

Sharp Fano resonances in THz metamaterials

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Abstract: We report on the occurrence of sharp Fano resonances in planar terahertz metamaterials by introducing a weak asymmetry in a two gap split ring resonator. As the structural symmetry of the metamaterial is broken a Fano resonance evolves in the low-frequency flank of the symmetric fundamental dipole mode resonance. This Fano resonance can have much higher Q factors than that known from single gap split ring resonators. Supporting simulations indicate a Q factor of 50 for lowest degree of asymmetry. The Q factor decreases exponentially with increasing asymmetry. Hence, minute structural variations allow for a tuning of the Fano resonance. Such sharp resonances could be exploited for biochemical sensing. Besides, the strong current oscillations excited at the Fano resonance frequency could lead to the design of novel terahertz narrow band emitters.

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References and links

1. S. Prosvirnin and S. Zouhdi, "Resonances of closed modes in thin arrays of complex particles," in "Advances Electromagnetics of Complex Media and Metamaterials," S. Zouhdi et al., ed. (Kluwer Academic Publishers, 2003), pp. 281–290.
2. V. A. Fedotov, M. Rose, S. L. Prosvirnin, N. Papasimakis, and N. I. Zheludev, "Sharp trapped-mode resonances in planar metamaterials with a broken structural symmetry," *Phys. Rev. Lett.* **99**(14), 147401 (2007).
3. N. I. Zheludev, S. L. Prosvirnin, N. Papasimakis, and V. A. Fedotov, "Lasing spaser," *Nat. Photonics* **2**(6), 351–354 (2008).
4. E. Plum, V. A. Fedotov, P. Kuo, D. P. Tsai, and N. I. Zheludev, "Towards the lasing spaser: controlling metamaterial optical response with semiconductor quantum dots," *Opt. Express* **17**(10), 8548–8551 (2009).
5. K. Tanaka, E. Plum, J. Y. Ou, T. Uchino, and N. I. Zheludev, "Multifold enhancement of quantum dot luminescence in plasmonic metamaterials," *Phys. Rev. Lett.* **105**(22), 227403 (2010).
6. V. A. Fedotov, N. Papasimakis, E. Plum, A. Bitzer, M. Walther, P. Kuo, D. P. Tsai, and N. I. Zheludev, "Spectral collapse in ensembles of metamolecules," *Phys. Rev. Lett.* **104**(22), 223901 (2010).
7. U. Fano, "Effects of configuration interaction on intensities and phase shifts," *Phys. Rev.* **124**(6), 1866–1878 (1961).
8. A. E. Miroschnichenko, S. Flach, and Y. S. Kivshar, "Fano resonances in nanoscale structures," *Rev. Mod. Phys.* **82**(3), 2257–2298 (2010).
9. B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, and C. T. Chong, "The Fano resonance in plasmonic nanostructures and metamaterials," *Nat. Mater.* **9**(9), 707–715 (2010).
10. F. Hao, Y. Sonnefraud, P. V. Dorpe, S. A. Maier, N. J. Halas, and P. Nordlander, "Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance," *Nano Lett.* **8**(11), 3983–3988 (2008).
11. X. Xiao, J. Wu, F. Miyamaru, M. Zhang, S. Li, M. W. Takeda, W. Wen, and P. Sheng, "Fano effect of metamaterial resonance in terahertz extraordinary transmission," *Appl. Phys. Lett.* **98**(1), 011911 (2011).
12. J. B. Pendry, A. J. Holden, D. J. Robbins, and W. J. Stewart, "Magnetism from conductors and enhanced nonlinear phenomena," *IEEE Trans. Microw. Theory Tech.* **47**(11), 2075–2084 (1999).
13. T. J. Yen, W. J. Padilla, N. Fang, D. C. Vier, D. R. Smith, J. B. Pendry, D. N. Basov, and X. Zhang, "Terahertz magnetic response from artificial materials," *Science* **303**(5663), 1494–1496 (2004).
14. S. Linden, C. Enkrich, M. Wegener, J. Zhou, T. Koschny, and C. M. Soukoulis, "Magnetic response of metamaterials at 100 terahertz," *Science* **306**(5700), 1351–1353 (2004).
15. H. O. Moser, B. D. F. Casse, O. Wilhelm, and B. T. Saw, "Terahertz response of a microfabricated rod-splitting-resonator electromagnetic metamaterial," *Phys. Rev. Lett.* **94**(6), 063901 (2005).

16. A. K. Azad, J. M. Dai, and W. Zhang, "Transmission properties of terahertz pulses through subwavelength double split-ring resonators," *Opt. Lett.* **31**(5), 634–636 (2006).
17. W. J. Padilla, A. J. Taylor, C. Highstrete, M. Lee, and R. D. Averitt, "Dynamical electric and magnetic metamaterial response at terahertz frequencies," *Phys. Rev. Lett.* **96**(10), 107401 (2006).
18. H. T. Chen, W. J. Padilla, J. M. O. Zide, A. C. Gossard, A. J. Taylor, and R. D. Averitt, "Active terahertz metamaterial devices," *Nature* **444**(7119), 597–600 (2006).
19. H. T. Chen, J. F. O'Hara, A. K. Azad, A. J. Taylor, R. D. Averitt, D. B. Shrekenhamer, and W. J. Padilla, "Experimental demonstration of frequency-agile terahertz metamaterials," *Nat. Photonics* **2**(5), 295–298 (2008).
20. S. Zhang, Y. S. Park, J. Li, X. Lu, W. Zhang, and X. Zhang, "Negative refractive index in chiral metamaterials," *Phys. Rev. Lett.* **102**(2), 023901 (2009).
21. H. Tao, A. C. Strikwerda, K. Fan, W. J. Padilla, X. Zhang, and R. D. Averitt, "Reconfigurable terahertz metamaterials," *Phys. Rev. Lett.* **103**(14), 147401 (2009).
22. J. Gu, R. Singh, Z. Tian, W. Cao, Q. Xing, M. He, J. W. Zhang, J. Han, H.-T. Chen, and W. Zhang, "Terahertz superconductor metamaterial," *Appl. Phys. Lett.* **97**(7), 071102 (2010).
23. H. T. Chen, H. Yang, R. Singh, J. F. O'Hara, A. K. Azad, S. A. Trugman, Q. X. Jia, and A. J. Taylor, "Tuning the resonance in high-temperature superconducting terahertz metamaterials," *Phys. Rev. Lett.* **105**(24), 247402 (2010).
24. O. Paul, C. Imhof, B. Reinhard, R. Zengerle, and R. Beigang, "Negative index bulk metamaterial at terahertz frequencies," *Opt. Express* **16**(9), 6736–6744 (2008).
25. R. Singh, E. Plum, C. Menzel, C. Rockstuhl, A. K. Azad, R. A. Cheville, F. Lederer, W. Zhang, and N. I. Zheludev, "Terahertz metamaterial with asymmetric transmission," *Phys. Rev. B* **80**(15), 153104 (2009).
26. X. G. Peralta, E. I. Smirnova, A. K. Azad, H. T. Chen, A. J. Taylor, I. Brener, and J. F. O'Hara, "Metamaterials for THz polarimetric devices," *Opt. Express* **17**(2), 773–783 (2009).
27. M. Walther, A. Ortner, H. Meier, U. Löffelmann, P. J. Smith, and J. G. Korvink, "Terahertz metamaterials fabricated by inkjet printing," *Appl. Phys. Lett.* **95**(25), 251107 (2009).
28. F. Miyamaru, S. Kuboda, K. Taima, K. Takano, M. Hangyo, and M. W. Takeda, "Three-dimensional bulk metamaterials operating in the terahertz range," *Appl. Phys. Lett.* **96**(8), 081105 (2010).
29. R. Singh, A. K. Azad, J. F. O'Hara, A. J. Taylor, and W. Zhang, "Effect of metal permittivity on resonant properties of terahertz metamaterials," *Opt. Lett.* **33**(13), 1506–1508 (2008).
30. R. Singh, E. Smirnova, A. J. Taylor, J. F. O'Hara, and W. Zhang, "Optically thin terahertz metamaterials," *Opt. Express* **16**(9), 6537–6543 (2008).
31. J. F. O'Hara, R. Singh, I. Brener, E. Smirnova, J. Han, A. J. Taylor, and W. Zhang, "Thin-film sensing with planar terahertz metamaterials: sensitivity and limitations," *Opt. Express* **16**(3), 1786–1795 (2008).
32. C. Debus and P. H. Bolivar, "Frequency selective surfaces for high sensitivity terahertz sensing," *Appl. Phys. Lett.* **91**(18), 184102 (2007).
33. I. A. Al-Naib, C. Jansen, and M. Koch, "Thin film sensing with planar asymmetric metamaterial resonators," *Appl. Phys. Lett.* **93**(8), 083507 (2008).
34. N. Papisimakis, Z. Luo, Z. X. Shen, F. De Angelis, E. Di Fabrizio, A. E. Nikolaenko, and N. I. Zheludev, "Graphene in a photonic metamaterial," *Opt. Express* **18**(8), 8353–8359 (2010).
35. S. Y. Chiam, R. Singh, W. Zhang, and A. A. Bettiol, "Controlling metamaterial resonances via dielectric and aspect ratio effects," *Appl. Phys. Lett.* **97**(19), 191906 (2010).
36. B. Lahiri, A. Z. Khokhar, R. M. De La Rue, S. G. McMeekin, and N. P. Johnson, "Asymmetric split ring resonators for optical sensing of organic materials," *Opt. Express* **17**(2), 1107–1115 (2009).
37. S. Y. Chiam, R. Singh, J. Gu, J. Han, W. Zhang, and A. A. Bettiol, "Increased frequency shifts in high aspect ratio terahertz split ring resonators," *Appl. Phys. Lett.* **94**(6), 064102 (2009).
38. I. A. I. Al-Naib, C. Jansen, and M. Koch, "High Q -factor metasurfaces based on miniaturized asymmetric single split ring resonator," *Appl. Phys. Lett.* **94**(15), 153505 (2009).
39. R. Singh, Z. Tian, J. Han, C. Rockstuhl, J. Gu, and W. Zhang, "Cryogenic temperatures as a path toward high Q metamaterials," *Appl. Phys. Lett.* **96**(7), 071114 (2010).
40. R. Singh, I. A. I. Al-Naib, M. Koch, and W. Zhang, "Asymmetric planar terahertz metamaterials," *Opt. Express* **18**(12), 13044–13050 (2010).
41. C. Jansen, I. A. I. Al-Naib, N. Born, and M. Koch, "Terahertz metasurfaces with high Q -factors," *Appl. Phys. Lett.* **98**(5), 051109 (2011).
42. S. Zhang, D. A. Genov, Y. Wang, M. Liu, and X. Zhang, "Plasmon-induced transparency in metamaterials," *Phys. Rev. Lett.* **101**(4), 047401 (2008).
43. N. Papisimakis, V. A. Fedotov, N. I. Zheludev, and S. L. Prosvirnin, "Metamaterial analog of electromagnetically induced transparency," *Phys. Rev. Lett.* **101**(25), 253903 (2008).
44. R. Singh, C. Rockstuhl, F. Lederer, and W. Zhang, "Coupling between a dark and a bright eigenmode in a terahertz metamaterial," *Phys. Rev. B* **79**(8), 085111 (2009).
45. N. Liu, L. Langguth, T. Weiss, J. Kästel, M. Fleischhauer, T. Pfau, and H. Giessen, "Plasmonic analogue of electromagnetically induced transparency at the Drude damping limit," *Nat. Mater.* **8**(9), 758–762 (2009).
46. S. Y. Chiam, R. Singh, C. Rockstuhl, F. Lederer, W. Zhang, and A. A. Bettiol, "Analogue of electromagnetically induced transparency in terahertz metamaterial," *Phys. Rev. B* **80**(15), 153103 (2009).
47. P. Tassin, L. Zhang, T. Koschny, E. N. Economou, and C. M. Soukoulis, "Low-loss metamaterials based on classical electromagnetically induced transparency," *Phys. Rev. Lett.* **102**(5), 053901 (2009).
48. N. Papisimakis and N. I. Zheludev, "Metamaterial-induced transparency," *Opt. Photon. News* **20**(10), 22 (2009).
49. V. Yannopapas, E. Paspalakis, and N. V. Vitanov, "Electromagnetically induced transparency and slow light in an array of metallic nanoparticles," *Phys. Rev. B* **80**(3), 035104 (2009).

50. D. Grischkowsky, S. Keiding, M. Exter, and Ch. Fattinger, "Far infrared time domain spectroscopy with terahertz beams of dielectrics and semiconductors," *J. Opt. Soc. Am. B* **7**(10), 2006 (1990).
 51. CST Microwave Studio®, (<http://www.cst.com>)
 52. R. Singh, E. Plum, W. Zhang, and N. I. Zheludev, "Highly tunable optical activity in planar achiral terahertz metamaterials," *Opt. Express* **18**(13), 13425–13430 (2010).
 53. R. Singh, C. Rockstuhl, F. Lederer, and W. Zhang, "The impact of nearest neighbor interaction on the resonances in terahertz metamaterials," *Appl. Phys. Lett.* **94**(2), 021116 (2009).
 54. R. Singh, C. Rockstuhl, and W. Zhang, "Strong influence of packing density in terahertz metamaterials," *Appl. Phys. Lett.* **97**(24), 241108 (2010).
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1. Introduction

Metamaterials is a flourishing field of science and engineering that exploits the exotic optical properties of subwavelength metallic structures to manipulate light at ultra small length scales. These metallic micro or nanostructured objects derive most of their properties from their ability to support resonances. The possibility to couple electromagnetic radiation into subwavelength structures can have profound impact on light-matter interactions at a very fundamental level. In order to concentrate light in planar metamaterials, they should be able to support sharp resonances with high quality (Q) factor associated with high field concentrations in minute volume. Planar metamaterials are optically thin structures having modest quality factors since they do not have an inner resonating volume for high energy confinement. Besides, their resonating units are usually strongly coupled to free space which in turn causes high radiation losses. Several recent metamaterial works proposed to break the symmetry of split ring resonators (SRRs) and demonstrated sharp asymmetric Fano resonances mainly in the microwave and optical regime [1–6]. A Fano resonance arises from the constructive and destructive interference of a narrow discrete resonance with a broad spectral line. The resulting lineshape profile is asymmetric [7–11]. Before Fano resonances were discovered it was assumed that the symmetric Lorentzian lineshape was the fundamental profile of any resonance.

Terahertz planar metamaterials have emerged as an important active and passive device with different functionalities [12–28]. Unfortunately, they still suffer from low Q factors which limits their sensing capabilities and filter performance [15–19,21–31]. In particular for sensing applications high Q factors are desired. Only then small agent or sample induced shifts of a resonance frequency can be reliably detected [31–41].

The Q factor of a resonator is generally determined by the energy loss per cycle versus the stored energy. Demonstrating a high Q metamaterial resonator for terahertz or optical wavelengths is difficult since the radiation loss in these structures increases inversely with the resonator size. An attempt to obtain higher Q factors and low loss in terahertz metamaterials by tuning the conductivity of metallic SRRs had only limited success and did not lead to devices suitable for practical applications [22,23,29,39]. The problem of low Q factors in terahertz metamaterials can be tackled if the metamaterial structural design is engineered in such a way that it could support Fano resonances.

In this letter, we report on sharp Fano resonances arising from a gentle symmetry breaking in a two gap terahertz SRR structure. We describe the design, fabrication, measurement and supporting simulations of asymmetric planar SRR metamaterials to generate sharp high Q Fano resonances. With increasing degree of structural asymmetry between the two arms of the SRR we observe an increase in the strength of the asymmetric resonance but a gradual decline in its Q factor. Such "Fano metamaterials" can have applications in diverse areas ranging from micro photonics and biochemical sensing to cavity quantum electrodynamics since their ability to concentrate electromagnetic fields in an extremely small spatial region forms the key to strong terahertz radiation matter interaction. The intense coherent oscillations at the resonance may also pave the way for the design and development of subwavelength terahertz emitter or antennas with highly selective bandwidth. The sharp resonance could also be exploited for developing slow light devices by invoking an electromagnetically induced transparency (EIT)-like response in the metamaterials [42–49].

2. Experiment

The frequency dependent transmission through the metamaterial samples was determined using a typical terahertz time-domain spectroscopy (THz-TDS) system [50]. The planar metamaterial samples were fabricated on n-type silicon substrate using photolithography and then depositing 200 nm of Aluminum. Figure 1 shows pictures of the two gap split ring structures. Two types of structures were fabricated: the first type is a perfect symmetrical split ring (SSR) structure in which both the upper and lower arcs have the same lengths; i.e. both arcs span an angle of 160° (see inset of Fig. 1). In the second type of metamaterial, we gently break the symmetry between the two arcs. The longer arc spans 170° and the shorter arc 150° . These types of structures are called asymmetric split rings (ASRs) [1]. We denote the upper arc segment by α and the lower arc segment by β and define the asymmetry parameter $\delta = (\alpha - \beta / \alpha + \beta) * 100$. For the fabricated ASR sample $\delta = 6.25\%$. All the other structural features of the sample are indicated in Fig. 1. The sample size is $10 \times 10 \text{ mm}^2$.

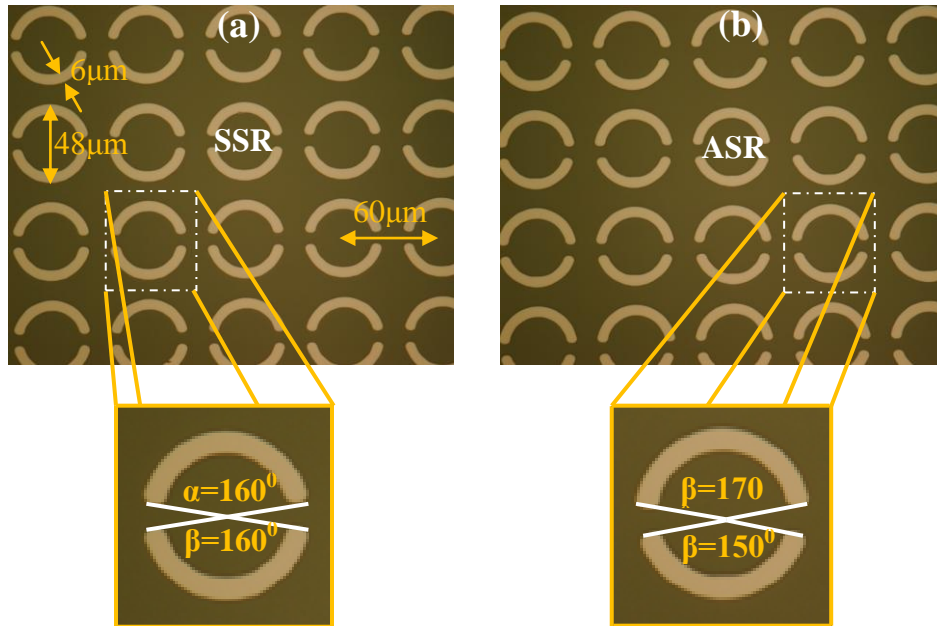


Fig. 1. Microscope image of a symmetric split ring resonator (a) and an asymmetric split ring resonator (b).

The THz TDS measurement setup has an $8f$ confocal geometry with a terahertz beam diameter of 3.5 mm at the focus. The signal to noise ratio is about 15000:1 for a single 17 picoseconds (ps) scan. For the reference scans a blank silicon wafer identical to the one on which the split rings were fabricated was used. The transmitted terahertz pulses were measured at normal incidence such that the electric (E) and magnetic (H) field of the incident radiation was in the metamaterial plane.

3. Measurement and Simulation

The measured amplitude transmission spectra through the SSR and ASR structures are shown in Fig. 2(a). The electric field in this case is oriented perpendicular to the two gaps, as indicated in the inset. The SSR sample shows only one broad symmetric resonance at 1.18 THz. The ASR structure shows two resonances, one which is identical to that of the SSR structure and an additional extremely sharp asymmetric resonance at 0.86 THz. The CST simulation shown in Fig. 2(b) is in good agreement with the measured spectra [51].

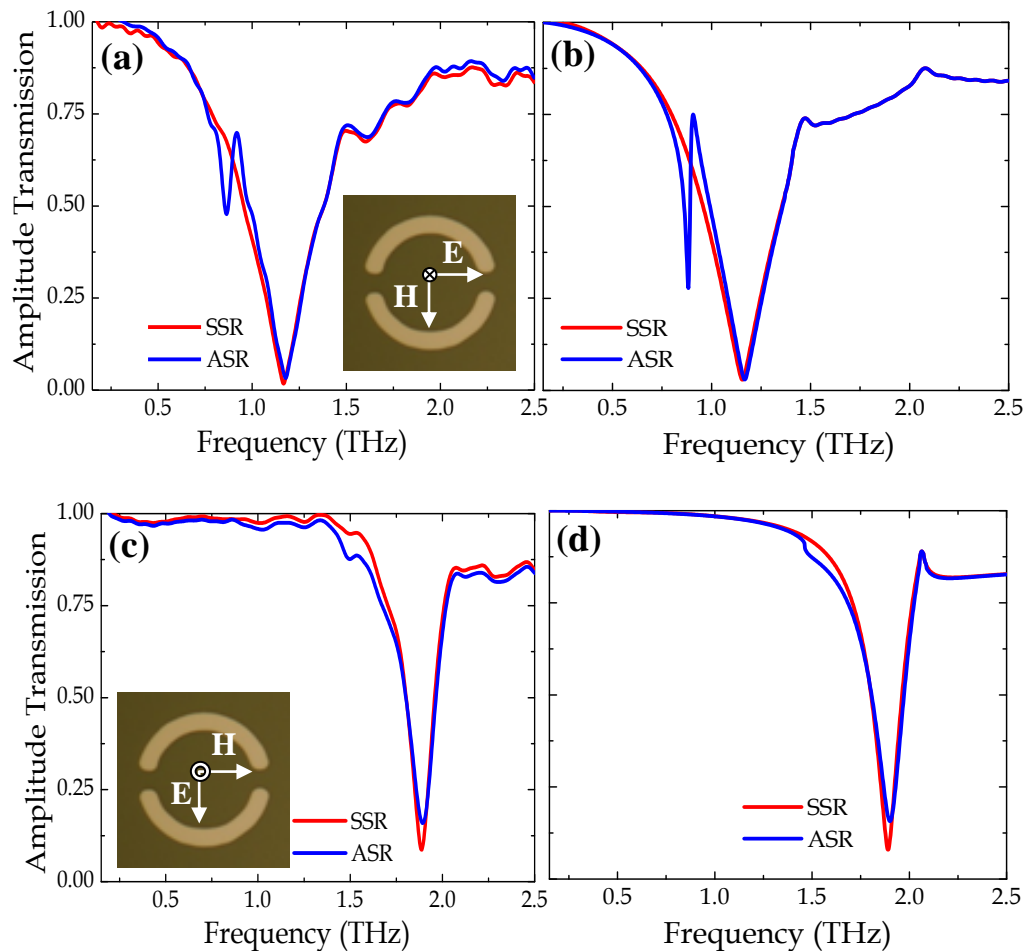


Fig. 2. Measured (a) and simulated (b) amplitude transmission spectra for symmetrical and asymmetric split ring array for an E field orientation perpendicular to the gap; measured (c) and simulated (d) spectra for an E field parallel to the gap. The insets show the E and H field orientation for each data.

In the case of the ASR structure one observes a slight difference between measurement and simulation regarding line width and minimum transmission of the sharp resonance at 0.86 THz. While the resonance line width is 50.3 GHz in the measurement it is 35 GHz in the simulation. This difference is mainly due to the limited time window of our measurement. Figure 3 shows two transmitted THz pulses. It is obvious that the oscillations in the pulse transmitted through the ASR metamaterial have not completely damped out after 17 ps. Yet, the terahertz pulse was truncated after 17 ps to cut off Fabry-Perot echos from the metamaterial substrate. Such a truncation of the time domain pulse leads to a limited spectral resolution after FFT. Consequently, sharp spectral features cannot be resolved very accurately. Hence, we see a difference between measurement and simulation regarding the sharpness of the asymmetric Fano resonance. The measured and simulated values for the Q factors are 13 and 15 respectively. The long lasting ringing in the blue curve reflects the presence of a high Q resonance in the ASR metamaterial. The ringing is absent in the red curve, i.e. for the pulse transmitted through the SSR metamaterial. Measurement and simulation for the other orientation when the E field is oriented along the gap of the SRR and

ASR metamaterials are shown in Figs. 2(c) and 2(d). In this case we excite just the broad symmetric resonance at 1.88 THz for both types of metamaterials.

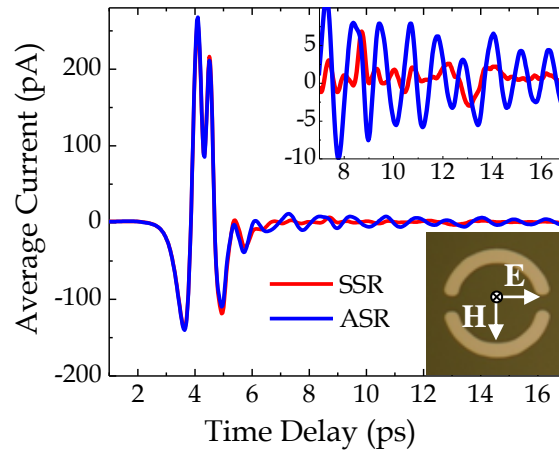


Fig. 3. Measured time domain terahertz pulse through the symmetric and asymmetric metamaterial.

4. Discussion

In order to understand the nature of resonances, we simulate the surface currents for the two fabricated geometries. The surface currents at the three resonances apparent from Fig. 2 are shown in Fig. 4. For the sharp asymmetric resonance at 0.86 THz which occurs for the first orientation we observe anti parallel currents in the top and bottom arcs. As the structure is only weakly coupled to the free space these currents are very pronounced. This particular resonance mode is similar in nature to the inductive capacitive (LC) resonance in a single gap SRR as both resonances result in current configurations that give rise to a magnetic dipole moment perpendicular to the metamaterial plane of the array. The currents oscillate coherently in all the ASRs at this particular frequency. The second broad symmetric resonance at 1.18 THz is due to a dipole-like parallel current distribution as seen in the simulation. The single resonance at 1.88 THz observed for the second orientation is also due to dipole-like parallel currents in the two arcs for both symmetric and the asymmetric types of metamaterials. These dipole resonances are strongly coupled to free space and, hence, are rather broad due to their highly radiative nature.

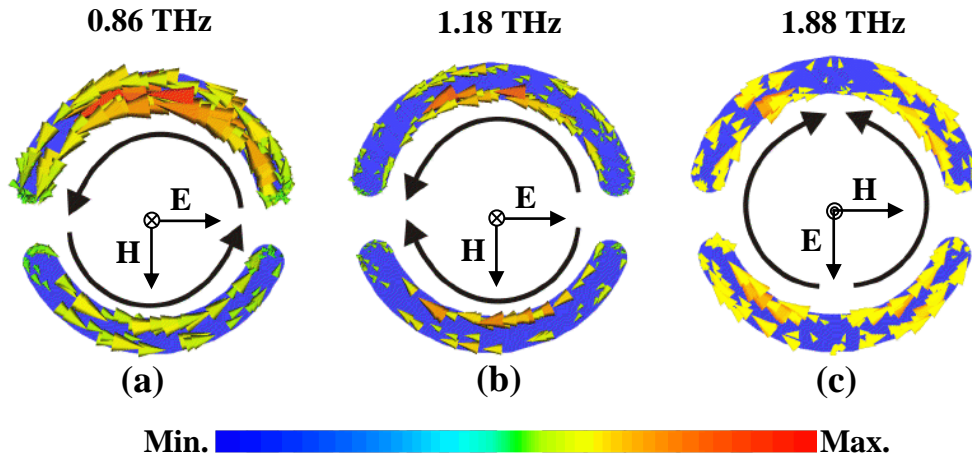


Fig. 4. Simulated surface currents at the three frequencies for which the resonances are observed.

The high Q asymmetric Fano resonance in the ASR arises from the structural asymmetry which leads to an interference between a sharp discrete resonance and a much broader continuum-like spectrum of dipole resonance. This narrow resonance arises from a subradiant dark mode for which the radiation losses are completely suppressed due to the structure's weak coupling to free space. Such dark modes are exploited to realize EIT-like effects in metamaterials which opens up avenues for designing slow light devices with high group index [42–49].

As can be seen from Fig. 2 the Fano resonance in our asymmetric metamaterial is sensitive to the polarization of the exciting field. This opens the route towards tunable devices which could base on the circular dichroism of terahertz waves mediated through a chiral arrangement of the planar metamaterial with respect to the incident terahertz field [52]. In the following we discuss the effect of the degree of asymmetry δ on the Q factor of the Fano resonance. The investigation is carried out through simulations the result of which is shown in Fig. 5. Figure 5(a) shows the calculated transmission spectra for various values of δ . It can be seen that the strength of the Fano resonance increases with increasing asymmetry parameter. The same is true for the width of the resonance. The sharpest resonance is observed for a small asymmetry of $\delta = 1.25\%$. In this case the line width is 14 GHz and the Q factor reaches 50. It should be stressed that such a high Q factor is almost an order of magnitude higher than that obtained in the regular LC resonance symmetric Lorentzian mode [30]. As δ increases, the resonance broadens since the ASR metamaterial couples more efficiently to the free space. Figure 5(b) shows that the Q factor decreases nearly exponentially as δ is increased from 1.25% to 12.5%; i.e. for the asymmetry range studied here. We observe this behavior mainly due to two simultaneous interactions in the ASRs. Firstly, the free space coupling increases with increasing degree of asymmetry. This leads to a lower transmission at the resonance frequency and to a broader resonance linewidth. Secondly, the interaction between the nearest neighbor ASRs in the metamaterial lattice changes with the asymmetry parameter [53]. The exponential decay in transmission at the LC resonance was recently observed in symmetric single ring SRRs with the increase in their packing density [54]. Yet, the decline of the Q factor in an exponential form had not been observed previously.

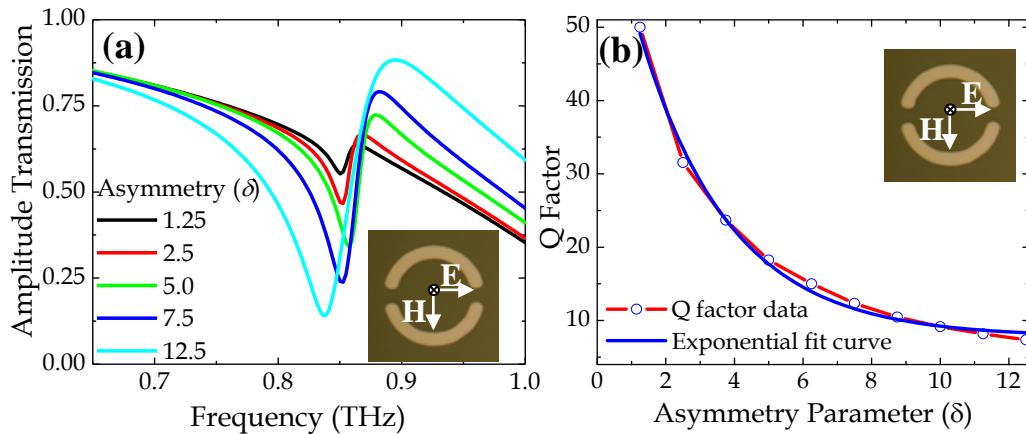


Fig. 5. Simulated amplitude transmission spectra (a), Q factor for different degrees of asymmetry (b). The red curve is just to guide the eye and blue curve is an exponential fit to the declining Q factor with increasing asymmetry.

Hence, ASR metamaterials with a weak asymmetry are likely to hold great potential for the use in tunable filters. Small changes in the local environment of the asymmetric SRR metamaterial supporting the Fano resonance would induce dramatic resonance frequency shifts. If those ASRs are fabricated on a substrate with gain, then the current oscillations at the Fano resonance frequency could lead to a very narrow band coherent terahertz radiation source following the concept of the lasing spaser [2–5].

5. Conclusion

In conclusion, we have experimentally and numerically shown that planar terahertz metamaterials with a small structural asymmetry can exhibit sharp Fano resonances. Theoretically Q factors of 50 can be achieved. These structures can have a multitude of applications including notch filters and highly selective narrowband THz emitters as well as highly sensitive terahertz based sensors for chemicals or bioagents.

Acknowledgements

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