Time- and Frequency-resolved Electrodynamics of Germanium Nanoantennas for Mid-infrared Plasmonics

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***Abstract*— We investigate the mid-infrared response of heavily doped germanium films and periodic arrays of nanoantennas by both continuous wave transmission/reflection spectroscopy and ultrafast pump-probe spectroscopy. We compare the data to finite-element modeling electromagnetic simulations of the subwavelength nanostructures. The plasma frequency of the doped or optically activated semiconductor extends in the 1000-2000 cm^{-1} range thus enabling access to molecular fingerprints.**

I. Introduction

PLASMONICS, or the study of free electron oscillations at optical frequencies, holds great promise for the development of future integrated photonic devices of subwavelength size, where the electric field intensity and phase distribution in space can be controlled by nanostructure geometry and then realized by nanofabrication techniques.

The plasmonic approach could is even more intriguing in the mid-infrared (IR) than in the near-IR or visible range, as it provides a route to near-field optics in a spectral window where fiber optics are not easy to fabricate. In addition, noble metals behave almost like perfect conductors and therefore subwavelengthnanostructures present high impedance mismatch to mid-IR radiation coupling [1]. The key ingredient to plasmonics in this frequency range is a material with plasma frequency in the mid-IR, low free carrier losses and high nanofabrication/integration potential.

In this work we study both electron-doped and intrinsic epitaxial germanium (n-Ge and i-Ge) films grown on silicon substrates by frequency- and time-resolved techniques. By Fourier transform infrared spectroscopy (FTIR) both in reflection and transmission geometry we demonstrate two orders of magnitude field enhancement factors in n-Ge nanoantennas. We assess that free carrier losses due to charged donor impurities and optical phonon scattering are extremely relevant in limiting the field enhancement factors. In parallel, we propose ultrafast activation by interband optical pumping of electron-hole pairs in i-Ge as a viable path to overcome both limitations, as charged impurities are not present in i-Ge and electron-phonon scattering times are longer than the time needed to establish plasma oscillations Moreover, ultrafast mid-IR pulses provide extremely high field intensities for nonlinear plasmonics. It remains to be seen how far the screened plasma frequency ω_p can be increased by doping, by optical pumping, or by a combination of the two methods. In the case of n-Ge at room-T one finds a Drude-like response with electron effective mass of conductivity $m^* = 0.12\ m_e$, infinity dielectric constant $\varepsilon_\infty \sim 16$ and (screened) plasma frequency $\omega_p \sim \sqrt{n/m^*\varepsilon_\infty}$ spanning in perspective the whole useful mid-IR molecular vibration fingerprint range (400-2000 cm^{-1}), as already found in doped Si [2,3] and InAs [4]. However, the plasmon decay time is found to be considerably shorter than the electron scattering time, i.e. the higher mobility of semiconductors compared to metals does not help in improving the quality factor of plasmonic resonators [5].

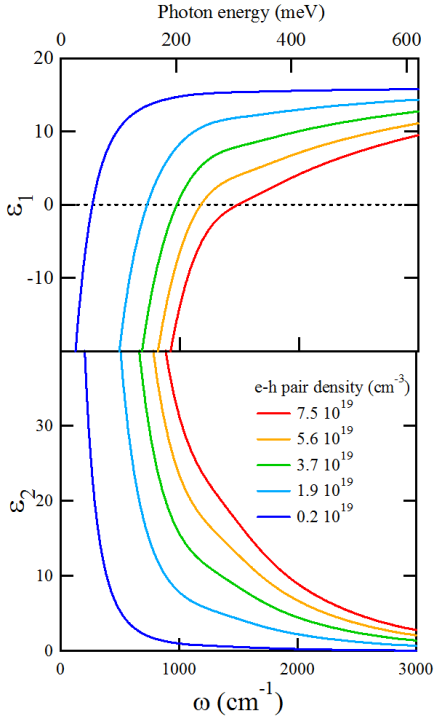

Figure 1. Calculated dielectric function of a plasma composed of both electrons and holes for different electron-hole pair excitation densities. The zero-crossing point of ε_1 is lower than that of a pure electron gas because of the larger average effective mass of holes.

II. Plasma Frequency under Optical Pumping

In our experiments, we investigate arrays of nanoantennas in the shape of rectangular rods, 1 μm thick, 800 nm wide and 2 or 3 μm long, either isolated (i.e. with distance among them larger than the near-field extension) or arranged in isolated pairs (inter-rod distance of 300 nm). Arrays of identical

geometry were fabricated on n-Ge films, to be analyzed by continuous-wave FTIR reflection/transmission spectroscopy in the entire far-to-near IR range (1-200 THz), and on i-Ge, to be optically pumped in the near-IR above the Ge direct gap (10 fs pulses centered at λ=1.02 μm) and probed by ultrafast mid-IR pulses (bandwidth 15-25 THz).

In order to describe active plasmonics in undoped semiconductors, where the free carriers are generated by optical pumping with ultrafast pulses of duration shorter than the plasmon decay time, we first have to define ω_p in the presence of both electron and hole gases. This is also needed to derive, from the mid-IR probe transmission spectra, the exact density of free carriers actually generated in the valence and conduction bands from the transmitted intensity of the spectroscopic probe pulse at pump-probe coincidence. The response of the hole gas can be modeled by a combination of light ($m^*_{LH} = 0.043\ m_e$) and heavy ($m^*_{HH} = 0.33\ m_e$) hole carriers resulting in a conductivity effective mass for holes of $m^* = 0.26\ m_e$ which is twice larger than that of electrons alone. Theoretical estimations of the dielectric constants for different electron-hole plasma are shown in Fig. 1 based on the results of steady-state spectroscopy of n-doped and p-doped Ge films. Finite-frequency transitions between the fully occupied split-off band and the partially unoccupied heavy- and light-hole valence bands fall in the mid-IR range (from 800 to 2000 cm^{-1}) further complicating the plasmonic response. Nevertheless, a clear advantage in terms of highest frequency of operation can be gained over n-Ge for pump fluence levels capable of exciting 10^{20} cm^{-3} electron-hole pairs.

III. Results

Epitaxial n-Ge and i-Ge films of 1 μm thickness are grown on silicon wafers by ultra-high vacuum chemical vapour deposition. The optical constants of the n-Ge film determined by FTIR returns $\omega_p \sim 1010$ cm^{-1} (or 30.5 THz) perfectly compatible with the doping level $n \sim 2.3 \cdot 10^{19}$ cm^{-3} determined by dc transport techniques. The frequency-dependent free carrier losses are extracted and compared to first-principle quantum calculations of electron-phonon and charged impurity scattering. Double-rod nanoantennas are fabricated by lithography and deep reactive ion etching on n-Ge and i-Ge films. Transmittance and reflectance spectra of n-Ge nanoantennas are studied by FTIR and two distinct localized plasmon resonances lie at 400-500 cm^{-1} and 800-900 cm^{-1}, according to the specific antenna length and single- or double-rod design. A clear dip in the reflectivity between the two resonances (i.e. around 700 cm^{-1} in the blue curve of Fig. 2a) is the clearest mark of antenna response.

Concerning the optical control experiments on i-Ge nanoantennas [1], the specular reflectivity when the incidence is fixed at the at Brewster angle for Ge is found to decrease strongly upon impulsive excitation of the plasma frequency. The optical response then starts to recover its equilibrium value first in the high-frequency region around 850 cm^{-1} and later on in the lower-frequency range around 500 cm^{-1}. The whole dynamics occur within few hundreds of ps. A possible interpretation for the observed behavior is the redshift of the plasma edge with increasing pump-probe delay, that in turns red-shifts the antenna resonances. In any case, the fact that reflectivity changes involve the spectral range above 850 cm^{-1} provides indication that the effective free carrier density reached by photoexcitation is larger than the one obtained by doping with $n \sim 2.3 \cdot 10^{19}$ cm^{-3} (as discussed above, in the n-Ge antennas the dip in the reflectivity was around 700 cm^{-1}). The high carrier density obtained in the the optical-control approach, combined with the advantage of a higher quality factor due to improved plasmon decay time by the lack of charged impurities, pave the way for efficient plasmonic antenna sensing in the mid-IR range.

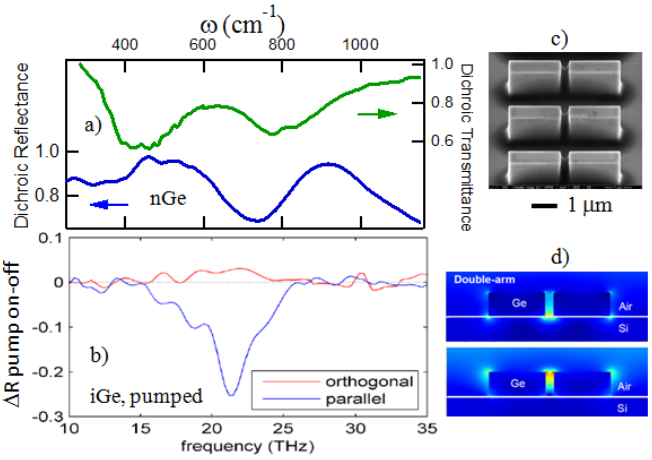

Figure 2 a) Linear dichroic ratio (ratio between spectra acquired with parallel/perpendicular polarization with respect to the antenna axis) of FTIR transmittance and reflectance spectra of n-Ge nanoantenna arrays. b) Pump-induced reflected intensity change probed at pump-probe coincidence with ultrashort mid-IR pulses. Pump wavelength is 1050 nm, pulse duration is sub-20 fs, pulse energy around 7 μJ. c) SEM image and d) Finite-difference time-domain modeling of the field intensity in the vertical section plane.

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