SUPPORTING INFORMATION -

ELECTRICALLY EXCITED PLASMONIC NANORULER FOR BIOMOLECULE DETECTION

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Supp. Note 1 Fowler-Nordheim Tunneling



Figure S1: nMOS energy band scheme shown in (I) depicts the accumulation state, if gate voltage Vg >0 V is applied. The resulting potential inside the stack yields in bending of the oxide potential and semiconductor bands which affect the tunneling mechanisms, depending on the work function of the materials and the oxide thickness. Calculated Fowler-Nordheim characteristics which are extended for direct tunneling effects are depicted in (II) for different oxide thickness. The associated quantum shot noise drives towards fluctuations that cover the visible regime as shown in (III).

The tunneling characteristics can be modeled similar to the approach in Watanabe et al.¹ By calculating the dependency of the energy band scheme (as in Fig. S1(I)) on the applied gate voltage Vg, it is possible to obtain the device characteristics regarding the tunneling process. All parameters (Eq. 1-4) are obtained by standard calculations in MOS semiconductor physics^{2,3}. Essentially, Eq. 1 describes the change of the electric fields and potential distribution inside the junction as function of the gate voltage.

$$V_{g} = V_{FB} + \varphi_{S} + \frac{\iota_{ox} \varepsilon_{Si}}{\varepsilon_{ox}} E_{ox}(\varphi_{s})$$
(1)

 V_g ...gate voltage (bias), V_{FB} ...flatband voltage, φ_s ...surface potential, t_{ox} ...oxide thickness, ε_{ox} ...oxide dielectric constant, ε_{Si} ...semiconductor dielectric constant, E_{ox} ...electric field in the oxide

Since the tunneling process is dominated by the properties of the oxide, the electric field inside the oxide has to be calculated as given in the following equation (material constants used in this work are listed in table 1):

$$E_{ox}(\varphi_{s}) = \pm \sqrt{\frac{2kTN_{D}}{\varepsilon_{Si}\varepsilon_{0}e}} \left\{ \exp\left(\frac{e\varphi_{s}}{kT}\right) - \frac{e\varphi_{s}}{kT} - 1 + \frac{n_{i}^{2}}{N_{D}^{2}} \left[\exp\left(-\frac{e\varphi_{s}}{kT}\right) + \frac{e\varphi_{s}}{kT} - 1 \right] \right\}^{1/2}$$
(2)

k ...Boltzmann constant, T ...temperature, N_D ...semiconductor doping, n_i ...intrinsic carrier concentration

With the obtained fields and potentials two tunneling mechanisms which are dominating the conduction mechanisms for thin film oxides at ambient conditions (Fowler-Nordheim tunneling (Eq. 3) and direct tunneling (Eq. 4)) were determined as comparison with the electrical experiments (see Fig. S1(II)).

$$I_{FN} = \frac{Ae^2}{8\pi\Phi_B} \frac{m_{si}^*}{m_{ox}^*} |E_{ox}|^2 \cdot \exp\left[-\frac{4\sqrt{2m_{ox}^*}}{3\hbar eE_{ox}} (e\Phi_B)^{3/2}\right]$$
(3)
$$I_{DT} = \frac{Ae^2}{8\pi\hbar\Phi_B} \frac{m_{si}^*}{m_{ox}^*} |E_{ox}|^2 \left[1 - \left(1 - \frac{E_{ox}t_{ox}}{\Phi_B}\right)^{1/2}\right]^{-2}$$

$$\cdot \exp\left\{-\frac{4\sqrt{2m_{ox}^{*}}}{3\hbar eE_{ox}}\left[(e\Phi_{B})^{3/2} - e(\Phi_{B} - E_{ox}t_{ox})^{3/2}\right]\right\}$$
(4)

 I_{FN} ...Fowler-Nordheim Tunneling, I_{DT} ...direct tunneling, A ...junction area, m_{Si}^* ...effective mass in silicon, m_{ox}^* ...effective mass in the oxide, Φ_B ...tunneling barrier height

For FEM simulations regarding the LETJ emission, the derivations of Uehara et al.⁴ were followed. As shown in **Fig. S1(III**), the power spectrum of the approximated oscillating dipole inside of the oxide layer can cover frequencies up to the visible regime. The resulting function of the power spectrum $|I(\omega)|^2$ (**Eq. 5**) is dependent on the LETJ structures material parameters

$$|I(\omega)|^{2} = \frac{Ae^{3}}{h^{2}\Phi_{B}} \frac{m_{si}^{*}}{m_{ox}^{*}} |E_{ox}|^{2} \left\{ \left(\frac{\hbar\omega}{e\Phi_{B}} + 1\right)^{1/2} - 1 \right\}^{-2}$$

$$\cdot \exp\left[-\frac{2\sqrt{2m_{ox}^{*}}(e\Phi_{B})^{3/2}}{3\hbar e|E_{ox}|} \left\{ \left(\frac{\hbar\omega}{e\Phi_{B}} + 1\right)^{3/2} + 1 \right\} \right]$$
(5)

 $|I(\omega)|^2 =$ power spectrum, ω ...angular frequency,

parameter	value	parameter	value
Φ _{Au}	5 [eV]	n _i	$1.45 \cdot 10^{10} [\text{cm}^{-3}]$
χ _{si}	4.05 [eV]	N _D	$2 \cdot 10^{19} [\text{cm}^{-3}]$
Α	$4 \cdot 10^{-2} [\text{cm}^2]$	Т	300 [K]
m [*] _{ox}	0.33 · m ₀ [kg]	ε _{ox}	9.6
m _{si} *	0.19 · m ₀ [kg]	ε _{Si}	11.9

Table S1: material parameters used in the calculations of tunneling mechanisms and power spectra



Figure S2: Plane wave excitation of gap modes at an incident angle of 60° . The spectra are shown for different separations of the substrate and nanoparticle [1, 3, 5, 10, 20] nm with their corresponding peak shift. The resulting peak position as function of the separation is in agreement with results that were obtained in the main article and validate the similarity of external and electrical excitation. To evaluate the influence of the refractive index of the organic layer, calculations were done without a shell around the particle (n_{sur} = 1.0) and a shell with high refractive index (n_{sur} = 1.5). As visible, an offset is occurring due to the increased refractive index of the surrounding shell n_{sur} , whereas the overall separation dependency is not influenced. The competing nature of the resonance shift induced by changes in the refractive index and the shift induced by changing the nanoparticle-substrate separation has to be considered for the evaluation of the detection scheme. In the case of a plasmonic nanoruler for biomolecule detection the separation is changing in the few nanometer range where the assumption of a gap-mode dominated resonance shift is fullfilled.

Supp. Note 3 Optimization of device parameters



Figure S3: Schematic of different parameters of the LETJ structures, which were prepared and tested for their performance. Placement of the LETJ junctions on the chip with eight independent junctions on one Si –chip.

Supp. Note 4 Influence of electrode material on the direct emission

The direct emission from the LETJ is altered by implementation of different electrode materials (Fig. S4). The altered emissions origin in the different work functions and dielectric functions of the metals. Specifically, the work function changes the initial conditions of the tunneling barrier, whereas the difference in the dielectric functions, alter the boundary conditions for coupling of SPP.



Figure S4: Spectra of the measured directly emitted light from LETJ structures with electrodes made of different material.





Figure S5: Dependency of the cutoff wavelength of the emitted light from LETJ chips on the applied voltage across the junction. (a) Spectra for different voltages (b) graph of the edge of the spectral emission as a function of the voltage. The cutoff was determined to be the wavelength, where the emitted intensity is larger than 5-times the noise standard deviation.

Supp. Note 6 Nanoparticle Distribution on top electrode of LETJ structure

The distribution of nanoparticles on the top electrode was analyzed by atomic force miscopy and dark-field microscopy. Nanoparticles were mainly adsorbed on the surface as single nanoparticles but also in the form of aggregates, which is represented by the AFM image in Fig. S6. The adsorbed nanoparticles had an average density of $7 \cdot 10^5$ particles/mm², which was estimated from the dark field images. The AFM images also shows that the NP induce strong inhomogeneity (height ~ 80 nm) on relatively flat substrate with average roughness RMS = 1.9 nm (obtained by AFM).



Figure S6: AFM image of the intrinsic roughness of the sample surface and after nanoparticle adsorption showing a sectional height profile of the nanoparticles. Dark-field image of larger scale to show the distribution of adsorbed nanoparticles.

Supp. Note 7 Relative LETJ spectra modification by metal nanoparticle

To identify the origin of LETJ enhancement, a new parameter is introduced, i.e. relative enhancement $\Delta I(w)$. It is obtained by the following equation, with the direct emission $I_D(w)$ and the nanoparticle enhanced emission $I_{NP}(w)$:

$$\Delta I(w) = \frac{I_{NP}(w)}{I_D(w)} / \left| \frac{I_{NP}(w)}{I_D(w)} \right| - 1$$
(6)

As visible, the resonance positions for electrical and optical excitation are in good agreement.



Figure S7: Graphs of the relative enhancement for the graphs in Figure 3(I) and Figure 3(II) in comparison to the resonance that is present for external illumination.

Supp. Note 8 Signal Stability and Peak Fitting

Prior to all measurements with nanoparticles, the spectra of bare LEIT junctions were recorded and served as reference to ensure their equality in emission characteristics. Tunneling current was set to 20 mA and the voltage was logged every second. The spectral integration time was set to 300 s to ensure long-term stability of the samples and optimize the signal-to-noise ratio of the recorded spectra. Deviations of the background spectral emission by noise and instability were found to be < 5 % of the total emission intensity. Thus, structural equality of the different LETJ junctions was assumed.



Figure S8: (I) Averaged spectral emission of an LEIT junction with 7 nm oxide thickness at 20 mA current. The deviation of 10 different measurements with integration time of 300 s is plotted as gray area. Summed up, the deviation is less than 5 % of the total emission. (II) Experimental data points of the gap mode peak shift induced by BSA and BSA/IgG coating of the nanoparticles. The curves are fitted polynomials for the quantitative determination of the observed shift.

The used method for determination of the peak positions in the spectra was implemented according to Dahlin et al.⁵ The functions were fitted by a polynomial function of 10th order and the systematic noise of the detector was subtracted. Subsequently, the spectral data cropped at 70 % of the peaks maximum to minimize peak fitting errors due to arbitrary features and outliers in the signal. This fitted signal was then analyzed as center of gravity by weighted, trapezoidal integration over the given spectral interval.

References

- (1) Watanabe, J.; Uehara, Y.; Murota, J.; Ushioda, S. Jpn J Appl Phys Part 1 Regul Pap Short Notes Rev Pap1993, 32 (1A), 99.
- (2) Sze, S. M.; Ng, K. K. Physics of semiconductor devices; John Wiley & Sons, 2006.
- (3) Hehenberger, P. Advanced Characterization of the Bias Temperature Instability, Technische Universität Wien, 2011.
- (4) Uehara, Y.; Watanabe, J.; Fujikawa, S.; Ushioda, S. Phys Rev B1995, 51 (4), 2229.
- (5) Dahlin, A. B.; Tegenfeldt, J. O.; Höök, F. Anal. Chem.2006, 78 (13), 4416.