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ARTICLE

Secondary Electron Imaging of Light at the Nanoscale

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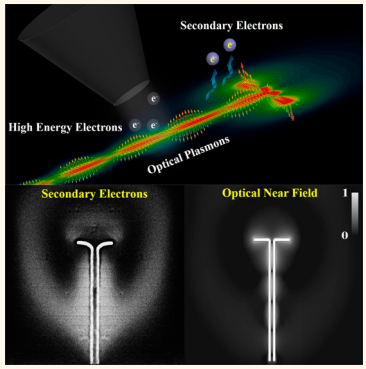
Supporting Information

ABSTRACT: **The interaction of fast electrons with metal atoms may lead to optical excitations. This exciting phenomenon forms the basis for the most powerful inspection methods in nanotechnology, such as cathodoluminescence and electron−energy loss spectroscopy. However, direct nanoimaging of light based on electrons is yet to be introduced. Here, we experimentally demonstrate simultaneous excitation and nanoimaging of optical signals using unmodified scanning electron microscope. We use high-energy electron beam for plasmon excitation and rapidly image the optical near fields using the emitted secondary electrons. We analyze dipole nanoantennas coupled with channel nanoplasmonic waveguides and observe both surface plasmons and surface plasmon polaritons with spatial resolution of 25 nm. Our experimental results are confirmed by rigorous numerical calculations based on full-wave solution of Maxwell's equations, showing high correlation between optical near fields and secondary electrons images. This demonstration of optical near-field mapping using direct electron imaging provides essential insights to the exciting relations between electrons plasmons and photons, paving the way toward secondary electron-based plasmon analysis at the nanoscale.**



KEYWORDS: *scanning electron microscopy, plasmonics, photonics, nanoimaging, nanoantennas, plasmon waveguides*

Surface plasmon polaritons (SPPs) are optically excited charge density waves, propagating along metal−dielectric interfaces.[1] Surface plasmon nanophotonics grants the speed and bandwidth of photonics with dimensions of integrated electronics and enables light−matter interaction on a deep nanoscale.[2−4] These properties have recently propelled a rapid extension of interest from both fundamental and applicative perspectives. This includes ultrafast nanophotonics,[4−6] solar energy conversion,[7−9] biomedical sensing and imaging,[10−13] as well as superlensing[12,14,15] and metasurface holography.[16] Characterization of optical plasmons requires proper excitation and detection schemes. Excitation of SP is usually performed optically and requires momentum matching devices as prisms,[17] gratings,[18] or nanoantennas.[19] Unfortunately, these techniques do not easily allow for a high localization and accurate positioning of the radiation source. In contrast, plasmons can be generated using irradiation with electron beam, inherently enabling excitation with nanoscale resolution.[20−22] Detection of SP can be realized on both optical and electrical domains. Optical nanoimaging is commonly performed using scanning near-field optical microscope (SNOM), where the probe is used for direct collection of the field in aperture mode[23] or used as a scatterer in scattering SNOM (s-SNOM).[24] Optical detection is also enabled by coupling the plasmons to radiating photons and using diffraction limited optics,[25] as the combination of electrical excitation with far field optical detection is demonstrated *via* cathodoluminescence (CL).[20,26−28] Indirect electrical detection of SPPs at the far field was reported using electron energy loss spectroscopy (EELS),[29−31] with time-resolved measurements demonstrated using laser excited photo cathodes in electric microscopy.[32,33] As CL and EELS use an electron beam of a scanning electron microscope (SEM) for plasmons excitation, both require large dwell times[34−36] and major modifications for optical imaging. In addition to standard SEM, CL requires parabolic mirror and CL spectrograph, as EELS mostly involves transmission electron microscopy (TEM), electron spectrometer, and a monochromator.[37−39] Recently reported approaches for direct-electron-based plasmon nanoimaging include Kelvin probe force microscopy (KPFM)[4,40−42] and photoemission electron microscopy (PEEM).[43−46] Both methods require optical illumination, where KPFM maps the surface work function and PEEM images the emitted electrons. In SEM, a tightly focused electron beam with energies typically up to 50 keV hits the specimen to excite various signals, which mainly include secondary electrons emission (SEE), high-energy backscattered electrons, and characteristic X-rays. Secondary electron-based SEM, the basis for our experimental measurements, is essential in a huge variety of applications including

Received: January 24, 2017
Accepted: March 6, 2017
Published: March 6, 2017

DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281

high-resolution surface potential imaging,[47] stem cell studies,[48] biomedical imaging,[49−51] and topography examination of nanostructures.[4,25,40] In this work, we experimentally demonstrate direct excitation and nanoimaging of optical signals, entirely based on unmodified SEM. As illustrated in Figure 1,

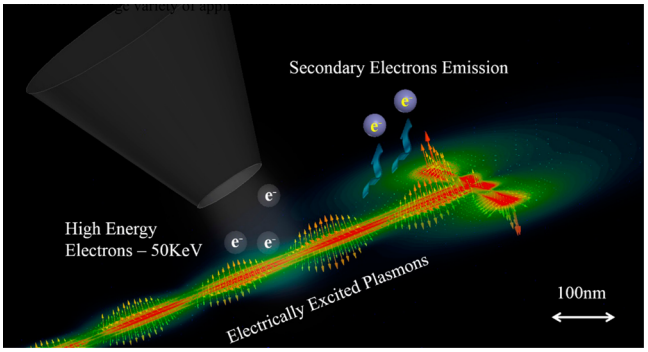


Figure 1. Illustration of electron-based plasmon generation and imaging in SEM. A high-energy electron beam illuminates the device, a nanoantenna coupled with channel waveguide. Optical plasmons are excited and decay to generate the emitted secondary electrons.

we use an electron beam as a nanoscale source of electromagnetic radiation and base our optical mapping on the emitted secondary electrons. We ascertain that the resulted near-field images are dependent on the sample conditions and discuss appropriate fabrication considerations. Our approach provides rapid intensity maps (1 μS/pixel) of optical near fields, with decreased sensitivity to nanofabrication inaccuracies due to the broad spectral nature of the electron beam. We image SPPs in channel plasmon waveguides with a slot width varying between 20 nm and 60 nm, in addition to localized plasmons excited at a variety of dipole nanoantennas and optical surface waves on dielectric substrates. Broadband SPP mode properties and antenna emission patterns are imaged with deep subwavelength resolution. Our experimental results are in excellent agreement with electromagnetic calculations, based on a 3D numerical solution of Maxwell's equations. Furthermore, we present an analytic description for the excitation of SPPs by swift electrons and provide a semi-empirical estimation for the plasmon contribution to the SEE. The theoretical origin of this work lies in the fact that the passage of a fast electron can excite localized plasmons in metallic nanoparticles as well as SPPs on planar metallic surfaces or in metal nanowires.[52−54] These plasmons can partially decay *via* inelastic channels that involve electronic excitations, including $e-h$ pair creation and SEE.[54−57]

The electromagnetic field of a point charge moving in vacuum can be regarded as an evanescent source of radiation that permits exploring regions of momentum−energy space that lie outside the light cone. For swift electrons with a constant velocity, ϑ, and a momentum k that interact with a thin specimen, the frequency domain electron charge density becomes $-2\pi\delta(\omega - k \times v)$, where $\omega = 2\pi f$ is the angular frequency. This approximation is well suited for our experimental conditions, which include 25 nm-thick metallic devices bombarded by 50 keV electron beam. Hence, we can obtain the electromagnetic fields produced by a swiftly charged particle moving inside a homogeneous medium by a direct solution of Maxwell's equations in the frequency−momentum space. Specifically, the electric field as a function of distance R from the beam takes the form of[54] (for detailed derivation, see Supporting Information)

$$\mathbf{E}_j^{\text{bulk}}(\mathbf{r}, \omega) = \frac{2e\omega}{v^2\varepsilon\gamma} e^{i\omega z/v}\left[\frac{i}{\gamma_e}K_0(u)\hat{z} - K_1(u)\hat{\rho}\right] \quad (1)$$

where $\gamma_e = (1 - \vartheta^2/c^2)^{-0.5}$ is the Lorentz contraction factor, ω is the angular frequency, $r = (\rho, z)$ and $u = \omega R/\vartheta\gamma_e$. The modified Bessel functions K_m describe an exponential decay of the field intensity with R for $\omega R/\vartheta\gamma_e > 0.2$.[54] Hence, we see that the moving electron acts as a broadband source of electromagnetic radiation, with the frequency components of the field moving with velocity ϑ along the electron trajectory. Using boundary conditions for the electromagnetic fields at the interfaces, we obtain the SPP excitation probability for incident electron beam with energies of 50 keV and 100 keV,[52,54] shown in Figure 2a (Figure 2a implements eq 19 in the Supporting Information).

In metals, secondary electronic excitations establish a dominant decay channel for localized and propagating plasmons, capable of producing electrons above the vacuum level that contribute to the detected SEE.[54−56] Both ion[58−60] and electron beam[55−57] induced plasmon assisted secondary electron emissions from metals were extensively investigated. Detailed analytical formulation of plasmon decay role in

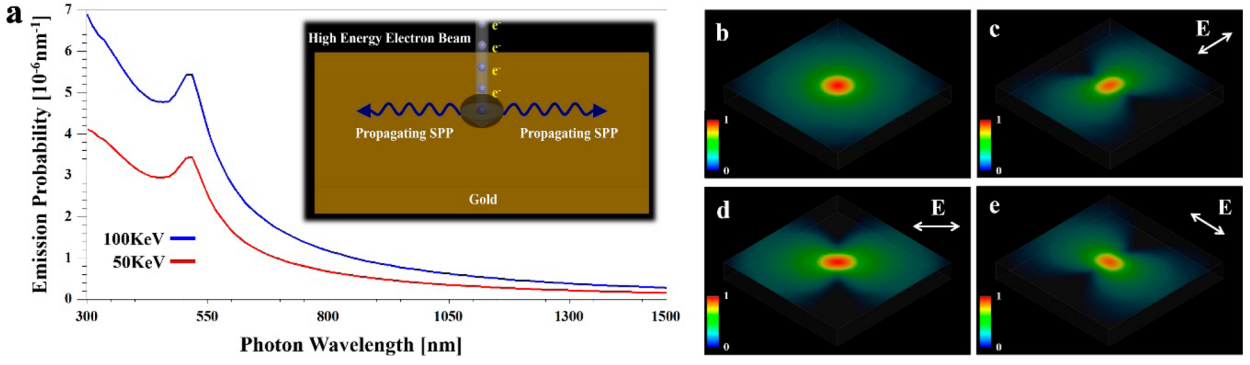


Figure 2. Plasmon excitation *via* electron beam-theoretical analysis. (a) Generation rate of SPP as a function of wavelength per incoming electron. The rates are calculated for 50 keV (red) and 100 keV (blue) electrons incident on a gold surface. Inset: the analyzed geometry (b). Numerical calculation of an optically modeled electron beam (50 keV, 1 nm radius), illuminating the geometry described in (a), showing the electric-field magnitude |E| on the surface (c). Numerically calculated |E| for a linearly polarized broad optical source at 45° polarization angle (d). Excitation with horizontal polarization (e). Excitation with linear polarization with −45° polarization angle.

DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281

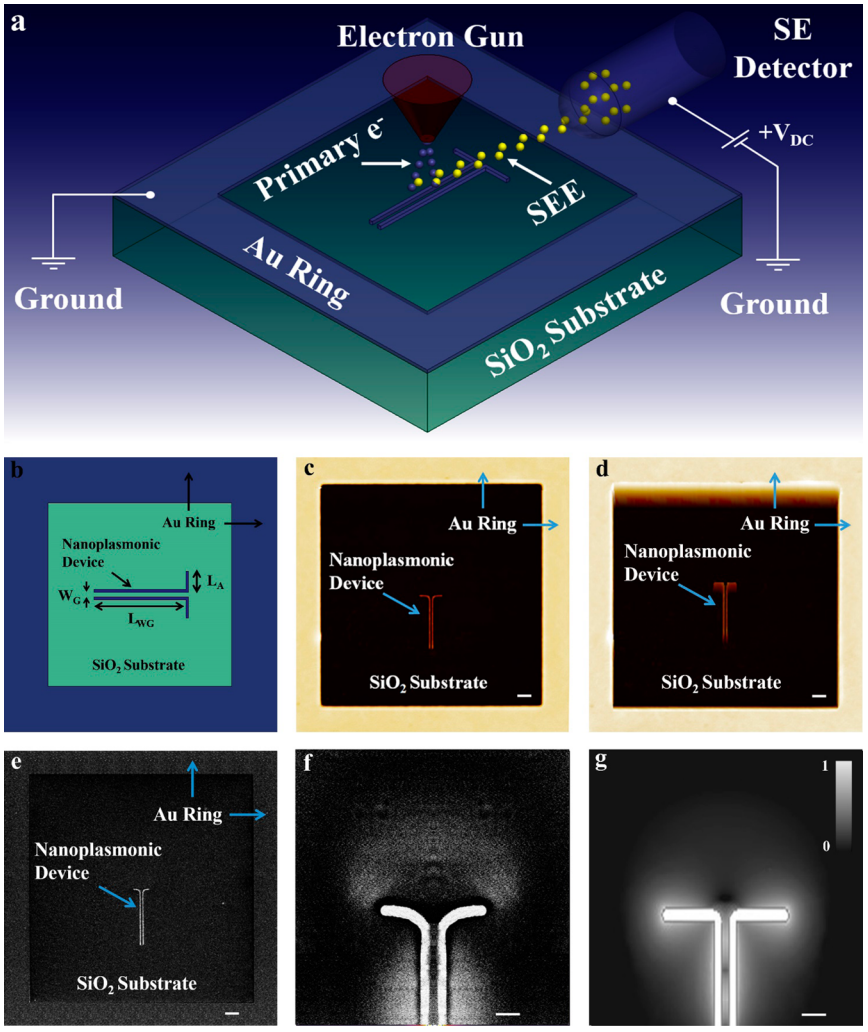


Figure 3. Electrical excitation and imaging of optical nanoplasmons. (a) Schematic illustration of our experimental setup. (b) Description of the analyzed nanoplasmonic devices. Dipole nanoantenna with an arm length 'L_A' and gap 'W_G', connected to a channel waveguide of length L_{WG}. The devices are made of Au on a SiO_2 substrate and surrounded by a Au square ring, which controlled the SE emission rate toward the detector. (c) 2D high-resolution AFM topography map of the analyzed device. (d) 3D high-resolution AFM topography map of the device. (e) SEM topography mapping of an identical device obtained with low beam energy (5 keV) and current (25 pA). (f) SEM (SEE) response of the device under excitation *via* high energy, focused electron beam (50keV, 1 nm). (g) 3D numerical simulation showing the electric-field magnitude |E| of the device, when excited by a 50 keV, 1 nm electron beam. Scale bar: 100 nm.

secondary electron emission in the nearly free-electron metals was reported,[55] showing a strong dependency on the incident beam angle and electron velocity. In this work, we use a normal incident angle, with incident electron velocity corresponding to an accelerating voltage (V) of 5− 50 keV ($\theta = 90°$; $\vartheta_0 = (2\ eV/m)^{0.5}$, see ref 54). The metals in use are described by their in plane complex dielectric function ($\varepsilon_{\parallel} \equiv \varepsilon_r + i\varepsilon_i$) using the Drude model, which gives good agreement for Au within the 300−1200 nm wavelength range.[61] Since $\omega \gg \Gamma \sim 1 \times 10^{13}$ ($\Gamma = 1/\tau$ is the damping rate constant), the in plane relative permittivity can be written as $\varepsilon_{\parallel} = \varepsilon_B - \omega_p^2/\omega^2 + i\omega_p^3/\omega^2\tau$, where ε_B is the contribution of bound electrons and ω_p is the plasma frequency.[40] The numerical calculations are performed using the finite element method (FEM) solution of Maxwell's equations (HFSS V15).[4,15,40] The electron beam was modeled (using eq 1) as a broadband source of electromagnetic radiation ranging from 300−1000 THz in frequency steps of 20 THz. The unpolarized[54] nature of the electron beam was modeled by incoherently summing the results from two separated calculations performed with orthogonal, linearly polarized sources using $|E|^2 = 0.5|\vec{E}_s|^2 + 0.5|\vec{E}_p|^2$. The quantity $|E|^2$ is the time averaged electric field intensity of the unpolarized beam source, $\vec{E}_s$ and $\vec{E}_p$ are the horizontally and vertically polarized sources, respectively (for a detailed derivation, see Supporting Information). Figure 2b−e presents simulation results of the electric field generated from an optically modeled high-energy (50 keV) electron beam impinging on Au−air interface, showing the frequency-aggregated electric-field magnitude, $|\mathbf{E}| = 1/N\sum_{\omega_1}^{\omega_N}|\mathbf{E}(\omega_i)|$. To enable excitation of SPPs, we created a subwavelength circular aperture of 50 nm radius at the center of the Au sample.[1] Figure 2b shows |E| for an electron beam excitation, with polarization-dependent results shown for different states in Figure 2c−e. As expected, a localized hot spot appears at the circular interface, followed by SPP propagation with respect to the electric-field polarization. The experimental setup used in this work is schematically illustrated in Figure 3a. Our image formation process is identical to the broadly used SEM for topography mapping.[62−66] To form the image, high-energy electrons are focused into a fine beam,

DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281

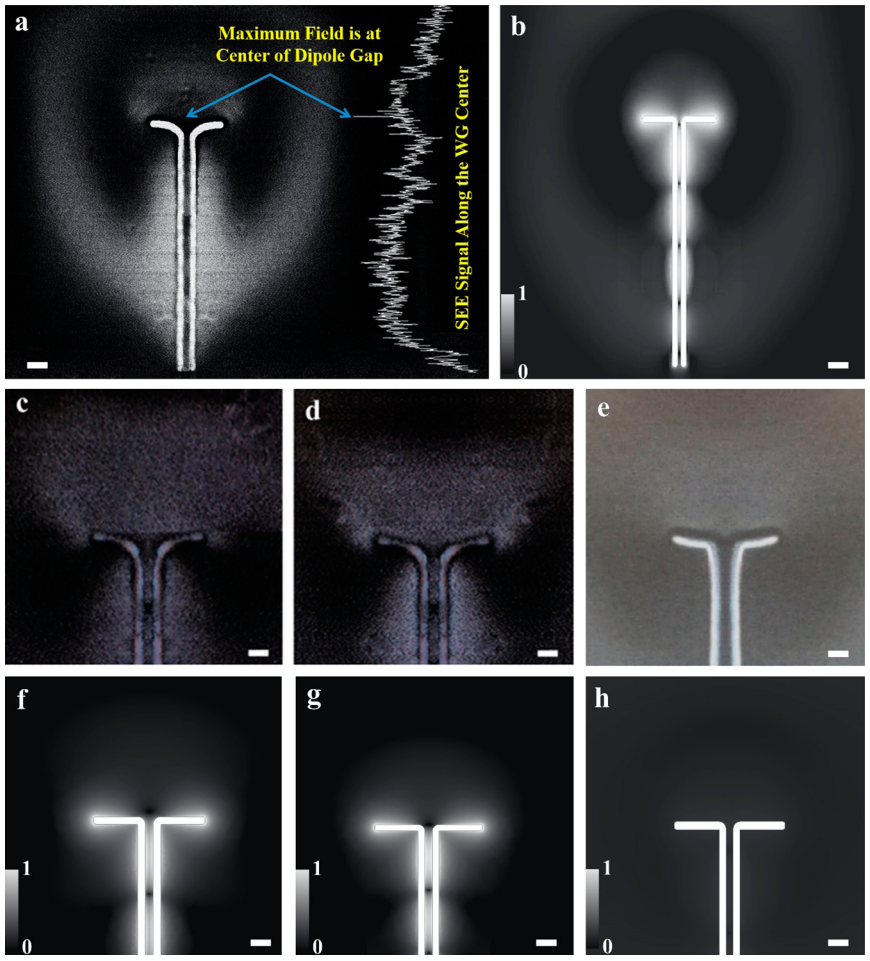


Figure 4. Optical near-field nanoimaging base on SEE. (a) SE imaging of the device, excited by a high impact-focused (50keV, 1 nm) electron beam. The field along the yellow line is shown in decibels (dB) at the right. (b) 3D numerical simulation showing the electric-field magnitude |E| of the device in (a). (c) SEE map of a device designed for resonance at 530 nm, under excitation *via* electron beam (50keV, 1 nm). (d) SEE map of a device designed for off-resonance behavior, under excitation *via* electron beam (50keV, 1 nm). (e) SEE map of the device in (d) excitation *via* 10keV electron beam. (f–h) Numerically calculated |E| of the device in (c–e), respectively. Scale bar: 100 nm.

which is scanned across the surface of the specimen. For each illuminated pixel, a positively biased-synchronized detector collects the excited SE and produces the image by mapping the operation that transmits information from the specimen space to the display space with controlled time averaging. We show that the SE fields can have the shape and dispersion properties of both plasmons and surface photons. We investigate hybrid devices of dipole nanoantennas integrated with channel plasmonic waveguides as shown in Figure 3b.

In addition to their importance for a large variety of applications,[4,15,40] analyzing these devices enables the mapping of both localized and propagating plasmons. The structures where fabricated on a SOI substrate by electron beam lithography (EBL), ion beam sputtering (Cr, 3 nm Au, 22 nm), and lift off. To minimize the effects of conventional charging on the field patterns, we chose the well-known approach of designing an intrinsically high-conductivity sample.[67−69] Hence, the devices were fabricated inside square apertures with dimensions of 6 μm × 6 μm; keeping over 99.9% of the sample surface as grounded Au (see Figure 1 and Supporting Information). The 6 μm × 6 μm aperture dimensions were chosen empirically to provide the highest quality images. To verify the fabrication process, we investigated the samples using high-resolution atomic force microscopy (AFM) with a tip diameter of 5 nm. Figure 3c,d, respectively, presents 2D and 3D topography images of the fabricated device, with geometrical dimensions of L_{WG} = 1500 nm, L_A = 200 nm, and W_G = 25 nm. The AFM study confirms the success of our fabrication process, showing clean waveguide channels and almost no residual particles in the regions of interest. The metallic square frame surrounding the device is also captured. Figure 3e shows topography mapping of the analyzed device, obtained using SEM at low (5keV) beam energy. The topography resembles the 2D AFM image, with no additional signals observed along the sample besides those that correspond to the actual device structure. However, when the beam energy is increased above a few tens of keV, optical plasmons are excited at the metal−dielectric interfaces along the device. These plasmons partially decay and transfer their energy to produce SE.[54−56] Figure 3f shows the nanoplasmonic device under excitation with a high-energy (50keV) electron beam, focused to 1 nm radius. Alongside the device topography, we observe enhanced fields at the metal−dielectric interfaces, which arise from plasmon excitation along the device. Additionally, the well-known dipolar optical-field pattern emitted from the nanoantenna[4,40] is clearly captured in the SE image. The experimental results are strongly supported by numerical calculations. The calculated electric-field magnitude, |

DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281

|E|, which is proportional to the SE excitation efficiency,[55−58] is shown in Figure 3g. Similar to the SE map, dipolar emission pattern from the nanoantenna as well as plasmonic enhancement at the metallic interfaces are well observed. Figure 4 shows quantitative analysis of the plasmonic devices with nanoscale resolution and broad frequency range. Figure 4a presents a 2D SE field map of the analyzed structure, where the field along the waveguide center is shown at the right-hand side of the device in logarithmic scale. The SE field along the waveguide center shows a standing wave pattern with the maximum field intensity located exactly at the nanoantenna gap, represented by a strong peak in the SE signal as expected for similar devices.[4,40,41] The field outside the device shows a different behavior, where the dipolar shaped emission is coupled to the surface and forms a standing wave pattern, exponentially decaying as a function of the distance from the metallic structure. The corresponding optical calculation of the electron image is shown in Figure 4b. The experiments and theoretical calculations are of high correlation, providing direct evidence to the coupling of both surface photons and free electrons from the nanoantenna to the sample surface, with directive propagation governed by the emission pattern. We note that a few of the oscillatory fields observed in Figure 4a do not appear in Figure 4b, mainly due to the non-continuous nature of the FEM calculations, where each frequency component excites the oscillatory mode.[40] Improved calculation results will be obtained by using time domain methods (FDTD) or increasing the frequency-sampling rate. Figure 4c shows the SEE field map for a device designed for resonance at the wavelength that maximizes plasmon excitation probability (Figure 2a), with corresponding dimensions of L_A = 180 nm, W_G = 25 nm. The SEE map for an off-resonance device (L_A = 210 nm, W_G = 30 nm) is shown in Figure 4d. The corresponding calculated |E| is presented in Figure 4f,g, respectively. The resonance device shows a 4 dB stronger field enhancement at the nanoantenna gap, and its emitted field extends significantly more into the substrate compared with the off-resonance device. The plasmons are coupled to optical surface waves also from the exterior waveguide interfaces, as observed in both experimental and calculation results. To provide additional evidence for the proficiency of the proposed method, we recorded SEE maps of the device excited with lower beam energy. Figure 4e shows the SEE analysis of the device in Figure 4d, captured with a beam energy of 10keV, with the corresponding calculation results shown in Figure 4h. As expected, the plasmon generation is significantly less pronounced compared to the case of excitation with the 50 keV beam, supported by both theory and experiments. To quantify the plasmon contribution to the SE signal, we characterize similar devices fabricated from SiO_2, a dielectric material that does not support plasmon excitation. Figure 5a shows an SE image of the SiO_2 device captured under identical conditions to the described experiments above, with the corresponding calculated |E| shown in Figure 5b. As expected, enhanced SE is observed only from the device topography with no additional SE signals detected; unlike the case of the plasmonic (Au) device. This shows that the enhanced SEE outside the device topography is mainly material related, which results in excited optical plasmons. For each pixel, the quotient of SE signals from the plasmonic (Figure 4c) and dielectric (Figure 5a) devices is the plasmon contribution to the SEE. For our images, the described ratio varies between 1.5 dB and 23 dB (for a dwell time of 1 μS per pixel). This means that the plasmon contribution enhances the SE emission by a factor varying from 1.4 to 200. Figure 5c shows a SE map of the plasmonic device, where the field along the dipole axis (yellow line) is presented. Note that the measured signal level at the right interface is slightly higher compared to the left interface, attributed to nanofabrication inaccuracy. The field contributions from the left (LI) and right (RI) dipole interfaces are clearly resolved, demonstrating spatial resolution in the region of 25 nm. We suggest several effects originated in the SE detector, which may possibly contribute to the minor differences between the experimental and theoretical SE images. The SE detector is located at a distance of ∼54 mm from the analyzed specimen with a relative angle of 21° (see also Figure S6); this relative position may create a shift in both delay and spatial distribution of the SE hitting the detector in comparison to their real values. In addition, finite signal-to-noise ratio and dynamic range of the detector (measured to be approximately 15 and 30 dB, respectively) may add to the slight smearing of the waves observed in the experimental SEE maps and does not appear in the numerically calculated images.

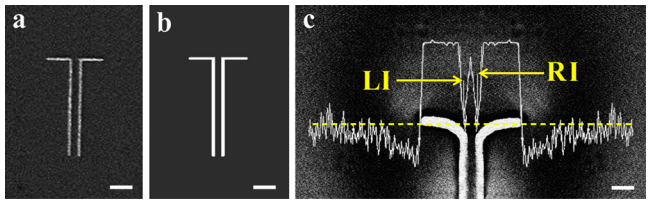


Figure 5. Control experiment and demonstration of the SEE spatial resolution. (a) SEE analysis of a similar device as in Figure 4a fabricated from SiO_2. (b) 3D numerical simulation showing the electric-field magnitude |E| of the device in (a). (c) SEE analysis of the plasmonic device excited by a 50 keV electron beam. The field along the dashed yellow line is presented, showing the capability of the SEM to resolve the field contribution of the left (LI) and the right (RI) waveguide interfaces, separated by 25 nm. Scale bars: (a, b) 100 nm; (c) 50 nm.

CONCLUSIONS

In summary, we introduce an approach for optical excitation and nanoimaging based on unmodified secondary electron microscopy. The proposed method facilitates ultrafast, simultaneous mapping of optical near fields and device topography, with both displayed in a single image. Based on secondary electrons as the fundamental imaging particle, our proposed method enables high spatial resolution; potentially outperforms the 25 nm resolution experimentally demonstrated in this work. Our experimental results are confirmed by rigorous numerical calculations, showing good agreement between secondary electron field maps and optical near fields, and offer rare insights into the tight relations between electrons photons and plasmons. Our findings provide the path for fundamental and applicative horizons of electron beam plasmonics, such as ultrafast broadband nanoimaging, molecular energy transfer, and optically inspired secondary electron cloaking.

METHODS

Devices Fabrication. The SOI sample was spin-coated with poly(methyl methacrylate) (PMMA 950 A2) by electron-beam resist, providing a thickness of 100 nm. The samples coated with PMMA were subsequently baked for 120 s on a hot plate at 180C. The desired pattern was exposed in the PMMA layer using a CRESTEC CABLE-

DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281

9000C high-resolution electron-beam lithography system using different doses to control line and gap widths. Then the samples were developed for 90 s using "methyl isobutyl ketone" (MIBK) and rinsed with IPA. The samples were subsequently exposed to Ar plasma to etch 10 nm in order to remove leftovers from the pattern, sputtered using BESTEC 2″ DC magnetron to deposit 3 nm Cr and 22 nm Au, and then immersed in 180 kHz ultrasonic bath with NMP for 3 h for resist liftoff.

SEM Characterization. Both topography and functional measurements were carried out simultaneously using a CRESTEC CABLE-9000C high-resolution electron-beam lithography system with integrated SEM, with vacuum levels of ∼10−5. The samples surface (Au) was grounded to zero DC potential, as it was vector scanned (x,y) using a high-energy (50 keV) electron beam, focused to 1 nm radius with controllable beam currents varied between 5 pA and 250 pA. We used nominal scan rates of 50−200 mS/frame for analog and digital scans. The emitted secondary electrons were collected *via* SE detector, biased to 10 kV. In our experiments, the horizontal (x) axis is defined as the "fast axis", with the vertical (y) is the slow axis. To reduce noise and increase the image resolution, we used a pixel averaging of 4 points per pixel as well as frame averaging of four frames per image. Combined pixel and frame averaging reduces the effects of high and low spatial frequency noises, respectively. All of the SEM images, micrograph, intensities, and counts in this work are presented in logarithmic scale.

AFM Measurements. All measurements were performed at room temperature and free ambient conditions (no vacuum), using a Dimension Icon AFM system with NanoScope V controller (Bruker). We used NanoWorld probes SSS-NCH, SuperSharpSilicon - Non-contact/Tapping mode - high resonance frequency, with a typical diameter of 2 nm, resonance frequency of 320 kHz, and spring constant of 42 N/m.

Numerical Simulations. The numerical results are obtained by using the software package ANSYS HFSS V15, the industry standard simulation tool for 3D full-wave electromagnetic-field simulation. HFSS solves Maxwell's equations *via* the finite element method (FEM) using an adaptive mesh refinement process for tailored accuracy requirements. The field's solutions are calculated with the metallic (Au) plasmonic structures being deposited on a homogeneous SiO_2 substrate. The sample is illuminated by optical source at spectral range of 300−1000 THz, which is modeled as a focused beam with 1 nm characteristic radius. The electric field is of controlled polarization as the wave vector K is normal to the surface. A selectively dense meshing is assigned in the metallic and waveguiding regions, with a maximum cell size of 1 nm and 750,000 FEM tetrahedral cells. To provide maximum accuracy, the model is terminated as follows: The interface with free space is bounded by a broad band perfectly matched layer (PML) absorbing boundary conditions (ABC), while the metallic and SiO_2 terminations are done *via* layered impedance (LI) ABC. The minimum number of adaptive meshing iterations was set to 12, with a convergence condition of 1% maximum energy variance between adjacent iterations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b00548.

Detailed derivation of the analytical formulation of an electron beam radiation source and its associated electromagnetic fields; sample design for minimization of charging effects; and additional experiments conducted with scanning axis rotation (PDF)

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Author Contributions

M.C. initiated and designed the studies, carried out the theoretical design and analysis, performed the experiments, and wrote the manuscript. Y.A. fabricated the devices and performed the experiments. R.S. contributed the computational facility. Z.Z. reviewed the manuscript and participated in the results analysis.

Funding

The authors declare that no funding was provided for any of the authors for this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

M.C acknowledges Prof. Javier Garcia De Abajo for the great discussions, enhancing the authors understanding and knowledge in this fascinating field.

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DOI: 10.1021/acsnano.7b00548
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DOI: 10.1021/acsnano.7b00548
ACS Nano 2017, 11, 3274−3281