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Hazardous materials sensing: An electrical metamaterial approach

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ABSTRACT

Metamaterials are recently emerging materials exhibiting amazing properties such as extremely miniaturized antennas, waveguides, optical couplers, multiplexers and filters. Such structures also respond to the variation in their ambient conditions when exposed to toxic and hazardous materials, which are especially hazardous to human health. Through this manuscript, we document our studies on three different high energy materials; namely 2- bromo-2nitropropane-1,3-diol (BNP), bis (1,3-diazido prop-2-yl) malonate (AM) and bis (1,3-diazido prop-2-yl) glutarate (AG). A Complementary Split Ring Resonator has been fabricated at resonant frequency of 4.48 GHz using copper on FR4 substrate. The energetic materials were exposed to the sensor and results were monitored using Vector Network Analyzer. The volume of liquids was varied from 0.5 μL to 3 μL. Prominent and explicit shifts in the transmission resonant frequency and amplitude was seen as a signature of each energetic material. The signatures were not only sensitive to the specific toxic group in the material but also to the volume of the liquid subjected to this sensor. The results are correlated with the simulation results, basic chemistry of the materials and permittivity measurements. The ultra-fast reversibility and repeatability, with good sensitivity and specificity of these devices project their applications in sensitive locations, particularly to combat for human security and health issues.

1. Introduction

Given any application in any industrial sector, sensors play a significant role in any instrumentation, processing and manufacturing cycle. In this context, metamaterials [1,2] are set to establish a new class of materials which could revolutionize the scope of science and range of applications. These artificially engineered structured materials are also envisaged for high end applications such as cloaking and superlens [3,4]. They are being explored due to their unique capability to manipulate the basic electromagnetic parameters along the entire electromagnetic spectrum and also offer extreme miniaturization. A simple antenna of such structures can be implemented in the size much less than conventional $\lambda/2$ sized-device. This is a unique opportunity to achieve miniaturized devices.

Amongst a wide range of sensors, high energy materials (HEMs) detection is one of the biggest branches of R&D, wherein a continuous need of improvement is there [5,6]. They are extremely vital for national security, especially in terms of chemical and biological warfare diagnostics (CBW). HEM sensors are broadly categorized into electrochemical, mass, optical and biosensors depending on the type of measurement. These types of sensor are fast, easily reproducible, inexpensive, highly sensitive with a potential option for miniaturization. But there are many challenges. Most explicit requirements for a sensor at on-site detection can be stated as: high sensitivity, high selectivity, low response time, easy reproducibility, reusability, low deployment cost, fast recovery, reversibility and room-temperature sensing. Such HEMs are also detected using spectrophotometric methods which include ion mobile spectroscopy, mass spectroscopy, laser induced breakdown spectroscopy, Raman and Tera-Hertz spectroscopy; which are expensive and bulky and hence not suitable for on-site detection [7,8]. In this sense, improvement of sensors is still much needed. Metamaterials have just recently been explored for sensing applications in various spectral regimes i.e. microwave, terahertz, infrared to optics [9,10]. The resonators at terahertz and infrared regime though being accurate and fast with high sensitivity and selectivity, have huge shortcomings of complex designing and fabrication, as they require sophisticated fabrication tools, which lead to high cost [11]. Microwave regime however is still considered a suitable choice for various applications, including

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sensing because they offer various other advantages which include high sensitivity, selectivity, label free, quick response time and low fabrication costs [12]. Metamaterial resonators we propose here, resonate at λ/12 i.e. corresponding to 83% size reduction than conventional microwave resonators (λ/2), and hence are also known as electrically small resonators. They have been explored for various sensing applications such as biosensing, displacement, rotation, strain, chemical and gas sensing [13–18]. On the other hand, Complementary Split Ring Resonators [CSRRs] [19] interact with the electric fields of electromagnetic wave exhibit negative permittivity and have better sensitivity than SRRs [20], therefore being more suitable choice for sensing applications. Till now, CSRRs have been explored for dielectric characterization of planar materials, liquids, antennas and filters [20–24].

In this manuscript, we have explored the application of CSRR circuits for sensing of HEM, one of which is of propellant category [25]. The sensing studies show that the sensitivity and reversibility of the sensors is extremely high. The results have been carefully attributed to the dielectric properties of the various energetic materials and the effect of polarizability and loss of the material, which induce the observed changes in the resonant frequency. Simulation studies have been done to show the good agreement with the experimental data. It can be envisaged from these studies that metamaterial based sensors show extremely good promise for chemical and biological warfare (CBW) diagnostics; especially for propellant and explosive detection. CSRR structures were fabricated using standard UV photolithography technique with copper on conventional FR4-epoxy substrate which is low cost and has loss tangent independent of frequency upto 12 GHz [26,27]. Three different materials namely 2- bromo-2nitropropane-1,3-diol (BNP), bis (1,3-diazido prop-2-yl) malonate (AM) and bis (1,3-diazido prop-2-yl) glutarate (AG) were sensed using the CSRR based microstrip device using Vector Network Analyser (VNA, Agilent PNA N2225A). The results were simulated in CST Microwave Studio (Electromagnetic FDTD solver software). The dielectric measurements were done using Agilent Dielectric Probe Kit (85070E). Extremely fast response and recovery time, small size, real time, label free, highly sensitive, low profile and easily integrated microstrip-based CSRR sensor is hence projected for HEMs sensing.

2. Design, theory and simulation

CSRR structures are considered as dual complements of SRRs [28] which exhibit negative permittivity by electric field excitation. Since CSRRs are excited by electric field perpendicular to its plane, they are more sensitive to change in permittivity of the surroundings and have better sensitivity than SRRs. The simplest way to excite the CSRR with the electric field is to excite it through microstrip transmission line. The electric field lines in this case interact with the CSRR, giving a sharp dip in transmission around the resonant frequency of the CSRR structure. In this work, CSRR based microstrip device was first designed, modeled and simulated. The resonant frequency selected was initially set to 4.5 GHz. The CSRR was etched out at the ground of the microstrip which behaved as a band stop filter [19]. Fig. 1(a) shows the copper structure which was fabricated on a commercially available FR4 epoxy ($\varepsilon r = 4.4$ thickness $h = 0.8$ mm) substrate. The dimensions were fixed as $a = 5.24$ mm, $c = 0.5$ mm, $d = 0.6$ mm and $g = 0.92$ mm.The upper plane conductor strip had a width 1.4 mm, corresponding to a characteristic impedance of 50 Ω. The complete size of the device was 4 cm × 2 cm. Fig. 1(b) shows the equivalent circuit of the fabricated structure. The fabricated CSRR was soldered with SMA connectors at both ends and thereafter connected to the VNA. The sensing set up is shown in Fig. 1(c). Theoretically, the physical dimensions necessary to achieve this frequency was calculated by using the following design formulas [29]:

$$\omega_0 = 2\pi f_o = \left(L_c C_c\right)^{-1/2} \tag{1}$$

ω_0 is the angular resonant frequency L_C and C_C are inductance and capacitance of the CSRR. The capacitance C_C is dependent mainly on real part of permittivity ε and is directly proportional to it whereas L_C is dependent on permeability μ.

From the circuit, the dispersion relation can be obtained by simple calculation as follows:

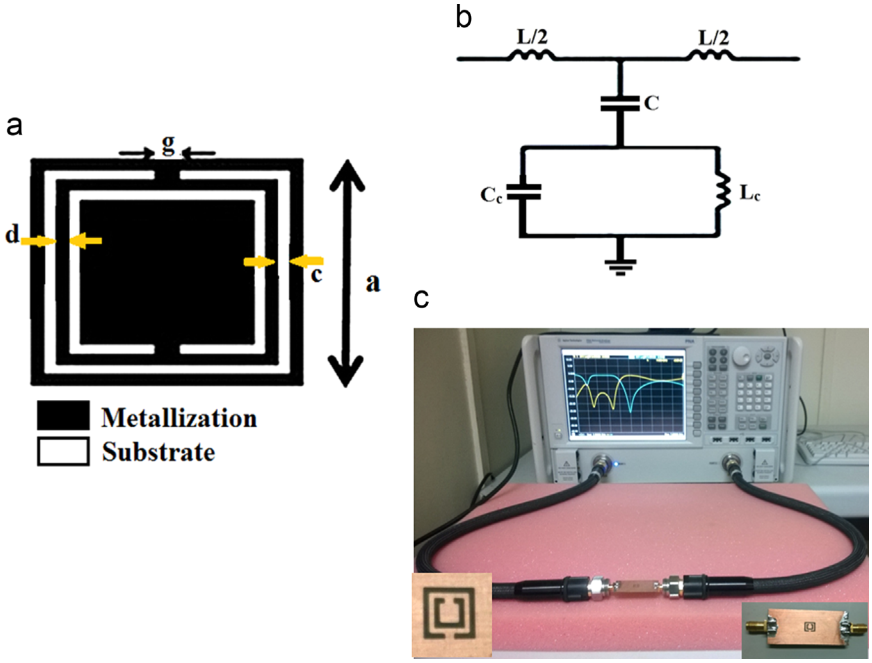

Fig. 1. (a) shows the design of Complementary Split Ring Resonator (CSRR) along with the dimensions (b) shows the equivalent circuit of CSRR (c) shows the experimental setup. The inset shows enlarged view of CSRR based microstrip (bottom right) and enlarged view of CSRR (bottom left).