Anisotropic change in THz resonance of planar metamaterials by liquid crystal and carbon nanotube

J. H. Woo, 1 E. Choi, 1 Boyoung Kang, 1 E. S. Kim, 1 J. Kim, 1 Y. U. Lee, 1 Tae Y. Hong, 2 Jae H. Kim, 2 Ilha Lee, 3 Young Hee Lee, 3 and J. W. Wu 1,∗

1Department of Physics and Quantum Metamaterials Research Center, Ewha Womans University, Seoul 120-750, South Korea
2Department of Physics, Yonsei University, Seoul 120-749, South Korea
3Department of Physics, Sungkyunkwan University, Suwon 440-746, South Korea
∗jwwu@ewha.ac.kr

Abstract: THz metamaterials are employed to examine changes in the meta-resonances when two anisotropic organic materials, liquid crystal and carbon nanotubes, are placed on top of metamaterials. In both anisotropic double split-ring resonators and isotropic four-fold symmetric split-ring resonators, anisotropic interactions between the electric field and organic materials are enhanced in the vicinity of meta-resonances. In liquid crystal, meta-resonance frequency shift is observed with the magneto-optical coupling giving rise to the largest anisotropic shift. In carbon nanotube, meta-resonance absorptions, parallel and perpendicular to nanotube direction, experience different amount of broadening of Lorentzian oscillator of meta-resonance. Investigation reported here opens the application of metamaterials as a sensor for anisotropic materials.
© 2012 Optical Society of America

OCIS codes: (160.3918) Metamaterials; (160.3710) Liquid crystals.

References and links
1. W. Withayachumnankul and D. Abbott, “Metamaterials in the terahertz regime,” IEEE Photon. J. 1, 99–118 (2009).
2. T. Driscoll, G. O. Andreev, D. N. Basov, S. Palit, S. Y. Cho, N. M. Jokerst, and D. R. Smith, “Tuned permeability in terahertz split-ring resonators for devices and sensors,” Appl. Phys. Lett. 91, 062511 (2007).
3. Y. Sun, X. Xia, H. Feng, H. Yang, C. Gu, and L. Wang, “Modulated terahertz responses of split ring resonators by nanometer thick liquid layers,” Appl. Phys. Lett. 92, 221101 (2008).
4. J. O’Hara, R. Singh, I. Brener, E. Smirnova, J. Han, A. Taylor, and W. Zhang, “Thin-film sensing with planar terahertz metamaterials: sensitivity and limitations,” Opt. Express 16, 1786–795 (2008).
5. C. Debus and P. H. Bolivar, “Frequency selective surfaces for high sensitivity terahertz sensing,” Appl. Phys. Lett. 91, 184102 (2007).
6. N. Vieweg, C. Jansen, M. Shafkat, M. Scheller, N. Krumbholz, R. Wilk, M. Mikulics, and M. Koch, “Molecular properties of liquid crystals in the terahertz frequency range,” Opt. Express 18, 6097–6107 (2010).
7. T.-I. Jeon, K.-I. Kim, C. Kang, S.-I. Oh, J.-H. Son, K. An, D. Bae, and Y. Lee, “Terahertz conductivity of anisotropic single walled carbon nanotube films,” Appl. Phys. Lett. 80, 3403 (2002).
8. R. Singh, E. Smirnova, A. Taylor, J. O’Hara, and W. Zhang, “Optically thin terahertz metamaterials,” Opt. Express 16, 6537–6543 (2008).
9. W. J. Padilla, M. T. Aronsson, C. Highstrete, M. Lee, A. J. Taylor, and R. D. Averitt, “Electrically resonant terahertz metamaterials: theoretical and experimental investigations,” Phys. Rev. B 75, 041102 (2007).
10. S. Jewell, E. Hendry, T. Isaac, and J. R. Sambles, “Tuneable Fabry-Perot etalon for terahertz radiation,” New J. Phys. 10, 033012 (2008).
1. Introduction

Metamaterials are artificial materials engineered to provide properties which are not readily available in nature. Among applications of metamaterials, frequency selective surface (FSS) received attention as high sensitivity sensors, mainly due to the ease of tailoring characteristics of meta-resonance such as the resonance frequency and polarization dependence. Importantly, the quality factor of FSS meta-resonance can be tailored by a structural design to enhance the sensitivity of sensor. In practice, dielectric materials are placed on top of micron-size patterned FSSs, and changes in terahertz (THz) resonance characteristics are examined.

Variety of FSS structures have been introduced to relate a change in THz transmission spectra with the dielectric properties of materials placed on top of FSSs [1]. With an array of single split-ring resonators (SRR), effects on the THz transmission spectra of a weak solution of silicon nanospheres [2], and dielectrics such as water, ethanol, and chloroform [3] are investigated. The observed red-shifts of resonant absorptions are attributed to an increase in capacitance of ring-resonators for low-energy inductance-capacitance resonance and also to an increase in the effective electron mass for high-energy electric dipole resonance. In an array of double SRR structures, a similar behavior of resonance red-shift is observed [4]. By introducing an asymmetric ring structure in FSS instead of a symmetric SRR structure, a high-sensitivity THz sensing is achieved [5]. In all the above examples, the resonance red-shift is investigated in an isotropic configuration, where solution or dispersion of dielectrics are deposited on top of the FSS. Noting that resonance characteristics of inductance-capacitance or electric dipole of a SRR are dependent on the incident electromagnetic wave polarization direction in general, the SRR is a metamaterial structure where an anisotropic change in the absorption resonances can be investigated for dielectrically anisotropic molecules.

In this study, we address the polarization-dependent change in the THz resonance in micron-sized metamaterial FSSs as anisotropic sensors. In doing so, we employ two FSSs, namely anisotropic and isotropic metamaterials. As the probe materials, we adopt anisotropic organic materials, i.e., liquid crystal and carbon nanotubes.

![Microscope pictures of (a) double split-ring resonator metamaterial A and (b) isotropic metamaterial B.](image)
2. Metamaterials and time-domain THz measurement

We examine how the resonance frequencies of polarization-sensitive anisotropic and polarization-insensitive isotropic metamaterials are affected by the presence of dielectrically anisotropic organic materials. We adopted organic molecules possessing a strong structural anisotropy, namely, liquid crystal and carbon nanotube, which exhibit dielectric anisotropy in THz regime. It is known that the torsional mode of liquid crystal survives down into THz regime with a significant contribution to the dielectric response and the refractive index of carbon nanotube varies in the range of 4.0-9.0 in 1 THz range [6, 7]. This suggests that THz metamaterials are appropriate meta-surfaces to sense the presence of liquid crystal and carbon nanotube near FSSs. Furthermore, we can monitor how the director of liquid crystal molecules and the cylindrical symmetric axis of carbon nanotube are oriented relative to anisotropic FSSs at THz frequency range.

We introduce two metamaterials shown in Fig. 1. The first metamaterial A is composed of double split-ring resonators, which possesses a magneto-electric coupling at low frequency

![Fig. 2. Metamaterial A and THz transmission spectra.](image)

![Fig. 3. Metamaterial B and THz transmission spectra.](image)
resonance for THz wave polarization parallel to the gap bearing arm. The lowest resonance is LC resonance and the higher resonances are dipole resonances, and the excitation of each resonance is polarization sensitive [8]. The second metamaterial B is composed of a four-fold rotational symmetric split-ring resonator, with the symmetric axes of x- and y-axis. It possesses the same resonance frequency for polarizations parallel & perpendicular to the gap bearing arm, hence polarization insensitive [9]. Substrate is p-doped silicon wafer, and a 10nm-thick titanium was deposited as adhesion layer, and a 200nm-thick Au was deposited on top. After the standard photolithography by use of mask aligner, the lift-off process provided the final metamaterials. Meta-particle is in the size of 36μm×36μm with the lattice constant of 50μm.

Time-domain terahertz transmission measurements were carried out with a TeraView TPS Spectra 3000 Spectrometer at a resolution of 1.2 cm⁻¹ at room temperature in vacuum. THz dipolar radiation from emitter is highly linear-polarized with less than 0.5% depolarization. By use of an aperture with diameter in size of 8mm, the central part of Gaussian beam is selected to ensure a plane wave propagation of ps pulse. The time-domain pulse duration is about 2 ps, leading to the accessible spectral range of 0.1-3 THz (3-100cm⁻¹). A fast Fourier transformation of time-domain signal provides the transmission spectrum. By dividing the sample spectrum by the p-doped silicon wafer spectrum, we obtain the amplitude and phase spectra. THz transmission spectra are shown in Fig. 2 and Fig. 3.

3. Liquid crystal and carbon nanotube on metamaterials

In order to study the polarization-dependent changes in THz resonance, we adopted dielectrically anisotropic nematic liquid crystal (LC) and carbon nanotube (CNT). Since THz transmission of metamaterial A is polarization-dependent, nematic LC and CNT, when placed along two orthogonal directions on top of metamaterial A, will modify THz resonance differently. On the other hand, nematic LC and CNT on top of metamaterial B will give rise to an isotropic change in THz resonance. We fabricated three samples with nematic LC and CNT, respectively.

3.1. Sample fabrication and measure of anisotropy

Nematic liquid crystal E7 (Merck, nematics at room temp.) is adopted, which has the ordinary and extra-ordinary refractive indices n_o=1.609 and n_e=1.761 in THz range of 0.2-1.2 THz [10].

![Fig. 4. Schematic drawing of LC on metamaterials. Director of LC is (a) parallel and (b) perpendicular to the gap-bearing arm of metamaterial A. (c) LC is on metamaterial B. (d) Picture of sample cells fabricated with LCs.](image-url)
In THz regime, the electromagnetic response of LC originates predominantly from vibrational and torsional modes of the molecule, which do not occur at optical frequencies [6, 11, 12]. Nematics E7 is reported to exhibit a birefringence of $\approx 0.17$ (0.2-1.2 THz) [13]. An LC alignment polyimide layer is prepared on a fused silica substrate to fabricate an LC cell. After rubbing process, an LC cell is constructed by sandwiching the fused silica substrate and metamaterial A or B with 12 $\mu$m spacer. Nematic LC filled the cell by a capillary action. By changing the rubbing direction, the director of nematic LC is oriented either parallel or perpendicular to the gap-bearing arm on metamaterial A. For metamaterial B, the director is oriented simply parallel to one of the gap-bearing arms. Figure 4 shows schematic drawings of nematic LCs on metamaterials A and B along with pictures of sample fabricated with LC.

To prepare CNT, a mixture of semiconducting and metallic ones was drawn from a sidewall of multi-walled nanotube forests formed on a silicon substrate [14]. After removing from silicon substrate, CNT yarn was attached to the metamaterial by drying out ethanol spayed on CNT yarn placed on metamaterial. CNT is multi-walled carbon nanotube sheet with diameter in the range of 10-15 nm, and is dichroic in THz absorption. When the polarization of THz wave and nanotube direction are in parallel configuration, there occur more absorption than in perpendicular configuration [7]. We attached CNT sheet to metamaterial A with the nanotube direction oriented either parallel or perpendicular to the gap-bearing arm. On metamaterial B the nanotube direction is oriented simply parallel to one of the gap-bearing arms. Figure 5 shows schematic drawings of CNTs on metamaterials A and B along with pictures of sample fabricated with CNT.

Now we introduce a measure of anisotropy in the THz spectra [15]. For liquid crystal, the size of liquid crystal cell gap is in the order of 10 $\mu$m, while the length of nematics is in the order of a few nanometers. When the anisotropy is measured with a linearly-polarized THz plane wave, the orientations of nematics relative to the polarization direction as well as relative to the beam propagation direction has to be taken into account, which leads to the measure of anisotropy as

$$\text{Anisotropy} = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}.$$ 

For carbon nanotube, nanotubes are attached on top of the metamaterials, forming a 2 dimen-
sional structure. Hence, the orientation of nanotubes relative to the polarization direction of a linearly-polarized THz plane wave solely contributes to the anisotropy, and the measure of anisotropy is defined as

\[
\text{Anisotropy} = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}.
\]

3.1.1. Liquid crystal on double split-ring resonator metamaterials

Once LC cells are prepared, we carried out THz-TDS measurements in configurations of different polarization directions of THz wave relative to directions of gap-bearing arm of metamaterial A and director of nematic LCs. Transmission spectra are shown in Fig. 6 corresponding to \(E\parallel\), and Fig. 7 corresponding to \(E\perp\). Here \(E\parallel\) and \(E\perp\) stand for the electric field parallel and perpendicular to the gap-bearing arm of metamaterials. Blue arrow corresponds to the beam propagation direction and solid black arrow corresponds to the polarization direction of incident THz wave. In both Fig. 6 and Fig. 7, nematic LC director is along dotted black arrow in

![Graph](image1)

Fig. 6. LC on metamaterial A, \(E\parallel\).

![Graph](image2)

Fig. 7. LC on metamaterial A, \(E\perp\).
Fig. 6(a) & 7(a), and along solid black arrow in Fig. 6(b) & 7(b). Since nematic LC is optically uniaxial with extra-ordinary and ordinary refractive indices, \( n_e \) and \( n_o \), THz wave experiences \( n_o \) in Fig. 6(a) & 7(a) and \( n_e \) in Fig. 6(b) & 7(b).

Furthermore, we compare the absorbance for \( n_e \) and \( n_o \) for a given relative configuration between the polarization direction and the gap-bearing arm direction in order to estimate the efficiency of metamaterial \( A \) as anisotropic sensor. We plot the absorbance spectra obtained from the transmission measurement, and calculate the anisotropy, namely, \( \text{Anisotropy} = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \), which is shown in Fig. 8. Change in the sign of Anisotropy along THz frequency means that the difference of red-shifts in \( n_e \) and \( n_o \) case changes sign. High anisotropic sensitivity can be achieved at the spectral region possessing large Anisotropys. Value of Anisotropy around 0.08 is observed in \( E_{\perp} \) configuration, and overall \( E_{\perp} \) is more efficient than \( E_{\parallel} \) in discerning the orientation of nematic LC director in terms of change in absorption differences near resonance frequency of metamaterial \( A \).

3.1.2. Liquid crystal on isotropic metamaterials

Transmission spectra measured for an isotropic structure is shown in Fig. 9. Blue arrow corresponds to the beam propagation direction. Solid black arrow corresponds to the polarization direction of incident THz wave. Nematic LC director is along dotted black arrow in Fig. 9(a), corresponding to \( n_o \) case, and is along solid black arrow in Fig. 9(b), corresponding to \( n_e \) case. We find that there exists a difference in transmission spectra between Fig. 9(a) and 9(b), which is from the fact that the refractive indices experienced by THz wave are different even though metamaterial is isotropic. As in the double split-ring resonators, we compare the absorbance for \( n_e \) and \( n_o \) in isotropic metamaterials, which is shown in Fig. 10.

Since transmission change is more pronounced in spectral shift than in absorption when nematic LC is present on top of metamaterials, we introduce a measure of spectral shift \( \Delta \omega \)

![Graph](image-url)
Fig. 9. LC on metamaterial B.

Fig. 10. Anisotropy (dark blue curve) is plotted, namely, Anisotropy = \((I_\| - I_\perp)/(I_\| + 2I_\perp)\) when nematic LC is present on top of metamaterial B.

defined as below.

\[
\Delta \omega = \frac{\omega_{LC} - \omega_0}{\omega_0} \times 100
\]

Negative value of \(\Delta \omega\) corresponds to a red-shift of resonance frequency, which is not directly related to the measure of anisotropic sensitivity of metamaterial Anisotropy = \((I_\| - I_\perp)/(I_\| + 2I_\perp)\), introduced in Fig. 8. Table 1 summarized the amount of red-shift \(\Delta \omega\) obtained from Fig. 6, Fig. 7, and Fig. 9. We find that the magneto-electric coupling resonance goes through large red-shifts, which indicates that nematic LC residing near the gap of double-split rings strongly distorts an asymmetric current flows responsible for magneto-electric coupling when the electric field of THz wave is applied along the direction of gap-bearing arm.

Regarding to the sensitivity of metamaterial assessing the anisotropy of materials, we note
Table 1. Red-Shift in Resonance Frequency of Metamaterial in the Presence of Nematic LCs

| metamaterial | resonance freq. | $n_\parallel$ case | $n_\perp$ case |
|--------------|-----------------|-------------------|----------------|
| A            | $E_\parallel$: 0.49THz | -6.5%          | -7.8%         |
|              | $E_\parallel$: 1.55THz | -3.7%          | -3.7%         |
|              | $E_\perp$: 1.25THz   | -5.1%          | -5.6%         |
| B            | 0.85THz          | -5.9%          | -6.0%         |

that Anisotropy = $(I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$ in the range of 0.05 is readily observed for 12μm thick nematic liquid crystal E7 cell, while the corresponding phase shift of $4 \times 10^{-3}$ of $2\pi$ is hardly observable in a usual polarization transmission measurement unless we adopt an interferometry setup.

3.1.3. Carbon nanotubes on double split-ring resonator and isotropic metamaterials

Figure 11(a) and 11(b) show transmission spectra of CNT prepared on the double split-ring resonator metamaterial when the polarization of light is parallel and perpendicular to the gap bearing arm, respectively. Figure 12(a) shows transmission spectra of CNT samples prepared with the isotropic metamaterial. In both metamaterials, we observed that the absorption gets larger and broader in parallel case (blue curve) than in perpendicular case (green curve). Noting that the FWHM of metamaterial resonance is determined by dissipation coming from Drude damping and radiative damping [16], we find that the presence of CNT on top of metamat-
Fig. 12. THz transmission spectra for CNT on isotropic structure along with bare isotropic structure spectra (red curve) is shown. Blue arrow corresponds to the beam propagation direction. Carbon nanotube is parallel (blue curve) and perpendicular (green curve) to the polarization direction.

Table 2. Oscillator Strength Changes in Resonance Absorption of Metamaterial in the Presence of CNTs

| metamaterial | resonance freq.  | parallel case | perpendicular case |
|--------------|------------------|---------------|-------------------|
| A            | $E_\parallel$: 0.49THz | -31.2%        | -36.2%            |
|              | $E_\parallel$: 1.55THz  | -36.2%        | -18.4%            |
|              | $E_\perp$: 1.25THz    | -54.8%        | -48.9%            |
| B            | 0.85THz           | -68.3%        | -64.7%            |

Figure 13 shows Anisotropy = $(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ for the parallel and perpendicular cases of the CNT alignment and polarization with absorbance spectrum of bare sample (dark blue). Figure 13(a) and 13(b) show Anisotropy for double split-ring resonator metamaterial when the polarization of light is parallel and perpendicular to gap bearing arm, and Fig. 13(c) shows Anisotropy for isotropic metamaterial. We find that the anisotropic absorption of CNT has been enhanced around the resonance frequency. To see the effect more clearly, we replotted Fig. 14 with the reference spectra (CNT on top of the bare Si substrate). For the reference sample, transmission spectra when CNT is parallel and perpendicular to the polarization are measured separately, and Anisotropy is calculated, which exhibits a rather flat response over the measured THz spectral range. When compared with Anisotropy of the reference sample (black curve), Anisotropy of metamaterial samples (red, blue, and green curves) exhibit very pronounced changes. In other words, the anisotropic absorption of CNT has been strikingly enhanced in the proximity of anisotropic meta-resonances of the metamaterial, which is of great use for metamaterials as anisotropic sensor.

Since transmission change is more pronounced in absorption than in spectral shift in the presence of CNT on top of metamaterials, we introduce a measure of oscillator strength change $\Delta \alpha$ defined as below.

$$\Delta \alpha = \frac{\alpha_{\text{CNT}} - \alpha_0}{\alpha_0} \times 100,$$

Negative $\Delta \alpha$ value corresponds to the decrease in resonance oscillator strength, which is the absolute measure of the sensitivity of metamaterial as sensors. These results are summarized in Table 2. In metamaterial A, $E_\perp$ configuration, corresponding to symmetric current flow in
Anisotropy $=(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ of CNT samples is shown with absorbance spectra of bare sample (dark blue curve). (a) Double split-ring resonator at $E_\parallel$ configuration. (b) Double split-ring resonator at $E_\perp$ configuration. (c) Isotropic structure.

the metamaterial, suffers a larger increase in the absorption than $E_\perp$ configuration for both polarizations parallel and perpendicular to CNT direction. When metamaterials A and B are compared, resonance absorption in metamaterial B goes through a much larger increase.

4. Summary

Anisotropic and isotropic THz metamaterials are employed to examine changes in the meta-resonances when two anisotropic organic materials, liquid crystal and carbon nanotubes, are placed on top of metamaterials. In both metamaterials, anisotropic interactions between the electric field and two organic materials are enhanced in the vicinity of meta-resonances. In liquid crystal, meta-resonance frequency shift is observed with the magneto-optical coupling giving rise to the largest anisotropic shift. In carbon nanotube, meta-resonance absorptions, parallel and perpendicular to the cylindrical axis, experience different amount of broadening of Lorentzian oscillator of meta-resonance. In case of liquid crystal, red-shift of metamaterial resonance spectrum is attributed to a change in the dispersive part of refractive index, while an increase in absorption of metamaterial resonance observed in carbon nanotube is from a change in the absorptive part of refractive index. Anisotropic interactions between metamaterials and anisotropic organic materials can be utilized in the application of metamaterials as a sensor for anisotropic materials.
Fig. 14. Anisotropy $= (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ of CNT samples shown in Fig. 13 is plotted all together with the reference spectra of CNT on top of bare Si substrate.

Acknowledgments

JWW acknowledges support from Quantum Metamaterial Research Center program as well as CNRS-Ewha International Research Center program and YHL acknowledges support from WCU program (R31-2008-000-10029-0) of the National Research Foundation of Korea funded by Ministry of Education, Science, and Technology, Republic of Korea.