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Mid-Infrared Sensing Using Heavily Doped Germanium Plasmonics on Silicon Substrates

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Heavily-doped semiconductor films are very promising to produce mid-infrared plasmonic devices for a wide range of sensing applications because the real part of the dielectric function of the film is negative and broadly tunable in this wavelength range. In this work, we investigate, n-type doped Ge epilayers grown on Si substrates. We design and realize Ge nano-antennas on Si substrates demonstrating the presence of localized plasmon resonances, and exploit these resonances for molecular sensing in the mid-infrared.

Introduction

The quest for novel plasmonic materials has been a lively area of research over the last few years [1]. To-date, surface plasmon polaritons and localized surface plasmons have been almost exclusively based on metals such as gold, aluminium and silver, which display plasma frequencies close to the visible and near infrared spectral region [1-2]. At these wavelengths, surface plasmons have shown interesting properties to enable future communication architectures, high performance sensors, and high-resolution systems. Recently, there has been particular interest in extending these plasmonic structures to other wavelength regions such as the mid-infrared (MIR). This is due to the fact that many molecules have unique vibrational resonances in the atmospheric transmission window of 8-13 μm wavelength. One of the main challenges to enable MIR plasmonics is related to the fundamental properties of these commonly used metals, which radically change their properties in the wavelength region of interest.

An alternative to metals that has been suggested is to use highly doped semiconductors [3-4]. Nominally un-doped semiconductors usually have a plasma frequency in the far-infrared [5], whereas doping levels $\geq 10^{19} \text{ cm}^{-3}$ are required for the MIR [1]. In order to enable cheap integrated plasmonic sensors the semiconductor structures should ideally be compatible with CMOS processes to take advantage of mature Si foundry technology. Ge meets this criterion and has been suggested as a

suitable plasmonic candidate for the MIR because it is optically transparent over this region and already used in Si photonics foundries for photodetectors [6-7]. Compared to Si, Ge also has the advantage of having a lower effective mass for electrons. Recently, it has been experimentally demonstrated that n-type Ge can be used for sensing in the MIR through the exploitation of plasmon resonances from nano-antenna structures [3-4].

Experiment

In this paper, we report on the growth, fabrication, and optical characterization of heavily-doped n-type Ge antennas on Si substrates. We then demonstrate that these structures can be exploited for the sensing of analytes. The highly doped n-Ge plasmonic material was epitaxially grown by low-energy plasma-enhanced chemical vapor deposition on a Si (001) substrate [8]. The n-Ge was grown at 500 °C and in-situ doped by a phosphine gas precursor to achieve an active doping concentration of $N_D \sim 2.5 \times 10^{19} \text{ cm}^{-3}$, which corresponds to a plasma frequency of $\sim 1,000 \text{ cm}^{-1}$ ($\sim 10 \mu\text{m}$ wavelength). Fabrication of the plasmonic n-Ge antennas was performed by electron-beam lithography and HSQ resist [9-10]. Subsequently, an inductively coupled plasma tool was used to etch the antennas using SF_6 and C_4F_8 in a mixed chemistry process [9] which has been demonstrated to produce low electrical damage in the fabrication of Si nanowire devices [10]. Figure 1(a) demonstrates a scanning electron microscope (SEM) image of fabricated $1 \mu\text{m}$ thick double n-Ge antennas with lengths of $2 \mu\text{m}$ and a gap of 300 nm [11]. Figure 1(b) presents a tilted (85°) SEM image of the double antenna structure. The optimized dry-etch process results in an anisotropic etch profile.

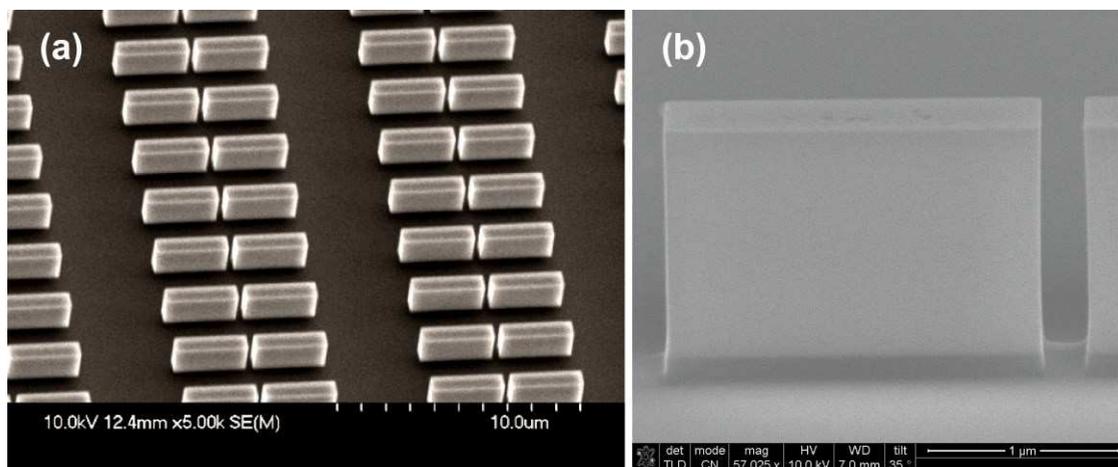


Figure 1. (a) A SEM image of the fabricated n-Ge plasmonic double antenna array. (b) A higher magnification SEM image of the n-Ge double antennas at 85° tilt.

The MIR response of the fabricated antenna structures has been characterized by Fourier transform infra-red (FTIR) spectroscopy. A broadband MIR source was used to illuminate the sample under analysis and the signal was collected with an MCT detector. The absorbance spectra of the antennas are demonstrated in Figure 2. In the following, we identify two different polarisations; co-polarisation (co-pol) and cross-polarisation (cross-pol), where the field is aligned along or across the antenna arm direction, respectively. The experimental results obtained clearly display a resonance peak R2 at $\sim 800 \text{ cm}^{-1}$ and R1 at $\sim 450 \text{ cm}^{-1}$ for the highly doped n-Ge antennas. The undoped reference Ge is also displayed and demonstrates no such resonances. These resonances correspond to hot-spots located at the Ge-air interface. The resonance peaks appear only

for the co-pol spectrum of the dipole antenna with high doping (red continuous line). The sharp spectral feature around 610 cm^{-1} that can be observed in all spectra is due to the Raman-active Si phonon, which couples to IR light because of defects in the Si substrate. The remaining narrow peaks that appear are partly due to impurities in the silicon wafers.

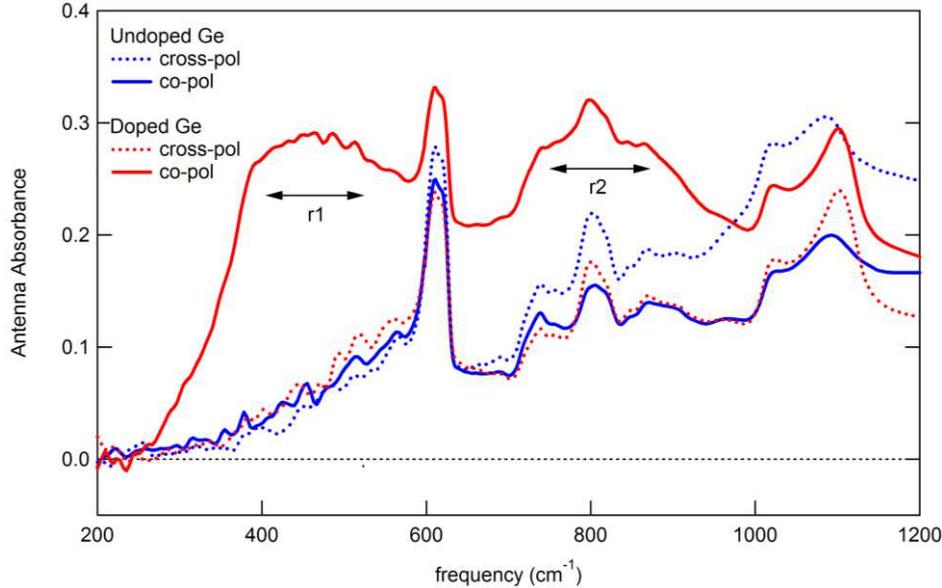


Figure 2. FTIR absorbance spectra of the fabricated $1\ \mu\text{m}$ thick n-Ge double antenna structures (red). Two broad resonance peaks are identified in co-polarization and are labelled as R1 and R2. The undoped Ge double antenna reference is also displayed (blue).

The potential for sensing by using the plasmonic properties of these n-Ge double antenna structures was investigated. The R2 resonance for the sensing of thin solid-state layers with vibrational fingerprints in the spectral window was demonstrated. This was achieved by using a polydimethylsiloxane (PDMS) layer, which features a vibrational absorption resonance at 800 cm^{-1} . This absorption line matches well with the spectral position of the R2 near-field resonance. By spin-coating highly diluted PDMS and further curing, we obtained a PDMS thickness below 40 nm . The transmission spectra for the antenna samples are displayed in Figure 3. A comparison between the transmission spectra of the clean antennas and of the spin-coated antennas reveals that the PDMS layer induces two changes in the spectra. There is a slight redshift of the plasmonic resonance due to the increased refractive index in the antenna surroundings, and there is also the appearance of an asymmetric spectral line around 800 cm^{-1} . Through this experiment, it is demonstrated that the line-shape around 800 cm^{-1} is completely different for parallel and perpendicular polarization and that the line-shape obtained for perpendicular polarization is similar to the one obtained from nominally undoped antenna samples. This observation clearly highlights the electromagnetic coupling between PDMS and the longitudinal plasmon resonances. We also calculated the ratio between the experimental spectra acquired from PDMS-coated antennas with parallel and perpendicular polarization, both for the doped and undoped samples. Noticeably, the 800 cm^{-1} vibrational feature from PDMS completely disappears in the undoped antennas after such normalization, meaning that no PDMS-antenna interaction is taking place irrespective of the field polarization when doping is absent in identical undoped Ge antennas.

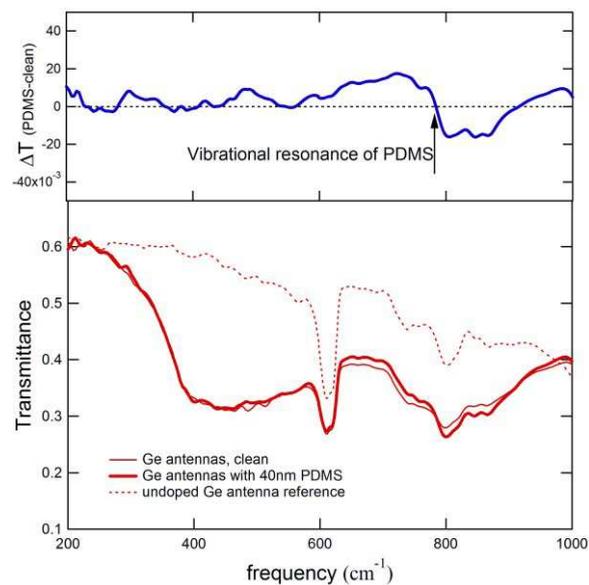


Figure 3. The FTIR transmission spectra acquired after PDMS is spin coated onto the double antenna structures (solid lines) and reference spectra from the clean samples. The undoped reference Ge antennas are also displayed (dash line). The upper plot shows the transmission spectra obtained after subtraction of the clean n-Ge antennas from antennas coated with PDMS.

Conclusions

We have demonstrated localized plasmon resonances in n-Ge double antennas and exploited the fabricated devices for sensing experiments based on the resonant detection of molecular vibrational fingerprints of PDMS. This leads to enhancement factors of up to two orders of magnitude for the PDMS located in the antenna hotspots [3][4]. The developed technology holds great promise for the realization of CMOS-compatible mid-IR devices for substance-specific molecular sensing.

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