was stirred for 15 min at 70 °C. The resultant homogenous mixture was hydrolyzed by adding the mixed solution of H_2O, C_2H_5OH, and HCl in the molar ratio 4:1:0.011 per mole of alkoxide, respectively. Finally, a 30 min stirring provided the conversion of this sol to $5Al_2O_3 \cdot 95SiO_2$ (mol %) aluminosilicate gel. The sol, just before its gelation point, was then placed on the top of the microchannel glass samples (donated by State Optical Institute, St. Petersburg, Russia) and 30 mbar vacuum assisted filtration resulted in the formation of MT inside the channels. Following drying at room temperature for one day and further annealing at 500 °C for 2 h, the fabricated MTs [Fig. 1(a)] were isolated by the mechanical destruction of the template [Fig. 1(b)]. This thermal treatment regime resulted in highly emissive air-stable samples which display broad visible photoluminescence (PL) originating from carbon substi-

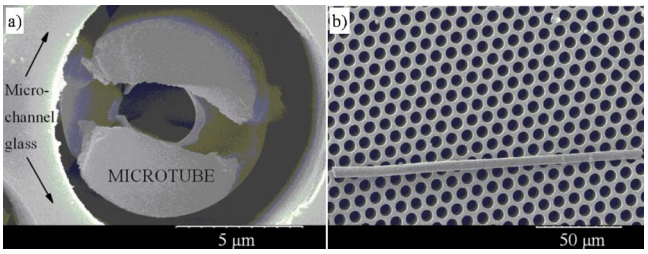

FIG. 1. (Color online) SEM images of aluminosilicate microtubes inside and outside the matrix.

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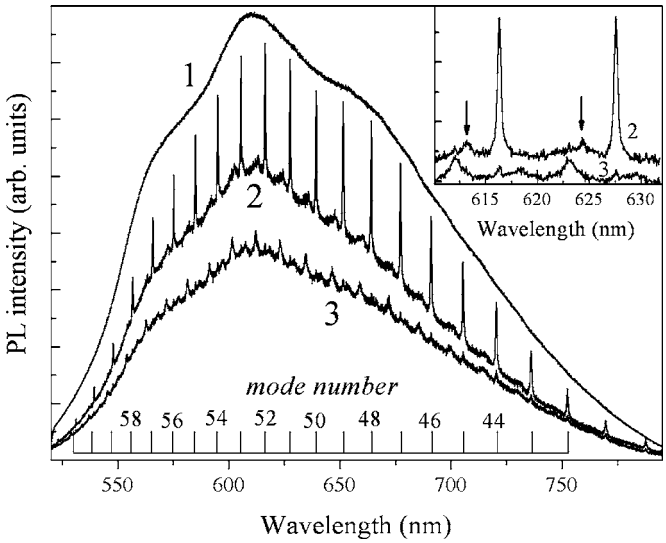

FIG. 2. Room-temperature PL spectra of single microtube accommodated in matrix (1) and freestanding microcavity with polarizer orientation parallel to the microtube axis (2) and polarizer rotated by 90° (3). The upper inset shows a region around TM_{52} WGM with subtracted PL background.

tutional defects for silicon.[8] An elemental analysis study of the annealed aluminosilicate gel showed carbon and hydrogen contents of 0.32% and of 0.56%, respectively. Scanning electron microscopy (SEM) imaging analysis showed that the fabricated MTs have an inner diameter of $\sim 2\ \mu$m. The maximum length of a single MT was 200 μm. The formation of aluminosilicate MTs by the vacuum filtration of gel can be explained by the fact that the cohesive driving forces for complete microchannel filling are substantially weaker than the adhesive forces to the pore walls. Similar phenomena were reported for the formation of polymer nanotubes by wetting of ordered porous templates using a polymer melt.[9]

The optical spectra of the fabricated MT were analyzed by spatially resolved microphotoluminescence (micro-PL) at room temperature. Our micro-PL experimental setup is described elsewhere.[10] An Ar^+ laser (wavelength of 514.5 nm) was used as the optical pump source. A polarizer inserted into the optical beam path in front of the detection system was used in the polarization experiments.

When embedded into the matrix, we observe a broad PL band associated with carbon defects in the MT (Fig. 2, curve 1). In contrast to this broad PL band of the MT embedded in a microporous glass matrix (Fig. 2, curve 1), the emission spectra of single freestanding MTs exhibit very sharp periodic structure (Fig. 2, curves 2 and 3). When separated from the matrix, the MT is much more optically dense than its surrounding medium allowing light propagating inside the MT to be spatially constrained to travel along the rim of a cross section of the MT, and therefore it is said to be trapped in a WGM. The presence of sharp emission peaks in the spectrum of a single MT is an immediate result of this optical confinement (Fig. 2, curves 2 and 3) These peaks correspond to optical resonance locations and reflect the fact that transition probabilities are increased for emission wavelengths near resonance.

In the samples under study, the WGM peaks are superimposed on a background signal arising from part of the emission which does not match any WGM of the MT (Fig. 2). The placement and spacing between WGM peaks are determined by the diameter (D) and refractive index (m) of the microcavity while the spectral intensity distribution depends on the parameters of the emitting species and can be easily modified by doping of the original aluminosilicate gel, for example, by rare earth ions. In order to identify peaks in the observed WGM structure, we have adopted the boundary-value solution to the problem of scattering of plane electromagnetic waves by a dielectric microcylinder.[11] In the framework of this approach WGM of a concentric cylinder can be ascribed to the transverse electric and transverse magnetic (TM) resonant cavity modes with a different angular quantum number n and a radial quantum number l. The most striking feature of the spectra presented in Fig. 2 is the strong polarization properties. The sharp peaks dominating in the spectrum for a polarizer orientation parallel to the MT axis (Fig. 2, curve 2) correspond to linear polarized light with the electric vector vibrating parallel to the axis of cylinder. Rotating the polarizer by 90° results in strong quenching of these WGMs (Fig. 2, curve 3) unambiguously indicating their TM character. The results of the mode identification (TM_n^l) for $m=1.48$ and $D=7.65\ \mu$m are shown in Fig. 2. If we fit the WGM peaks by a Lorentzian function, we find quality factors defined by $Q=\lambda_0/\Delta\lambda$ ranging between 2000 and 3200 with the maximum Q value obtained for the peak centered at 616 nm. The quality factor reflects how long a photon can be stored in the microcavity before leaking out. Since the cavity Q factor is directly related to the lifetime of the photon in the cavity $\tau_{cav}=Q/\omega_0$ (where ω_0 is the resonant frequency), we can estimate a time constant $\tau_{cav}\approx 1$ ps. Physically, the high-Q value results in a small linewidth thereby enhancing the modification of spontaneous emission rate inside the microcavity, which can be characterized by the Purcell factor F.[12] For the investigated MT, the estimated mode volume is in the range of $V\approx 10(\lambda/n)^3$. Together with the obtained Q values, the enhancement of the spontaneous emission rate $F=(3Q(\lambda/n)^3)/(4\pi^2V)$ can be calculated and enhancement factor up to 24 can be expected. This value implies the weak-coupling regime of cavity quantum electrodynamics (CQED) with these MT samples. However, in the context of CQED experiments, the coupling of photons to WGM can be optimized by changing the overall and inner diameters of the MT and by this way eliminating the uncoupled PL emission.

Subtraction of PL background allows us to reveal the presence of satellites: broader peaks of the same polarization, which are blueshifted with respect to the identified WGMs (indicated by arrows in Fig. 2). The separation between these satellites homogeneously increases with wavelength ranging between 8 and 18 nm and is identical to the WGM spacings. Therefore the observed secondary structure cannot be attributed to the WGM of higher l, for which smaller mode spacings are expected. Observation of two resonances of the same mode type can be explained by taking into account the fact that modes other than WGM can be supported by the MT cavity. The presence of the second, inner surface has significant influence on the emission pattern of microcavity systems. As a result, the MT mode structure is more complex than in a single boundary microcavity. Along with WGM originating from total internal reflection at the outer boundary there will be a different kind of mode penetrating the inner region at specific values of inner and outer diameters and refractive index.[3] Weaker photon confinement may led to enhanced losses and therefore to a broadening of these modes. To monitor the surface quality and homogeneity of

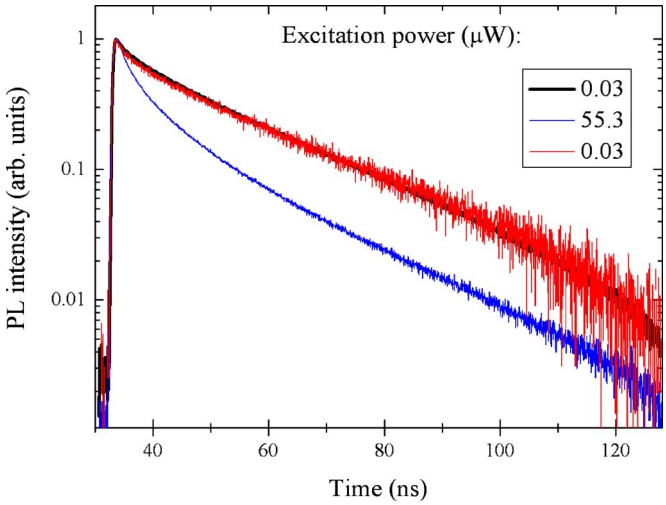

FIG. 3. (Color online) Time-dependent PL intensity decays of a single microtube at varying excitation powers.

the fabricated MT we have studied the micro-PL spectra obtained for different positions of the exciting laser spot along MT axis. It turned out that the WGM positions shifts less than 2 nm over a distance of 10 μm. From our calculations, we have determined that this shift is a result of a difference in MT diameter of only 20 nm.

In order to understand the emission process further, we have studied the micro-PL spectra and lifetime of the PL as a function of intensity (I_{pump}). The MT was excited by 480 nm picosecond pulses at 5 MHz repetition rate generated by LDH-480 laser head controlled by a PDL-800B driver (PicoQuant). In our studies of $I_{\text{PL}}=f(I_{\text{pump}})$ dependence we were not able to demonstrate either threshold behavior of I_{PL} or narrowing of the WGM emission linewidth. The overall spectrum presented in Fig. 2 is unchanged when going into the high intensity regime showing that mode selection and lasing have not occurred. However, the results presented in Fig. 3 confirm that an increase of excitation power leads to a very significant increase of the emission decay rate in the single MT cavity. In these experiments PL decays at varying excitation powers were measured using an Olympus IX71 microscope (40×0.65 Plan Achromat objective) combined with the time-correlated single photon counter (MicroTime200, PicoQuant). The emission was monitored in the region of the TM_{52}^{1} WGM using a narrow band filter. The excitation power was measured just before entering the objective using a calibrated power diode. The pump laser with its polarization parallel to the MT axis was tightly focused (beam size ~1 μm).

The shape of the decay curves (Fig. 3) is nonexponential but very reproducible: going back to low excitation level the original PL decay characteristics are restored. The much faster decay rate at high intensity is due to amplified spontaneous emission. It is noteworthy that ASE is a nonlinear optical phenomenon. As a result, the PL decay observed at higher excitation power is much more nonexponential as compared with this detected in lowexcitation regime (Fig. 3) This fact along with clear decrease in PL lifetime (Fig. 3) lends strong credence to the occurrence of ASE in the MT. The decrease of the emission decay time observed here is due to increased gain in the aluminosilicate glass and this decrease can be efficiently controlled by the excitation power. It is also noteworthy that after 60 ns in the high intensity measurement, the decay time is similar to the low intensity measurement showing that amplified spontaneous emission is no longer occurring at this point following the laser pulse. The decreased decay time at high pump intensity and the reversibility of the decay kinetics show that we have achieved ASE from the MT. This observation demonstrates the high optical quality of these materials and that they have strong potential to act as microlasers. The direct observation of lasing in which a single mode dominates has not been observed to date. In any case, the observation of a lasing threshold is problematic for three-dimensional microcavity structures in general. This is due to the strong coupling of the spontaneous emission to the cavity modes (i.e., the WGM in our case) and the lack of external mirrors.

To summarize, we have developed a simple and robust method for fabricating luminescent aluminosilicate MT and demonstrated the high-Q resonance modes in the emission spectra of a single microcavity. The method of preparation of such structures has the unique advantage of providing high-quality small three-dimensional cylindrical microcavities with strongly polarized emission. The decrease of the emission decay time observed at high excitation power confirms the occurrence of amplified spontaneous emission from a single MT. The fabricated high-Q microcavity structures have significant potential for photonic applications.

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[1]K. J. Vahala, Nature (London) **424**, 839 (2003).
[2]H.-J. Moon, Y.-T. Chough, and K. An, Phys. Rev. Lett. **85**, 3161 (2000).
[3]H. J. Moon, G.-W. Park, S.-B. Lee, K. An, and J. H. Lee, Opt. Commun. **235**, 401 (2004).
[4]R. A. Wallingford and A. G. Ewing, Anal. Chem. **60**, 1972 (1988).
[5]S. Blair and Y. Chen, Appl. Opt. **40**, 570 (2001).
[6]T. Kipp, H. Welsch, Ch. Strelow, Ch. Heyn, and D. Heitmann, Phys. Rev. Lett. **96**, 077403 (2006).
[7]M. Nogami and Y. Abe, J. Non-Cryst. Solids **197**, 73 (1996).
[8]W. H. Green, K. P. Le, J. Grey, T. T. Au, M. J. Sailor, Science **276**, 1826 (1997).
[9]M. Steinhart, J. H. Wendorff, A. Greiner, R. B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, and U. Gosele, Science **296**, 1997 (2002).
[10]Y. P. Rakovich, J. F. Donegan, N. Gaponik, and A. L. Rogach, Appl. Phys. Lett. **83**, 2539 (2003).
[11]M. Kerker and E. Matijevic, J. Opt. Soc. Am. **51**, 506 (1961).
[12]E. M. Purcell, Phys. Rev. **69**, 681 (1946).