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Near-Field Imaging of Free Carriers in ZnO Nanowires with a Scanning Probe Tip Made of Heavily Doped Germanium

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A novel scanning probe tip made of heavily doped semiconductor is fabricated and used instead of standard gold-coated tips in infrared scattering-type near-field microscopy. Midinfrared near-field microscopy experiments are conducted on ZnO nanowires with a lateral resolution better than 100 nm, using tips made of heavily electron-doped germanium with a plasma frequency in the midinfrared (plasma wavelength of 9.5 μm). Nanowires embedded in a dielectric matrix are imaged at two wavelengths, 11.3 and 8.0 μm , above and below the plasma wavelength of the tips. An opposite sign of the imaging contrasts between the nanowire and the dielectric matrix is observed at the two infrared wavelengths, indicating a clear role of the free-electron plasma in the heavily doped germanium tip in building the imaging contrast. Electromagnetic simulations with a multispherical dipole model accounting for the finite size of the tip are well consistent with the experiments. By comparison of the simulated and measured imaging contrasts, an estimate for the local free-carrier density in the investigated ZnO nanowires in the low 10^{19} cm^{-3} range is retrieved. The results are benchmarked against the scattering intensity and phase maps obtained on the same sample with a gold-coated probe tip in pseudoheterodyne detection mode.

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I. INTRODUCTION

In the last decade, scattering-type scanning near-field optical microscopy (SSNOM) [1,2], also called apertureless SNOM, has arisen as one of the most powerful techniques for material characterization at the nanoscale [3] with deeply sub- λ resolution of a few tens of nanometers [4–9], enabling midinfrared (mid-IR) spectroscopy (typically in the wavelength range $5 \mu\text{m} < \lambda < 15 \mu\text{m}$), and a noncontact measure of the electrical conductivity of nano-objects [10,11]. When applied to the study of nanowires (NWs), SSNOM has mostly been used to estimate the local free charge-carrier density N , a quantity of great importance in NW applications [12–14] that is extremely difficult to predict before NW growth [15] or to estimate from electrical or thermal transport measurements on nano-devices featuring metal contacts and junctions [16–19]. Because of its deeply sub- λ resolution, SSNOM can even

provide spatial profiles of N in single NWs by nano-spectroscopic detection of the scattering resonance of the free-carrier plasma [6,10,11], whose amplitude and frequency are both proportional to $\sqrt{N/m^*}$, m^* being the carrier effective mass. For high N values of the order of 10^{19} cm^{-3} , and for small- m^* semiconductor NWs like electron-doped InP ($m^* = 0.08 m_e$, where m_e is the bare electron mass) or GaAs ($m^* = 0.067 m_e$), the scattering resonance of the free-carrier plasma typically sits in the mid-IR range. In some important NW systems, e.g., ZnO NWs [11,14,15] now employed as nanolasers [20,21] and piezoelectric nanogenerators [22], however, the plasma resonance is not very evident in the SSNOM intensity spectra [11], either because the carrier relaxation time is very short [23] and, consequently, the intrinsic resonance line shape is too broad [24], or because N is inhomogeneous over length scales smaller than the typical lateral resolution of SSNOM [11], leading to extrinsic plasma resonance broadening. In electron-doped ZnO, moreover, $m^* = 0.29 m_e$ [24], which is a rather large value that leads to a weak plasma resonance and/or to a plasma frequency

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falling outside the typical SSNOM measurement range. Measurement of the phase and amplitude of the SSNOM signal provides higher sensitivity than simple intensity measurements [10–11], but this requires the pseudoheterodyne detection mode and a longer acquisition time per pixel [25,26]. Following along the lines of Refs. [25] and [26], it would be highly desirable to implement a practical version of homodyne SSNOM that can be used to get at least estimates of N in NWs made of ZnO and other materials not displaying sharp plasma resonances in the mid-IR range. To this aim, we introduce here an alternative type of probe tip made of heavily-doped semiconductor featuring its own plasma resonance in the mid-IR range [27].

In previous SSNOM experiments aimed at determining N in semiconductors, gold-coated pyramidal probe tips were used and broad IR frequency intervals were required for nanospectroscopy. For example, in Ref. [4] both terahertz and mid-IR data obtained with different laser systems are combined to measure N in silicon transistors in the 10^{18} – 10^{20} -cm $^{-3}$ range, while in Ref. [10] several mid-IR tunable lasers are employed to measure N in InP nanowires in the 10^{19} – 10^{20} -cm $^{-3}$ range by detecting the NW plasma resonance. More recently, both ultrabroadband IR synchrotron radiation [5,7] and IR supercontinuum radiation generated by femtosecond lasers [6,8] were coupled to SSNOM systems to study the electrodynamic response of nanocrystals and nanowires. In general, in a broadband spectroscopy approach to SSNOM, the tip is located at a few positions within the sample to acquire IR spectra and detect sample resonances therein [5–10]. In this case, the broadband spectrum typically displayed by pyramidal gold-coated probe tips [28], which lack sharp electromagnetic resonances, is a positive feature if one aims at unambiguously identifying the resonance(s) belonging to the sample. In the present work, instead of broadband gold-coated tips, we employ engineered probe tips made of heavily electron-doped germanium (n -Ge) with a plasma frequency in the mid-IR range [27,29,30], with the aim of estimating N in NWs that do not display a clear plasma resonance. The scattering intensity maps are recorded at two IR frequencies, one above and one below the plasma frequency of the engineered n -Ge tip, which then features either a negative or a positive dielectric permittivity. The comparison of the two maps with an electromagnetic model based on the optical properties of the tip, precisely measured on the high crystal-quality epitaxial n -Ge material before probe fabrication, allows for an estimate of N in a ZnO NW sample (N_{ZnO}) and for free-carrier-density profiling along the NWs. The estimate and the profile are benchmarked against those obtained from phase and amplitude measurements on the same NWs with a conventional gold-coated monolithic probe tip in the pseudoheterodyne detection mode, and they are found to be in good agreement.

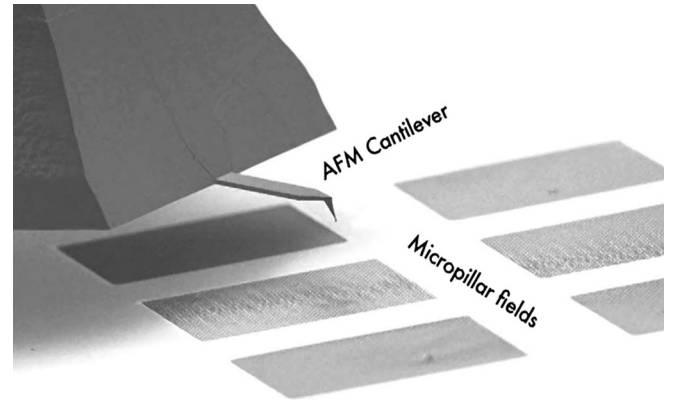
II. RESULTS AND DISCUSSION

The presentation of the results starts from a description of the engineered doped semiconductor probe, including the experimentally determined response function of the material and electromagnetic simulations of the tip. Then, a scattering near-field microscopy experiment on a ZnO nanowire is presented and it is compared to electromagnetic models, with the aim of determining a range of values for the free-carrier density in the nanowire.

A. Doped semiconductor tip engineering

Sophisticated probe tips have been engineered for a variety of different purposes [28,31–34]: for instance, gold-coated cones [31] and pyramids [32] have been attached to cantilevers and used as scanning resonant antennas for SSNOM microscopy, while gold nanorods with engineered length and shape have been employed to perform SSNOM molecular vibrational nanospectroscopy [28]. To realize the probe employed in this work, we have first attached n -Ge layer blocks to silicon cantilevers to be used for SSNOM, and then we have nanosculptured pyramidal tips by focused ion beam milling [35]. The SSNOM probe engineering technique is presented in Video 1. In the mid-IR range, n -Ge displays no interband optical transitions (like many other electron-doped semiconductors [8]) hence, it approximately behaves as an ideal Fermi liquid [29], with a complex dielectric function written according to the Drude model as

$$\tilde{\epsilon}_{\text{tip}}(\omega) = \epsilon'_{\text{tip}} + i\epsilon''_{\text{tip}} = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\gamma^2 + \omega^2} \right) + i \frac{1}{\omega} \left(\frac{\epsilon_{\infty} \omega_p^2 \gamma}{\gamma^2 + \omega^2} \right), \quad (1)$$



VIDEO 1. Nanofabrication process of the n -Ge tip. The n -Ge epitaxial layer grown on a Si wafer is first patterned into micropillars. The extremity of an AFM cantilever probe, with the tip apex intentionally removed by focused-ion-beam milling, is placed in contact with the top surface of one of the micropillars. The probe is glued to the pillar by electron-beam-induced deposition of a platinum-carbon composite. The pillar base is subsequently cut by ion milling and the n -Ge epitaxial layers are detached from the Si wafer using the silicon cantilever itself as a manipulation probe. Finally, the n -Ge layer is shaped into a four-side pyramid with curvature radius of about 50 nm [27].

where ω_p is the (screened) plasma frequency of the tip, ϵ_∞ is the dielectric screening constant due to valence electrons oscillating at higher frequencies, and $\gamma \ll \omega_p$ is the electron energy relaxation rate. In Eq. (1), one sees that a crossover exists from a negative permittivity $\epsilon'_{\text{tip}} < 0$ at frequency $\omega < \omega_p$, to a positive permittivity $\epsilon'_{\text{tip}} > 0$ at $\omega > \omega_p$. In the mid-IR range below ω_p , a doped semiconductor displays a very small negative value of ϵ'_{tip} and an intrinsic spheroid-polarizability resonance is established [30], at odds with wirelike resonances of mid-IR antennas made of noble metals with ω_p in the visible range [28,33,34,36], for which the wire length determines the resonance frequency. Given the present-day *n*-Ge thin-film growth technology, tips with any value of ω_p up to $\approx 3000 \text{ cm}^{-1}$ could be engineered and adapted to specific SSNOM experiments. In Fig. 1(a) we plot the complex dielectric function of the specific *n*-Ge material used in this work for SSNOM probe engineering, which displays $\omega_p = 1050 \text{ cm}^{-1}$ and is well described by the Drude model (dashed lines). From the data in Fig. 1(a) the complex polarizability of a *n*-Ge sphere of radius $r \approx 50 \text{ nm}$, approximating the tip apex, is calculated in the quasistatic limit as $\tilde{\alpha} = 4\pi r^3(\tilde{\epsilon}_{\text{tip}} - 1)/(\tilde{\epsilon}_{\text{tip}} + 2)$ and it displays a maximum in its absolute value just below ω_p accompanied by a phase-delay peak exceeding $\pi/4$ [see Fig. 1(b)].

We now consider the behavior of a doped semiconductor tip for SSNOM on both a high-*N* and a low-*N* ZnO sample surface. To do this, we use the image point-dipole (IPD) model, in which the tip is considered as a small spherical dipole inducing an image dipole in a semi-infinite homogeneous sample plane [1,37]. The sample optical properties are chosen to reproduce those of ZnO with very high *N* and very low *N*, in both cases with a short Drude relaxation time of the InP NW of Ref. [10] is 1.0 ps). The moduli of the calculated scattering cross sections of the tip-surface image-dipole system $|\tilde{S}(\omega)|$ strongly increase below ω_p and then fall abruptly above ω_p [see continuous curves in Fig. 1(c)]. The scattering phases $\phi_s(\omega) = \arg[\tilde{S}(\omega)]$ have a sharp peak at ω_p approaching $\pi/2$ [dashed curves in Fig. 1(c)]. This behavior of the scattering functions mirrors the ones already observed by SSNOM on NW samples, however, we remark that the plasma resonance here belongs to the tip and not to the sample. Importantly for the aim of the present work, the sharp features seen in the scattering cross sections for a high- N_{ZnO} sample in Fig. 1(c) (purple curves) decrease in strength with decreasing N_{ZnO} (red curves), and this effect may provide a contrast mechanism for carrier-density mapping. On the other hand, in Fig. 1(c) almost no difference is seen among high- N_{ZnO} , low- N_{ZnO} , and dielectric samples at frequencies far away from ω_p . We shall then conduct SSNOM experiments at two IR frequencies close to ω_p ($\omega_{\text{IR1}} \lesssim \omega_p$ and $\omega_{\text{IR2}} \gtrsim \omega_p$).

We perform finite-difference time-domain (FDTD) simulations to estimate the plasmon resonance spectrum

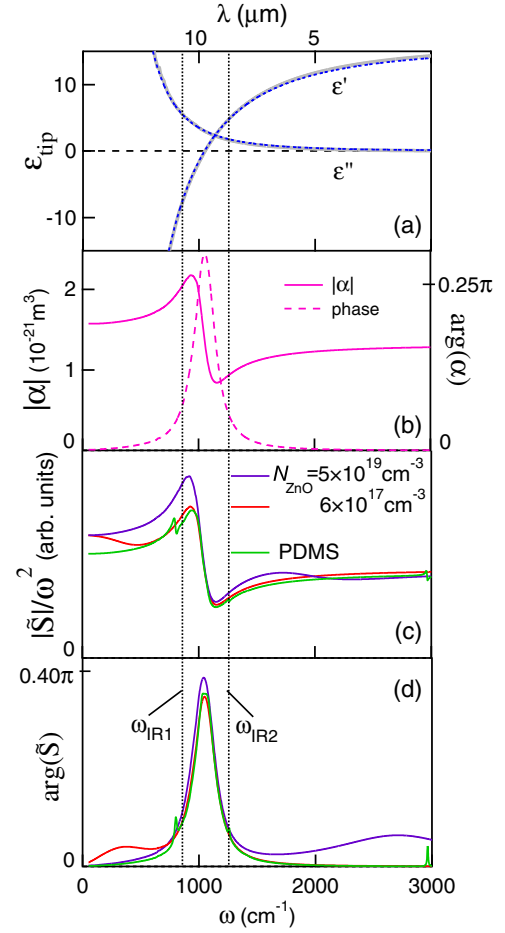


FIG. 1. Image point-dipole model. (a) Dielectric function of the epitaxial electron-doped germanium film used in this work for scanning probe-tip engineering. Gray thick lines, IR experiment [27]; dashed lines, Drude fit with $\omega_p = 1050 \text{ cm}^{-1}$, $\gamma = 205 \text{ cm}^{-1}$, $\epsilon_\infty = 16.0$. (b) Polarizability amplitude and phase of a sphere of radius $r = 50 \text{ nm}$ made of *n*-Ge. (c) Scattering amplitude and (d) phase of the *n*-Ge sphere when positioned 10 nm from a semi-infinite plane made of ZnO, calculated in the framework of the image dipole model. Two carrier-density values have been considered for ZnO: $N_{\text{ZnO}} = 5 \times 10^{19} \text{ cm}^{-3}$ (“good” conductor, purple curves) and $N_{\text{ZnO}} = 6 \times 10^{17} \text{ cm}^{-3}$ (“bad” conductor, red curves). The scattering amplitude is also calculated for a semi-infinite plane made of the dielectric matrix material used in this work (PDMS, green curve, almost overlapping with the one of the “bad” ZnO conductor, red curve). For PDMS we use a multi-Lorentzian model with $\epsilon_\infty = 2.0$. For ZnO we use $\epsilon_\infty = 3.7$, $\gamma = 600/1500 \text{ cm}^{-1}$ for the red (purple) curve, and $m^* = 0.29 m_e$. The amplitude contrast between good and bad conductors around 900 cm^{-1} is exploited in this work for SSNOM imaging. The two vertical dotted lines mark the two measurement frequencies ω_{IR1} and ω_{IR2} .

of the scanning probe tip used in this work, shown in Fig. 2(a). The tip is a *n*-Ge square-base pyramid with a height of about $1.5 \mu\text{m}$, side of about $1.0 \mu\text{m}$, and curvature radius of the tip apex $r \approx 50 \text{ nm}$. The field-enhancement map is reported in Fig. 2(b) for $\omega_{\text{IR}} = 850 \text{ cm}^{-1}$. The

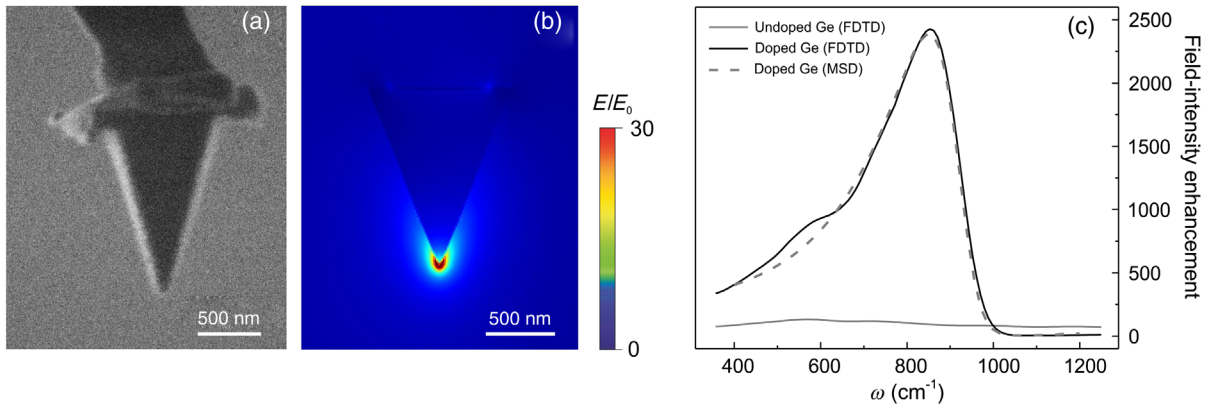


FIG. 2. Doped semiconductor tip engineering. (a) Image of the engineered tip during nanosculpturing of the pyramidal tip, taken with the focused ion beam at low ion currents. (b) Finite-difference time-domain (FDTD) electromagnetic simulations of the electric-field enhancement E/E_0 as a function of position in space at the peak enhancement frequency $\omega_{\text{IR}} = 850 \text{ cm}^{-1}$. (c) Field-intensity enhancement $|E/E_0|^2$ as a function of ω_{IR} at a position 25 nm below the tip apex calculated with FDTD and with the multispherical dipole model described in the text. Simulations of doped Ge use the dielectric function of Fig. 1(a), those of undoped Ge use $\epsilon = 16.0 + 0.001i$.

electromagnetic field enhancement at the apex is calculated in Fig. 2(c) (black solid line) as a function of ω_{IR} in the range 400–1250 cm^{-1} ($\lambda \sim 8\text{--}25 \mu\text{m}$) using illumination conditions identical to those of the SSNOM experiment. The maximum field enhancement found at 850 cm^{-1} is clearly related to the resonant excitation of the free-electron plasma in $n\text{-Ge}$, because it is absent when instead the dielectric function of undoped Ge $\epsilon = 16.0 + 0.001i$ is considered [gray solid line in Fig. 2(c)] [30]. It is then convenient to use the reliable CO_2 laser technology emitting at $\omega_{\text{IR}1} = 884 \text{ cm}^{-1}$ in conjunction with a $n\text{-Ge}$ tip with $\omega_p = 1050 \text{ cm}^{-1}$.

B. Near-field imaging experiment

We prepare a test sample made of doped ZnO NWs embedded in a polydimethylsiloxane (PDMS) matrix. Conductive-AFM measurements indicate that the different NWs have a large spread of conductivity values, and indeed in the hydrothermal crystal-growth process the expected doping level varies widely in the range $N_{\text{ZnO}} \sim 10^{17}\text{--}10^{20} \text{ cm}^{-3}$ [15]. Figure 3(a) shows a SEM image of a single ZnO NW transferred onto a silicon substrate before blending it with PDMS, and Fig. 3(b) shows the cross section SEM image of another NW embedded in the same PDMS matrix. Embedding the NWs in a matrix is crucial for eliminating high topography steps that may impact on the scattering function producing artifacts in the SSNOM maps [38,39]. Also, there is an intrinsic technology interest in studying the conductivity of NWs embedded in a matrix because they form the building block of foldable nanophotonic and nanoelectronic devices [20,21]. We use a commercial SSNOM setup (neaSNOM by Neaspec GmbH) where the doped semiconductor tip with $\omega_p = 1050 \text{ cm}^{-1}$ is illuminated at a grazing incidence with the electric-field

vector oriented at an angle of 30° with respect to the surface normal. A mid-IR detector is aligned so as to measure the radiation intensity backscattered in the far field. The sample is scanned in the x, y plane and the detector output voltage $u(x, y)$ is measured [2]. The voltage u is proportional to the backscattered light intensity that depends on the background (stray light) interfering with the near-field signal. The experimental near-field signal $u_{(i)}$ is therefore isolated by demodulation of the detector voltage at the i th harmonic of the cantilever tapping frequency Ω for $i \geq 2$, resulting in SNOM maps $u_{(i)}(x, y)$ like those demonstrated in Figs. 3(g)–3(j) for $i = 2$. The pseudoheterodyne technique described in Ref. [2], which allows a direct retrieval of $\phi_{s,(i)}$, could not be applied to the $n\text{-Ge}$ tip, mainly because of an increased mechanical noise of our nanoengineered probe if compared to monolithic scanning probes. This is attributed essentially to the weak mechanical link between the $n\text{-Ge}$ pyramid and the silicon shaft, producing an increased noise power density at a low modulation frequency below a few tens of kHz, which prevents the use, in the neaSNOM microscope, of the Michelson interferometer with an oscillating mirror at around 300 Hz to demodulate the phase information [2]. Phase-stabilized homodyne SNOM [25,26] or monolithic probe-tip fabrication may represent a solution to this problem for future studies.

We image the NW of Fig. 3(a), of a radius of $R_{\text{NW}} \sim 200 \text{ nm}$ and buried under $h \sim 60 \text{ nm}$ of PDMS [see Fig. 3(b)]. Two IR lasers are used, one emitting at $\omega_{\text{IR}1} = 884 \text{ cm}^{-1} < \omega_p$ and one emitting at $\omega_{\text{IR}2} = 1250 \text{ cm}^{-1} > \omega_p$. For direct comparison, the same NW is imaged with a gold-coated probe characterized by identical mechanical properties of the cantilever. The SEM images of the two probe tips are shown in Figs. 3(c)–3(d).

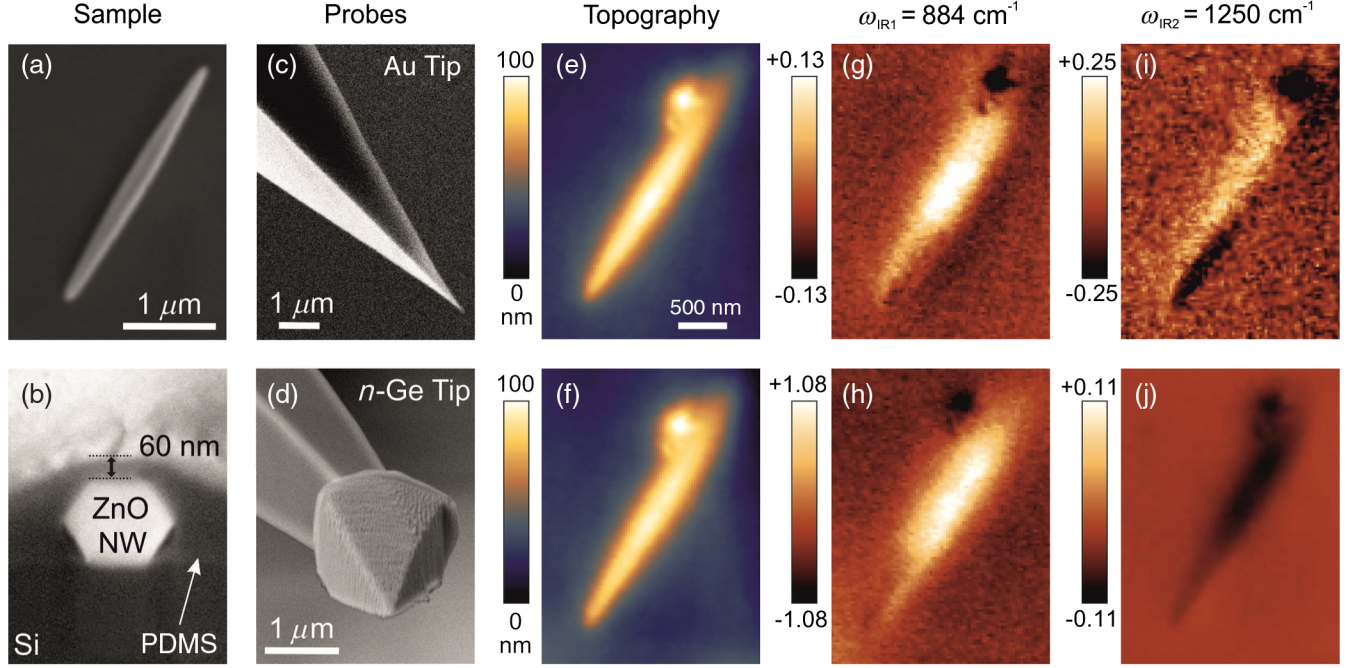


FIG. 3. SNOM imaging of a nanowire. (a) SEM image of the ZnO nanowire dispersed on a silicon wafer. (b) Slice-and-view section of one of the NWs from the same sample buried under 60 nm of PDMS matrix. (c), (d) SEM images of the gold-coated silicon tip (c) and of the n -Ge tip (d) used for mid-IR nanoimaging. (e), (f) AFM topography of a selected NW on the test sample obtained with the two tips. (g)–(j) Maps of the SSNOM signal $u_{(2)}$ taken at two different IR frequencies (884 and 1250 cm^{-1}) with the two tips. When imaged with the n -Ge tip (h), (j), the nanowire displays contrast on the dielectric matrix of a different sign at the two IR frequencies. Linear plane fit is applied. In (i), a 2×2 Gaussian smoothing algorithm is also applied due to a higher noise.

The respective AFM topography maps of the NW [Figs. 3(e)–3(f)] do not display significant differences between each other and they confirm the expected smooth variations of the topography. In the case of the gold-coated tip, the pseudoheterodyne detection mode is applied. For simplicity, we focus on a specific location at the center of the NW, indicated in Fig. 4. The measurements of the SSNOM intensity contrasts and phase shifts with respect to the PDMS background are shown in Figs. 4(a)–4(b) as black dots, and they are compared to the IPD model predictions with a gold-coated tip calculated for different free-carrier parameters of the NW [10–11]. A free-carrier density $N_{\text{ZnO}} = 2.5 \times 10^{19} \text{ cm}^{-3}$ with an electron mobility of $25 \text{ cm}^2/\text{V s}$ gives a good fit to the data.

In Figs. 3(g)–3(j), the SSNOM intensity maps $u_{(2)}(x, y)$ collected with either tip are shown for ω_{IR1} and ω_{IR2} . For each map, one can define the maximum experimental near-field contrast as

$$\Delta u_{(i)} = \frac{u_{(i)}^{\text{NW}} - u_{(i)}^{\text{PDMS}}}{u_{(i)}^{\text{PDMS}}}, \quad (2)$$

where $u_{(i)}^{\text{NW}}$ is measured at the center of the NW, and $u_{(i)}^{\text{PDMS}}$ is the average over the PDMS matrix surrounding the NW. The SSNOM maps obtained with the gold-coated tip at ω_{IR1} and at ω_{IR2} both display a positive $\Delta u_{(2)}$ at the center of the NW that corresponds to the positive ΔS calculated in

Fig. 4(a). Turning to the SSNOM maps collected with the doped semiconductor tip, at $\omega_{\text{IR1}} < \omega_p$ a positive $\Delta u_{(2)} \approx +0.50$ is observed at the center of the NW [Fig. 3(h)], while at $\omega_{\text{IR2}} > \omega_p$ a negative $\Delta u_{(2)} \approx -0.11$ is found [Fig. 3(j)], demonstrating that the near-field interaction of the doped semiconductor tip with the ZnO NW is very different from that of the gold-coated tip. Understanding the precise reason for this difference requires electromagnetic modeling.

C. Electromagnetic model

The comparison between the experimental data of Fig. 3 and the IPD model of Fig. 1(c) must be done carefully, because in the present experiment with the n -Ge tip the scattering phase and amplitude could not be separately measured due to technical limitations of the nanoengineered tip explained above. Therefore, the demodulated voltage signal at each frequency ω actually depends on the background amplitude $B_0(\omega)$ and phase $\phi_b(\omega)$, which are not related to the specific tip-sample interaction [2]:

$$u_{(i)}(\omega) \approx 2\kappa(\omega)B_0(\omega)|\tilde{S}(\omega)|_{(i)} \cos[\phi_b(\omega) - \phi_{s,(i)}(\omega)], \quad (3)$$

where $\kappa(\omega)$ is the detector sensitivity. Now, B_0 can be considered as a constant over the investigated area of size much smaller than λ , while ϕ_b smoothly varies with x and y

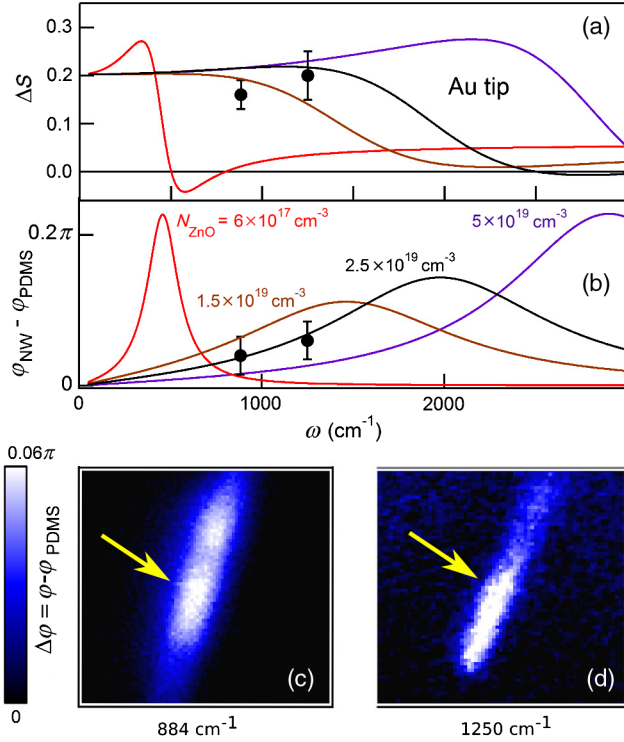


FIG. 4. Scattering phase and amplitude measured with the gold-coated tip. (a),(b) The scattering amplitude (a) and phase (b) contrast between a ZnO NW with different free-carrier density calculated from the IPD model with a Au sphere of radius $r = 50$ nm (color curves) and measured in the pseudoheterodyne detection mode (black dots), referring to the position at the NW center indicated by arrows in panels (c),(d). The electron mobility values are the same as Figs. 1(c)–1(d), i.e., $62 \text{ cm}^2/\text{Vs}$ for $N_{\text{ZnO}} = 6 \times 10^{17} \text{ cm}^{-3}$ and $25 \text{ cm}^2/\text{Vs}$ for the other curves. (c),(d) Scattering phase contrast maps at 884 cm^{-1} (c) and 1250 cm^{-1} (d). The map size is $2 \times 2 \mu\text{m}^2$. The amplitude maps are reported in Fig. 3(g) for 884 cm^{-1} and 3(i) for 1250 cm^{-1} . The formula used for the calculations in (a),(b) is reported in the Supplemental Material, $z = 70$ nm where z is the tip to sample distance is used.

because of the smooth topography variations of the PDMS matrix in which the NW is embedded. Also, from an inspection of Fig. 1(d), one should have a similar value of ϕ_s for both PDMS and the nanowire at each measurement frequency. Indeed, using a doped semiconductor probe tip on weakly resonant samples results in a scattering phase variation with the frequency driven by the tip and, as such, almost independent of the sample material. Within these approximations the cosine term in Eq. (3) can be considered constant over each entire map (see the Appendix). The observed SSNOM image contrasts, almost entirely determined by the scattering amplitude, can now be compared with the IPD model calculation of the scattering intensity contrast $\Delta S = [|\tilde{S}^{\text{NW}}(\omega)|_{(i)} - |\tilde{S}^{\text{PDMS}}(\omega)|_{(i)}] / |\tilde{S}^{\text{PDMS}}(\omega)|_{(i)}$ where the values of $|\tilde{S}(\omega)|_{(i)}$'s are taken from the IPD model data for

the doped semiconductor tip on a ZnO half-plane. Within the IPD model, at $\omega_{\text{IR1}} = 884 \text{ cm}^{-1}$ the contrast ΔS is strong and positive for very high N_{ZnO} , weak and positive for very low N_{ZnO} . At $\omega_{\text{IR}} \sim 1250 \text{ cm}^{-1}$, a strong negative contrast is not expected for any N_{ZnO} value, and this is at clear odds with the observation of Fig. 3(j). To overcome this contradiction, one should be reminded that the IPD model may not be accurate enough to reproduce the SSNOM contrast determined by finite-size effects due to the nanostructured sample [40–43], to the engineered probe tip itself [28], or to both. In previous works that went beyond the IPD model, the scattering function of the tips is either calculated in the prolate spheroid approximation [41–46], or it is directly measured [28]. Here, instead, we simulate the n -Ge tip by using several n -Ge spheres of decreasing radii mimicking the decrease of the pyramid cross section towards the tip apex. The number of spheres and their radii are selected in order to fit the near-field FDTD simulation data and to mimic the actual n -Ge tip geometry in Fig. 2(a): the smallest sphere has almost the same curvature radius, and the other spheres follow the pyramid angle. In comparison with the prolate spheroid approximation, both the finite size of the tip and the small curvature radius at the apex can be taken into account [44,45]. Moreover, we simulate the ZnO NW by a further ZnO sphere embedded in a PDMS layer. All the spheres and the layers are considered in mutual polarization interaction, i.e., they are all affected by both the incident electric field and by the electric field radiated by the other spheres and layers. To do that, we employ a multiple-scattering code introduced in Ref. [47], which is a semianalytical model and therefore its calculation is fast enough to provide the explicit dependences of the image contrast value with N_{ZnO} as a free parameter in the model. This multispherical dipole (MSD) model is here adapted to the doped Ge tip of the present experiments by choosing the four spheres of decreasing radii (240, 120, 60, and 30 nm) sketched in Fig. 5(a), a choice that nicely reproduces the shape of the tip as well as the FDTD resonance frequency spectrum [see the dashed line in Fig. 2(c)] using the dielectric function $\epsilon_{\text{tip}}(\omega)$ given in Fig. 1(a). The fitting to the FDTD data and to the experimental results is achieved by considering only the dipole term in the multipole field expansion. We recall that, in the IPD model, the tip was modeled by a single sphere of radius $r = 50$ nm, and the FDTD spectrum of Fig. 2(c) cannot be reproduced by a single sphere [37].

For the application of the MSD model to SSNOM, we calculate the intensity of the backscattered radiation $|\tilde{E}_s|^2$ for many tip-sample distance values $z(t) = (z_{\text{max}}/2) [1 + \cos(\Omega t)]$ reproducing tapping-mode operation of the probe ($z_{\text{max}} \sim 100$ nm). Then, the i th components of the t -dependent Fourier transform $|\tilde{E}_s|_{(i)}^2$ are computed for comparison with the experimental $u_{(2)}$ and $u_{(3)}$. The NW

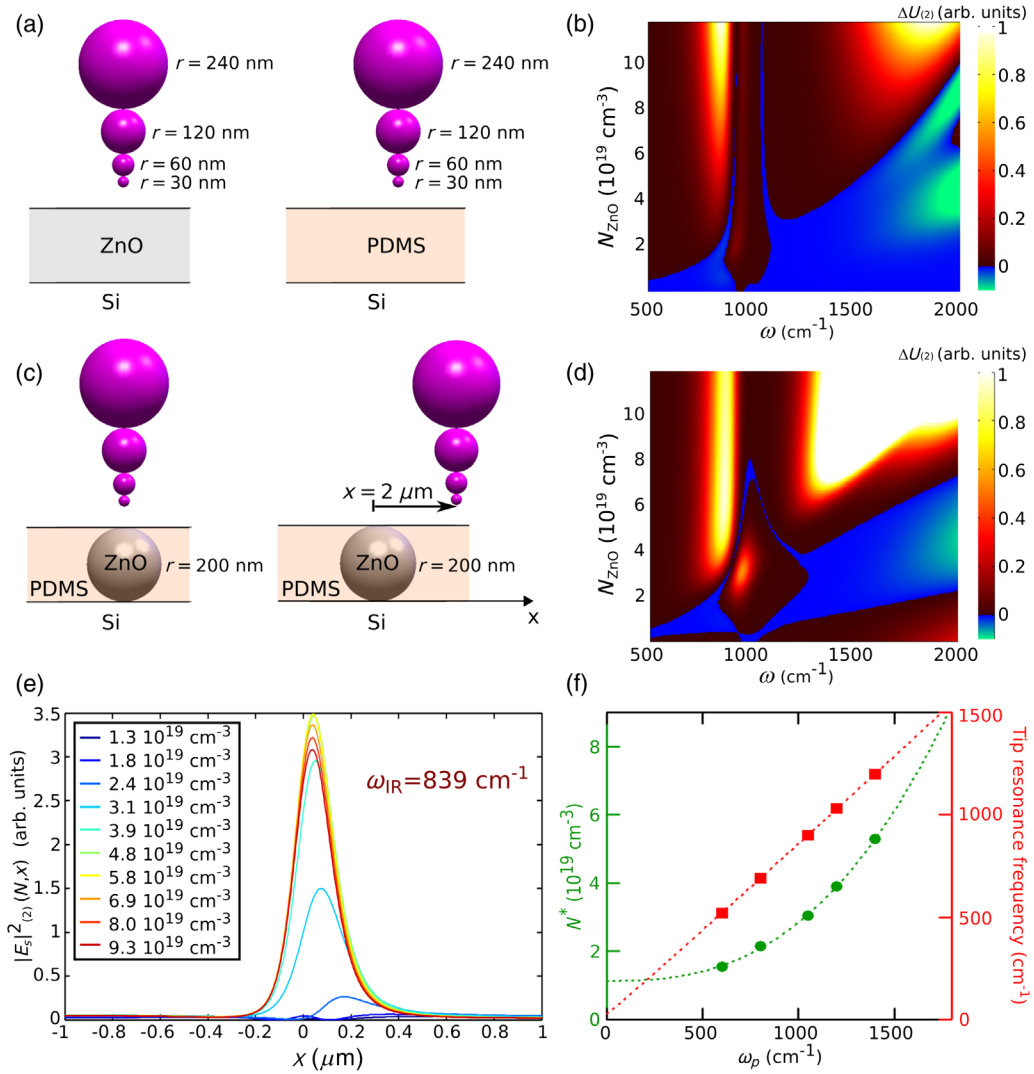


FIG. 5. Multi-spherical-dipole model of the SSNOM experiment. (a) The scattering function of the engineered tip over a ZnO layer and over a PDMS layer, both on a Si substrate, is simulated by using four spheres of different radius for the Ge tip. (b) The calculated scattering intensity contrast $\Delta u_{(2)}^{\text{calc}}$ is color plotted vs the values of ω_{IR} and N_{ZnO} (red hot, positive contrast values; blue-green, negative contrast values). (c) The simulation is repeated by adding a ZnO sphere of radius $R_{\text{NW}} = 200$ nm representing a nanowire embedded in a PDMS matrix. The scattering intensity contrast is calculated for several displacements x of the n -Ge tip from the ZnO sphere and the zero-contrast condition [i.e., intensity identical to that of the geometry outlined on the right-hand side of panel (a)] is reproduced for $x > 2 \mu\text{m}$. The contrast $\Delta u_{(2)}^{\text{calc}}$ between $x = 0 \mu\text{m}$ and $x = 2 \mu\text{m}$ is then color plotted in (d). (e) The scattering intensity for $i = 2$ plotted vs x for different values of N : the asymmetric SSNOM profile of the ZnO sphere shows imprints of the illumination direction along x [41]. (f) A threshold carrier density N^* for NW visibility is defined from the data in (e) and from identical simulations where the plasma frequency ω_p of the n -Ge tip is varied (green dots). The plasmon resonance of the n -Ge tip is also plotted (red squares), dashed lines are guides to the eye. In all simulations, $\epsilon^{\text{PDMS}} = 2.0$, the n -Ge tip dielectric function is taken from Eq. (1) and the Drude parameters other than N_{ZnO} used to reproduce the ZnO dielectric function are $\epsilon_{\infty} = 3.9$, $m^* = 0.29m_e$, $\gamma = 600 \text{ cm}^{-1}$ [23].

dielectric function includes N_{ZnO} as a free parameter. The sample is either considered as a 400-nm-thick ZnO layer on a semi-infinite Si substrate [Fig. 5(a)], or as a sphere of ZnO of 400-nm diameter embedded in PDMS and deposited on a semi-infinite Si substrate [Fig. 5(c)], in order to directly assess the possible role of sample-related finite-size effects. For comparison with the experiment of Figs. 3(h) and 3(j), we calculated the SSNOM intensity contrast of the buried NW over the PDMS matrix:

$$\Delta u_{(i)}^{\text{calc}}(\omega_{\text{IR}}, N_{\text{ZnO}}) = \frac{||\tilde{E}_s^{\text{ZnO}}(\omega_{\text{IR}}, N_{\text{ZnO}})|_{(i)}|^2 - ||\tilde{E}_s^{\text{PDMS}}(\omega_{\text{IR}})|_{(i)}|^2}{E_0^2}, \quad (4)$$

which is a real function of N_{ZnO} and ω_{IR} . In Figs. 5(b) and 5(d), the contrast for $i = 2$ is color plotted as a function of N_{ZnO} and ω_{IR} for the two situations sketched in Figs. 5(a) and 5(c), respectively.

Looking at Fig. 5(b), one sees that the contrast $\Delta u_{(2)}^{\text{calc}}$ (homogeneous ZnO sample case) displays a clear imprint of the plasmon resonances of the *n*-Ge tip at 850 cm^{-1} , whose intensity increases for higher N_{ZnO} without any significant frequency shift. Also, for very low N_{ZnO} and for $\omega > \omega_p$, $\Delta u_{(2)}^{\text{calc}}$ is almost zero (areas of dark red color), and it even turns negative (areas of blue-green color), indeed matching the experimental observation of Fig. 3(j), hence indicating that the effects due to the finite size of the tip, which are accounted for in the MSD model and not in the IPD model, cannot be neglected in the calculation of the total scattering function. The negative contrast for $\omega > \omega_p$ is not surprising, as scattering suppression was previously observed in SSNOM performed with gold tips on the high-frequency side of vibrational [38,40] or plasma [10] resonances of the sample. Here, instead, the resonance resides in the tip material, but it becomes more evident in the SSNOM maps as N_{ZnO} increases [see Fig. 5(b)]. If one now adds the effect of the finite size of the ZnO sample [Fig. 5(d)], one sees that the overall picture is confirmed: at $\omega_{\text{IR1}} = 884 \text{ cm}^{-1}$ one gets strong positive contrast for high N_{ZnO} , while at $\omega_{\text{IR2}} = 1250 \text{ cm}^{-1}$ one instead gets weak negative contrast in the low 10^{19}-cm^{-3} range of N_{ZnO} . Since Figs. 5(b) and 5(d) are not fundamentally different at any $\omega_{\text{IR}} \leq 1250 \text{ cm}^{-1}$, we derive that the sample-related finite-size effects are not significant in our experiments. Instead, at $\omega_{\text{IR}} > 1600 \text{ cm}^{-1}$ a clear difference between Figs. 5(b) and 5(d) is observed in the bright spots for very high N_{ZnO} (top right corner of the color plots), which can indeed be tentatively assigned to sample-related finite-size effects becoming important for shorter wavelengths [40].

For an absolute evaluation of N_{ZnO} based on the MSD model of the experiment in Fig. 3, we define a free-carrier-density threshold value N^* such that, for any $N_{\text{ZnO}} > N^*$, a ZnO NW becomes clearly visible in a transverse SSNOM line-scan [see Fig. 5(e)]. For the *n*-Ge tip discussed in this work, one finds from the MSD model that $N^* \approx 2 \times 10^{19} \text{ cm}^{-3}$. The good visibility in Fig. 3(h) of the NW with unknown N_{ZnO} implies that, therein, $N_{\text{ZnO}} > N^*$. The negative contrast observed at 1250 cm^{-1} [Fig. 3(j)], globally compared to Figs. 5(b) and 5(d), suggests that N_{ZnO} should not approach $\sim 10^{20} \text{ cm}^{-3}$. One can then provide a final estimate for N_{ZnO} in the low 10^{19}-cm^{-3} range, which is in good agreement with the result ($N_{\text{ZnO}} \approx 2.5 \times 10^{19} \text{ cm}^{-3}$) obtained on the same NW with the gold-coated tip using the pseudoheterodyne detection mode, shown in Fig. 4. The noticeable feature of our engineered tips is that one could choose a tip material with ω_p optimized to be sensitive to different NW materials and carrier-density ranges: Fig. 5(f) shows the plasmon resonance frequency of *n*-Ge probe tips, simulated within the MSD model, linearly scaling with ω_p . The corresponding value of N^* , also determined from the MSD model, has a superlinear but monotonic dependence on ω_p , indicating

that engineered probe tips with high (low) ω_p will be more sensitive to the response of NWs with higher (lower) N_{ZnO} .

D. Imaging resolution of free-carrier profiling

It has been recognized [19] that, beyond the absolute value of the conductivity, the free-carrier-density profile in NWs is also extremely difficult to be reliably determined by contact-based methods. Noncontact optical methodologies have then been proposed, including Raman, photoluminescence, and cathodoluminescence spectroscopy [48,49]. Note that structural methodologies like secondary ion mass spectroscopy and atom probe only provide the density of dopant atoms, which may be very far from the actual free-carrier density due to partial dopant activation [18]. Among optical methodologies, the approaches based on SSNOM [6,10,11] directly provide the local free-carrier-density profile through determination of the Drude model parameters with subwavelength lateral resolution [10], which we demonstrate in the following also for our engineered doped semiconductor tips.

In Fig. 6 the maps and the line profiles along the NW axis of the near-field signal are shown for ω_{IR1} and ω_{IR2} . Therein, the signal $u_{(3)}$ is plotted instead of $u_{(2)}$, because $u_{(3)}$ has a weaker background interference and is therefore better suited for a quantitative analysis [50]. Figure 6(a) displays the SSNOM image taken at ω_{IR1} where the NW has a high positive image contrast, as already seen in Fig. 3(h) for the $u_{(2)}$ map. Line profiles measured across the NW for different positions along the axis [27,37] indicate a SSNOM lateral resolution of $100 \pm 20 \text{ nm}$ at both $\lambda_{\text{IR1}} = 11.3 \mu\text{m}$ and $\lambda_{\text{IR2}} = 8.0 \mu\text{m}$ hence $\sim \lambda/100$. The lateral resolution is only slightly broader than both the embedding depth $h \sim 60 \text{ nm}$ and the radius of curvature $r \sim 50 \text{ nm}$, as typically obtained in the SSNOM imaging of buried nanostructures [8]. The SSNOM line profile at ω_{IR1} along the NW axis [oblique coordinate ξ , Fig. 6(c)] shows a high signal in the central portion of the NW, almost constant with ξ , and a slow decrease towards the NW ends. At ω_{IR2} [Figs. 5(b) and 5(d)], again the NW shows a negative image contrast as in Fig. 3(j) but the signal-to-noise ratio is even better than that at ω_{IR1} . The slow decrease of the scattering contrast from $\xi = 0.5 \mu\text{m}$ to $\xi = 0.1 \mu\text{m}$, and then from $\xi = 1.2 \mu\text{m}$ to $\xi = 1.5 \mu\text{m}$, in both Figs. 6(c) and 6(d), is probably due to the increasing h or the decreasing R_{NW} value towards the ends of the NW [see the cigarlike shape of the NW in Fig. 3(a)], both impacting on the strength of the near-field interaction of the doped semiconductor tip with the NW [50–52]. Importantly, the profile of the phase shift measured with the gold-coated tip, extracted from the phase map in Fig. 4(c) and reported in Fig. 6(c) with an offset, displays exactly the same features as the intensity profiles measured with the *n*-Ge tip, confirming that the profile variations at constant h and R_{NW} in the central portion of the NW (from $\xi = 0.5 \mu\text{m}$ to $\xi = 1.2 \mu\text{m}$) are likely due to free-carrier-density variations. A constant

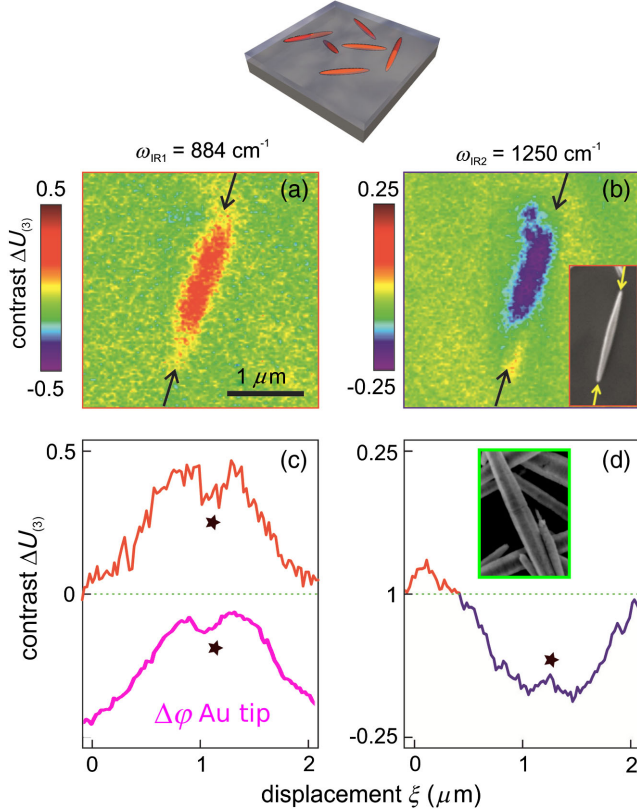


FIG. 6. Assessment of the resolution of free-carrier profiling. (a),(b) Maps of the SNOM contrast of a ZnO nanowire (NW) over the surrounding PDMS matrix observed at two IR frequencies. In the inset of (b) we show the SEM image of the same NW. (c),(d) SNOM signal profile cuts between the two NW extremities indicated by the black arrows in (a),(b) and by the yellow arrows in the inset of (b). The abscissa of (c),(d) is the displacement coordinate ξ along the NW axis. The dashed green line represents the average value of the contrast observed on the surrounding PDMS matrix. The lower end of the NW ($\xi < 0.5 \mu\text{m}$) is buried under a larger thickness of PDMS and it is not visible in the present SSNOM maps and profiles. The pink curve in panel (c) is the phase contrast profile measured with the gold-coated tip, extracted from Fig. 4(c). The pink curve is offset and scaled to match the red curve in the panel above. In panel (c), the higher noise level in the n -Ge tip profile (red curve) if compared to the Au tip (pink curve) is due to the higher mechanical noise of the nanoengineered tip. The stars in (c),(d) correspond to a position with slightly lower carrier density in the NW. This feature is attributed to the initial growth seed of the NW, with higher crystal defect density. In the inset of panel (d), a SEM image of another similar NW is shown, where the initial growth seed position is seen as a transversal indent in the middle of the NW.

N_{ZnO} is found along the NW axis, apart from a dip at the position around $\xi = 0.8 \mu\text{m}$, marked by stars in Figs. 6(c) and 6(d), which points towards a local depletion of the free carriers, perhaps due to the presence of a structural nucleation defect like the one visible in the inset of Fig. 6(d). This type of nucleation defect often correlates to local suppression of the free-carrier density in ZnO NWs grown with the hydrothermal method [53]. We notice that

the signal decrease at the NW ends and the dip at $\xi = 0.8 \mu\text{m}$ are identically seen at both ω_{IR1} and ω_{IR2} , independently on the sign of the image contrast (positive for $\omega_{\text{IR1}} < \omega_p$ and negative for $\omega_{\text{IR2}} > \omega_p$), confirming that the doped semiconductor tip presented in this work features clear near-field interactions with the sample, both above and below its plasma frequency ω_p , and is able to capture small local variations in N_{ZnO} .

III. CONCLUSIONS

Scanning near-field optical microscopy has been performed with purposely engineered doped semiconductor tips featuring a plasma frequency in the midinfrared range. The intrinsic plasma resonance in the tip material (epitaxial heavily electron-doped germanium) provides a strongly wavelength-dependent scattering intensity contrast displaying a clear correlation with the free-carrier density in ZnO nanowires with a very short Drude relaxation time. The free-carrier-density range of a single ZnO nanowire could be estimated by comparing the image contrast of the near-field microscopy maps acquired at two wavelengths, one above and one below the plasma wavelength of the tip, to the image contrast calculated using a semianalytic multipole model of the near-field microscopy experiment. The results are positively benchmarked against those obtained with a conventional gold-coated tip in the more precise pseudoheterodyne detection mode, where both phase and amplitude are measured. The model has also clarified that the shape and size of the doped semiconductor tip strongly affect the scattering image contrast, while the shape and size of the nanowire have a lower impact. Our doped semiconductor tips therefore provide the same kind of information as that provided by the commonly used gold-coated tips for specific SSNOM experiments. In the future, the monolithic fabrication of scanning probes made of epitaxial material layers may open alternative avenues in near-field optical microscopy and scanning probe microscopy in general.

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APPENDIX: METHODS

Scanning probe tips made of doped semiconductors are fabricated by modifying commercial visible-apex silicon probes (Nanosensors ATEC-NC) as described in Video 1. These tips had been previously used to perform AFM topography imaging in contact and tapping mode, micro-photoluminescence emission, and SSNOM tests [27]. The epitaxial germanium layers used in this work are grown on silicon wafers by plasma-enhanced chemical vapor deposition using GeH_4 and PH_3 as gas precursors. A 2- μm -thick undoped Ge buffer layer is followed by the growth of a 2- μm -thick electron-doped n -Ge layer with reduced defect density. The activated doping level $n \approx 2.5 \times 10^{19} \text{ cm}^{-3}$ is determined by Hall transport measurements [29]. Heavily electron-doped germanium has $m^* = 0.12 m_e$, $\epsilon_\infty = 16$, and with these values the plasma frequency can be predicted from the free-carrier density from $\omega_p^2 = n/m^* \epsilon_\infty$. Heavily doped n -Ge films can nowadays be epitaxially grown in few- μm -thick layers perfectly suited for the fabrication of scanning probe tips, and the value of ω_p can be widely tuned in the mid-IR range up to about 2500 cm^{-1} , as verified by IR spectroscopy on different semiconductor wafers [29].

Electromagnetic simulations are conducted using a commercial software (Lumerical Inc. FDTD Solutions v8.9 software) for the FDTD data in Fig. 2 and with a homemade code for Green's function formalism [37] for the MSD data in Fig. 5 [51]. The NW dielectric function is calculated from the Drude model with parameters suitable for ZnO: $m^* = 0.29 m_e$, $\epsilon_\infty = 3.7$, and different values of N in the 10^{17} – 10^{20} cm^{-3} range. Illumination conditions replicate the Neaspec reflective objective at grazing incidence, with a 90° total horizontal opening angle, 20° vertical opening angle, and 60° incidence angle.

ZnO nanowires are grown by the hydrothermal method at 90°C in an equimolar aqueous solution (5 mM) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$. Nanowires are immersed in a liquid solution of polydimethylsiloxane (PDMS) diluted 1:40 in n -heptane, which is then spun at 5000 rpm onto silicon wafers and thermally cured on hotplate at 80°C to form a conformal elastomeric matrix (thickness ranging from $\sim 60 \text{ nm}$ on top of the NWs to 180 nm in the empty matrix areas).

SSNOM is performed with a scanning-sample AFM where the tip is illuminated with a focused laser beam (neaSNOM by Neaspec GmbH). The laser systems employed in this work are a CO_2 gas laser at 884 cm^{-1} , and a quantum cascade laser with emission at 1250 cm^{-1} . The detector of the backscattered radiation is a liquid nitrogen-cooled mercury and cadmium telluride (MCT) photovoltaic sensor. The scattered intensity signals $u_{(2)}$, $u_{(3)}$ are amplified by lock-in demodulation at 2Ω and 3Ω , in order to isolate the contribution due to the near-field tip-sample interaction ($\Omega \sim 70 \text{ kHz}$, cantilever chips by Nanosensors, model ATEC-NC). Measurement on test

samples conducted with the n -Ge tip demonstrated the near-field nature of the signal [37]. In order to maximize the SSNOM contrast, the collection optics is aligned with the tip on a position far from the NW, and ϕ_B is set to smoothly vary around values close to 0 (i.e., the cosine term in Eq. (3) is maximized to smoothly vary around a value close to 1, considering that $\phi_S \cong 0$ on the weakly absorbing PDMS matrix). In this way, the problem of low-frequency mechanical noise of the n -Ge tip that prevents pseudo-heterodyne detection is partly circumvented. The pseudo-heterodyne detection is instead performed with a gold-coated Nanosensors ATEC-NC tip, with the Michelson interferometer built into the neaSNOM microscope, with the moving mirror oscillating at 300 Hz.

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