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Abstract. The use of heavily doped semiconductors to achieve plasma frequencies in the mid-IR has been recently proposed as a promising way to obtain high-quality and tunable plasmonic materials. We introduce a plasmonic platform based on epitaxial n-type Ge grown on standard Si wafers by means of low-energy plasma-enhanced chemical vapor deposition. Due to the large carrier concentration achieved with P dopants and to the compatibility with the existing CMOS technology, SiGe plasmonics hold promises for mid-IR applications in optoelectronics, IR detection, sensing, and light harvesting. As a representative example, we show simulations of mid-IR plasmonic waveguides based on the experimentally retrieved dielectric constants of the grown materials. © *The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI.* [DOI: 10.1117/1.JNP.9.093789]

1 Introduction

Over the last two decades, the development of plasmonics for operation around the visible spectral window has heavily relied on gold as the preferred material, mainly because of its excellent properties in terms of stability, easy chemical synthesis, and biocompatibility.[1–6] Already in these high-frequency ranges, however, other metals have sometimes been preferred when it comes to specific spectral regions, in particular, Ag and Al for the blue region and, more recently, the near-UV region.[7,8] Longer midinfrared (mid-IR) wavelengths have also been approached by exploiting gold,[9–13] which in the IR range behaves as a very good conductor, with low penetration depths for the electromagnetic fields. Strictly speaking, however, the equivalent of a plasmonic metal in the mid-IR would possess carrier densities in the 10^{19} to 10^{20} cm^{-3} range, something that can be achieved by heavily doping the semiconductor. Indeed, a few seminal works have already outlined the very interesting possibilities that will be opened by the use of such materials for mid-IR plasmonics.[14–16] The idea of turning attention to semiconductors as "metals" in the mid-IR comes from the dependence of the plasma frequency (marking the onset of conducting behavior) on the carrier density n, according to the relation $\omega_p \propto \sqrt{n/m^*}$, where m^* represents the effective mass of the free carriers involved in the plasma oscillations.

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Another relevant issue when it comes to the use of plasmonic interfaces in optoelectronics and integrated devices is the compatibility with the existing Si photonics and CMOS platforms, something that cannot be solved with Au-based nanostructures. A natural choice in terms of semiconductor materials, from the point of view of integration, points toward Si and Ge.[17–19] Between these two, Ge should be preferred both in standard mid-IR photonic devices, due to its inherently lower losses, and for plasmonic applications based on heavy doping, since the lower effective mass ($m* \approx 0.12$ for Ge compared to $m* \approx 0.26$ for Si) allows a higher plasma frequency to be reached for a given doping level.

2 Material Growth and Characterization

We grow epitaxial Ge on standard Si wafers by low-energy plasma-enhanced chemical vapor deposition (LEPECVD).[20,21] In an LEPECVD reactor, as sketched in Fig. 1(a), the wafer is exposed to a high intensity plasma, leading to growth rates of several nanometers per second through a very efficient decomposition of the reactive molecules. Since the plasma is obtained by a low-voltage arc discharge, the ion energies are in the range of tens of eV, low enough to allow the growth of crystalline materials. The plasma source is connected to a UHV chamber and the geometry of the plasma is designed by a grounded anode in the lower part of the growth chamber and by a magnetic field induced by a combination of coils and permanent magnets. The reactive gases, SiH_4, GeH_4, B_2H_6, and PH_3, are fed into the growth chamber through a gas dispersal ring placed above the anode. The dopant gases are diluted in Ar, respectively, 1% and 5%. The substrate is kept at a fixed potential with respect to ground and its temperature is adjusted between 200°C and 750°C by radiation heating. The deposition chamber has a base pressure of 10^{-9} mbar, while the working pressure is much higher, reaching 10^{-2} mbar. The growth rate is mainly controlled by the plasma density and by the gas flows and it is almost independent from the substrate temperature. For this reason, the growth rate and the surface diffusivity of the adatoms are completely decoupled and they can be optimized separately, a key issue in achieving a high concentration of activated dopants. Moreover, since the decomposition of the reactive molecules is dominated by the plasma, the surface chemistry between the substrate and the reactive molecules plays a modest role in the determination of the alloy composition, which can be easily controlled by the gas flows. The investigated samples were grown on p-type Si(001) substrates with a resistivity of 5 to 10 $\Omega \cdot$ cm. Before the heteroepitaxy, the native oxide was removed by dipping the substrate in aqueous hydrofluoric acid solution. All samples
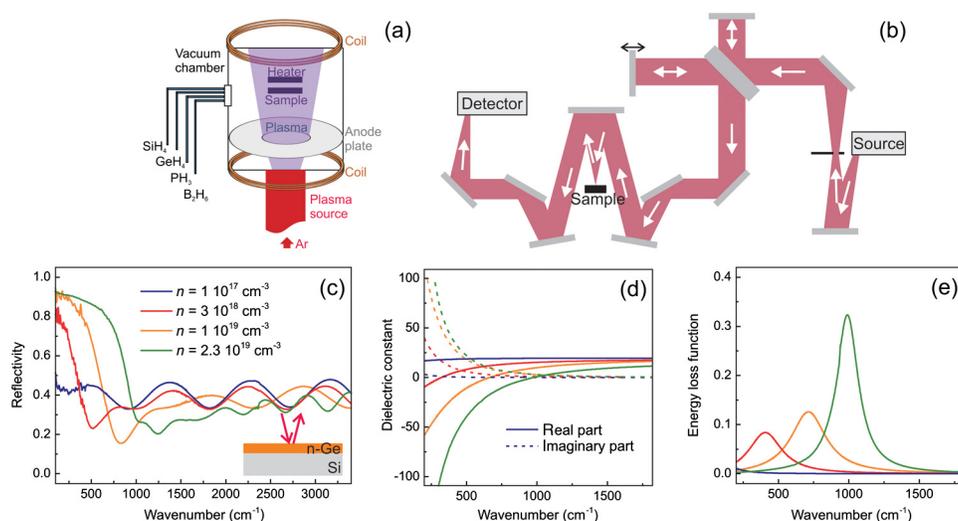

Fig. 1 (a) A sketch of the low-energy plasma-enhanced chemical vapor deposition reactor; (b) a sketch of the Fourier-transform infrared spectroscopy setup; (c) the reflectivity spectra for samples with different doping levels; (d) the dielectric constant of the investigated samples extracted from the reflectivity data; (e) a plot of the energy loss function, highlighting the position of the plasma frequency in the investigated materials.

were deposited at 500°C at a growth rate of ∼1 nm/s, with a GeH_4 flux of 20 sccm. The highest investigated doping ($\sim 2.3 \times 10^{19}$ cm^{-3}) was achieved *in situ* by adding 0.15 sccm of PH_3.

The mid-IR response of materials with different levels of doping in the 10^{17} to 10^{19} cm^{-3} range has been characterized by means of Fourier-transform infrared spectroscopy based on a Michelson interferometer, as sketched in Fig. 1(b). Figure 1(c) shows the reflectivity data acquired at near-normal incidence from each sample, after normalization to the reflectivity of a gold mirror. It can already be appreciated that the reflectivity drops from nearly 100% to about 35% when the plasma frequency of the material is crossed and the material's behavior accordingly turns from metallic (at low frequencies) to dielectric (at high frequencies). In the dielectric region, clear Fabry–Pérot fringes appear because of the finite thickness of the Ge film (1 to 2 μm for the different investigated samples). By applying a fitting procedure based on multilayer reflectivity and the Drude model, we extract the dielectric function from the experimental data, as demonstrated in Fig. 1(d). In agreement with the above discussion, it can be observed that the real part of the dielectric constant of each sample becomes negative below the corresponding plasma frequency, signifying metallic (plasmonic) behavior. To better highlight the plasmonic response of each material, we plot in Fig. 1(e) the energy loss function, calculated as $\text{Im}(1/\varepsilon)$, which peaks around the plasma frequency because of the energy loss channel opened by bulk plasmons in doped Ge. It can be discovered that the highest doping achieved in this series of samples ($n \sim 2.3 \times 10^{19}$ cm^{-3}) places the plasma frequency of Ge around 1000 cm^{-1} (around 10-μm wavelength), thus paving the road toward applications of this material platform in mid-IR plasmonics. Doping just above the 3×10^{19} cm^{-3} level is technically achievable and would be sufficient to enable sensing throughout the whole of the important 8 to 13 μm mid-IR window where many chemical and biological molecules have unique stretching and bending mode molecular absorption lines.

3 Example: Dielectric-Loaded Plasmonic Waveguides

As a representative example, we consider subdiffraction mode confinement below the dielectric cut-off in coupled metal-dielectric waveguides. In general, the strong reduction of the mode cross section in plasmonic waveguides, which is accompanied by a reduced effective wavelength as well, comes together with significantly increased losses, so that a trade-off between mode volume and propagation length always needs to be considered. For this reason, while standard dielectric waveguides are likely to be the preferred choice for on-chip transmission of signals over footprints that are much larger than the wavelength, plasmonic waveguides could be a choice when strong field confinement, even if only over small distances, is a premium feature, e.g., in integrated sensing applications. From this point of view, the use of a Ge-on-Si platform in the mid-IR allows for the realization of both low-loss dielectric waveguides, with intrinsic Ge already being proposed as one of the key materials for mid-IR waveguiding,[19] and plasmonic waveguides, by exploiting heavy n-type doping with P, As, or Sb atoms.

Figure 2(a) shows representative data obtained by finite-difference frequency-domain methods[22] of the quasidegenerate transverse-magnetic (TM) and transverse-electric (TE) fundamental modes supported by a square dielectric Ge waveguide on a Si substrate, as a function of the side L of the waveguide. It can be observed, as expected, that the mode index decreases with the decreasing cross section of the waveguide, until it approaches the index of the substrate and cut-off is reached. For the wavelength $\lambda = 16$ μm used in these simulations, guided modes exist only for waveguide cross sections larger than about 4×4 μm^2, with the TM_0 mode being the last one to reach cut-off. A standard geometry for subdiffraction plasmonic waveguiding is the so-called dielectric-loaded waveguide,[23–25] where a thin dielectric slab is placed on top of a plasmonic film. Figure 2(b) shows that, by exploiting this concept, a Ge dielectric waveguide with a cross section as small as 4×1 μm^2 on top of an n-doped Ge film can sustain a propagating plasmonic mode. The dielectric constant of the n-doped Ge is taken from experimental data for the $n \sim 2.3 \times 10^{19}$ cm^{-3} doping level and the index of the supported plasmonic mode is about $5.0 + 1.9i$, confirming that the strong confinement is achieved at the expense of extremely large losses, as is common in most plasmonic waveguides. In perspective, more favorable waveguide geometries allowing for lower losses can be designed.
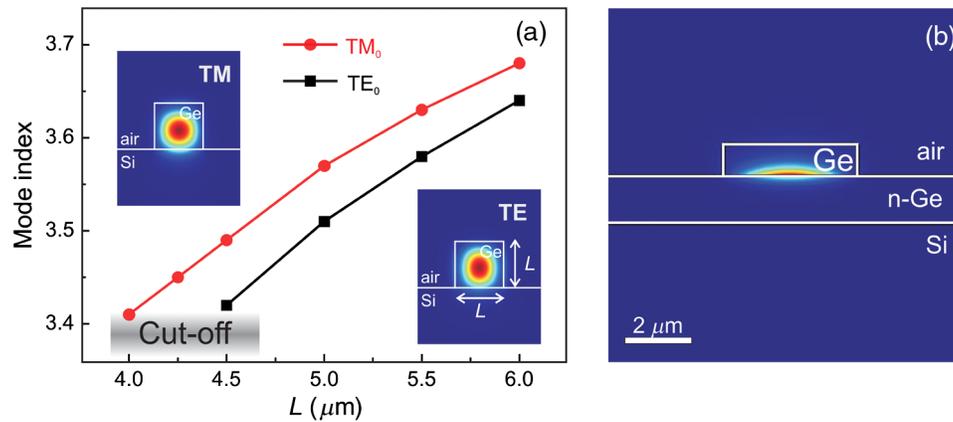
Fig. 2 (a) The effective index of the TM_0 and TE_0 modes in a dielectric Ge waveguide of varying square cross section fabricated on Si; the cut-off is reached for a cross section of about 4×4 μm^2; (b) a dielectric-loaded plasmonic waveguide realized with a 4×1 μm^2 dielectric Ge slab on top of a 2-μm thick n-doped Ge film.

4 Conclusions

Heavily doped semiconductors might open a new era in mid-IR plasmonics due to the high quality of the material and the possibility of tuning the plasmonic response by controlling the carrier concentration with electrical or optical means. In this frame, the development of a group-IV plasmonic material platform would further benefit from the large integrability and low costs allowed by the compatibility with the Si photonics and CMOS platforms. The present materials already allow operation in the 10 to 20 μm window, thus, e.g., covering part of the so-called fingerprint region which is of special interest for sensing applications. Future efforts along this road need to be focused on increasing the doping level of Ge and on understanding the sources of losses at mid-IR frequencies in order to optimize the plasmonic material and possibly enter the 5 to 10 μm wavelength window.

Acknowledgments

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