Benchmarking the use of heavily-doped Ge against noble metals for plasmonics and sensing in the mid-infrared

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Abstract—**Despite the recent introduction of heavily-doped semiconductors for mid-infrared plasmonics, it still remains an open point whether such materials can compete with noble metals. We employ a whole set of figures of merit to thoroughly assess the use of heavily-doped Ge on Si as a mid-infrared plasmonic material and benchmark it against standard noble metals such as Au. In doing this, we design and model high-performance, CMOS compatible mid-infrared plasmonic sensors based on experimental material data reaching plasma frequencies up to about 1950 cm^{-1}. We demonstrate that plasmonic Ge sensors can provide signal enhancements for vibrational spectroscopy above 3 orders of magnitude, thus representing a viable alternative to noble metals.**

I. Introduction

THE direct targeting of the molecule vibrational fingerprints demands for new enhanced sensors operating in the mid-infrared (mid-IR) range. In this framework, plasmonic devices have been proposed as a way to achieve increased light-molecule interaction leading to the so-called surface-enhanced infrared absorption (SEIRA) spectroscopy. Even though most research efforts focused their attention on gold platforms so far, heavily-doped semiconductors have recently demonstrated their potential as fabrication materials for mid-IR sensing devices [1]. The most relevant advantages include the high material quality obtained with the epitaxial growth and the potential for on-chip CMOS integration of group-IV semiconductors. Yet, in order to obtain high-performance sensing platforms, it is crucial to reach an accurate characterization of the plasmonic properties of the material and achieve a sensor design capable of providing high local field enhancements over large and uniform areas.

II. Results

We design and model, by means of a multilayer finite-element method, free-standing nano-slit arrays based on heavily-doped Ge epitaxially grown on Si. Such devices are well within the capabilities of modern fabrication technologies developed for semiconductor membranes on silicon chips. The plasmonic properties of the Ge can be evaluated in terms of field confinement and propagation length [2]. In this context, Ge compares favorably to other semiconductors and demonstrates mid-IR enhancement properties within one order of magnitude of those typically displayed by noble metals in the visible range. Moreover, we exploit a set of three different figures of merit to capture all the different aspects of plasmonic enhancement under realistic experimental conditions. The metrics are defined

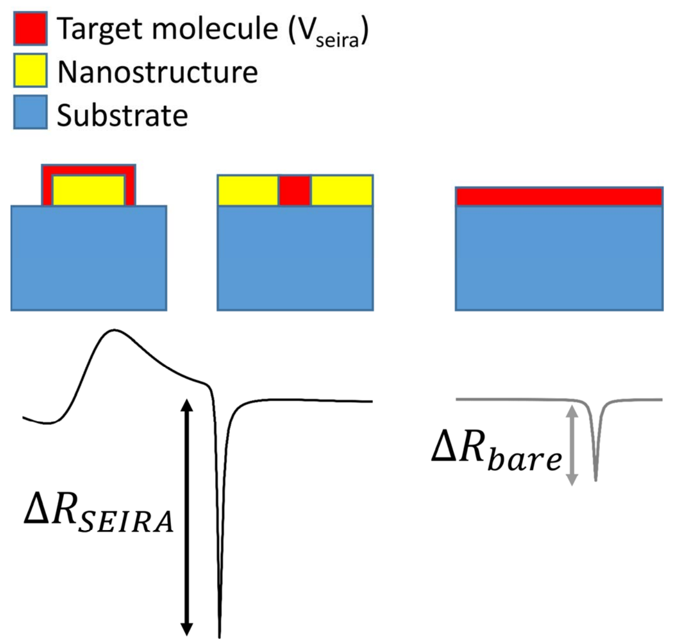

Fig. 1. Schematic representation of nanoantenna and nanoslit SEIRA sensing platform and corresponding baseline corrected reflectance SEIRA signal (ΔR_{SEIRA}), along with the reference reflectance signal for the same volume V_{SEIRA} of target molecules deposited on the bare substrate (ΔR_{bare}).

as a function of two quantities determined in a far field reflection geometry, and represent an improvement on different approaches based on local field quantities that are biased towards large area coverages in spite of large signal enhancements. The first introduced quantity is defined as $\Delta R_{\mathrm{SEIRA}}$ and corresponds to the baseline-corrected SEIRA signal of a volume V_{SEIRA} of target molecules interacting with the plasmonic platform. The second quantity ΔR_{bare} coincides with the vibrational signal arising from the same volume of molecule V_{SEIRA} deposited on a bare substrate [Fig. 1]. In this framework the first introduced figure of merit is simply defined as $\mathrm{fom_{SNR}} = \Delta R_{\mathrm{SEIRA}}$. The metric serves as a proxy of the measured signal intensity, allowing for the monitoring of the platform signal-to-noise ratio, which can be approximately expressed as $\mathrm{SNR} \propto (\Delta R_{\mathrm{SEIRA}})^{1/2}$. The second proposed metric is defined as the ratio of the baseline-corrected SEIRA signal amplitude to the one of the bare target molecules, i.e. $\mathrm{fom_{SEIRA}} = \Delta R_{\mathrm{SEIRA}}/\Delta R_{\mathrm{bare}}$. The metric monitors the SEIRA enhancement performance and is solely related to the intrinsic signal enhancement properties of the sensing device. The last

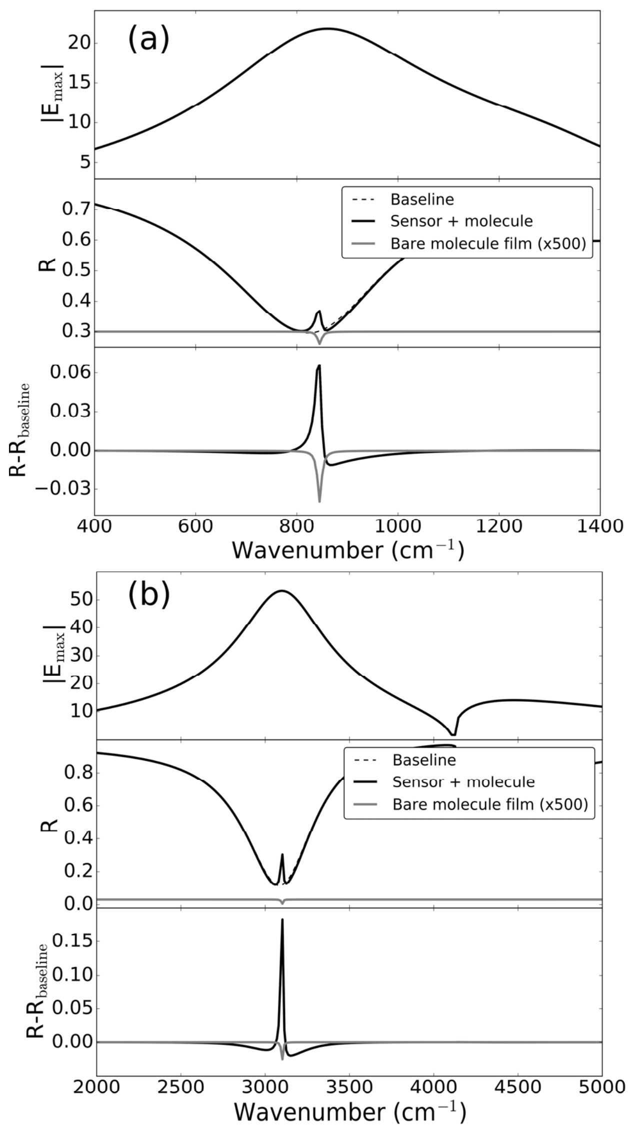

Fig. 2. (a) Local field enhancement and typical SEIRA signal for a Ge sensing platform operating at 845 cm^{-1}. (b) Local field enhancement and typical SEIRA signal for a Au sensing platform operating at 3100 cm^{-1}.

devised metric aims at the description of the measured SEIRA signal under realistic experimental conditions. In a typical experiment, a volume $V_{\mathrm{tot}} = V_{\mathrm{SEIRA}} + V_{\mathrm{bare}}$ of analyte is usually delivered to the sensing platform and a reference substrate, where for the sensing device only a limited volume (V_{SEIRA}) of the target molecules interacts with the plasmonic nanostructure, while the remaining volume fraction (V_{bare}) experiences no significant signal enhancement. In order to track the signal enhancement between the sensing platform and the reference substrate, starting from the quantities $\Delta R_{\mathrm{SEIRA}}$ and ΔR_{bare}, it is then necessary to consider a normalization coefficient including the relative volume fraction of sensitized molecules, finally obtaining:

$$\mathrm{fom}_{\mathrm{exp}} = \left(\frac{\Delta R_{\mathrm{SEIRA}}}{\Delta R_{\mathrm{bare}}}\right) \times \left(\frac{V_{\mathrm{SEIRA}}}{V_{\mathrm{bare}}}\right).$$

As a practical example, we model and compare the performance of Au-based, state-of-the-art SEIRA platforms [3] against the newly-designed Ge-based sensing devices. We demonstrate that the adopted Ge nano-slit design allows for SEIRA signal enhancements, tracked by means of the $\mathrm{fom}_{\mathrm{SEIRA}}$ metric, above 3 orders of magnitude in the 400-1000 cm^{-1} energy range [Fig. 2(a)], with uniform field enhancement inside the nano-slits. The signal enhancement compares favorably with the 3 to 4 orders of magnitude gain typically obtained with best performing Au-based platforms characterized by comparable geometrical parameters [Fig. 2(b)]. This indicates that plasmonic Ge sensors represent a viable alternative to noble metals for integrated plasmon enhanced vibrational spectroscopy in the mid-infrared range.

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