Influence of plasmons on terahertz conductivity measurements

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Time-domain terahertz spectroscopy allows measuring the complex conductivity spectrum of materials at frequencies on the order of 1 THz (terahertz). Typically, terahertz studies produce conductivity spectra that are different from those predicted by the classical Drude model, especially in nanostructured materials. We claim that plasmon resonances in particles that are small compared to the THz wavelength cause these deviations. This is supported by measurements on photoexcited silicon, in bulk as well as in μm-sized particles. In the latter, the behavior is vastly different and strongly dependent on charge carrier concentration.

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The electrical resistance of metals and semiconductors, or its inverse, the conductivity, is dependent on the concentration of charge carriers—electrons and holes—in the material and on how easily these can flow through the material. The latter is affected by scattering processes such as collisions with other charge carriers and interactions with the crystal lattice. These processes typically result in a spectral signature in the lower THz range. Since it is possible to generate THz radiation as freely propagating beams,[1] THz spectroscopy is an ideal tool to measure the conductivity and obtain knowledge about charge-carrier behavior without the need for electrical contacts. The material properties can be expressed either as a complex-valued conductivity or the fully equivalent complex-valued dielectric function. The contribution of the charge carriers to the dielectric function can be described by the Drude model,[2] which assumes that the velocity of the charge carriers is damped with a damping time τ_D. Often, small deviations are found that imply that this damping does not have a single time constant.[3–5]

The deviations from the Drude model become more dramatic in nanostructured materials, such as photoexcited TiO_2 nanoparticles,[6] InP nanoparticles,[7] semiconducting polymer molecules,[8,9] and carbon nanotubes.[10,11] In these studies, conductivities were found that represent an oscillatory motion of the charge carriers rather than a damped linear motion. This behavior was attributed to charge-carrier backscattering,[6,7] charge-carrier pairs bound in excitons,[8,9] and resonances with a Lorentzian lineshape.[10–12] An exception is a study on CdSe nanoparticles,[13] where Drude-like behavior was found.

The cause of these deviations seems to be related to the fact that one measures an effective dielectric function of the structured material, which is not simply the sum of the contributions of its components. In Refs. 10–13, these effective dielectric functions are evaluated in a more thorough way. Still, in the latter three studies it was necessary to assume the existence of a resonance, without a clear physical origin being stated. The backscattering model, used in some studies,[6,7,11] is somewhat inconsistent: in the original paper, N. V. Smith[14] proposed that charge carriers might scatter anisotropically (the Drude model assumes isotropic scattering), and found that this effectively leads to Drude behavior with a different time constant. To explain the observed deviations from the Drude model one needs to assume that each charge carrier scatters only once, which has no clear physical basis.

We propose that there is a different explanation for these strong deviations from the Drude model in structured materials. In a THz experiment, one essentially applies an electric field to a sample and measures the resulting current. Since there are no electrical contacts, this current will lead to a surplus of positive charge at one side of the sample or the constituting particles, and a surplus of negative charge at the other side. This change in the charge distribution leads to an electrostatic force that drives the charge carriers back to their original position, which results in a damped harmonic oscillation. The exciton explanation[8,9] could be considered as a special case of this proposed mechanism.

In this letter, we speak in terms of the complex conductivity σ that defines the relation between the electric current density J and an electric field with angular frequency ω and amplitude E_0 according to $J(t) = \mathrm{Re}[\sigma(\omega)E_0 e^{-i\omega t}]$. The conductivity of a sample is obtained from an experiment by comparing the time-dependent electric field $E(t)$ of a THz pulse that has propagated through a sample with the incoming original field E_{in}. For the simplest possible experimental geometry, a thin slab with thickness d embedded in a medium with refractive index n, it can be derived[15] that

$$J(t) = -\frac{2\varepsilon_0 cn}{d}[E(t) - E_{\mathrm{in}}(t)], \tag{1}$$

where c is the speed of light and ε_0 is the permittivity of vacuum. The conductivity is then $\sigma(\omega) = \tilde{J}(\omega)/\tilde{E}(\omega)$, where $\tilde{J}$ and $\tilde{E}$ are the Fourier transforms of their time-domain counterparts.

In the Drude model,

$$\sigma(\omega) = \frac{\tau_D e^2 N/m}{1 - i\omega\tau_D}, \tag{2}$$

where τ_D is the damping time of the charge carrier motion, e is the elementary charge, N is the number density of the charge carriers, and m is their effective mass. Knowing the conductivity of a medium, one can describe its interaction with radiation. An essential quantity is the plasma frequency $\omega_p = (ne^2/\varepsilon_0 m)^{1/2}$. In the Drude conductivity model, radiation can propagate through a material if $\omega \gg \omega_p$, and will be absorbed if $\omega \ll \omega_p$. This is under the implicit assumption that the system under study is much larger than the wavelength of the radiation. This assumption is not correct in the case of

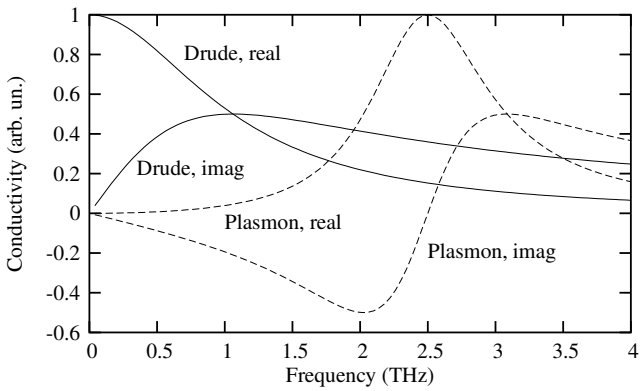

FIG. 1: The real and imaginary parts of the conductivity according to (1) a pure Drude model and (2) a damped plasma resonance [Eq. (4)] as would be measured in a THz measurement. Here, $\tau_D = 0.15$ ps and $\omega_0/2\pi = 2.5$ THz. A larger τ_D would lead to a sharper resonance.

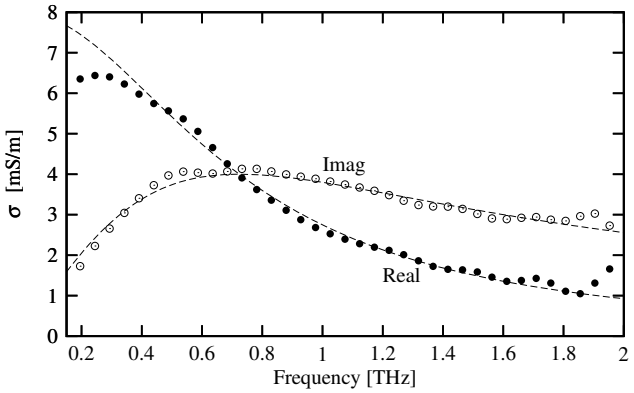

FIG. 2: Conductivity of a photoexcited silicon wafer, excited with 22 μJ/cm^2 at 800 nm. Above 0.4 THz, the spectrum exhibits a Drude behavior. For comparison, a Drude model with $\tau_D = 0.22$ ps is shown (dashed lines). The data for other excitation intensities differed only in amplitude.

THz measurements on particles that are small compared to the wavelength, where charges cannot pass the boundaries of the particles. This leads to a plasmon resonance at a frequency (for a spherical particle)[16] $\omega_0 = \omega_p/\sqrt{3}$. (The dielectric constants of the particle and the surrounding medium would lead to an additional scaling factor, which we do not take into account in this more qualitative discussion.) Hence, as we already mentioned in the beginning, the equation of motion for the charge carriers takes the form of a damped harmonic oscillator,

$$x'' + \frac{1}{\tau_D}x' + \omega_0^2 x = \frac{eE_0}{m}e^{-i\omega t}, \tag{3}$$

where x is the excursion of the charge carriers from their equilibrium position. From this, we can derive the conductivity

$$\sigma(\omega) = \frac{\tau_D e^2 N/m}{1 - i\omega\tau_D(1 - \omega_0^2/\omega^2)}, \tag{4}$$

which reduces to the Drude model for $\omega \gg \omega_0$. Figure 1 shows the difference between Drude-like conductivity and a plasmon-like conductivity. Although this model is not very refined, it can be expected that its qualitative features are correct, for example the fact that the imaginary part of σ crosses the frequency axis at ω_0. The resulting conductivity is qualitatively similar to that resulting from a Lorentz-like resonance,[10–12] but the latter would be more appropriate for a quantum-mechanical two-level system.

We examined the effect of sample morphology on the measured conductivity experimentally. A 0.5 mm thick wafer of crystalline undoped silicon was cut in half. One half was ground to a powder with particle sizes between 1 and 30 μm. The powder was mixed with a viscous solution of polyvinylpyrrolidone (PVP) in ethanol. The mixture was painted on a fused-silica substrate and was allowed to dry, resulting in a 40 μm film consisting of silicon particles embedded in a PVP matrix. The volume fraction of silicon was estimated to be below 0.1. The transmittance of the Si:PVP film was 0.5 at 800 nm. The THz conductivity was measured with a setup similar to the one used by Beard *et al.*[5] The THz radiation was focused onto the sample (focus diameter approx. 2 mm), and the sample was excited with laser pulses with a wavelength of 800 nm and a spot diameter of 15 mm. We ensured that the central part of the excitation spot had a homogeneous intensity in order to prevent the THz probe pulse from being diffracted and causing artifacts. The delay between the excitation pulse and THz pulse was 100 ps, to allow for thermalization of the charge carriers within the conduction band.

The measured conductivity $\sigma(\omega)$ in the silicon wafer is shown in Fig. 2. The conductivity follows approximately a Drude model, except for the lower frequencies, where we cannot rule out that the small size of the probed region, only 2 times the wavelength at 0.3 THz, affects the measurement. At the edges of the THz focus, electrical charges are built up, which would result in effects that are somewhere between the bulk limit (system dimensions are much larger than the wavelength) and the small-particle limit [Eq. (4)].

As expected, the conductivity in the silicon-powder sample is completely different, as is shown in Fig. 3. There is a good qualitative agreement between the measured conductivities and the plasmon model. At the lowest excitation intensity, the data can be described with a Drude damping time $\tau_D = 0.15$ ps. We estimate from the penetration depth of 9.8 μm[17] that the electron–hole pair concentration is $N/2 = 7.6 \times 10^{15}$ cm^{-3}. This agrees with the findings in reference 3, which lists $\tau_D = 0.20$ ps for electrons and 0.08 ps for holes at comparable concentrations.

The plasmon frequency can be recognized as the frequency at which $\mathrm{Im}(\sigma)$ crosses the frequency axis and $\mathrm{Re}(\sigma)$ is maximal. At higher concentrations N, the plasmon frequency should increase proportionally to $\sqrt{N}$. The experimental results for 22 and 101 μJ/cm^2 agree well with this expectation, but those between 1.9 and 22 μJ/cm^2 do so only approximately for reasons not clear to us. We also note that the Drude damping time τ_D decreases as the excitation intensity

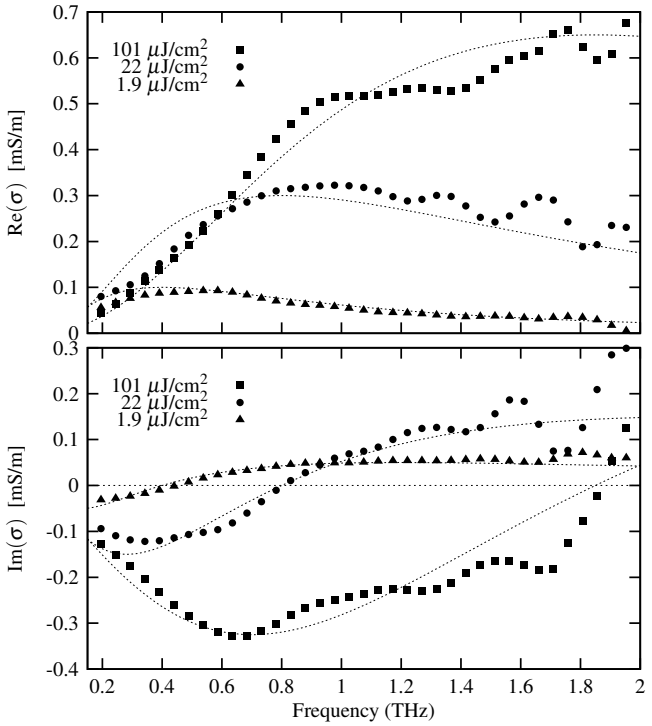

FIG. 3: Conductivity of PVP with embedded silicon particles after photoexcitation. The dashed lines represent the plasmon model in Eq. (4), with Drude damping times τ_D of 0.15, 0.08, and 0.038 ps, plasmon resonance frequencies $\omega_0/2\pi$ of 0.4, 0.8, and 1.85 THz,at excitation intensities of 1.9, 22, and 101 μJ/cm^2, respectively.

increases, which agrees with observations in Ref. 3.

The agreement between measured and calculated conductivity is only qualitative; there are clear differences. We attribute the differences to the inhomogeneous character of the sample and excitation conditions. Since the excitation light is attenuated in the sample, a lower concentration of charge carriers is created in the deeper-lying particles. Also, particles larger than the penetration depth (9.8 μm at 800 nm[17]) of the excitation light are mainly photoexcited on one side. Furthermore, we calculated the plasmon frequencies based on spherical particles; other particle geometries will have different plasmon frequencies. Finally, we assumed only one type of charge carriers, while in our measurements, both electrons and holes participate in the movements of the charges.

Summarizing, we have shown that plasmon resonances in small particles can explain the strong non-Drude behavior of the frequency-dependent conductivity obtained from THz time-domain spectroscopy. For low charge carrier concentrations, which lead to a low plasmon frequency, the measured conductivity is representative for the conductivity of the particle material. For higher concentrations, one could in principle model plasmon resonances and separate the true conductivity from the plasmon effects.

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