Mesoporous Thin-Film on Highly-Sensitive Resonant Chemical Sensor for Relative Humidity and CO_2 Detection

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Mesoporous Silica Thin-Film Synthesis Details

In a typical synthesis, a silica sol-gel was first prepared by an acid-catalyzed process.[15] A prehydrolyzed solution containing 10.4 g of tetraethyl orthosilicate (TEOS, ≥ 99.0%, Sigma-Aldrich), 5.4 g of diluted hydrochloric acid (pH 2) and 12 g of ethanol was stirred vigorously at room temperature for 20 min. This sol-gel was then added to a solution containing a structure-directing agent, a poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) block copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Sigma-Aldrich). The block copolymer solution was prepared by dissolving 1.4 g ~ 2.75 g of P123 in 8 g of ethanol (EtOH). The final mixture was aged between 10 min and 3 h under a stirring condition at room temperature. The amount of triblock copolymer and the aging time are critical in determining the phase morphology, such as lamellar, 3D cubic, and hexagonal structures.[15] Continuous thin films (80 ~ 150 nm in thickness) were then formed by dip-coating at a speed of 6 mm/min on the device, which were left in an ambient condition for 24 h to increase the silica cross-linking. Subsequently, the surfactants were removed by heating the as-deposited thin films at a rate of 1°C/min to 400°C and then holding for 4 h.

APTES-Functionalized Mesoporous Silica Thin-Film Synthesis Details

To prepare APTES-functionalized thin films using the EISA procedure in acidic condition, it is important to neutralize -NH_2 with a strong acid to inhibit fast hydrolysis between TEOS and APTES in the presence of water.[16] A prehydrolyzed solution containing 3.75 g of TEOS in 4.15 g of EtOH, 0.54 g of H_2O and 0.15 ml of 0.01M HCl was vigorously stirred at 60°C for 1 h. 0.5 g of 2M HCL, 2.2 g of H_2O and 18 g of EtOH were added to the prehydrolyzed solution where 0.44 g of (3-aminopropyl) triethoxysilane (APTES, ≥ 98%, Sigma-Aldrich) was immediately added dropwise. 2.75 g of P123 dissolved in 8 g of EtOH was then added to the solution, which was aged for 5 h under a stirring condition. The as-deposited thin-films prepared by dip-coating at a speed of 6 mm/min were left in an ambient condition for 24 h to increase the silica cross-linking. The applied films were calcined by heating at a rate of 1◦C/min to 400◦C and holding for 4 h.

Chemicals

All chemicals were used as received from Sigma-Aldrich (St. Louis, MO, USA) without further purification.

Table S1. Summary of the prepared CMUT sensors with variations in the functionalization layer.

Sample	**Functionalization Layer**	**Synthesis**			
		P123	**Aging Time**	**Calcination Temp**	**Mesophase**
I	Sputtered Oxide	-	-	-	-
II	Non-templated Oxide	0 g	3 hr	400°C	-
III	Mesoporous Silica	1.4 g	20 min	400°C	3D ($P6_3/mmc$)
IV	Mesoporous Silica	2.75 g	3 hr	400°C	2D ($p6mm$)
V	10% APTES Functionalized Mesoporous Silica	2.75 g	5 hr	400°C	2D ($p6mm$)

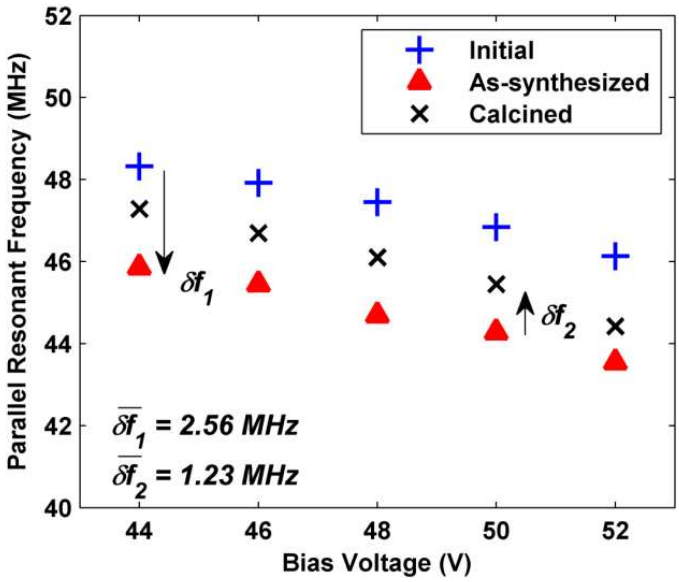

Figure S1. Plot of parallel resonant frequencies at different bias voltages of the CMUT resonant sensor before functionalization, after depositing the as-synthesized film, and after calcination. The measurement resolutions and accuracy of the resonant frequency and the bias voltage are 3.75 kHz with 0.002% (Agilent Technologies, Model 4294A, Palo Alto, CA) and 1 V with 0.05% (Stanford Research Systems, Model PS310, Sunnyvale, CA), respectively.

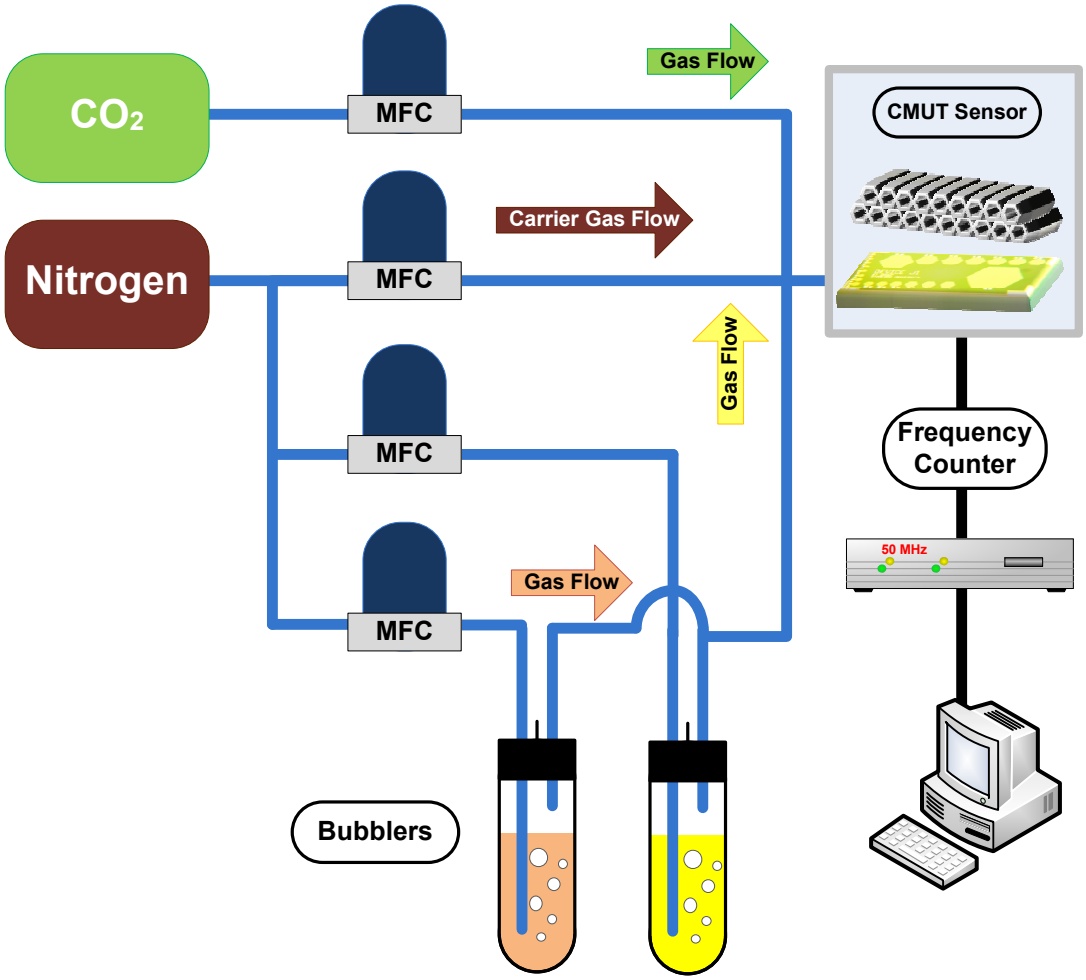

Figure S2. Schematic of the experimental setup. The carrier gas (N_2, Praxair, Danbury, CT) is passed through a mass flow controller which adjusts the flow rate of N_2 injected into a bubbler containing water. The outlet from the bubbler is merged back with the carrier gas and the final mixture of a certain level of relative humidity is delivered to a chamber enclosing the functionalized CMUT sensor. To generate different CO_2 concentrations, the flow rate of CO_2 from the CO_2 gas cylinder (Praxair, Danbury, CT) is adjusted by a mass flow controller and is merged with the carrier gas.

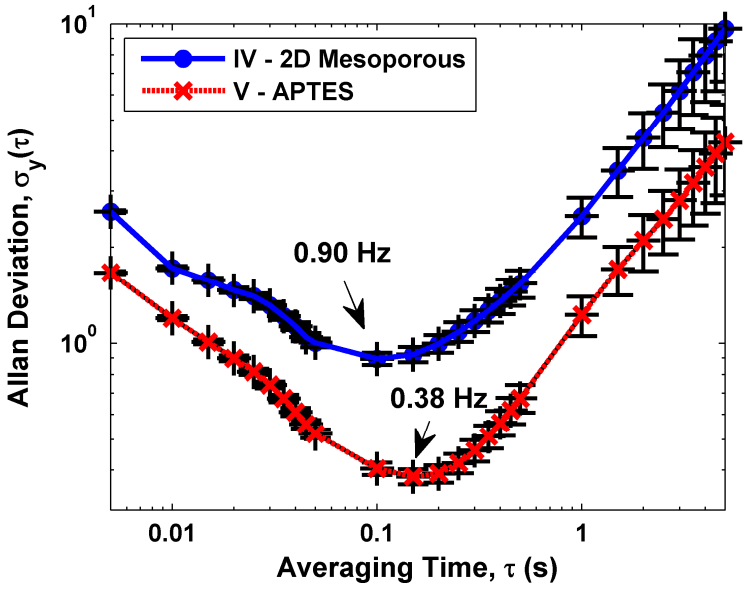

Figure S3. Plot of overlapped Allan deviation calculated from the frequency counter data with a gate time of 5 ms (Stanford Research Systems, Model SRS620, Sunnyvale, CA) over different averaging time. The lowest noise numbers for the oscillators based on the CMUTs functionalized with 2D and APTES-functionalized mesoporous silica thin-films are 0.90 and 0.38 Hz, respectively. The error bars indicate the 1-sigma confidence level.

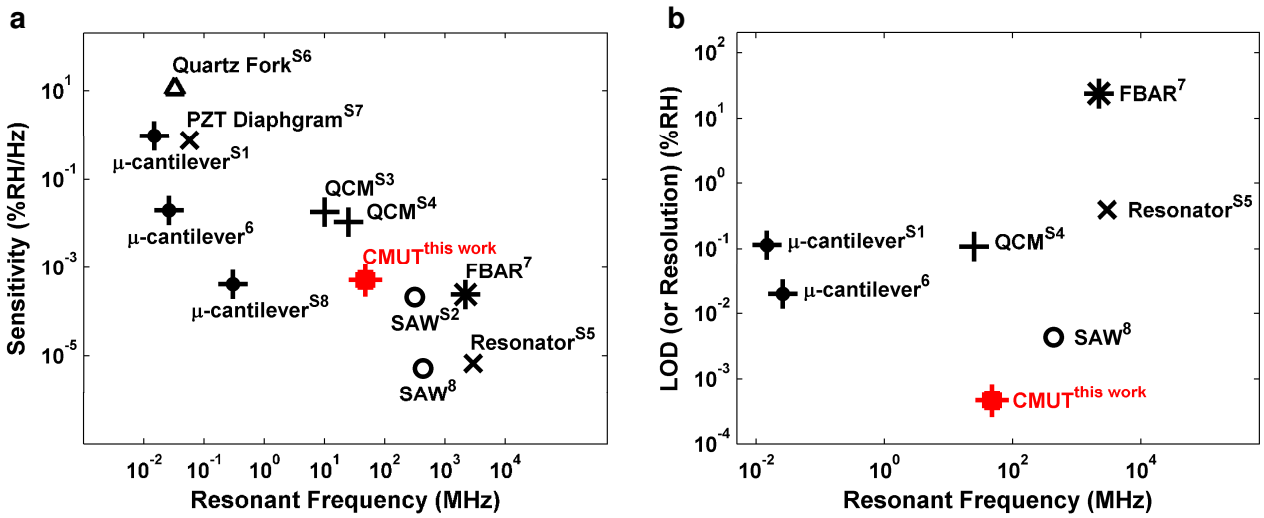

Figure S4. Plot of (a) volume sensitivities and (b) volume resolutions to relative humidity against the operating frequency of the resonant sensors in the literature. Only the works that stated the frequency noise level are presented in (b). The volume resolutions were computed based on the 1-sigma confidence of the frequency noise.

Supplementary References

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