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# Anomalous Transmission through Highly-Doped Conducting Polymer PPy(PF6) Films with Two-Dimensional Periodic Subwavelength Hole Array

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Since Ebbesen *et al.* reported the phenomenon of "anomalous transmission" through optically thick metallic film perforated with two-dimensional subwavelength hole array [1], many studies have been carried out with various goals ranging from fundamental interest to device application [1-13]. The transmission, T of perforated films has been found to be higher by about three orders of magnitude than the expected value predicted by the conventional aperture theory (Bethe's theory) [14], where T scales as $(r/\lambda)^4$ (here r is the hole radius and $\lambda$ is the wavelength). It has been also found that the absolute transmission efficiency, namely T divided by the holes area fraction, surprisingly exceeds the value of one. This implies that there is an enhancement mechanism of light transmission due to the hole arrays. Indeed the angular dependence of T spectrum agrees very well with the dispersion relation of surface plasmon polariton (SPP) on both film surfaces, and thus it is believed that the field enhancement is caused by SPP at the metal-dielectric interfaces.

Most of the research on "anomalous transmission" has been focused on 'good' metals such as Ag, Al, Au, Cr [3], Ni [5], as well as heavily doped semiconductors such as Si [12] and InPb [13]. Here we report the observation of "anomalous transmission" in film of another type of conductor, namely heavily-doped conducting polymer. Doped conducting polymers such as polyacetylene, polyaniline and polypyrrole, show metal-insulator transition at high doping level of few %. Among the class of conducting polymers, heavily-doped polypyrrole with PF6 [PPy(PF6)] is the most conductive [15-17]. Here we report for the first time the observation of "anomalous transmission" in the THz spectral range of a heavily doped PPy(PF6) film with two-dimensional subwavelength hole array (Fig.1(a)) [18].

The free-standing 25 μm thick PPy(PF6) film with a room-temperature DC conductivity of

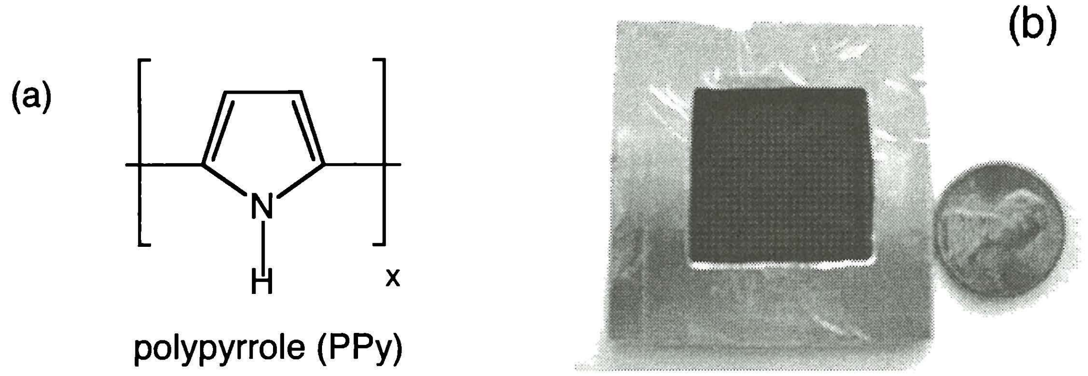


Fig. 1: Molecular structure of polypyrrole and picture of hole array on PPy(PF6) film.

215/(Ω cm) were prepared electrochemically at –40 C. It has been postulated that heavily doped PPy(PF6) has two plasma frequencies, where the lower frequency seems to be caused by a Drude type free electrons with plasma frequency in the THz range [13-15]. The hole arrays were fabricated using a laser machining system (Optec, MicroMaster), which is based on a pulsed excimer laser. The periodicity and diameter of the holes were 1 mm and 0.5 mm, respectively. The area fraction of the holes is thus ~ 20%.

We used a conventional THz time-domain spectroscopy (THz-TDS) setup [19] for measuring the transmission characteristics through the film. Photoconductive devices were used for both THz generation and coherent detection. The sample was placed at the center of the two off-axis parabolic mirrors of the optical system. The THz beam was normally incident on the sample and polarized parallel to the aperture rows. Reference transmission spectra were measured without the sample for normalization. THz-TDS

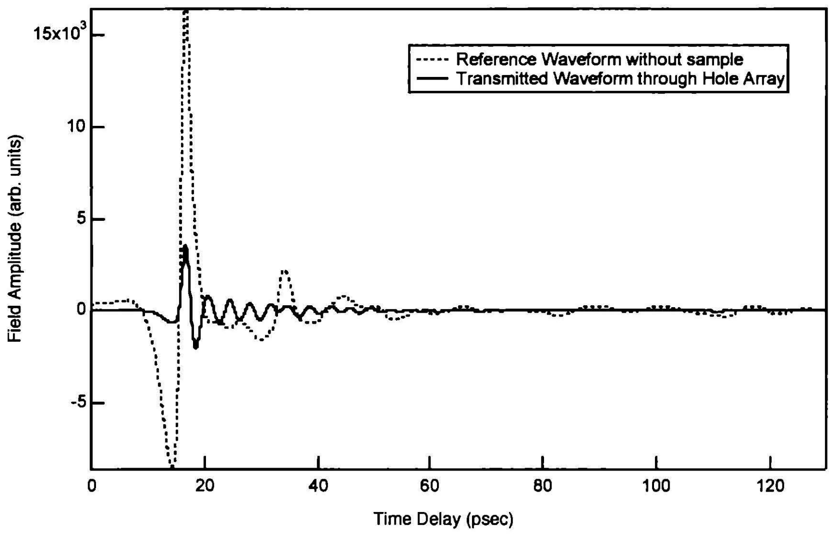


Fig. 2: Transient THz response through the free-standing 25 μm thick PPy(PF6) film with two-dimensional hole array (full line), and without the sample (dashed line) for normalization.

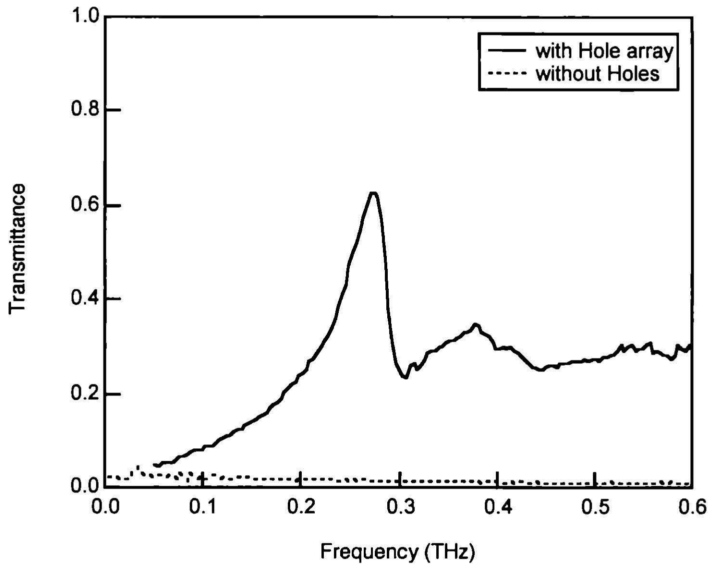


Fig. 3: Frequency-domain transmission spectrum through the free-standing PPy(PF6) film with (full line) and without (dashed line) the perforated two-dimensional hole array.

technique allows to directly measure THz electric field, so that both amplitude and phase information can be obtained. Figure 2 shows the measured transient response of THz radiation through the perforated PPy(PF6) film, and without the sample for reference. Applying Fourier-transform to the time-resolved responses into the frequency-domain, both magnitude and phase of the transmission spectrum are obtained.

Figure 3 shows the Fourier-transformed frequency-domain transmission spectra through the free-standing PPy(PF6) film with and without the perforated hole array. It is apparent from this figure that without the perforated hole array the PPy(PF6) film is almost opaque. However with the hole array, some peaks are observed in the transmission spectrum. At around 0.27 THz, the transmittance is almost 60%, which is much higher than the holes area fraction (~ 20%); this implies that anomalously enhanced transmission was obtained. The transmission peaks, $\lambda_{SP}$ agree very well with the theoretical model based on SPP dispersion for small holes, which can be expressed as [1]

$$\lambda_{SP} = \frac{a_0}{\sqrt{i^2 + j^2}} \left( \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right)^{1/2}, \qquad (1)$$

where $\varepsilon_m$ and $\varepsilon_d$ are the dielectric constants of the metal (that is PPy(PF6)) and dielectrics surrounding the metal (that is air), $a_0$ is the hole array lattice constant, and i and j are integers. Using Eq. (1) with $\varepsilon_m = -1.2\times10^4 + 2.5\times10^3 i$ the transmission peaks at about 0.27, 0.38 and 0.55 THz correspond to (i, j) = (1, 0), (1, 1) and (2, 0), respectively, and therefore we conclude that these anomalous transmission peaks are indeed caused by SPP.

In conclusion, we observed for the first time "anomalous transmission" through heavily doped organic conducting polymer PPy(PF6) that was perforated with two-dimensional subwavelength hole array.

It is expected that the transmission peaks show some tunability such as frequency shift, transmission height and bandwidth by changing the doping level of the PPy film. Further experiments are been completed at present and will be discussed elsewhere. Moreover, it is also conceivable that using the phenomenon of anomalous transmission as a spectroscopic technique, we would be able to better understand the doping process and transport mechanism in highly-doped conducting polymer, which is still actively debated.

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