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Resonantly-enhanced transmission through a periodic array of subwavelength apertures in heavily-doped conducting polymer films

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We observed resonantly-enhanced terahertz transmission through two-dimensional (2D) periodic arrays of subwavelength apertures with various periodicities fabricated on metallic organic conducting polymer films of polypyrrole heavily doped with PF_6 molecules [PPy(PF6)]. The "anomalous transmission" spectra are in good agreement with a model involving surface plasmon polariton excitations on the film surfaces. We also found that the 'anomalous transmission' peaks are broader in the exotic metallic PPy(PF6) films compared to those formed in 2D aperture array in regular metallic films such as silver, showing that the surface plasmon polaritons on the PPy(PF6) film surfaces have higher attenuation. © *2006 American Institute of Physics.*
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Since Ebbesen *et al.* reported the phenomenon of "anomalous transmission" through optically thick metallic films perforated with two-dimensional (2D) subwavelength hole arrays,[1] numerous studies have been carried out to explore both fundamental issues and potential device applications.[1–16] In pursuing these goals, there has been significant interest in expanding the range of experimental conditions under which this phenomenon may be observed. For example, while much of the early work in this area focused on studies at optical frequencies, there have been several recent demonstrations reporting observations of enhanced transmission at mid-infrared,[9] terahertz (THz),[10–14] and microwave frequencies.[15] Over this broad range of the electromagnetic (EM) spectrum, arrays fabricated on metal films have been the most intensely investigated. Two-dimensional periodic structures in such films not only allow for reasonable coupling of freely propagating radiation to surface EM waves, or surface plasmon polaritons (SPPs), but also exhibit attenuation properties for these surface modes that are perceived as adequate. The attenuation length is particularly long in the THz and microwave EM spectral ranges. Recent materials in which anomalous transmission through 2D aperture arrays has been demonstrated include amorphous silicon at optical frequencies,[16] and semiconductors at THz frequencies.[10]

Here we report, for the first time the observation of anomalous transmission in 2D hole arrays perforated on films of another, more exotic class of conductors, namely heavily-doped conducting polymers. Doped conducting polymers such as polyacetylene, polyaniline and polypyrrole show a metal-insulator transition at high doping levels of a few percent.[17] Among the class of conducting polymers, polypyrrole [PPy] heavily-doped with PF_6 [PPy(PF6)] is one of the highly conducting polymers, with very good stability in air.[17–20] Also its conductivity is large (>100 S/cm) even as the temperature approaches 0 K. It has been postulated that heavily-doped PPy(PF6) has two plasma frequencies, where the lower frequency seems to be caused by a Drude free electron dielectric response with a plasma frequency in the THz spectral range. Our finding shows that SPP excitations can be formed on the surfaces of metallic conducting polymers; so in this sense these novel organic metallic films behave like regular metals. However, when comparing the anomalous transmission spectra of the heavily-doped polymeric films with those of regular metals such as Ag, we found that the SPPs in PPy(PF6) have much larger attenuation.

PPy films were polymerized and doped electrochemically with PF_6 molecules at −40 °C. From earlier studies[18] it is known that in fully doped films there exists one dopant PF_6 ion for every four PPy monomers in the polymer chain. Also the room-temperature dc conductivity of heavily-doped PPy(PF6) is ~200 S/cm. To fabricate the 2D aperture array, the PPy(PF6) films were peeled off the electrodes following polymerization yielding free-standing films with thicknesses of ~25 μm.

We first measured the complex dielectric constant spectrum of the unperforated PPy(PF6) film in the THz EM range using conventional THz time-domain spectroscopy (THz-TDS).[21,22] In our setup, photoconductive (PC) devices were used for both THz generation and coherent detection. The sample was placed at the center of two off-axis parabolic mirrors used to collect, collimate, and focus the THz EM radiation. The THz EM beam was normally incident on the film surface and linearly polarized. Reference spectra were measured without the sample for normalization purposes. A unique feature of the THz-TDS technique is that it allows for a direct measurement of the THz electric field, so that both amplitude and phase information are obtained simultaneously. By Fourier transforming the ps time-resolved PC data into the frequency domain, we can then evaluate both

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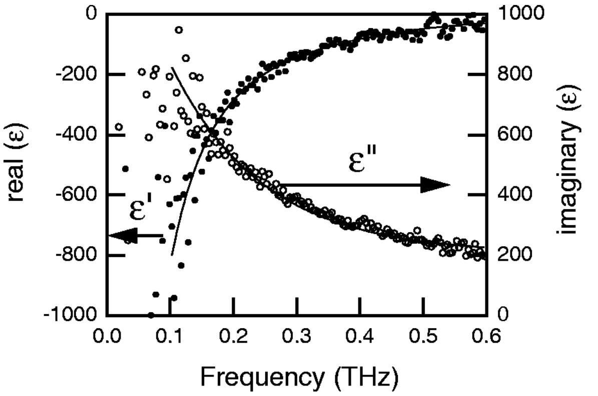

FIG. 1. Spectra of the real (ε'; filled circles) and imaginary (ε''; empty circles) components of the THz dielectric constant for the heavily-doped PPy(PF6) free-standing 25-μm thick film. The lines are to guide the eye.

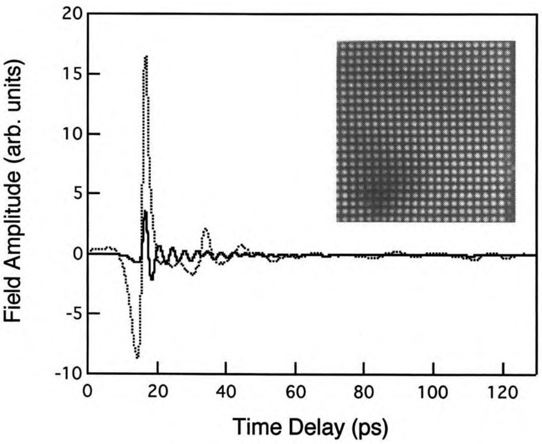

FIG. 2. Observed THz time-domain wave forms transmitted through the heavily doped free-standing PPy(PF6) film perforated with two-dimensional hole array (solid trace), and in the absence of the sample (dashed trace) for normalization. Inset: photograph of the free-standing 25-μm-thick PPy(PF6) film perforated with 2D hole array having 1-mm-square periodicity and 0.5 mm diameter.

real (n_r) and imaginary (κ) THz refractive indices from the resulting magnitude and phase spectra directly, without the need for Kramers–Kronig analysis. Using this information, we can obtain the real and imaginary dielectric constants from $\varepsilon=\varepsilon'+i\varepsilon''=n^2=(n_r+i\kappa)^2$ (here ε and $n=n_r+i\kappa$ are the complex dielectric constant and complex refractive index, respectively).

Figure 1 shows the measured real (ε') and imaginary (ε'') dielectric constant spectra of the heavily-doped PPy(PF6) film in the THz spectral range relevant to the resonant transmission measurements discussed below. We indeed found that ε' is negative over the spectral range of interest here, and this corresponds to "metallic" behavior. Thus the PPy(PF6) film should support SPP excitations. Our obtained dielectric spectra are consistent with those of Martens *et al.*[23] who found that the dielectric function of PPy(PF6) films is consistent with a Drude free carrier response with a very short scattering time of order 10 fs; we thus expect the SPP attenuation on such films to be relatively high.

Next, we examined the transmission characteristics of 2D periodic subwavelength aperture arrays fabricated on the PPy(PF6) films. The 2D hole arrays were fabricated on the polymer films using a pulsed excimer laser machining system (Optec, MicroMaster) in a square lattice geometry. We fabricated two samples with different periodicities, of 1 and 1.5 mm, on the heavily-doped PPy(PF6) film, with a corresponding hole diameter of 0.5 and 0.75 mm, respectively. The fractional aperture area was thus ~20% (inset of Fig. 2). The transmission characteristics of the two hole arrays were measured using the same THz-TDS technique discussed above. The polarization of the incident THz beam was parallel to the aperture rows, with the detector oriented to measure the same polarization. Figure 2 shows the typical measured transient response of THz radiation through the perforated PPy(PF6) film (solid trace), and in the absence of the sample (dashed trace) for normalization. These data were used to calculate the absolute amplitude transmission coefficient as a function of frequency, as explained above.

Figure 3 shows the Fourier-transformed frequency-domain transmission spectra through the free-standing heavily-doped PPy(PF6) film perforated with hole array of 1 mm (full line) and 1.5 mm (dotted line) periodicities. The transmission spectrum for the unperforated film is also shown (dashed line) for comparison. It is seen that without the perforated hole array the 25-μm-thick PPy(PF6) film is nearly opaque. However, with the hole array, transmission peaks are observed in the spectra. For the sample with 1 mm periodicity at the peak frequency of 0.27 THz, the transmittance is almost 60%. This is much larger than the fractional aperture area (~20%), implying that anomalously enhanced transmission was obtained.

The transmission peaks, $\lambda_{\rm SPP}$ agree well with the conventionally used model for such structures. In this model, the SPP dispersion relation for a perforated film is approximated by the dispersion relation for an unperforated film, and may be expressed as[24]

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

where ε_m and ε_d are the dielectric constants of the metal [i.e., PPy(PF6)] and the dielectrics surrounding the metal (i.e., air), a_0 is the hole array lattice constant, and i and j are integers. For the 1 mm 2D periodicity two prominent transmission peaks and another that is less prominent may be identified in Fig. 3. The transmission peaks are seen at $\nu_1=0.27$ THz; $\nu_2=0.38$ THz; and $\nu_3=0.55$ THz, which correspond to $\lambda_1=1.11$ mm; $\lambda_2=0.79$ mm; and $\lambda_3=0.55$ mm, respectively. These wavelength values are in excellent agree-

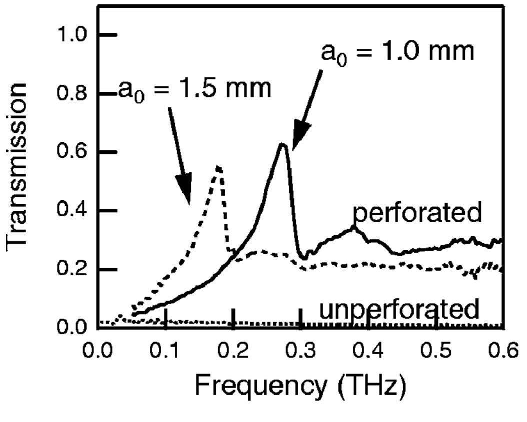

FIG. 3. Frequency-domain transmission spectra for free-standing PPy(PF6) films of heavily-doped films with 1 mm (solid trace) and 1.5 mm (dashed trace) periodicity, and an unperforated film (dotted trace).

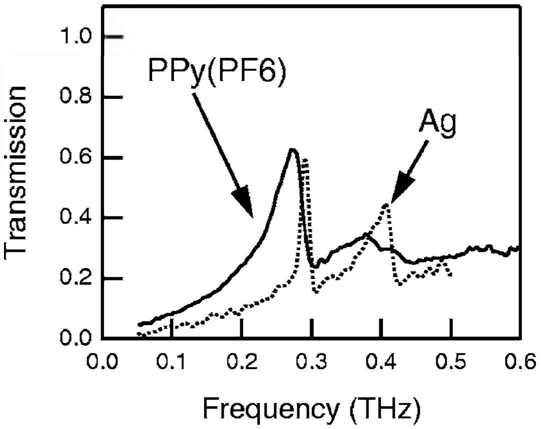

FIG. 4. Frequency-domain transmission spectrum through the free-standing heavily-doped PPy(PF6) film with 1 mm periodicity (solid trace) and a stainless steel foil over coated with Ag (dotted trace) having the same periodicity.

ment among themselves when calculating λ's using Eq. (1) for $(i,j)=(\pm 1,0)$, $(\pm 1,\pm 1)$, and $(\pm 2,0)$, respectively. Also their absolute values are consistent with Eq. (1) using the dielectric response given in Fig. 1. We therefore conclude that these anomalous transmission peaks are related to resonant interactions with SPP. By changing the periodicity of the 2D hole array, the transmission peaks shift to a correspondingly lower frequency, as observed by the dashed trace in Fig. 3. Prominent transmission peaks are now observed at $\nu_1=0.18$ THz and $\nu_2=0.25$ THz; no other resonantly enhanced peak can be identified for this film. These peaks correspond to $\lambda_1=1.67$ mm and $\lambda_2=1.20$ mm, respectively. The locations of these peaks agree perfectly with the new periodicity using Eq. (1) when taking into account the increase factor of 1.5 in the lattice constant periodicity a_0; they are also consistent among themselves. Thus, this simple, commonly used model can adequately explain our experimental observations. Our results indicate that heavily-doped conducting polymers contain large density of "free carriers" that allow direct excitation of SPP similar to normal metals, in spite of intrinsically disordered quasi-one-dimensional systems.

We note that the bandwidth of the lowest order transmission peak for the PPy(PF6) samples is much broader than the corresponding peaks observed for 2D hole arrays in regular metallic films.[11] In Fig. 4 we compare the anomalous transmission spectra for a 2D hole array in the doped PPy(PF6) film with 1 mm periodicity (solid trace) and a similar hole array fabricated in a stainless steel foil over coated with Ag (dotted trace) having the same periodicity. Although the transmission peaks have roughly the same value (~60%) in both samples, nevertheless the lowest order [namely $(\pm 1,0)$] resonant peak in the perforated PPy(PF6) film is broader by a factor of ~3 compared to the corresponding width of the lowest transmission band in the perforated Ag film. Also the frequency of the lowest order peak in the PPy(PF6) film is redshifted compared to that in the Ag film. We attribute the broader transmission resonance band for the PPy(PF6) sample to the fact that SPP excitations experience greater propagation losses in the doped conducting polymer compared to that in the metal film. The reason for the redshifted resonance in the perforated PPy(PF6) film compared to the Ag film is less clear.

In conclusion, we observed, for the first time, anomalous transmission through heavily-doped organic conducting polymer PPy(PF6) films that were perforated with 2D subwavelength hole array with various periodicities. The resonance transmission bands are in good agreement with a model of SPP excitations on the perforated films. By using organic conducting polymers, whose properties may be widely varied by chemical synthesis, we should be able to fabricate a variety of novel optical devices that may not be possible using metallic films. 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 heavily-doped conducting polymer. These topics are still being actively debated in the field.

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