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Solid analyte and aqueous solutions sensing based on a flexible terahertz dual-band metamaterial absorber

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Abstract. A high-sensitivity sensing technique was demonstrated based on a flexible terahertz dual-band metamaterial absorber. The absorber has two perfect absorption peaks, one with a fundamental resonance \( f_1 \) of the structure and another with a high-order resonance \( f_2 \) originating from the interactions of adjacent unit cells. The quality factor \( Q \) and figure of merit \( f_2 \) are 6 and 14 times larger than that of \( f_1 \), respectively. For the solid analyte, the changes in resonance frequency are monitored upon variation of analyte thickness and index; a linear relation between the amplitude absorption with the analyte thickness is achieved for \( f_2 \). The sensitivity \( S \) is 31.2% refractive index units (RIU\(^{-1}\)) for \( f_2 \) and 13.7% RIU\(^{-1}\) for \( f_1 \). For the aqueous solutions, the amplitude of absorption decreases linearly with increasing the dielectric constant for the ethanol–water mixture of \( f_1 \). These results show that the designed absorber cannot only identify a solid analyte but also characterize aqueous solutions through the frequency shift and amplitude absorption. Therefore, the proposed absorber is promising for future applications in high-sensitivity monitoring biomolecular, chemical, ecological water systems, and aqueous biosystems. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.OE.56.2.027104]

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1 Introduction

Nondestructive, highly sensitive sensing techniques are desirable in detecting new chemical and biological samples, especially for ecological water systems and aqueous solutions. Detection techniques for new chemical or biological materials have been employed through numerous physical and chemical methods.\(^1\)\(^-\)\(^4\) However, such approaches often require adding an appropriate marker, which may cause the sample to be modified before its reaction with materials.\(^5\)\(^-\)\(^9\) Therefore, it is necessary to develop the detection techniques for reliable and effective label free testing.

Terahertz (THz) metamaterial sensors have attracted considerable interest as a promising detection tool because of the THz wave characteristics of low photon energy, which can be detected without damage to materials.\(^10\)\(^-\)\(^17\) Recently, THz metamaterial sensors have been used in the nondestructive and label-free detection of materials.\(^14\)\(^-\)\(^18\) However, the sensitivity of the previously reported metamaterial biosensors is relatively lower due to the radiative and nonradiative loss. Most detection techniques were carried by different shifts in resonance frequency and rarely considered the changes in amplitude resonance. Furthermore, few reports are available on aqueous solution sensing based on THz metamaterials.\(^19\)\(^-\)\(^24\)

In this paper, we report a highly sensitive sensing technique for monitoring materials by THz dual-band metamaterial absorber. We propose the absorber based on double-cross metallic lines owing to the symmetry with sixfold rotational symmetry and the sensing capabilities in terms of the change in resonance frequency and the amplitude absorption. There are two strong narrowband absorption peaks of fundamental resonance \( f_1 \) and another with a high-order resonance \( f_2 \). In addition, the quality factor \( Q \) and figure of merit (FOM) of \( f_2 \) are 6 and 14 times larger than that of \( f_1 \), respectively. Most importantly, a linear relation between the amplitude absorption and the analyte thickness was achieved for the resonance \( f_2 \). By studying the ethanol–water mixture, we also demonstrated that the amplitude absorption decreased linearly when increasing the dielectric constant for the resonance \( f_1 \). Therefore, the proposed THz metamaterial absorber can be applied to identify biomolecular, chemical, and explosive solvent types and to determine the corresponding concentrations.

2 Sensor Design and Discussion

2.1 Terahertz Metamaterial Absorber

The proposed THz flexible absorber is illustrated in Fig. 1(a) and consists of three layers. The top layer includes a double-cross metallic line structure patterned on the flexible polyimide (PI) film with a thickness of 10 \( \mu \)m, and the bottom layer and metallic line structure are 200-nm-thick gold film. The dielectric constant and loss tangent of PI are 3.1 and 0.05, respectively. The thickness of the designed flexible absorber is 10.4 \( \mu \)m. The unit cell of the absorber is shown in Fig. 1(b), and the geometric parameters are \( L = 72 \mu \)m, \( w = 6 \mu \)m, and \( p_x = p_y = 100 \mu \)m. Figure 1(c) shows the simulation absorption spectra of the absorber through CST Microwave Studio. The unite cell boundary conditions with a tetrahedral mesh were used in the frequency domain solver, in which case the wave ports were automatically added in the direction of normal incidence to the substrate. The amplitude of the transmission \( S_21 \) and the reflection \( S_{11} \) were obtained and the absorption was calculated using \( A = 1 - R \cdot T = 1 - S_{11}^2 - S_{21}^2 \), where \( S_{21} \) is zero across the entire frequency range due to the metallic ground plane.
The unit cell was subject to the periodic boundary conditions in the \( x \)- and \( y \)-directions and open for the \( z \)-direction in free space. The magnetic and the electric fields were parallel to the \( x \)- and \( y \)-axes, respectively.

Two distinct absorption peaks are located at around 1.08 (\( f_1 \)) and 2.77 THz (\( f_2 \)), with absorptions of over 99.4%. Their qualities \( Q \) were 8.9 for \( f_1 \) and 55 for \( f_2 \) (\( Q = f / \text{FWHM} \)), where FWHM is the full width at half maximum and \( f \) is the frequency of the absorption peak). The \( Q \) of resonance \( f_2 \) was six times larger than that of the resonance \( f_1 \).

Based on the analysis results, the \( Q \) characteristics of the resonance \( f_2 \) were superior to those of resonance \( f_1 \). To understand the physical mechanism of the designed absorber, we simulated the distribution of the electric field (\( |E| \)) and the magnetic field (\( |H| \)) at the resonances \( f_2 \) and \( f_1 \) using CST Microwave Studio (Fig. 2). As shown in Figs. 2(a) and 2(b), the electric field for the resonance \( f_1 \) was mainly focused on the sides of the metallic array along the direction of the electric field; however, the resonance \( f_2 \) was mainly focused on the sides of the metallic array and the area between the units. We also observed that the magnetic field (\( |H| \)) of the resonance \( f_1 \) was located on the dielectric layer, but the resonance \( f_2 \) was mainly focused on the middle of the unit cell and the area between the units. Consequently, the resonance \( f_1 \) was the fundamental resonance of the proposed structure, and the resonance \( f_2 \) originated from the interactions of adjacent unit cells as the high-order resonance. Thus, the \( Q \) of high-order resonance \( f_2 \) was superior to the fundamental resonance \( f_1 \). From the simulation analytical results, we also determined that the designed THz dual-band metamaterial absorber was capable of sensing for high-sensitivity monitoring of the materials.

![Fig. 1](https://ebooks.spiedigitallibrary.org/journals/Optical-Engineering) (a) Structure schematic of the proposed flexible absorber. (b) Unit cell of the absorber, the geometrical parameters are \( L = 72 \, \mu m \), \( w = 6 \, \mu m \), and \( p_x = p_y = 100 \, \mu m \). (c) Simulation absorption spectra of the designed flexible absorber.

![Fig. 2](https://ebooks.spiedigitallibrary.org/journals/Optical-Engineering) Distribution of the electric field (\( |E| \)) for the flexible absorber at the frequencies of (a) 1.07 and (b) 2.77 THz, respectively; distribution of the magnetic field (\( |H| \)) for the flexible absorber at the frequencies of (c) 1.07 and (d) 2.77 THz, respectively.
From Fig. 1(c), we also know that there is a third weak peak at about 1.69 THz. In order to explain the physical mechanism of this peak, we numerically simulated the electric field distribution of the resonances 1.07 and 1.69 THz, as shown in Fig. 3. The electric field of 1.07 THz was mainly focused on the sides of the metallic array along the incident electric field. For the resonance 1.56 THz, the electric field was mainly focused on the sides of the cross metal structure, where the angle between the two metal lines’ structure and incident electric field direction is 45 deg. Consequently, the third peak at the resonance 1.69 THz originated from the metal line structure as another fundamental resonance.

The designed flexible absorber was fabricated through evaporated, spin-coated, lift-off, and peel-off techniques, and the microscopic image of the absorber was shown in Fig. 4(a). The design absorber was also characterized by THz time-domain spectroscopy using a gold mirror as reference, as shown in Fig. 4(b). There are three absorption peaks at 1.04, 1.67, and 2.73 THz under normal incident angle, and the experimental result agreed with the simulation.

### 2.2 Solid Analyte Sensing

To explore the sensitivity for absorber, PI films of different thicknesses were spin coated on the absorber. The absorber sensor characteristics were simulated using CST Microwave Studio (Fig. 5). From the above analysis, we know that the third peak was relatively weak, so we mainly discuss the sensing characteristics for resonances \( f_1 \) and \( f_2 \). Figure 5(b) shows the simulated absorption spectra of the absorber under different thicknesses (t) of solid analyte; the red frequency shifts of the resonance \( f_1 \) for the film thicknesses 4, 8, and 12 \( \mu m \) were 90, 116, and 134 GHz, respectively. The frequency shifts of 198, 364, and 491 GHz for the 4, 8, and 12 \( \mu m \) thicknesses of the analyte for the resonance \( f_2 \) were significantly higher than those of frequency shift \( f_1 \). Additionally, the change in the amplitude absorption was apparent with the different thicknesses of the PI film for the resonance \( f_2 \).

Figure 5(c) reveals the frequency shifts with solid analyte thickness for the resonance \( f_1 \) (dots) and \( f_2 \) (stars) with simulated data; the red and blue lines show the exponential fits to the simulation data. The fitting functions are described for the resonance \( f_1 \) and \( f_2 \), where the total frequency shift saturated at approximately 150.8 and 984.7 GHz, respectively. The fitting functions are described by

\[
y_1 = 982.028 - 984.742e^{(-\frac{t}{17.243})} \quad \text{and} \quad y_2 = 160.059 - 150.806e^{(-\frac{t}{5.893})},
\]

respectively.

From Fig. 5(c), we also noted that the frequency shift became saturated at the analyte thicknesses over 10 and 25 \( \mu m \) of the resonances \( f_1 \) and \( f_2 \), respectively, and no further significant frequency shift was observed upon increasing the analyte thickness.

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**Fig. 3** Distribution of the electric field \( E \) for the flexible absorber at the frequencies of (a) 1.07 and (b) 1.69 THz, respectively.

**Fig. 4** (a) Microscopic image of a part of the THz flexible absorber and (b) measured and simulated absorption spectra of the THz flexible absorber.
As shown in Fig. 5(b), the amplitude absorption was different at the film thicknesses 0, 4, 8, and 12 μm for the resonance \( f_2 \). The relation between the amplitude absorption with the analyte thickness was also studied as shown in Fig. 5(d); a linear relation can be achieved for the resonance \( f_2 \), and the fitting functions are described as \( y_3 = 1 - 0.028/t \) for the resonance \( f_2 \). This effect provides an effective method to probe the dielectric properties of the overlayer.

We further characterized the absorber sensor for different refractive indices by CST Microwave Studio under a fixed analyte thickness \( t = 16 \mu m \) (Fig. 6). Figure 6(a) reveals the simulated absorption spectra of the absorber under different refractive indices. We found the red frequency shifts of the resonances \( f_1 \) and \( f_2 \) when the refractive index increased from 1.0 to 1.4. The frequency shifts of 0, 200, and 387 GHz for the resonance \( f_2 \) were significantly higher than that for resonance \( f_1 \). This is due to the higher \( Q \) factor of \( f_1 \).
Additionally, the change in amplitude absorption was achieved for the resonance \( f_2 \).

In Fig. 6(b), the relative frequency shift (RFS) in the refractive index for the resonances \( f_1 \) and \( f_2 \) was also studied, the RFS was defined as RFS = \( \frac{f_{\text{Ref}} - f_{\text{Abs}}}{f_{\text{Ref}}} \times 100\% \), where \( f_{\text{Ref}} \) is the resonance frequency of the flexible absorber without any analyte and \( f_{\text{Abs}} \) is the resonance frequency of the flexible absorber with analyte refractive index \( n \). The frequency sensitivity is defined as \( df/dn \), the slope of linear fitting function, where \( df \) is the change of resonance frequency and \( dn \) is the change of the refractive index. The sensitivity \( S \) is 31.2% refractive index units (RIU)\(^{-1} \) for the resonance \( f_2 \) and 13.7% RIU\(^{-1} \) for the resonance \( f_1 \). The amplitude absorption and the frequency shift with the different refractive indices were also characterized for the resonance \( f_2 \) [Fig. 6(c)], the fitting functions for the amplitude absorption are described by \( y_4 = 1.0827 - 0.0071e^{-\frac{\mu}{2z\mu}} \) and \( y_5 = 553 * n - 586 \), respectively. Therefore, this designed absorber can be applied to identify the unknown materials by the amplitude absorption change and the frequency shift. By applying the method, higher accuracy biosensor can be achieved as privileges over conventional through the frequency shift or the amplitude modulation. To quantitatively characterize the absorber sensor, we also calculated the FOM. The FOM was defined as \( \text{FOM} = S \times Q \), where \( S \) is the sensitivity of the THz flexible absorber and \( Q \) is the quality factor of the resonance \( f \). The FOM was 17.2 for the resonance \( f_2 \) and 1.2 for the resonance \( f_1 \). The FOM value of the high-order resonance is 7.5 times that of the recent results.\(^{14} \)

From the simulation analytical results, we determined that the designed THz dual-band metamaterial absorber was capable of sensing the solid analyte. From Fig. 5(c), we also noted that the frequency shift became saturated at analyte thicknesses over 10 \( \mu \text{m} \) for the resonance \( f_1 \) and \( f_2 \), respectively, and no further significant frequency shift was observed.

To qualitatively explain the properties, we simulated the electric field distribution in the \( x-z \) plane for the THz absorber (Fig. 7). The electric field fell off quickly away from the metamaterial absorber layer and can be neglected above 10 \( \mu \text{m} \) for the resonance \( f_1 \) and 30 \( \mu \text{m} \) for the resonance \( f_2 \). According to a previous report,\(^{25} \) the equivalent capacitance \( c_{\text{eff}} \) can be expressed as

\[
c_{\text{eff}} = \frac{Q_{\text{eff}}}{U_{\text{eff}}} = \frac{\int_{\Omega} \varepsilon_0 \varepsilon_r \tilde{E} \tilde{E} \text{dA}}{\int_{\Omega} \tilde{E} \tilde{E} \text{d}x} \propto \int \varepsilon_r(z) \tilde{E}(z) \text{d}z. \tag{1}
\]

Thus, the equivalent capacitance changes slightly with a further increase in coating thickness, and the frequency changes tend to be saturated.

### 2.3 Aqueous Solution Sensing

However, metamaterials for aqueous solution sensing are rarely reported; thus, we further characterized the designed THz absorber sensor for aqueous solutions. Figure 8(a) displays the simulated absorption for aqueous solutions of ethanol. The thickness of the aqueous layer was 15 \( \mu \text{m} \). The red frequency shifts of the resonance \( f_1 \) for the dielectric constants of 2.6 + 0.9i, 2.8 + 1.1i, and 3.2 + 1.3i were 124, 142, and 172 GHz, respectively.\(^{26} \) The frequency shifts of 140, 152, and 211 GHz of the dielectric constants for the resonance \( f_2 \) were higher than those of frequency shift \( f_1 \).

However, the resonance intensity \( f_2 \) becomes weaker with an increase in the dielectric constant of the ethanol–water mixture and the amplitude absorption of the resonance \( f_1 \) increased. From the above analytical results, we know that the resonance \( f_2 \) originated from the interactions of adjacent...
unit cells, and it has more sensitivity to the variation of the dielectric constant. Compared to solid analyte, aqueous solution has greater loss for larger imaginary part for the dielectric constants result in the becoming weak of resonance and the absorption amplitude and frequency shift of the resonance $f_2$ are different from that of the resonance $f_1$ varying with the dielectric constant of the aqueous solution.

The dielectric constant dependence of the amplitude absorption for the resonances $f_1$ and $f_2$ was also studied as shown in Figs. 8(b) and 8(c). Obviously, the amplitude absorption for the resonances $f_1$ and $f_2$ reduced linearly when increasing the dielectric constant of the ethanol–water mixture.

Therefore, the proposed metamaterial absorber also provided an effective method to probe the molecular or ionic concentrations and did not require the penetration of a water layer.

3 Discussion

We demonstrated a flexible THz dual-band metamaterial absorber, which exhibited sensitivity in sensing solid analyte and aqueous solutions through the frequency shift and the amplitude absorption. For the solid analyte, a linear relation was observed between the thickness of the analyte and the amplitude absorption for the high-order resonance $f_2$, and the exponential and line relation were obtained among the refractive index, the amplitude absorption, and the frequency shift of the high-order resonance $f_2$, respectively. For the aqueous solution, a linear relation was also achieved between the amplitude absorption and dielectric constant of the ethanol–water mixture of the resonance $f_1$. In the detection techniques for sensing materials, frequency shift at two resonances can enhance accuracy. The proposed THz absorber can be applied for highly accurate and sensitive monitoring of biomolecular chemical aqueous biosystems and ecological water systems in the future.

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X.Y. and L.J.L. performed numerical simulations and prepared the samples. All the authors wrote the paper. J.Q.Y. directed the research. The authors declare no competing financial interests. The research was supported by the National Natural Science Foundation (No. 61675147), the China Postdoctoral Science Foundation (No. 2015M571263), the Programe of Independent Innovation and Achievement Transformation Plan for Zaozhuang (No. 2016GH19), Science and Technology Program of Zaozhuang (No. 2016GJX31), and Zaozhuang Engineering Research Center of Terahertz and the Doctoral Foundation.

References

1. Y. Rivenson et al., “Overview of compressive sensing techniques applied in holography,” Appl. Opt. 52(1), A423 (2013).
2. N. Kida et al., “Characteristic effect of an anticancer dinuclear platinum (II) complex on the higher-order structure of DNA,” J. Biolog. Inorg. Chem. 15(5), 701–707 (2010).
3. V. Cassina et al., “Atomic force microscopy study of DNA conformation in the presence of drugs,” Biochem. Biophys. Res. Commun. 231(4), 495–501 (2006).
4. Q. Zhu et al., “Ultrasonic simultaneous detection of four biomarkers based on hybridization chain reaction and biotin–streptavidin signal amplification strategy,” Biosens. Bioelectron. 68(15), 42–48 (2015).
5. E. F. Aziz et al., “Interaction between liquid water and hydroxide revealed by core-hole de-excitation,” Nature 455, 89–91 (2008).
6. K. J. Tielrooj et al., “Cooperativity in ion hydration,” Science 328, 1006–1009 (2010).
7. X. X. Han et al., “Label-free indirect immunoassay using an avidin-induced surface-enhanced Raman scattering substrate,” Small 7, 316–320 (2011).
8. X. J. Wu et al., “Label-free monitoring of interaction between DNA and oxalatolin in aqueous solution by terahertz spectroscopy,” Appl. Phys. Lett. 101, 033704 (2012).
9. K. He et al., “Y-shaped probe for convenient and label-free detection of microRNA-21 in vitro,” Anal. Biochem. 499, 8 (2016).
10. S. Ebbinghaeus et al., “Protein sequence and pH-dependent hydration probed by terahertz spectroscopy,” J. Am. Chem. Soc. 130(8), 2374–2375 (2008).
11. P. U. Jepson et al., “Terahertz spectroscopy and imaging—modern techniques and applications,” Laser Photonics Rev. 5, 124–166 (2011).
12. J. S. Melinger et al., “Pulse-dependent characterization of terahertz vibrations of explosives and related threat materials,” Opt. Exp. 18(26), 27238 (2010).
13. E. Arik et al., “Dielectric properties of ethanol and gasoline mixtures by terahertz spectroscopy and an effective method for determination of ethanol content of gasoline,” J. Phys. Chem. A 118(17), 3081–3089 (2014).
14. L. Q. Cong et al., “Experimental demonstration of ultrasensitive sensing with terahertz metamaterial absorbers: a comparison with the metasurfaces,” Appl. Phys. Lett. 106, 031107 (2015).
15. R. J. Singh et al., “Ultrasonic terahertz sensing with high-Q Fano resonances in metasurface,” Appl. Phys. Lett. 105, 171101 (2014).
16. B. X. Wang et al., “A novel dual-band terahertz metamaterial absorber for a sensor application,” J. Appl. Phys. 117, 14504 (2015).
17. X. Wu et al., “Sensing self-assembled alkanethiol by differential transmission interrogation with terahertz metamaterials,” Appl. Opt. 52(20), 4877 (2013).
18. L. Q. Cong et al., “Fano resonances in terahertz metasurfaces: a figure of merit optimization,” Adv. Opt. Mater. 3, 1537–1543 (2015).
19. H. Tao et al., “Silk-based conformal, adhesive, edible food sensors,” Adv. Mater. 24, 1067–1072 (2012).
20. L. J. Xie et al., “Extraordinary sensitivity enhancement by metasurface in terahertz detection of antibiotics,” Sci. Rep. 5, 1038 (2015).
21. D. Kaikai et al., “Wavelength and thermal distribution selectable microbolometers based on metamaterial absorbers,” IEEE Photon. J. 7, 6909008 (2014).
22. B. Kearney et al., “AlSiOx/Al single and multiband metamaterial absorbers for terahertz sensor applications,” Opt. Eng. 52(1), 013801 (2013).
23. W. X. Yu et al., “Meta-microwindmill structure with multiple absorption peaks for the detection of ketamine and amphetamine type stimulants in terahertz domain,” Opt. Mater. Exp. 4, 234 (2014).
24. X. J. Wu et al., “Alkanethiol-functionalized terahertz metamaterial as label-free, highly-sensitive and specific biosensor,” Biosens. Bioelectron. 42, 626–631 (2013).
25. B. Reinhard et al., “Metamaterial near-field sensor for deep-subwave-length thickness measurements and sensitive refractometry in the terahertz frequency range,” Appl. Phys. Lett. 100, 221101 (2012).
26. X. J. Wu et al., “Self-referenced sensing based on terahertz metamaterial for aqueous solutions,” Appl. Phys. Lett. 102, 151109 (2013).