Microbead-assisted high resolution microwave planar ring resonator for organic-vapor sensing

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Microbead-assisted high resolution microwave planar ring resonator for organic-vapor sensing

Mohammad H. Zarifi,[1] Mohammadreza Fayaz,[2] Jordan Goldthorp,[1] Mohammad Abdolrazzaghi,[1] Zaher Hashisho,[2] and Mojgan Daneshmand[1]
[1]*Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada*
[2]*Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 2W2, Canada*

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A microbead-assisted planar microwave resonator for organic vapor sensing applications is presented. The core of this sensor is a planar microstrip split-ring resonator, integrated with an active feedback loop to enhance the initial quality factor from 200 to ~1 M at an operational resonance frequency of 1.42 GHz. Two different types of microbeads, beaded activated carbon (BAC) and polymer based (V503) beads, are investigated in non-contact mode for use as gas adsorbents in the gas sensing device. 2-Butoxyethanol (BE) is used in various concentrations as the target gas, and the transmitted power (S21) of the two port resonator is measured. The two main microwave parameters of resonance frequency and quality factor are extracted from S21 since these parameters are less susceptible to environmental and instrumental noise than the amplitude. Measured results demonstrate a minimum resonance frequency shift of 10 kHz for a 35 ppm concentration of BE exposure to carbon beads and 160 kHz for the polymer based adsorbent at the same concentration. The quality factor of the resonator also changed for different concentrations, but a distinguishable variation is observed for the BAC adsorbents. The high quality factor of the sensor provides the opportunity of real time monitoring of the adsorbent behaviors in remote sensing mode with very high resolution. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4907944]

The presence of volatile organic compounds (VOCs) in ambient air can result in negative effects on human health. For instance, toluene causes vertigo symptoms, benzene is carcinogenic, and many other VOCs cause headaches, dizziness, or eye irritation.[1] Prolonged exposure to VOCs can damage the liver and central nervous system.[2] VOCs can be captured and, in some cases, removed from the air through several techniques such as adsorption,[3] absorption,[4] oxidation,[5] incineration,[6] biofiltration,[7] condensation,[8] and membrane separation.[9] Compared to other control techniques, adsorption is more cost-effective and efficient.

Microwave resonators have been used for sensing applications in areas ranging from material characterization to environmental system monitoring.[10,11] Different types of microwave resonators have been studied for sensing purposes, but planar structures have gathered more attraction than others because of their simple structure, ease of fabrication, CMOS compatibility, and low cost. Their results have high reproducibility and demonstrate less sensitivity to the mechanical and thermal noise of the ambient environment.[12–16] A very attractive application for the microwave planar structure is gas sensing.[17–19] The permittivity of low concentrations of target gas molecules is not detectable by a bare microwave resonator, therefore, a separation process is performed to enable gas sensing. VOC adsorption on an adsorbent has been widely used for gas sensing, where changes in dielectric properties of the loading adsorbent can be monitored.[20] Adsorption occurs on the surface of adsorbent, therefore properties such as surface area and polarity play an important role in adsorption. To have high adsorption capacity, adsorbent should contain high surface area and high porosity. Depending on the size, porosity could be categorized into three major groups: micropores (less than 2 nm), mesopores (between 2 and 50 nm), and macropores (larger than 50 nm). Micropores are filled at low vapor pressures through pore filling mechanism. For larger pores, such as mesopores, capillary condensation is the dominant adsorption mechanism, where molecules condense on the layer of molecules previously adsorbed on the surface of the pore. In the adsorbent pores, the adsorbate molecules are in a liquid-like state. Therefore, adsorption is able to enhance gas sensing by concentrating gas molecules in a small volume.

In adsorption, the target gas molecules, penetrating into the pores, change the permittivity and electromagnetic conductivity of the blank adsorbent. The variation in the adsorbed material is here detected by the microwave resonator as an indication of the target gas concentration.

Different gas concentrations result in different level of pore filling and create different variations in permittivity and resistivity, which can be characterized as variations in the quality factor and resonance frequency of the resonator.[21,22] Mason *et al.*[23] have demonstrated a very powerful technique utilizing a microwave cavity to monitor and evaluate activated carbon bead lifetime. However, they used a 3D microwave cavity with beads inside, and passed the flow directly into the cavity in contact with the microwave device. In this work, a state of the art microwave planar microstrip resonator with an active feedback loop was designed and fabricated to perform the noncontact measurement of organic vapor concentrations. This is accomplished by monitoring the

microwave behavior of the beaded adsorbents once they are exposed to an organic vapor.

The selected adsorbents were microporous beaded activated carbon (BAC) (Kureha Corporation) and a microporous/mesoporous polymeric adsorbent (DOWEX Optipore V503). The BET surface area, total pore volume, and micropore volume of the BAC were 1371 m^2/g, 0.55 cm^3/g, and 0.50 cm^3/g, respectively. The BET surface area, total pore volume, and micropore volume of the polymeric adsorbent were 963 m^2/g, 0.79 cm^3/g, and 0.20 cm^3/g, respectively. These properties were determined with N_2 adsorption at 77 K (iQ2MP, Quantachrome). Also 2-butoxyethanol (BE) (ACROS ORGANICS) was selected as adsorbate.

The setup consisted of a tube, vapor generation system, gas detection system, and data acquisition and control (DAC) system. The adsorption tube was made of quartz (2.2 cm inner diameter) filled with 4.1 ± 0.1 g of virgin BAC, a fritted glass disk held the BAC bed in place. The vapor generation system consisted of a syringe pump (KD Scientific, KDS-220) that injected liquid solvent into a dry, 20 standard liters per minute (SLPM, measured at 25 °C and 1 atm) air stream to achieve the desired inlet concentration, ranging from 35 to 695 ppm_v. The air flow rate was set using a mass flow controller (Alicat Scientific). The gas detection system consisted of a photoionization detector (PID, Minirae 2000, Rae Systems) that monitored VOC concentration at the adsorption tube's outlet. The PID was calibrated before each test using the adsorbate stream generated with the vapor generation system. The BAC was fully loaded to its equilibrium adsorption capacity, during all adsorption experiments, as indicated by the PID measurements. The DAC system consisted of a LabVIEW program (National Instruments) and a data logger (National Instruments, Compact DAC) equipped with analog input and output modules for recording outlet VOC concentration. The sensor setup is shown in Figure 1(a).

The resonator was placed at a fixed distance of 1 cm away from the tube for all measurements.

The core of this noncontact sensor is a microwave split ring resonator (shown in Figure 2), which utilizes an active feedback loop with an active device to compensate the energy loss in the resonator and create a very high quality

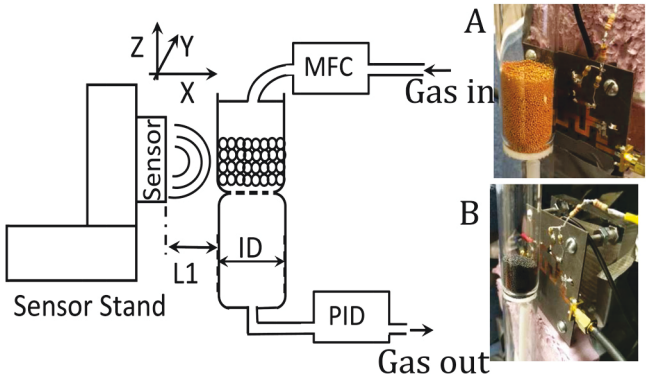

FIG. 1. Schematic for the measurement setup and beaded adsorbents in an adsorption tube in the vicinity of the sensor to perform the noncontact gas sensing (a) polymer based adsorbent (V503) and (b) beaded activated carbon. During the experiments, the weight of the samples was kept constant and because of the lower density of V503 it has higher volume than beaded activated carbon.

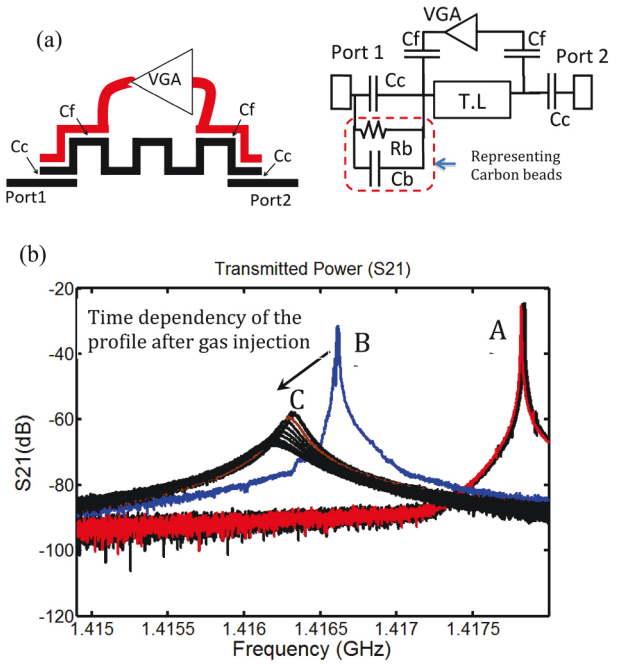

FIG. 2. (a) Resonator structure and the associated circuit model for the resonator and the adsorbent materials (b) S21 measurements for different media of (A) Air, (B) blank beaded activated carbon and tube, and (C) Time-based response of the sensor to gas injection in the tube.

factor in the resonator's resonance profile.[24,25] The electrical properties of the adsorbent material are modeled as a parallel RC circuit, where the change in permittivity affects the capacitor Cb and variation in the loss tangent impacts the resistor Rb. During the experiments, the DC bias voltage of the active device, which determines the quality factor of the sensor, was kept constant at 750 mV for the measurements.[24] The quality factor of the bare resonator, without any sample material, was measured to be around 900 K at the resonance frequency of 1.42 GHz. Having such a high quality factor significantly reduces the minimum detectable variations in the electrical permittivity, as shown in Eq. (1), and increases the resolution of the sensor[24]

$$|\Delta\varepsilon_{min}| = \frac{\alpha\varepsilon}{V_{omax}Q} \times \sqrt{4kTBR}, \tag{1}$$

where $k = 1.38 \times 10^{-23}$, T is the room temperature in Kelvin, B is the measured bandwidth, R is the resistivity of the device, ε is the permittivity, α is a compensation constant, and V_{omax} is the maximum amplitude of the resonance profile.[24]

The scattering parameters (S21) were measured using a vector network analyzer (VNA-E8362, Agilent Technologies). Real time measurements were performed while the gas was flowing inside the tube in the vicinity of the resonator, and automated data acquisition was performed using Labview software. The scattering parameters were measured and recorded for every 1 min until the beads reached their saturation adsorption capacity and the outlet gas concentration from the tube became equal to the inlet gas concentration. The saturation time for the beads depended on the initial concentration of the inlet gas and varied for different concentrations. The saturation time ranged

from 60 min for a relative pressure of 0.6 to 8 h for a relative pressure of 0.03. Figure 2 demonstrates the measured scattering profile of the sensor in different states, (A) with air ambient, (B) in the vicinity of the adsorption tube filled by blank beaded activated carbon with no gas flow, and (C) in presence of the constant concentration of gas inside the tube and the time dependency of the profile. The microwave sensor in air, with no adsorbing material nearby, showed a quality factor of 268 K at a resonance frequency of 1.4178 GHz. This measurement was performed several times prior to experiments and the resonance frequency and quality factor of the sensor remained constant in all measurements. Then, the blank sample (quartz crystal with beaded activated carbon) was placed at a constant distance from the sensor. Since the beaded activated carbon are lossy with high permittivity, quality factor and resonance frequency drop to 110 K and 1.4167 GHz, respectively. Introducing gas to the quartz tube affects both permittivity and loss tangent of the beads and creates a down shift in the frequency response of the sensor.

As shown in Figure 2, a simple circuit model can be drawn for the resonator including the adsorbent beads. The model for the adsorbents is shown with Cb and Rb. The beaded activated carbon is a lossy material with higher permittivity than air, therefore the equivalent permittivity in that medium can be considered as $\varepsilon = \varepsilon' - j\varepsilon''$, where ε'' is representative of loss in the ambient air. Loss tangent is a related quantity for a lossy material which is defined as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}. \tag{2}$$

According to Eq. (2) a relation between complex permittivity and loss tangent can be drawn

$$\varepsilon = \varepsilon'(1 - j\tan\delta). \tag{3}$$

Substituting Eq. (3) into a capacitor model, a parallel RC circuit with $Cb \propto \varepsilon'$ and $Rb = \frac{1}{C\times\omega\times\tan\delta}$ is obtained, as shown in Figure 2(a).

Having the adsorbent beads in quartz tube affect the resonance frequency and quality factor of the resonator by changing the permittivity of the sensor ambient. The proposed structure with an active device in the feedback loop has capability of retrieving the quality factor to a very high value by changing the bias voltage and gain of the transistor consequently. This initial value of the resonance frequency and the quality factor are used as the base line for the measurements. Introducing the gas through the tube and bed, affects the permittivity of the beads. Accumulation of gas molecules, in a liquid-like state, inside the pores resulted in increasing the permittivity and loss factor in the environment.

Therefore, changes in effective complex permittivity affect the resonance frequency as well as the quality factor of the sensor through variations of Cb and Rb. The designed sensor enables real time monitoring of the microwave behavior of beaded adsorbents in terms of loss and permittivity, as shown in Figure 3. In this figure, beaded activated carbon is used as the adsorbent material and two different relative vapor pressures (P/P_0) of 0.2 and 0.6 for 2–Butoxyethanol are compared. More changes in frequency and quality factor are observed for higher vapor pressures, which represent

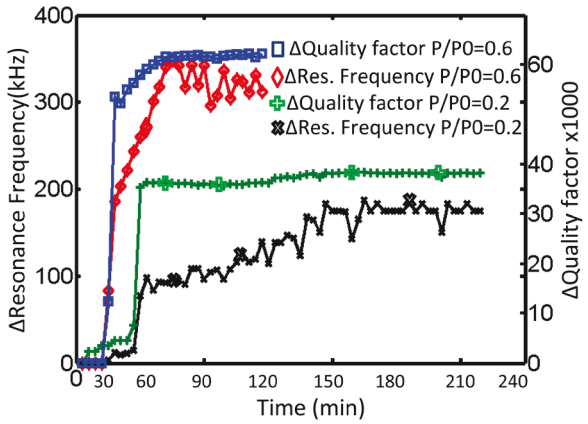

FIG. 3. Sensor transient behavior for the two different concentrations of 266 ppm (P/P0 = 0.2) and 654 ppm (P/P0 = 0.6) of 2-Butoxyethanol on BAC adsorbent. Transmitted power is measured and the quality factor and resonance frequency is extracted for duration of 4 1/2 h.

higher concentrations of gas. High concentrations of gas show faster response times than lower concentrations, which are explained by the adsorption mechanism. During our experiments, for P/Po = 0.6 to P/Po = 0.03, settling times of the sensor response between 1 h and 24 h are recorded. Quality factor measurement is performed as the ratio of the resonance frequency in S21 profile (where the amplitude has a peak value) to the −3 dB bandwidth, where the amplitude of the profile at associated frequencies drops to $1/\sqrt{2}$ of the maximum value of the amplitude.

The same sets of experiments were performed for the polymeric adsorbent (V503) at various gas concentrations for the same adsorbent, and the resonance frequency shift after stabilizing the gas was recorded (sensor's settling time varies between 1 h to 20 h for P/Po = 0.03 to P/Po = 0.6). The results are compared with those of BAC and presented in Figure 4. According to the measurements, BAC has higher electromagnetic loss compared to polymer based beads when loaded, but polymeric beads show a greater shift in resonance frequency which demonstrates the difference in their adsorption behavior. It is also observed that polymeric beads

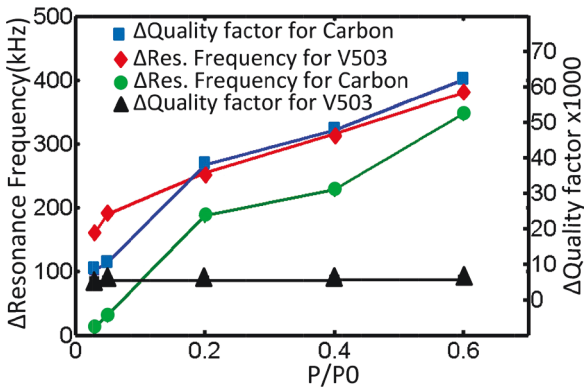

FIG. 4. Quality factor and resonance frequency variations of the microwave sensor for different concentrations of 2-Butoxyethanol in the presence of beaded activated carbon and polymeric beads. Measurements demonstrate that the polymeric beads create less change in the quality factor of the sensor, which shows their low loss tangent and superior transparency to microwave signals.

show more swelling than carbon beads. Since the microwave sensor is a volumetric device, this also contributes to a greater shift in the resonance frequency when compared to the carbon beads.

In conclusion, this work reports a state of the art, low cost, very high resolution sensor for noncontact gas sensing applications. The noncontact operation of the sensor makes it more attractive for dangerous and toxic gas detection, since the sensing platform does not need to be in the gas-flowing medium. The reported device also enables the precise, real time monitoring of the adsorbent beads to estimate their adsorbent behavior. The experimental results demonstrated a minimum variation of 10 kHz in the resonance frequency of the microwave resonator in the presence of the beaded activated carbon adsorbent. Noise and response time reduction are main challenges in sensor device implementation,[26] where in the reported device the main source of the noise is the thermal and high frequency noise of the active device. This means that the temperature effect on the sensor during condensing the gas molecules over the adsorbent beads must be considered. In the reported experiments, the temperature of the sensing environment is almost constant at room temperature. But the effect of temperature will be studied in the future work to reduce the frequency jitter effect and increase the accuracy of the sensor. Post-processing techniques, such as spectral analysis and Karhunen–Loève Transform,[27] can also be employed for the thermal noise and drift reduction in the proposed sensor. The post processing techniques can improve the readout in while the noise is deteriorated the frequency shift. The reported device has the advantage of easy miniaturization and compatibility with CMOS integrated circuits, which makes it implantable in handheld devices, gas masks, and environmental monitoring systems.

[1]X. Chen, L. Feng, H. Luo, and H. Cheng, "Analyses on influencing factors of airborne VOCS pollution in taxi cabins," Environ. Sci. Pollut. Res. **21.22**, 12868–12882 (2014).

[2]D. Das, V. Gaur, and N. Verma, "Removal of volatile organic compound by activated carbon fiber," Carbon **42**(14), 2949–2962 (2004).

[3]Z. Hashisho, H. Emamipour, M. J. Rood, K. J. Hay, B. J. Kim, and D. Thurston, "Concomitant adsorption and desorption of organic vapor in dry and humid air streams using microwave and direct electrothermal swing adsorption," Environ. Sci. Technol. **42**(24), 9317–9322 (2008).

[4]C. Y. Chiang, Y. Y. Liu, Y. S. Chen, and H. S. Liu, "Absorption of hydrophobic volatile organic compounds by a rotating packed bed," Ind. Eng. Chem. Res. **51**(27), 9441–9445 (2012).

[5]F. Tang and X. Yang, "A 'deactivation' kinetic model for predicting the performance of photocatalytic degradation of indoor toluene, o-xylene, and benzene," Build. Environ. **56**, 329–334 (2012).

[6]P. Stehlik, R. Dvorak, L. Bebar, and T. Parizek, "Up to date technologies for off-gas cleaning," in *Proceedings of the 2008 Global Symposium on Recycling, Waste Treatment and Clean Technology, REWAS* (2008), pp. 1367–1372.

[7]S. Detchanamurthy and P. A. Gostomski, "Biofiltration for treating VOCs: An overview," Rev. Environ. Sci. Biotechnol. **11.3**, 231–241 (2012).

[8]R. F. Dunn and M. M. El-Halwagi, "Selection of optimal VOC-condensation systems," Waste Manage. **14**(2), 103–113 (1994).

[9]S. Schnabel, P. Moulin, Q. T. Nguyen, D. Roizard, and P. Aptel, "Removal of volatile organic components (VOCs) from water by pervaporation: separation improvement by Dean vortices," J. Membr. Sci. **142**(1), 129–141 (1998).

[10]H. J. Lee, H.-S. Lee, K.-H. Yoo, and J.-G. Yook, "DNA sensing using split-ring resonator alone at microwave regime," J. Appl. Phys. **108**(1), 014908 (2010).

[11]O. Korostynska, A. Mason, and A. Al-Shamma'a, "Microwave sensors for the non-invasive monitoring of industrial and medical applications," Sens. Rev. **34**(2), 182–191 (2014).

[12]A. A. Abduljabar, S. Member, D. J. Rowe, A. Porch, and D. A. Barrow, "Novel microwave micro fluoidic sensor using a microstrip split-ring resonator," IEEE Trans. Microwave Theory Tech. **62**(3), 679–688 (2014).

[13]H.-J. Lee, J.-H. Lee, and H.-I. Jung, "A symmetric metamaterial element-based RF biosensor for rapid and label-free detection," Appl. Phys. Lett. **99**(16), 163703 (2011).

[14]A. Oprea, N. Barsan, U. Weimar, M. Bauersfeld, D. Ebling, and J. Wollenstein, "Capacitive humidity sensors on flexible RFID labels," Sensors Actuators B Chem. **132**(2), 404–410 (2008).

[15]K. Saeed, A. C. Guyette, I. C. Hunter, and R. D. Pollard, "Microstrip resonator technique for measuring dielectric permittivity of liquid solvents and for solution sensing," *IEEE/MTT-S International Microwave Symposium 2007* (2007), pp. 1185–1188.

[16]H. J. Lee, J.-H. Lee, H.-S. Moon *et al.*, "A planar split-ring resonator-based microwave biosensor for label-free detection of biomolecules," Sensors Actuators B Chem. **169**, 26–31 (2012).

[17]R. A. Potyrailo, N. Nagraj, C. Surman *et al.*, "Wireless sensors and sensor networks for homeland security applications," Trends Analyt. Chem. **40**(4), 133–145 (2012).

[18]R. A. Potyrailo and W. G. Morris, "Multianalyte chemical identification and quantitation using a single radio frequency identification sensor," Anal. Chem. **79**(1), 45–51 (2007).

[19]M. H. Zarifi, A. Sohrabi, P. Mojir Shaibani, M. Daneshmand, and T. Thundat, "Detection of volatile organic compounds using microwave sensors," IEEE Sens. J. **15**, 248 (2014).

[20]W. T. Chen, K. M. E. Stewart, J. Carroll, R. Mansour, and A. Penlidis, "Novel gaseous phase ethanol sensor implemented with underloaded RF resonator for sendor-embedded passive chipless RFIDS," *The 17th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS & EUROSENSORS XXVII), 2013 Transducers & Eurosensors XXVII* (IEEE, 2013), pp. 2059–2062.

[21]S. Lowell and J. E. Shields, *Powder Surface Area and Porosity*, 3rd ed. (Chapman & Hall, London, New York, 1991), p xii, 250 p.

[22]C. B. Roop and M. Goyal, *Activated Carbon Adsorption* (Taylor and Francis, 2005).

[23]A. Mason, O. Korostynska, S. Wylie, and A. I. Al-Shamma'a, "Non-destructive evaluation of an activated carbon using microwaves to determine residual life," Carbon **67**, 1–9 (2014).

[24]M.-F. Joubert, S. A. Kazanskii, Y. Guyot, J.-C. Gâcon, and C. Pédrini, "Microwave study of photoconductivity induced by laser pulses in rare-earth-doped dielectric crystals," Phys. Rev. B **69**(16), 165217 (2004).

[25]A. M. Jones, J. F. Kelly, J. Tedeschi, and J. S. McCloy, "Design considerations for high-Q bandpass microwave oscillator sensors based upon resonant amplification," Appl. Phys. Lett. **104**, 253507 (2014).

[26]R. H. Farahi, A. Passian, L. Tetard, and T. Thundat, "Critical issues in sensor science to aid food and water safety," ACS NANO **6(6)**, 4548–4556 (2012).

[27]V. V. Zaharov, R. H. Farahi, P. J. Snyder, B. H. Davison, and A. Passian, "Karhunen-Loeve treatment to remove noise and facilitate data analysis in sensing, spectroscopy and other applications," Analyst **139**(22), 5927–5935 (2014).