Local electric field enhancement at the heterojunction of Si/SiGe axially heterostructured nanowires under laser illumination

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Jose Luis Pura1, Julián Anaya2, Jorge Souto1, Ángel Carmelo Prieto1, Andrés Rodríguez3, Tomás Rodríguez3 and Juan Jiménez1

1 GdS Optronlab, Dpt. Física de la Materia Condensada, ed. i+d, Parque Científico, Universidad de Valladolid, Paseo de Belén 1, 47011 Valladolid, Spain
2 Centre for Device Thermography and Reliability, HH Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8 1TL, Bristol, UK
3 Ingeniería Electrónica, ETSI de Telecomunicación, Universidad Politécnica de Madrid, Avenida Complutense 30, 28040 Madrid, Spain

E-mail: J.AnayaCalvo@bristol.ac.uk

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Abstract
We present a phenomenon concerning electromagnetic enhancement at the heterojunction region of axially heterostructured Si/SiGe nanowires when the nanowire is illuminated by a focused laser beam. The local electric field is sensed by micro Raman spectroscopy, which allows the enhancement of the Raman signal arising from the heterojunction region to be revealed; the Raman signal per unit volume increases at least ten times with respect to the homogeneous Si and SiGe nanowire segments. In order to explore the physical meaning of this phenomenon, a three-dimensional solution of the Maxwell equations of the interaction between the focused laser beam and the nanowire was carried out by finite element methods. A local enhancement of the electric field at the heterojunction was deduced. However, the magnitude of the electromagnetic field enhancement only approaches the experimental one when the free carriers are considered, showing enhanced absorption at the carrier depleted heterojunction region. The existence of this effect promises a way of improving photon harvesting using axially heterostructured semiconductor nanowires.

Keywords: Si/SiGe heterojunction, electromagnetic enhancement, nanowires, photogenerated carriers

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductor nanowires (NWs) are attracting a great deal of attention because of the increasing number of potential applications based on their unique properties [1]. Most of these properties arise from the NW confined dimensions, the diameter, as compared to some characteristic lengths, e.g. exciton Bohr radius, phonon mean free path, wavelength of the incident electromagnetic (EM) waves, etc [2]. In particular, there is great interest in the interaction between semiconductor NWs and light, as their optical properties make them optimal candidates for nanophotonic devices [3, 4]. The broad range of unique optical properties of semiconductor NWs has been reported, e.g. waveguiding [5], optical resonances [6], and antenna effects, among others [7]. All these effects emerge because light interacts with the NWs in different ways depending on the NW diameter, wavelength, and the dielectric properties of the NW and the surrounding media. One of the most relevant properties concerning light/NW interaction is the ability of NWs to enhance their optical
absorption/scattering for certain diameters, which are characterized by large local electric fields inside the NW [8]. The absorption/scattering resonances deal with different phenomena recently reported, including, among others, the enhanced photocurrent response of the NWs [7], enhanced elastic and inelastic light scattering by Si NWs [9], light extinction [10], light emission in different semiconductor NWs [11, 12], and second harmonic generation [5]. Since the Raman intensity is proportional to the excitation light intensity and the scattering volume, an experimental study of the interaction of light with matter at the nanoscale can be carried out by its Raman response [13]. This makes Raman spectroscopy an excellent probe for sensing the local electric field induced inside the NW under incident light. In addition, it is possible to take advantage of its capabilities as a powerful non-destructive technique for the characterization of the structure, composition, stress, thermal, electronic, and optical properties of semiconductor NWs [6, 14–18]. It is worth noting that up to now research interest in light/NW interaction has been focused mainly on homogeneous single NWs and/or core–shell heterostructured NWs [19]. However, the response of axially heterostructured NWs to EM waves is still unexplored. These types of structures are attracting increasing interest since heterojunctions (HJs) are necessary for the development of semiconductor NW based devices [20]. In the junction of these NWs a jump in the complex refractive index due the abrupt change of materials is expected, which therefore may change the EM response of the NW. In addition to the HJ built-in electric field, which can locally change the polarizability, the oscillator strength and the presence of free carriers, either native or photogenerated, could also affect the electric field distribution inside the NW. To further advance in this subject, we present in this work a study of the distribution of the EM field in axially heterostructured Si/SiGe NWs, paying special attention to the role of the HJ in the optical response of the NW. This is carried out experimentally by using its Raman response as a sensor of the local electric field. The experimental data are compared to the output of a three-dimensional (3D) solution of the Maxwell equations characterizing the EM laser/NW interaction by finite element methods (EM-FEM), enabling us to explain the role of the HJ in the EM interaction.

2. Experimental description and samples

Axially heterostructured NWs were grown by the vapour–liquid–solid (VLS) method using SiH$_4$ and GeH$_4$ as precursor gases and alloyed Ga–Au metal droplets of different compositions as catalysts. The as-grown NWs were sonicated in an ultrasonic bath and suspended in methanol; subsequently the NWs were deposited on an Al substrate by dropcasting. For more details on the growth of these NWs see [21] and [22]. High resolution transmission electron microscopy (TEM) and energy dispersive x-ray (EDX) analyses of the HJ were carried out. High resolution TEM images of the HJ region of SiGe/Si HJs did not show structural discontinuities at the junction, stacking faults, or other structural defects, see figure 1(a). The EDX profile shows a compositionally graded HJ with a width of around 30 nm, of the order of the NW diameter, ≈ 32 nm for the NW shown in figure 1(b).

The micro Raman spectra of several individual Si/SiGe NWs were recorded using a high resolution Labram UV-HR 800 Raman spectrometer from Horiba-JovinYvon. The excitation and the scattered light collection were performed by means of a confocal metallographic microscope with a high magnification objective (100X and 0.95 numerical aperture (NA)). The excitation was carried out with a frequency doubled Nd:YAG laser (532 nm). The measured laser beam diameter at the focal plane for these conditions was ~1 μm, thus slightly bigger than the ∼700 nm given by the Abbe’s formula ($w_{1/2} \propto 1.22\lambda/NA$) and several times larger than the typical NW diameter studied here, which ranges from 30 to 100 nm. The NWs deposited on a metallic substrate were found to enhance the Raman signal with respect to free standing NWs. The metallic substrate also allows better heat dissipation, reducing the laser induced heating of the NWs [23]. The Ge concentration in the SiGe segment of the NW, measured by EDX and confirmed by the Raman measurements, lies at around 10% for all the studied NWs. Prior to the

![Figure 1.](image-url)
Raman measurements the dimensions and morphology of the NWs were characterized using a scanning electron microscope (SEM). The Raman spectra were acquired by scanning the laser beam along and across the NW axis in steps of 100 nm. The transverse scanning across the NW allows the optimization of the excitation conditions, i.e. maximum Raman signal with negligible laser induced heating [23]. The longitudinal scanning permits localization of the HJ, and also the study of the Raman intensity profiles along the NW, and more interestingly around the HJ.

3. Experimental results

Four Raman spectra recorded at different positions along an axially heterostructured Si/SiGe NW are shown in figure 2. Spectrum 1 was taken on the Si segment of the NW, while spectrum 4 was recorded on the SiGe segment. Spectra 2 and 3 were recorded with the laser beam sharing the two pure segments and the HJ. When these spectra are compared, a dramatic change is observed in the spectral shape of 2 and 3 with respect to 1 and 4. Spectra 1 and 4 show a typical Lorentzian peak, with the spectral parameters characteristic of Si and Si$_{0.9}$Ge$_{0.1}$ NWs respectively [24, 25]. Meanwhile, the spectra recorded in positions 2 and 3 appear broadened and asymmetric as a consequence of the overlapping contribution to the Raman spectrum of the different regions of the NW being simultaneously excited by the laser beam. In order to analyse this signal, spectral deconvolution was thus carried out to ascertain the different contributions of the pure Si and SiGe segments of the NW, and also the contribution of the HJ region. For this deconvolution we used spectra 1 and 4, corresponding unequivocally to the Si and Si$_{0.9}$Ge$_{0.1}$ pure NW segments, as the reference spectra for the fitting of spectra 2 and 3. However, when using a weighted Gaussian convolution (from the focused laser intensity distribution) of the two bands corresponding to the two pure segments it was not possible to reproduce the Raman spectra recorded when the laser beam was sharing the three NW regions, i.e. spectra 2 and 3 (see figure 3 inset).

Figure 3 shows that a third band is necessary to achieve a satisfactory fit of the spectra recorded with the participation of the HJ, e.g. 2 and 3. This third contribution, which has a peak width and frequency intermediate between those recorded for the pure Si and Si$_{0.9}$Ge$_{0.1}$ NW segments, should arise exclusively from the very narrow HJ region. It should be noted that the HJ region in VLS NW growth does not present a sharp composition change, but it follows a compositionally graded transition from the nominal 10% Ge of the SiGe segment to the pure Si segment (see figure 1(b)). The thickness of this transition region is of the same order of magnitude as the NW diameter, and it is consequence of the Ge reservoir effect on the catalyst droplet. Once the GeH$_4$ gas source had been switched off, this reservoir continues depositing Ge during the growth up to Ge exhaustion in the catalysts droplet [3, 26, 27]. Thus, in order to explain the Raman signal detected in the HJ region, we should first consider this transition volume as the source of the observed third band in the Raman spectrum. The Raman intensity is correlated to the volume of the material probed by the laser beam [14], which in our case gives a ratio of ~1:0.1:1 (Si:HJ:SiGe) between the three probed regions for a 50 nm diameter NW when the laser beam spot shares the three parts of the NW (when it is centred around the HJ). Therefore, the high intensity of the Raman band arising from the HJ region (see figure 3), which is similar in amplitude to the ones corresponding to the Si and SiGe NW segments, cannot be explained in terms of a simple convolution of the signals.
weighted by their scattering volumes. Indeed, the high intensity recorded in the HJ, when translated in terms of Raman intensity per unit volume, results in a Raman signal enhancement for the HJ contribution of at least one order of magnitude with respect to the signals recorded in the two single NWs segments. This means that there is a significant enhancement of the induced local EM field at the HJ of the NW. Furthermore, the Raman intensity along the heterostructured NW is not only amplified at the HJ, but the presence of the HJ seems to pull up the overall Raman signal. This is shown in figure 4, in which the integrated Raman intensities of the different contributions, namely Si, HJ and SiGe, as determined from the deconvolution of the experimental Raman spectra, are plotted as a function of the position of the laser beam along the NW. Here the Raman intensity reaches a maximum when the laser beam crosses the HJ, evidencing that the presence of the HJ enhances the overall Raman intensity, and thus affecting the distribution of the electric field inside the NW even when the laser beam is not directly illuminating the HJ. We should note that this behaviour was observed for all of the several axially heterostructured NWs that we studied. On the other hand, the decrease in the SiGe signal on the right-hand side of the plot in figure 4 is the consequence of the reduced scattering volume and Gaussian intensity profile of the laser at the end of the NW (see the SEM image of figure 4). The same effect occurs on the other end of the NW (Si segment) but it is not plotted here.

4. Laser/NW interaction using EM-FEM simulations

To study the quantitative interaction between the focused laser beam and the NWs, and thus to unravel the distribution of the EM field inside the HJ NW, one needs to solve the Maxwell equations for the laser/NW system. This has been typically carried out by means of the Lorenz–Mie theory, in which the NW is described as an infinitely long cylinder immersed in a homogeneous and isotropic non-absorbing medium [28]. In the framework of this formalism, the calculation of the absorption and scattering efficiencies, $Q_{abs}$ and $Q_{sc}$ respectively, has revealed a strong dependence of these coefficients on the NW diameter, presenting resonances for certain diameters [6, 17]. Alternatively, we have analysed the NW/laser beam interaction by solving the equivalent 2D Maxwell equations using the radio-frequency module of the COMSOL Multiphysics simulation software, contrasting our results with the solution of the Lorentz–Mie equations and obtaining an excellent agreement [29]. However, because of the symmetry-breaking in the presence of the HJ, the simulation of the axially heterostructured NWs cannot be performed by a 2D approach like the ones typically used when studying the light/NW interaction for homogeneous and core–shell heterostructured NWs [14, 15]. Instead, here we solved a 3D model accounting for the axial HJ and the finite length of the NW, as well as the presence of the metallic substrate. The EM model used here reproduces a HJ NW with the same characteristics as the one shown in figure 4, deposited on a metallic (Al) substrate and surrounded by air. The NW is illuminated by the same 532 nm Gaussian laser beam used in the experiments. The air/NW/substrate system was limited by Cartesian perfectly matched layers, which absorb all the outgoing radiation, thus eliminating secondary reflections on the boundaries. The complex refractive indexes were obtained from the Sopra database [30]. As a first step the response of a perfectly dielectric NW was calculated. This model was solved for different positions of the excitation laser beam along the NW axis in order to reproduce the experimental profile of figure 4. A particular solution of the model is shown in figure 5, where one observes the 3D distribution of the relative electric field intensity, defined as $E_r^2 = |E|^2/|E_{Incident}|^2$ (i.e. the electric field enhancement over the incident laser EM field), inside the heterostructured NW. In the same figure we also included the profile of this magnitude along the NW axis, highlighting the local enhancement at the HJ region. For each position of the laser beam the EM field distribution inside the NW is calculated. The volume integrals of the square of the electric field, $|E|^2$, in the three different regions, Si segment, SiGe segment and the HJ, are then calculated. The value of these integrals should therefore be proportional to the theoretical Raman signal arising from each NW region under the excitation beam [13]. It is remarkable that this model shows a similar amplification and localization of the EM field in the HJ region, see figure 5. However, the estimated amplification for the HJ region was lower than the one deduced from the experimental data (see figure 6, pink dots). In order to explain this discrepancy a more complete model accounting for the effect of the photogenerated carriers in the solution of the Maxwell equations was considered. This is needed since the presence of free carriers will contribute to the dielectric losses. For the excitation conditions of our measurements and a surface recombination velocity (SRV) of $S \approx 3 \times 10^5$ cms$^{-1}$ [31], this results in a photogenerated...
carrier concentration of $n \approx 10^{19}$ cm$^{-3}$, in agreement with other experimental estimations [31]. The dielectric losses will mainly affect the regions with free carriers, i.e. the two NW segments, since as a consequence of the carrier depletion at the HJ, this region will be free of the losses associated with the presence of free carriers. As a result, the dielectric losses will modify the electric field distribution inside the NW, lowering the electric field in the homogeneous segments with respect to the HJ, which yields an effective amplification of the HJ signal.

Once the free carriers were considered the model was solved for a carrier density ranging from $10^{16}$ to $10^{20}$ cm$^{-3}$. The results obtained for two representative carrier densities, $n = 8 \times 10^{18}$ cm$^{-3}$ and $n = 5 \times 10^{19}$ cm$^{-3}$, are shown in figure 6. From this it is clear that by including the effect of the photogenerated carriers in the model, the EM field is strongly localised in the HJ region, approaching the contribution observed in the experimental data of figure 4, and therefore explaining the origin of anomalous effect observed in the experiments. However, we should note that the experimental intensity of the SiGe segment is higher than the intensity measured for the Si segment, as opposed to what is observed in the EM-FEM model, which shows similar values for both segments. This discrepancy might arise by a difference of a few nanometres in the diameter of both segments, which due to the diameter dependent resonance in the Raman intensity, can be responsible for the observed difference [29]. In fact, diameter changes in the presence of axial HJs are common. Here, to simplify the problem, the data of figure 6 were calculated for an ideal cylindrical NW, without diameter change, and therefore the model does not account for these subtle differences in geometry.

Finally, and to fully validate the model, the hypothesis of including the photogenerated carriers as an important player in explaining the observed Raman intensity needs to be tested experimentally. In nanoscale systems the photogenerated carrier concentration is dominated by the surface recombination; therefore, by modifying the surface condition, one can change the SRV, which in return will induce a change in the free carrier density. Taking this into account, Si NWs were dipped in a 4% HF solution in order to remove the native oxide layer, changing their SRV. The chemical treatment removes the native SiO$_2$ external layer and does not react with the crystalline Si core, leaving a clean Si NW. The NWs were immediately deposited in the metallic substrate, and kept in a N$_2$ atmosphere up to the first Raman measurement. After this point the N$_2$ source is switched off and the oxidation process starts at room temperature. Immediately after the removal of the oxide layer the surface recombination states will be nearly suppressed, then the equilibrium photogenerated carrier density will rise, lowering the Raman signal because of the free carrier associated losses. As time goes on and the spontaneous oxidation process takes place, new surface recombination centres are created and the SRV increases, with the reduction of the free carrier density and the concomitant increase of the Raman signal. In our experiment, the Raman spectrum was periodically recorded for one week of measurements, albeit the Raman signal became fully stable after the second day. The Raman signal evolution for this Si NW can be seen in figure 7, showing that the intensity starts to reach a stable value after the first 24 hours. This is in good agreement with the time needed for the formation of the first stable oxide layer in Si at room temperature, which lies around 25–30 hours [32]. This therefore shows the evolution of the Raman signal with the change of the SRV, which progressively increased due to the oxidation. It should be noted that this experimental configuration warrants the same excitation conditions and photogeneration rate for all the measurements, and thus shows that the change in the photogenerated carrier concentration is controlled by the SRV. In addition, the Raman signal rises rather quickly in the first hours of oxidation, suggesting that the creation of a full oxide layer is not needed to enhance the surface recombination, but the creation of sparse defects at the surface is enough to spoil the...
homogeneity of the Si surface, and create surface states. With the presence of surface states, the equilibrium photocarrier concentration decreases and the Raman signal is progressively recovered. Therefore this result highlights the role played by the free carriers in the laser/NW interaction, and supports the good agreement observed between theoretical and experimental results obtained in the heterostructured NWs when the photogenerated carriers are considered in the EM interaction.

5. Summary

We have presented here a local EM amplification phenomenon in the HJ region of axially heterostructured Si/SiGe NWs when interacting with a laser beam. This nanoscale effect has been systematically studied by recording the Raman signals of the heterostructured NWs, which show a significant enhancement at the HJ region with respect to those obtained in compositionally homogeneous NWs of the same dimensions. The Raman intensity of the HJ presents an intensity per unit volume at least ten times higher than the pure segments of the NW. These experimental observations were contrasted with the results obtained by the 3D solution of the Maxwell equations for the interaction between the dielectric NW and the focused laser beam using an EM-FEM model. The model accounts for the above experimental observations, and shows the possibility of locally modifying the EM field in the HJ. However, the calculated electric field enhancement at the HJ is substantially lower than the one observed experimentally by the Raman signal. A more complete physical description considering the contribution of the photogenerated free carriers has been implemented, showing a good agreement with the experimental observations. The role of the photogenerated carriers on the Raman response of the NWs observed in the model has been revealed by experiments changing the photocarrier recombination dynamics by modifying the surface recombination velocity. The local electric field inside the NW can be modulated by the presence of the HJ and the surface states. This EM field enhancement at the HJ of axially heterostructured NWs suggests a path to optimizing light-sensitive devices as photo-detectors, sensors, solar cells, among others.

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