SAND2014-17869R

SAND20XX-XXXXR
LDRD PROJECT NUMBER: 14-2449
LDRD PROJECT TITLE: Non-resonant Nanoscale Extreme Light Confinement
PROJECT TEAM MEMBERS: Ganapathi Subramania, Dale Huber

ABSTRACT:

A wide spectrum of photonics activities Sandia is engaged in such as solid state lighting, photovoltaics, infrared imaging and sensing, quantum sources, rely on nanoscale or ultrasubwavelength light-matter interactions (LMI). The fundamental understanding in confining electromagnetic power and enhancing electric fields into ever smaller volumes is key to creating next generation devices for these programs. The prevailing view is that a resonant interaction (e.g. in microcavities or surface-plasmon polaritions) is necessary to achieve the necessary light confinement for absorption or emission enhancement. Here we propose new paradigm that is non-resonant and therefore broadband and can achieve light confinement and field enhancement in extremely small areas [~(λ/500)^2]. The proposal is based on a theoretical work[1] performed at Sandia. The paradigm structure consists of a periodic arrangement of connected small and large rectangular slits etched into a metal film named double-groove (DG) structure. The degree of electric field enhancement and power confinement can be controlled by the geometry of the structure. The key operational principle is attributed to quasistatic response of the metal electrons to the incoming electromagnetic field that enables non-resonant broadband behavior. For this exploratory LDRD we have fabricated some test double groove structures to enable verification of quasistatic electronic response in the mid IR through IR optical spectroscopy. We have addressed some processing challenges in DG structure fabrication to enable future design of complex sensor and detector geometries that can utilize its non-resonant field enhancement capabilities.].

INTRODUCTION:

Confining electromagnetic energy into small (nanoscale) volumes/areas can significantly enhance light-matter interaction. Through confinement electric field can be enhanced and energy squeezed significantly into subwavelength volumes thereby substantially increasing interaction cross-section with matter of interest. This enhancement of light matter interaction has practical implications in a number of application areas in photonics such as sensors, detectors, light sources etc. Current approaches to electromagnetic confinement rely on resonant approaches like surface plasmon polaritons in metals such as that described in extra ordinary optical transmission EOT phenomenon[2]. A typical EOT structure consists of a periodic array of subwavelength holes etched into a thin metal film. This phenomenon was demonstrated for the first time in a thin silver film patterned with subwavelength sized cylindrical holes and it is so named because the transmitted light is beyond the expectations of Bethe's theory[3] and twice the amount predicted from a simple analysis based on the area fraction of the holes. This mechanism behind this behavior is attributed due either to the excitation of surface plasmons [4] in the metal or dynamic diffraction or a combination of both. EOT structures thus exhibit field enhancement inside the subwavelength apertures which makes it attractive in enhancing light matter interaction. However, the resonant nature also makes EOT inherently narrowband which might not be suitable for certain applications. Furthermore, while electric field can be enhanced my reducing the size of the aperture it reduces the overall transmission through the structure resulting in lower signal-to-noise when used in device applications. In other words, the field enhancement and light transmission are coupled inversely. Therefore it would be of great interest to explore the possibility if we can achieve light confinement and electric field enhancement while simultaneously achieving a broadband operation.

It turns out that it is indeed possible to decouple the two by employing a novel non-plasmonic paradigm that is based on an inherently non-resonant phenomenon. As a result they can operate in broadband across a wide wavelength range in the mid infrared. This was demonstrated theoretically by our group and collaborators[1]. The paradigm structure consists of a periodic array of connected small and large apertures fabricated in a thin metal film. Shown in Figure 1, we call this the double-groove (DG) structure. This structure while superficially resembling traditional metal based plasmonic structures operates on an entirely different principle. Instead of exciting surface plasmon resonance modes, the metal electrons experience a quasistatic response broadband. This can be understood by considering a single unit cell of the DG structure wherein one can observe that the left and right half are electrically disconnected (figure 1b). The typical optical transmission response for three separate cases of the DG structure is plotted in figure 1c. The electrons are therefore free to move in the vertical direction (Y) on either side but are restricted to edges along the horizontal (X). When the electric field is polarized along X direction, charge accumulations occurs at the edges resulting in the generation of a potential. Since the potential difference in the small and large small gap is nearly same, the electric field is much larger in the small gap, enabling light transmission By adjusting the relative sizes of the small (W_{x1}) and large gap (W_{x2}) apertures along with their periodicity a large field enhancement (~ 20X-100X) in highly subwavelength areas [~(λ/500)2] has been predicted. In this work we have successfully achieved process development for fabricating the double groove structures and obtained some preliminary optical response that compare well with theoretical prediction which are detailed in subsequent sections.

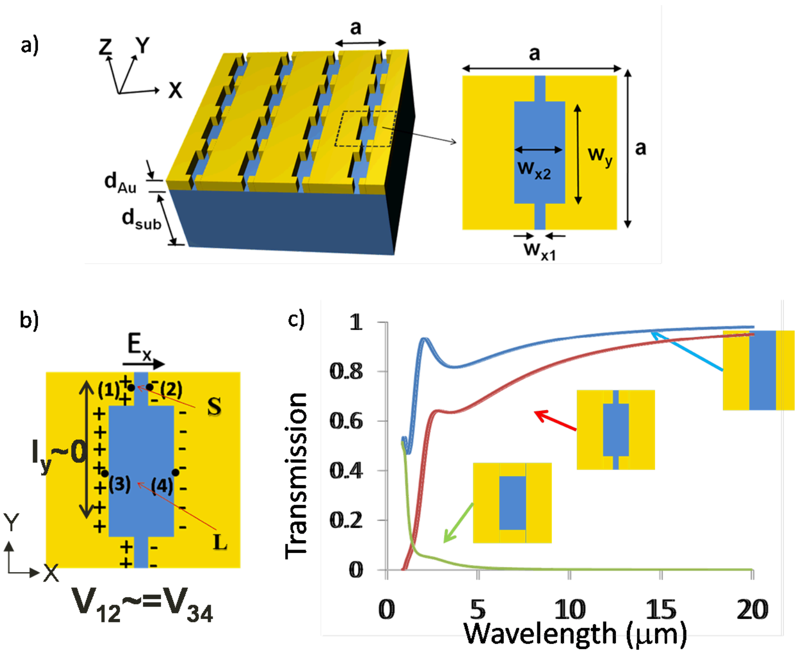

Figure1:(a) Schematic of a double-groove (DG) structure. (b) schematic of the quasistatic response. (c) Simulated transmission response for DG structure with maximum gap (w_{x1}=w_{x2}) , moderate gap and no gap (W_{x1}=0).

DETAILED DESCRIPTION OF EXPERIMENT/METHOD:

A main goal of this project is develop a process to fabricate across a large area (~ 1mm x 1mm) double groove structure to enable optical spectroscopy using fourier transform infrared (FTIR) to characaterize optical transmission for different structural geometries. The methods/experiments used to achieve this involves i) electromagnetic simulations based on finite difference time domain (FDTD) technique ii) nanfabrication based on electron beam lithography iii) Optical spectroscopy.

In order to increase the potential for success in this short term project (~ 3months) we decided to fabricate DG structures on a 50nm thick gold film with a periodicity of 800nm with varying gap widths which would reduce processing difficulties. To determine the optical response of this structures we performed finite difference time domain simulations using a commercial software package (Lumerical® FDTD solutions). We utilized 800nm X 800nm X 3000nm cell size with a uniform mesh size of 4 nm x 4 nm x 4 nm in the X, Y and Z direction. Due to the periodic nature of the structure we applied periodic boundary condition(PBC) along the X and Y direction and perfectly matched layer (PML) boundary conditions along the Z direction which is the light input direction. We employed a broadband pulsed plane wave source covering a broad spectral region between 1-20 μm wavelengths. The structure was placed in the middle of the simulation region. Two monitors were placed to record transmission and field distributions. The first monitor was placed near the back of the simulation region to record transmission response as a function of wavelength and the second one cutting the middle of the metal region to record the spatial distribution of the electric field at the desired wavelength.

The samples were fabricated on CaF_2 and BaF_2 substrates. First a layer of polymethylmethacrylate (PMMA) which serves as the electron beam resist was spin-coated on top of the substrate and baked for 15min at 170C. Either 3% and 4% PMMA in chlorobenzene was spun at 3000rpm which gave a thickness of ~ 160nm and ~250nm respectively. The choice of the resist concentration is determined by the balance of sufficient resist thickness that is essential for a successful metal lift-off and the e-beam dose latitude need to create the small gaps of the DG structure to be < 150nm. Resist coated samples were patterned in the JEOL 6300FS electron beam lithography system at CINT. Since CaF_2 and BaF_2 samples are non-conductive an additional charge dissipation layer of ~ 100A^o of thermally evaporated Au was also deposited to mitigate any charging effects during exposure. Dose range was varied from 450 to 900

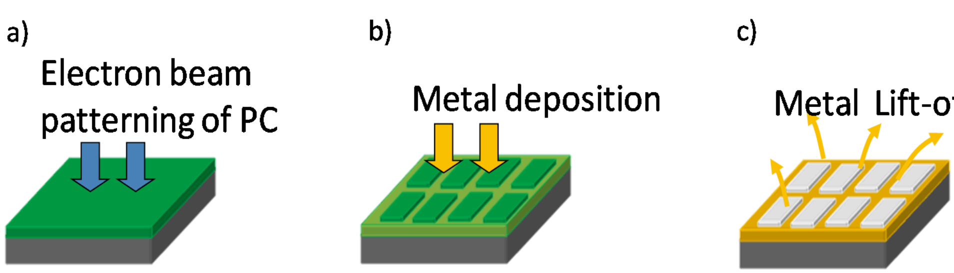

Figure2: Schematic of fabrication process for the double-groove (DG) structure.

μC/cm^2 written at 6nA and 2nA current settings. After exposure the charge dissipation layer was stripped in aqueous KI/I solution followed by development in 1:3 solution of methyl isobutyl ketone (MIBK) in isopropanol. Following development 50nm of Au was evaporated using e-beam evaporation. The sample was then soaked for several hours in n-methyl pyrrolidone (NMP) at 80^{o}C with mild stirring and/or mild sonication.

Finally, a spray of pressurized acetone is applied. This enables the lift-off of the metal from the unpatterned regions leaving behind the desired DG structure. A condensed form of the schematic is shown in figure 2. Optical spectroscopy was performed using a Bruker FTIR spectroscopy system. The typical beam size at the focal point of the sample is ~ 2 mm. The individual sample sizes however are 1mm x 1mm placed in an array 1.5 mm apart. In order to address each device individually a specialized sample holder was fashioned using rapid prototyping printer with a aperture that was slightly smaller than the sample size (~ 0.9 mm x 0.9 mm) to get the most signal through the device while preventing any light leakage around the device to the detector. The holder also has sliding sample holder that can translate the sample along the X and Y direction to enable selecting the desired device from the array for measurement. A broadband wire-grid polarizer was also introduced in the beam path to measure the optical response of the sample to polarized input light.

RESULTS:

We performed FDTD simulation of the nominal structure we fabricated. We utilized a lattice constant of 800nm and performed simulation for different parameters of small gaps. Based on the theoretical prediction of reference [1] the field enhancement achievable in the small gap region in the long wavelength limit is ~ a/W_{x1} . For instance, a small gap width of W_{x1} = 40 nm at lattice constant of a= 800nm is expected to give a field enhancement of ~ 20X in the small gap. Figure 3a shows a typical simulated transmission response for the case of a=800nm , W_{x1} = 40nm , W_{x2}=133 nm, W_y=266nm with d_{Au} =50nm and d_{sub}=600nm. Figure 3b shows the electric field distribution inside the aperture region at λ ~ 10 μm. A feature size of 40nm though quite challenging given the short time of this exploratory project we felt was a potentially achievable goal.

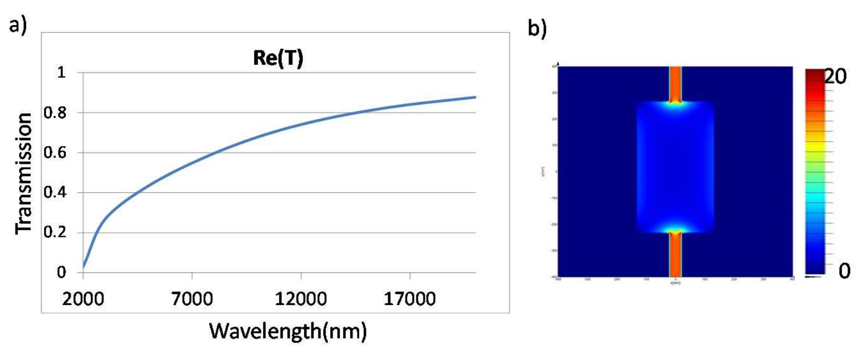

Figure 3: a) Simulated transmission response for DG structure with a=800nm and W_{x1}=40nm. (b) Electric field distribution in the DG structure at 10 mm wavelength.

We chose BaF_2 and CaF_2 windows that were commercially available due their broadband transparency in the midinfrared region. CaF_2 has good transmission only till ~ 10μm wavelength while BaF_2 is transparent well beyond 10 μm making it more suitable as substrate from the optical standpoint. However, BaF_2 does have materials limitations that made processing more difficult which will be discussed in the next section. Different variation of the DG structure were designed in the CAD layout and patterned in the

EBL. The gap was varied between the two extremes from maximum gap (W_{x1}=W_{x2}) wherein the structure is essentially a wire grid polarizer to no gap (W_{x1}=0) where in the structure is a rectangular hole array structure. On the BaF_2 substrates doses in the ranging from 450 to 650 $\mu C/cm^2$ were attempted. During the early attempts utilizing the lower concentration e-beam resist (3%) which nominally gives a thickness of ~ 160 mm large lift-off problems were noticed. Majority of the regions of the device the metal did not lift off (figure 4) from the unexposed parts of the resist when soaked in solvent. On subsequent attempts we used higher concentration PMMA (4%) to obtain a nominal thickness of 250nm. In this case however even at the lowest dose the gaps failed to open for the DG structure. However, the maximal gap or the wire grid structure did lift-off (figure 5). Further process improvements such as lowering of dose or

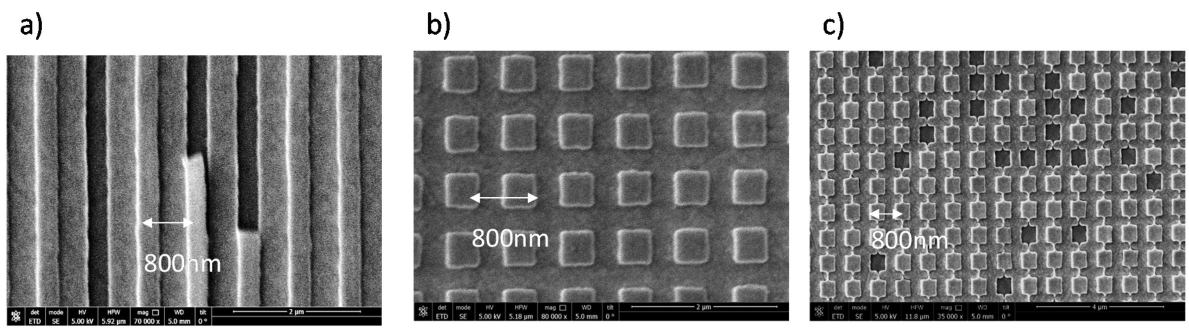

Figure 4: Scanning electron microscopy (SEM) images of structures fabricated on BaF_2 using 3% PMMA. a) wire grid b) rectangular hole c) DG structures.

modifications to CAD patterns are necessary and will be discussed in the next section.

On CaF_2 substrates we spun higher concentration PMMA (4%). Exposure was performed in the 750 to 900 $\mu C/cm^2$ dose range. Two variants of the DG structures to obtain a nominal gap widths of 60 nm and 100nm were initially designed in the CAD layout. Variation in e-beam does would provide a range of gap widths. Metal lift-off occurred successfully on this substrate. However, there were small regions of few microns in size where some lift-off issues were observed in some of the devices. At the lowest dose the maximum gap (W_{x1}=W_{x2}) wire grid structure were 350nm wide. On the double groove structure the small gap width (Wx1) ranged from ~150nm at the lowest e-beam dose regime to about ~ 80nm at the high dose in the

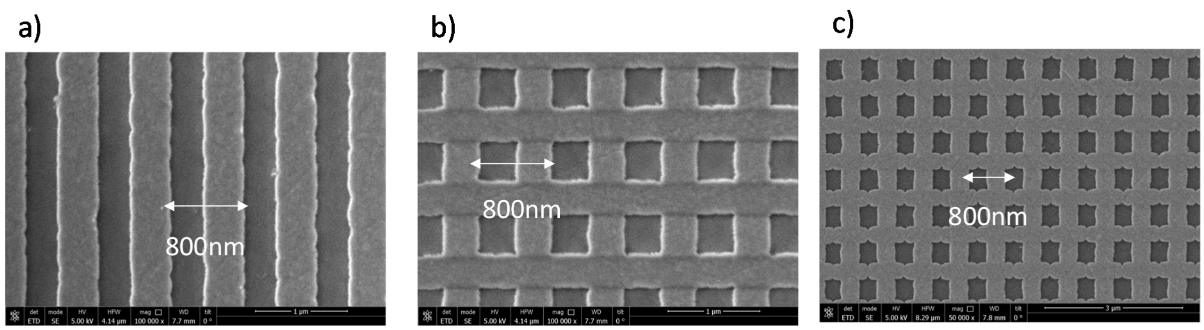

Figure 5: Scanning electron microscopy (SEM) images of structures fabricated on BaF_2 using 4% PMMA and sonication exhibiting successful metal lift-off. a) wire grid b) rectangular hole c) DG structures.

fabricated devices (figure 6) . The size of the rectangular opening within the unit cell (W_{x2} X W_y) were nominally 520 (±20) nm x 530 (±20) nm.

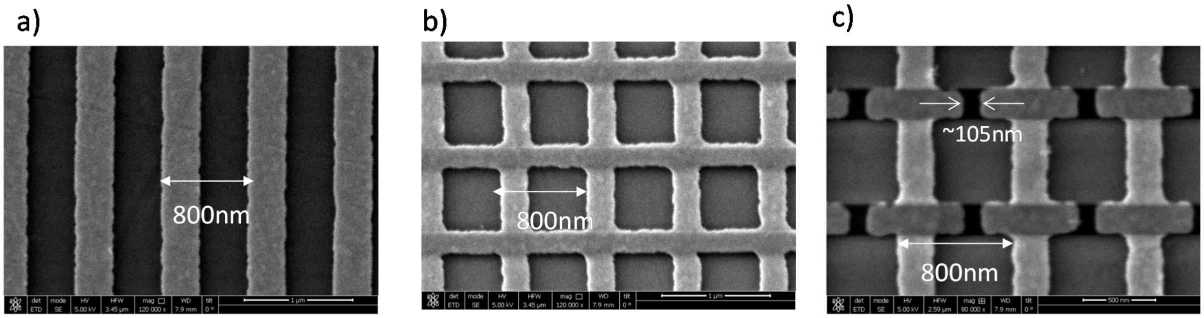

Figure 6: Scanning electron microscopy (SEM) images of structures fabricated on CaF_2 using 4% PMMA exhibiting successful metal lift-off. a) wire grid b) rectangular hole c) DG structures.

After we were able to successfully fabricate the DG structures which we achieved towards the end of this project we measured the infrared optical response in particular the transmission spectrum of the devices patterned on the successful CaF_2 substrate on the Bruker FTIR system. Optical transmission spectrum for three devices wire-grid (the maximum gap $W_{x1}=W_{x2}$), double-groove ($W_{x1}\sim$ 105nm) and rectangular aperture ($W_{x1}=0$) is shown in figure 7. A broad band transmission is seen in the midIR region from 2-9 μm wavelength for the wire-grid as well as the DG device. The transmission of the wire-grid ranges from ~ 0.7-0.8 and is somewhat larger than that for the DG structure which also shows transmission of ~ 0.6-0.7 in most of the measurement region. The transmission roll off towards shorter wavelength is faster for the DG structure than for the wire-grid structure which is expected. The rectangular aperture structure shows low transmission (0.2) throughout the region. At the longer wavelength side (> 7

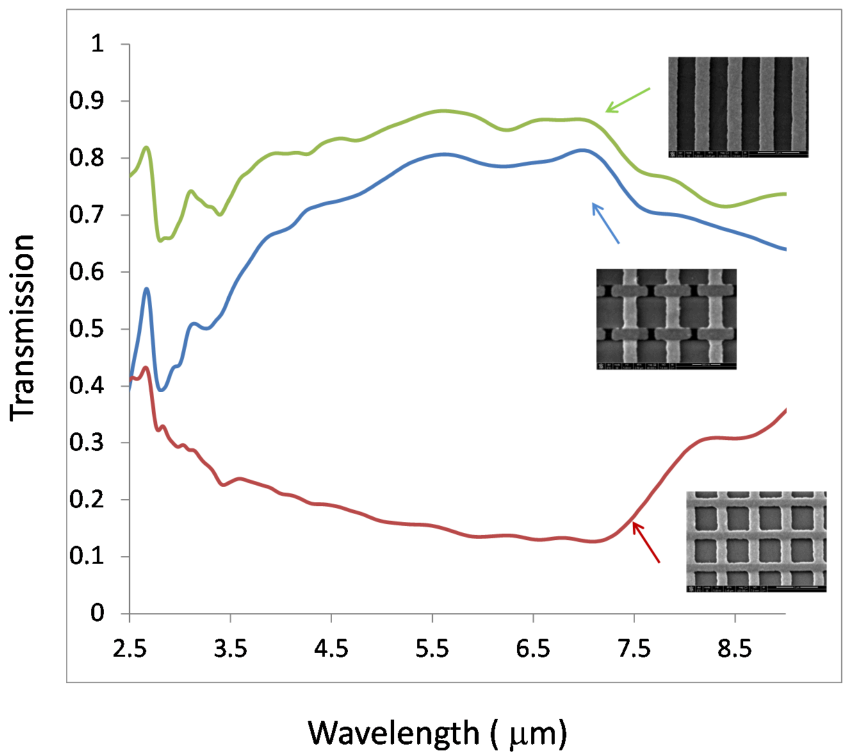

Figure 7: Fourier transform infrared (FTIR) transmission response for a typical DG structures ranging from closed to open gap structures.

μm) the DG and wire-grid shows drop in transmission and the rectangular aperture starts to increase. Similar behavior is also seen at the short wavelength side as well (< 3 μm). This can be explained and is discussed in the next section.

DISCUSSION:

In the theoretical work[1] inspiring this project a DG structure with a lattice constant 'a' of 300 nm was used an example to illustrate the various concepts of broad band field enhancement. The advantage of smaller lattice constant is the bandwidth of the behavior. In other words the transmission roll-off happens at shorter wavelengths (~ < 2 μm) and is sharper . However, this also implies that the minimum feature sizes required to achieve field enhancements are also small. For instance, 20X field enhancement requires ~ 15nm gap size. Due to the short duration and limited resources available for this project we relaxed the requirement of the lattice constant to 800nm. It means that this also relaxes the minimum feature size requirements to ~ 40nm. The trade-off comes in the form of tranmission roll-off that is more gradual and starts at much longer wavlengths (~5-6 μm) (figure 3a). Nevertheless, this demonstration would serve as an important proof-of-concept providing valuable information with regards to process development for nanofabrication.

BaF_2 is the ideal choice for substrate onto which to fabricate the DG structure as it has a low refractive index (n~ 1.5) and is transparent up to ~ 14 μm. Due to large atomic number of Ba compared to Ca it also requires considerably lower electron beam dose for exposure due to higher backscatter effect. However, as mentioned in the previous section BaF_2 also posed some material challenges such as higher solubility in water as well as cleaving or shattering easily under mechanical or thermal stress. This was particularly problematic during resist baking step as well as ultrasonication during metal lift off step when substrates tended to crack restricting further processing or subsequent optical characterization. However, it was shown that the structures can be fabricated if process steps are controlled. Although DG gap was not seen for the BaF_2 case reducing the dose further is very likely to be successful which will be attempted in subsequent writes. The CaF_2 samples were more robust but required higher e-beam doses to create the structures due to its lower atomic number. Although these structures were developed for large dimensional features many processing techniques developed can be applied to smaller lattice constant devices with minimal modification.
The optical transmission spectra for the wire-grid, DG and the rectangular hole array shows expected behavior based on theory where-in both wire-grid and DG structure show high transmission in the 3 to 7 μm wavelength range with DG structure transmission rolling off faster than wire-grid. However, there is also a drop in transmission beyond 7 μm. This is due to the intrinsic absorprtion of the CaF_2 substrate. At wavelengths smaller than 3 μm there is once again a rise in transmission although theory predicts a sharp drop in transmission. This is due to the fact the sample aperture material starts to become transparent and is no longer successfully masking the device region. This can be addressed by metallizing aperture material. Likewise, the transmission for the rectangular aperture is low (< 0.2) but not near zero as one would expect theoretically and it also exhibits similar anomalies like the wire-grid and the DG transmission. The reason for non-zero transmission of the rectangular aperture could be due to misalignment of

the aperture or the device region has physical damage where in a few 10s of micron size region has no structure enabling light to leak through. Further reducing the aperture size would be one approach to address this however, that also reduces signal to noise ratio. Alternatively larger device size could be used which ofcourse increases the e-beam write time. As successful fabrication was achieved towards the final phase of the 3 month exploratory project the optical measurements presented are at a preliminary stage. Nonetheless, they are encouraging as they seem to reflect closely the theoretical prediction. More optimized set-up as well as careful measurements which are being conducted presently will provide improved sets of data.

Finally, a fundamental scientific question of interest is the direct experimental probe of the quasistatic response as described in the introduction (figure 1b) using pump-probe spectroscopy. The broadband transmission is attributed to quasistatic response of electrons to the incoming electromagnetic field. This effect can be studied by directly modulating the carrier concentration in the small gap which can be achieved optically. The DG structure can be fabricated on semiconducting substrate such as silicon whose carrier concentrations can be modulated by an incoming pump beam whose wavelength is shorter than its bandgap. A probe beam that is slightly time delayed from the pump beam and of longer wavelength where the DG structure is expected to transmit measures the transmission as a function of generated carriers. This dynamic transmission response to carrier density will provide valuable information for scenarios when DG structures can be incorporated into devices or sensors. Since in the experimental set up the probe beam wavelength is expected to be around 2.5 μm a smaller lattice constant device (~ 300 nm) are needed which are challenging to fabricate. We were able to make some progress towards fabricating such structures during the time of writing this report but further process optimization will be necessary to obtain devices for characterization.

ANTICIPATED IMPACT:

In contrast to resonant techniques, non-resonant approach to extreme light confinement is novel and unexplored. In addition to broadband behavior, unlimited field enhancement (subject to onset of quantum effects) and extreme power confinement can be achieved without sacrificing light throughput. This approach can be highly transformative in understanding and manipulating light absorption and emission phenomena.

Thus far the theoretical structure described in the PRL[1] work has not been experimentally demonstrated. In this work we have demonstrated real fabricated double groove structure at 800 nm lattice constant and small gap region (region of electric field enhancement) < 100 nm whose preliminary optical response shows relatively good agreement with theoretical predictions. This is a significant milestone and is a key first step towards designing in the future more complex structures that can be incorporated into detectors and sensors. A detailed optical characterization of these structures is expected to lead to publications in the near future as well as presentations in conferences. Continued theoretical exploration of this structure has also provided interesting resonant response behavior on the shorter wavelength regime (near-infrared and visible) which can lead to publications. The logical next step involves measurement of enhancement in absorption features of organic thin films coated on DG structures due to the broadband field enhancement effects. This can also provide an indirect determination of the field enhancement in conjunction with theoretical modelling. This is useful preliminary experiment to evaluate the potential of this approach for broadband sensing applications. Futhermore, with fabricated

devices now available it may also be possible to directly measure field enhancements using near field optical microscope which has not been demonstrated thus far. Most importantly experimentally demonstrating this structure by developing a fabrication approach has afforded the preliminary success necessary to position us favorably for future internal and external funding. An expanded version of this work was proposed for full internal LDRD funding and was also a component of a Grand Challenge proposal for FY15. Although these proposals were not funded they received excellent technical feedback. Progress made during this exploratory LDRD will be significant in strengthening future proposal submissions that will enable to go further in our achievable goals. In particular successful fabrication of this structure now opens the possibility of making a quantum leap towards incorporating them on to detector structures made from 2D materials such as graphene. These detector structures can be small, lightweight and tunable in the mid infrared which align with many Sandia mission activities as well as detection at the limit Research challenge.
Non-resonant approach to field enhancement can not only offer new physical insights like broadband Purcell enhancement but also have significant advantages over its resonant counterpart by potentially enabling devices with large operational bandwidth, faster response and robustness. Initial success of this proposal will pave the way to providing quantitative answers to more deeper questions in the future : What is the practical maximum electric field enhancement achievable? What is realistic bandwidth of complete absorption that can be achieved in a desired and useful region? Conversely can broadband emission enhancement be achieved? To what extent non-linearity can be enhanced? Answers to these fundamental questions will in turn open up new research directions that will have important technological imlications and impact. Sandia has a significant investment in photonics based mission activities (e.g., solid state lighting, detection, imaging, photovoltaics, communication). Developing novel, out-of-the-box concepts and approaches strengthens the fundamental knowledge base essential for Sandia's future and global leadership. Success of this project will pave the way for technological impacts for instance, in IR detection in the next 5years.

CONCLUSION:

Extreme light confinement i.e., squeezing electromagnetic energy into increasingly smaller volumes has been key to the success of modern photonic devices. Current approaches rely on resonant techniques to achieve this based on plasmonic structures or metamaterials which have limitations. The goal of this project was to experimental verification of the theoretical work described in reference [1]. The paradigm structure consists of a periodic arrangement of connected small and large rectangular slits etched into a metal film named double-groove (DG) structure. Utilizing the quasistatic response of the metal electron to the incoming field this structure enables broadband optical transmission while enhancing electric field and squeezing electromagnetic power within an ultrasubwavelength gap. The degree of electric field enhancement and power confinement can be controlled by the geometry of the structure.

Towards experimentally demonstrating this phenomenon we have successfully developed a nanofabrication approach based on e-beam patterning and metal lift-off . We have successfully fabricated the DG structures with a lattice constant of 800nm with gaps < 100 nm that can potentially exhibit > 10X field enhancement on CaF_2 subtrates that are transparent across broad wavelength range in the midinfrared. We utilized electromagnetic modeling and theoretical calculations to design the DG structure and to predict the optical response. We performed FTIR spectroscopy to optically characterize the devices. Preliminary measurements demonstrate broadband optical transmission in the 3- 8 μm that matches well with theoretical predictions. This successful demonstration in the future will enable fabrication of more complex structures as wells incorporation in detector and sensor geometries to improve their performance. It will further enhance our understanding of light-matter interaction critical for future photonic devices.

REFERENCES:

1. Subramania, G., S. Foteinopoulou, and I. Brener, *Nonresonant Broadband Funneling of Light via Ultrasubwavelength Channels.* Physical Review Letters, 2011. **107**(16): p. 163902.
2. Ebbesen, T.W., et al., *Extraordinary optical transmission through sub-wavelength hole arrays.* Nature, 1998. **391**(6668): p. 667-669.
3. Bethe, H.A., *Theory of Diffraction by Small Holes.* Physical Review, 1944. **66**(7-8): p. 163.
4. Ghaemi, H.F., et al., *Surface plasmons enhance optical transmission through subwavelength holes.* Physical Review B, 1998. **58**(11): p. 6779.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.