n-Ge on Si for Mid-Infrared Plasmonic Sensors

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***Abstract*—The detection and amplification of molecular absorption lines from a mustard gas simulant is demonstrated using plasmonic antennas fabricated from n-Ge epitaxially grown on Si. Approaches to integrated sensors will be presented along with a review of n-Ge compared to other mid-infrared plasmonic materials.**

I. Introduction

Plasmonic materials [1] have the free electron oscillations in a metal coupled to photons and allow near field amplification of radiation below the plasmon edge [2] defined in wavenumbers ($\frac{1}{\lambda}$) as

$$\tilde{\nu}_p = \frac{1}{2\pi c}\sqrt{\frac{q^2 N}{\epsilon_0 \epsilon_\infty m^*}} \qquad (1)$$

where N is the doping density, m^* is the effective mass, ϵ_0 is the permittivity of free space, ϵ_∞ is the high frequency dielectric constant, q is the electron charge, c is the speed of light and λ is the wavelength. Metals such as Au and Ag can be used for visible wavelengths but these materials are incompatible with silicon foundries due to fast diffusion and the deep level trap states formed. Heavily doped semiconductors well above the Mott metal-insulator transition criteria can be used as plasmonic materials for the mid-infrared wavelengths where many molecules have strong molecular absorption lines related to the bonds which allow identification. Here n-Ge epitaxially grown on Si substrates is used as a mid-infrared plasmonic material and plasmonic antennas are demonstrated to provide amplification of specific molecular absorption lines of chemical weapon simulants. Examples of mid-infrared plasmonic sensors will be presented with potential applications for healthcare, environmental and chemical, biological, radiological, nuclear and explosives (CBRNE) security sensing.

Low-energy plasma enhanced chemical vapour deposition [3] was used to grow the n-Ge epilayers on high resistivity Si (001) substrates. Fig. 1 demonstrates the increase in the wavenumber (decrease in wavelength) of the plasmon edge as the doping density increased for n-Ge epilayers of thicknesses between 600 nm and 1000 nm [2][4][5]. The lowest wavelength of ~ 3.1 μm was achieved for an activated doping density of 2.1×10^{20} cm^{-3} at 300 K. This is sufficient to enable

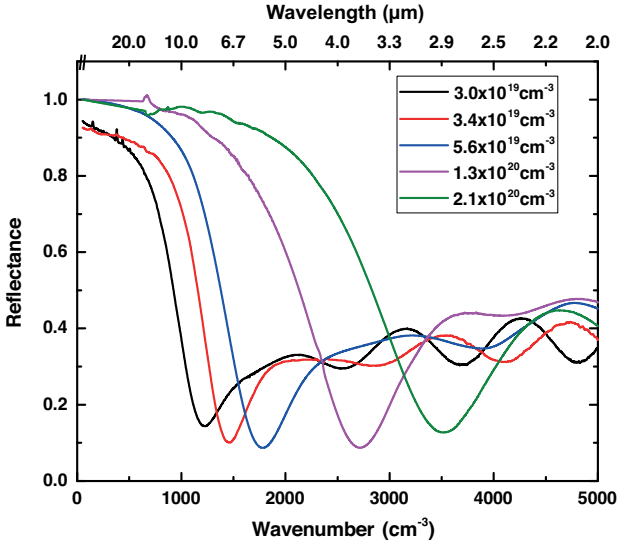

Fig. 1. The reflectance of 5 different n-Ge doped layers all with thickness between 600 nm and 1000 nm at 300 K.

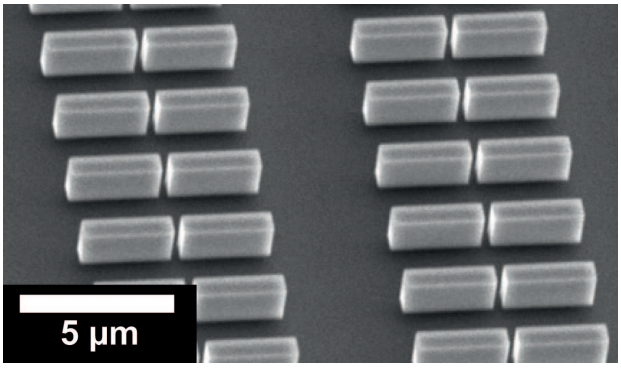

Fig. 2. A SEM image of an array of gap antennas with 3 μm long n-Ge sections and 300 nm gaps fabricated on top of a Si substrate.

the whole of the important 6.7 to 20 μm molecular fingerprint region and almost the whole of the 3 to 5 μm gas detection window. The former window has only really been successfully used with Fourier transform infrared (FTIR) systems.

A range of single and gap antennas were fabricated using

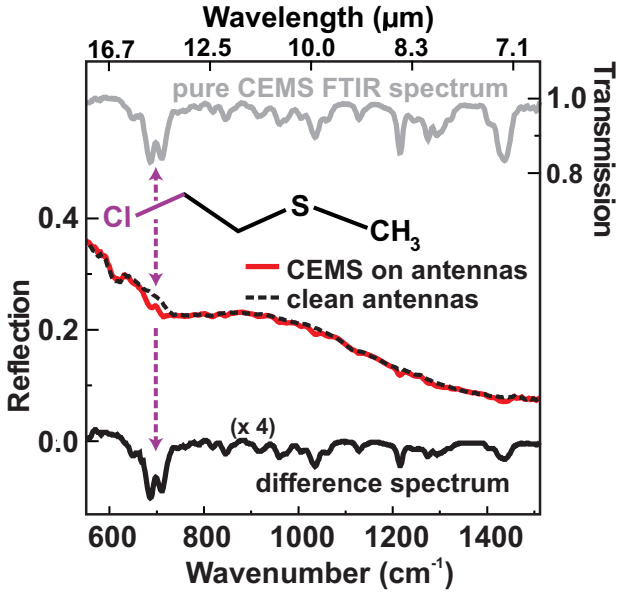

Fig. 3. Top: the transmission spectrum of CEMS measured by FTIR. Middle: the reflection spectrum of a n-Ge plasmonic antenna array without CEMS (dashed black line) and the array with CEMS (red line). Bottom: the difference between the clean and CEMS coated plasmonic antenna spectrums.

electron beam lithography and reactive ion etching from the 1000 nm thick n-Ge material [4] into arrays over a 5×5 mm^2 array. The n-Ge thickness is comparable to the skin depth in the 10 to 20 μm wavelength region. Fig. 2 provides a scanning electron microscope (SEM) image of a set of gap antennas. Antennas with lengths from 1 to 4 μm were produced since the substrate side plasmonic resonance can be tuned through varying the antenna length allowing the targeting of specific molecular absorption lines for identification [4].

An example of a chemical weapons detection application is demonstrated in Fig. 3 using the n-Ge antennas in Fig. 2. The FTIR spectrum of chloroethyl methyl sulphide (CEMS - see Fig. 3 insert for chemical structure) has a C-Cl bond absorption doublet at approximately 14 μm wavelength. The spectroscopic fingerprint region of 6.7 to 15 μm is where most explosives, chemical and biological weapons have unique molecular bonding absorption lines. A few drops of CEMS liquid mustard gas simulant was deposited on a set of antennas (red line in Fig. 3) and the difference was taken from a clean set of antennas (black dashed line) to leave the difference spectrum of CEMS (solid black line at bottom of Fig. 3). Since the plasmon edge was 10 μm for this material doped at 2.3×10^{19} cm^{-3}, only the absorption lines for longer wavelengths are amplified by the plasmonic antennas. Signal enhancements up to two orders of magnitude have been demonstrated at 12.5 μm wavelength using the n-Ge antennas to measure absorptions in polydimethylsiloxane (PDMS) [4].

Physical doping is not the only way large carrier densities can be achieved for plasmonic behaviour. Low or undoped semiconductors can be optically pumped to generate carriers which can provide tuning of plasmonic behaviour through optical gating [6]. We will present results on ultrafast plasmonic switching properties where fs pulses are used to demonstrate optical carrier densities up to 1.6×10^{20} cm^{-3} [6]. This is enabling for a wide range of new integrated mid-infrared sensors through accessing switchable plamonic behaviour with full control over the confinement of light and the field enhancement.

As demonstrated using analysis of time and frequency dependent n-Ge measurements, only electron-phonon and electron-charged impurity scattering dominate the decay of the plasmons and underdamped plasmon excitations are observed in the mid-infrared even at room temperature [5]. We have compared the plasmonic performance of n-Ge to the more common plasmonic metals of Au, Ag and Al. The higher electrical conductivity of Au and Ag do provide lower losses than n-Ge in the mid-infrared region investigated but this is counterbalanced by a significantly higher degree of field confinement in n-Ge since the doped semiconductor demonstrates true plasmonic behaviour [5].

II. Conclusion

Physical doping and optical pumping have been used to demonstrate plasmonic behaviour in Ge on Si antennas down to $\sim$3.1 μm wavelengths. The paper will review the results to date with examples of chemical weapons identification, describe activated plasmonic devices and describe routes to integrated mid-infrared sensors on a Si platform.

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References

[1] A. Boltasseva and H. A. Atwater, "Low-loss plasmonic metamaterials," *Science*, vol. 331, no. 6015, pp. 290–291, 2011. [Online]. Available: http://science.sciencemag.org/content/331/6015/290

[2] P. Biagioni, J. Frigerio, A. Samarelli, K. Gallacher, L. Baldassarre, E. Sakat, E. Calandrini, R. W. Millar, V. Giliberti, G. Isella, D. J. Paul, and M. Ortolani, "Group-IV midinfrared plasmonics," *Journal of Nanophotonics*, vol. 9, no. 1, p. 093789, 2015. [Online]. Available: http://dx.doi.org/10.1117/1.JNP.9.093789

[3] G. Isella, D. Chrastina, B. Rössner, T. Hackbarth, H.-J. Herzog, U. König, and H. von Känel, "Low-energy plasma-enhanced chemical vapor deposition for strained Si and Ge heterostructures and devices," *Solid-State Electron.*, vol. 48, no. 8, pp. 1317–1323, Aug. 2004. [Online]. Available: http://linkinghub.elsevier.com/retrieve/pii/S0038110104000565

[4] L. Baldassarre, E. Sakat, J. Frigerio, A. Samarelli, K. Gallacher, E. Calandrini, G. Isella, D. J. Paul, M. Ortolani, and P. Biagioni, "Midinfrared plasmon-enhanced spectroscopy with germanium antennas on silicon substrates," *Nano Letters*, vol. 15, no. 11, pp. 7225–7231, 2015. [Online]. Available: http://dx.doi.org/10.1021/acs.nanolett.5b03247

[5] J. Frigerio, A. Ballabio, G. Isella, E. Sakat, G. Pellegrini, P. Biagioni, M. Bollani, E. Napolitani, C. Manganelli, M. Virgilio, A. Grupp, M. P. Fischer, D. Brida, K. Gallacher, D. J. Paul, L. Baldassarre, P. Calvani, V. Giliberti, A. Nucara, and M. Ortolani, "Tunability of the dielectric function of heavily doped germanium thin films for mid-infrared plasmonics," *Phys. Rev. B*, vol. 94, p. 085202, Aug 2016. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevB.94.085202

[6] M. P. Fischer, C. Schmidt, E. Sakat, J. Stock, A. Samarelli, J. Frigerio, M. Ortolani, D. J. Paul, G. Isella, A. Leitenstorfer, P. Biagioni, and D. Brida, "Optical activation of germanium plasmonic antennas in the mid-infrared," *Phys. Rev. Lett.*, vol. 117, p. 047401, Jul 2016. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevLett.117.047401