Squeezing Millimeter Waves through a Single, Nanometer-wide, Centimeter-long Slit

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We demonstrate broadband non-resonant squeezing of terahertz (THz) waves through an isolated 2-nm-wide, 2-cm-long slit (aspect ratio of $10^7$), representing a maximum intensity enhancement factor of one million. Unlike resonant nanogap structures, a single, effectively infinitely-long slit passes incident electromagnetic waves with no cutoff, enhances the electric field within the gap with a broad $1/f$ spectral response, and eliminates interference effects due to finite sample boundaries and adjacent elements. To construct such a uniform, isolated slit that is much longer than the millimeter-scale spot of a THz beam, we use atomic layer lithography to pattern vertical nanogaps in a metal film over an entire 4-inch wafer. We observe an increasing field enhancement as the slit width decreases from 20 nm to 2 nm, in agreement with numerical calculations.

Subwavelength apertures and gaps in metal surfaces can tightly localize electromagnetic waves well below the diffraction limit and lead to strong field enhancements1–4. Light-matter interactions in nanometer-scale gaps also reveal novel phenomena such as nonlocal electromagnetic effects, optical rectification, and inelastic electron tunneling5–12. The prerequisite for fundamental investigation of such phenomena and their practical utilization is reliable, high-throughput fabrication of these gaps, ideally with dimensions down to the single-digit nanometer scale. While electron-beam lithography can be used to pattern nanometer-scale point junctions in thin metal films13, it is not practical to extend a point junction into a long and uniform slit through optically thick metal films and to create a dense array of such slits at the wafer scale. Other approaches based on colloidal nanoparticle junctions14–16 or film-coupled nanoparticles17,18 allow the formation of sub-nanometer-scale gaps, but do not allow precise control of their shape and arrangement. Furthermore, to fully take advantage of strong light-matter interactions in the technologically important far-infrared and terahertz (THz) regimes, it is necessary to design and construct these nanogap structures over millimeter or centimeter scales to increase the coupling efficiency of long-wavelength radiation energy into the nanogaps.

Recent experiments by other groups showed a field enhancement factor of 800 at 0.2 THz in 40-nm-wide slits18–20. The ability to construct even thinner nanogaps along arbitrarily large in-plane geometries at the wafer-scale can tremendously improve the signal-to-noise ratio, throughput, and repeatability for these experiments; a necessity for exploring THz field enhancement of the narrowest slits. In addition, it is desirable to investigate the THz transmission process and the resultant giant field enhancements using an isolated single slit. When arrays of slits are illuminated with a millimeter-sized beam for THz spectroscopy, it is often difficult to separate out optical effects inside the gap from effects due to periodicity.

Extending a nanometer-wide gap into a centimeter-long slit in a metal film requires constructing a device with an aspect ratio exceeding $10^7$. To address this challenge, we developed a patterning technology that allows wafer-scale fabrication of vertically-oriented nanogaps, called atomic layer lithography21,22. This technique relies on atomic layer deposition (ALD)23–25 to define the lateral patterning resolution of the nanogaps. Each ALD cycle deposits a 1–2 Å-thick conformal alumina (Al2O3) layer on the vertical sidewalls of patterned metals, enabling Ångstrom-resolution control of nanogap width. The key strength of atomic layer lithography over electron-beam and FIB lithography is that the critical dimension — the gap width — is decoupled from the pattern size and density. One can thus, in principle, extend nanometer-wide gaps along the contour of arbitrarily large patterns. Another key

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strength of the fabrication process is the simplicity with which patterned metals can be planarized using adhesive tape.

Our previous work\(^{22}\) demonstrated that Al\(_2\)O\(_3\)-filled gaps with a lateral width as narrow as 1 nm can be produced in a metal film along the contour of sub-millimeter scale rectangle. Here, we push the limit of our patterning and planarization capabilities by demonstrating nanogaps along 2-centimeter-long contours, proving the robustness and scalability of this technique. The production of a centimeter-long metallic nanogap allows us to perform THz time-domain spectroscopy (TDS) through an isolated sub-wavelength slit (\(\lambda/1,000,000\)) covering only 0.0002% of the cross-sectional area of an incident THz beam (Fig. 1a). In this experiment, the measured THz wave passes exclusively through the single nanometer-wide gap. By examining the transmitted radiation in the far field, we deduce broadband, non-resonant field enhancement inside the nanogap, in agreement with two-dimensional (2D) computational modeling for an infinitely long slit.

**Results**

Using atomic layer lithography (Fig. 1b), we fabricated centimeter-long nanoslits. An array of rectangular patterns (0.8 cm \(\times\) 0.1 cm; center-to-center spacing = 1 cm, as shown in Fig. 1c) in a gold film (150 nm in thickness with a 3-nm Ti adhesion layer) was first made on a 4-inch Pyrex glass wafer using photolithography, metal deposition, and lift-off. ALD, at 250 °C, was then used to conformally deposit a thin layer of alumina (Al\(_2\)O\(_3\)) over the pattern. The alumina film thickness was precisely defined, with Ångstrom-scale resolution, by the number of ALD cycles (measured deposition rate of 1.1 Å per cycle). A second layer of gold (150 nm) was deposited by directional electron-beam evaporation to fill the pattern and form the nanogap between the first and second metal layer.

After depositing the second metal layer, excess metal must be removed to expose the nanogaps. This type of critical step is typically done through a series of complicated planarization techniques; however, the poor adhesion between noble metals and oxides led us to the simple and effective solution of merely peeling off the excess metal with adhesive tape (Fig. 1b). Many groups have utilized peeling or stripping techniques for patterned metal fabrication. For example, the PEEL process\(^{26}\) combines soft lithography and lift-off to produce free-standing metal films, while template stripping\(^{27,28}\) from silicon molds produces ultra-smooth patterned metals. In the case of atomic layer lithography, wafer-scale peeling with adhesive tape (e.g. 3M Scotch\(^{\text{TM}}\) tape) planarizes the vertically oriented nanogap patterns, dramatically simplifying the process flow. Considering that the second metal layer is only 100–200 nm thick and the width of the trench is on the millimeter scale, it would appear that planarization would be difficult. However, as long as we ensure that the tape does not contact the metal inside the trench, by gently applying it without any extra pressure, only the raised portion of the metal layer is removed. We tested structures with various sizes and shapes, and this tape-based planarization process works well for structures with lateral dimensions as large as 1 cm.

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**Figure 1** | Atomic layer lithography of centimeter-scale loop with nanometer-scale gaps. (a), Illustration of a single, non-resonant nanoslit, one side of the centimeter-scale loop, illuminated at normal incidence by a \(p\)-polarized, focused THz beam. (b), Photograph of the tape-stripping process to planarize the nanogap patterns. (c), Photograph taken from the back side of the nanogap loop structure (0.8 cm \(\times\) 1 cm). (d), Top-view scanning electron micrograph (SEM) of a 20 nm-wide gap in a gold film. (inset) Enlarged SEM image of the left image. (e), Cross-sectional tunneling electron micrograph (TEM) of a 2 nm-wide alumina layer between two gold layers.
Transmitted electric field amplitude spectra were obtained by Fourier-transforming time-domain signals, which were then normalized to the reference signal collected for transmission through the glass substrate. We infer near-field enhancement factors by normalizing the transmitted amplitudes by the slit coverage ratio, according to Kirchhoff diffraction theory\textsuperscript{19,32}. This can be done because the minimum slit width of 2 nm is larger than the charge screening length (< 1 nm). Figure 3b shows that the enhancement varies approximately as 1/f, where f is frequency, over the entire measured spectral range. Previous work showed that the field enhancement increases as the slit width decreases down to tens of nanometers, due to capacitive charge accumulation from light-induced currents at the sidewalls\textsuperscript{18–20,33}. Reducing the slit width to 2 nm allowed us to achieve a non-resonant electric field (|E|) enhancement of 1300 at f = 0.3 THz; this corresponds to a maximum intensity (∣E∣²) enhancement of 10⁶, the highest yet obtained in single-slit studies. This enhancement is entirely due to the large ratio between the free-space wavelength of the THz wave and the narrow slit width, and does not rely on any resonant effects. While the enhancement is smaller than that obtained for resonant ring apertures\textsuperscript{22,34}; it is highly broadband without any cut-off or interference effects, and is limited only by the frequency response of the metal.

We also carried out two-dimensional finite-element modeling (FEM) using COMSOL to estimate the electric field enhancement as a function of the gap size, w. (For details of the simulations, see Methods.) In Fig. 4a, the simulated field enhancement factors are in good qualitative agreement with the measured factors, showing capacitance-like 1/w dependence\textsuperscript{18,33}. Figure 4b shows a cross-section of the electric field distribution around a 2-nm-wide slit. The enhanced electric field within the gap is nearly constant along its entire thickness. Strongly confined electric fields with enhancement factors over 1,000 near the entrance and exit corners are also observed.

**Conclusions**

We produced a wafer-scale array of 2-cm-long and 2-nm-wide gaps through optically thick metal films by combining photolithography, ALD, and tape-based planarization. To demonstrate the utility of these extremely high-aspect-ratio (>10⁷) nanostructures, single-slit NIR transmission and THz-TDS were performed. Using these measurements we inferred a non-resonant field enhancement factor of 1300 when a millimeter wave passes through a single 2-nm-wide metal slit. As transmission through the gap and the resulting high field enhancements are non-resonant, they will be effective over a broad range of frequencies. The nanogaps could thus be used to enhance wave-mixing processes that involve extremely different frequencies, such as frequency conversion from the visible or NIR to the THz. Placing molecules and nanoparticles inside the gaps will lead to...
plasmon-enhanced luminescence; the extended slit length will make it possible to gather statistical data from a large number of single quantum emitters simultaneously. For sensing applications, cm-long nanogaps facilitate integration with a large array of microfluidic channels. Furthermore, by scaling up the loop length and packing density, it may be possible to study resonant transmission of micro-waves through nanogaps

### Methods

#### Nanogap fabrication via atomic layer lithography

The nanogap is fabricated using the atomic layer lithography method developed in our previous work. First, an array of 0.8 cm × 0.1 cm rectangular patterns in metal films are fabricated on a Pyrex glass substrate using negative resist (NR71-1500P) and photolithography, followed by metal deposition (150 nm Au with Ti adhesion layer) using electron-beam evaporation and lift-off in a solvent (1165 remover). After cleaning with acetone, methanol, and IPA and blowing dry with N₂ gas, the patterned metal film is conformally coated with a thin Al₂O₃ layer by ALD at 250 °C (Cambridge NanoTech Inc., Savannah™). Trimethylaluminum and H₂O vapor were sequentially pulsing through the ALD chamber and N₂ gas was used to purge the chamber after each injection. The thickness of the Al₂O₃ film is calibrated using ellipsometry on a Si reference wafer placed in the same chamber, and the measured deposition rate for Al₂O₃ is 1.1 Å/cycle. After ALD, the trenches are filled with second metal by directional metal evaporation (Temescal). The metal deposited outside of the trench is easily removed using adhesive tape (single-sided 3M Scotch Magic Tape™) without leaving any residue.

#### Electron microscopy sample preparation

TEM samples are prepared by FIB milling. A thin film of Au/Al₂O₃/Au is cut across a nanogap at one side of the rectangular pattern. The lamella is then picked up by an Omniprobe and was attached to a TEM copper grid. The lamella is further thinned with ion beam milling to less than 100 nm, and is imaged in a TEM (FEG-TEM, FEI Tecna G2 30). For preparation of SEM samples, the top alumina layers on the metal surface are etched using reactive ion etching (RIE) with an inductively coupled plasma (Plasmalab System100 ICP180, Oxford Ltd.), to avoid charging effects. The samples are then imaged in an SEM (FEG-SEM, JEOL 6700).

#### Near-infrared spectroscopy

A broadband fiber-coupled, laser driven light source (Energetiq, EQ-99FC) is used to illuminate single nanogaps through a 600 µm fiber, reflective collimator, polarizer, and condenser on top of an inverted microscope (Nikon Ti-S). Transmitted light is collected with a 50×, 0.9 NA objective and imaged onto the entrance slit of a 300 mm focal length imaging spectrometer (Acton SP2300i) equipped with a thermoelectrically cooled, 256-element InGaAs diode array (BaySpec Nunavut). The imaged nanogap length is 5 µm, and 5 measurements are obtained, for a total length of 25 µm. The incident light polarization is adjusted for maximum throughput (perpendicular to the nanogap contour). Spectra are background subtracted and normalized using the spectrum for direct transmission through the glass substrate.

#### Terahertz time-domain spectroscopy

A terahertz pulse with a few picoseconds pulse width is generated from a GaAs-based photoconductive antenna (Tera-SED, Gigaoptics, GmbH) illuminated by a femtosecond Tsapphire laser pulse train with a center wavelength of 780 nm, 80 MHz repetition rate, and 90 fs pulse width (Mai Tai XF, Newport Corporation). The p-polarized terahertz light passes through the nanogap samples at normal incidence and is detected by electro-optic sampling using a 1-mm-thick ZnTe crystal (INGCrys Laser System Ltd.).

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**Figure 4** Two-dimensional (2D) finite-element simulation of a single nanoslit. (a), Red squares indicate measured field enhancement of the nanogaps at 0.3 THz as a function of the gap size, performed by THz time-domain spectroscopy. Blue triangles indicate simulated field enhancements by 2D finite-element modeling. (b), (left) Calculated electric field amplitude around a 2-nm-wide slit in a 150-nm-thick gold film. (right) Enlarged electric field amplitude distribution around the exit of the nanoslit. The slit is filled with alumina (Al₂O₃).
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