

# Design of a plasmonic photonic crystal for single bio-molecule spectroscopy

Ryan M. Gelfand,\* Hooman Mohseni  
Bio-inspired Sensors and Optoelectronics Laboratory (BISOL)  
Department of Electrical Engineering and Computer Science  
Northwestern University, Evanston, IL

We present the design and initial characterization of a device geometry that is suitable for measuring the direct mid-infrared absorption of single molecules. The devices are based on a metal-dielectric-metal sandwich with optically thick gold cladding layers which squeeze the gap mode, the optical mode in the dielectric layer, in the electric field direction; with a photonic crystal cavity defect which can squeeze the gap mode in the planar direction. Simulations show a field enhancement of 10000 times the incident field in the cavity defect at an excitation frequency of 87 THz. Experimentally, devices with varying periods were made using a free standing  $\text{Si}_3\text{N}_4$  film of 15 nm or 50 nm as the inner dielectric. These devices show a red shift as the period is increased and more interesting there is also a red shift for the thinner dielectric devices showing that the field is further squeezed in this layer. By placing a molecule into the cavity, there should be a strong enough interaction between the light and the analyte so that its absorption spectra can be resolved.

**Keywords:** Plasmonic biosensing, Single molecule spectroscopy, Surface enhanced infrared absorption (SEIRA)

## 1. INTRODUCTION

Molecular identification on the sensitivity down to a single molecule would benefit many industries from explosives detection [1] and security; [2] to helping us discover new drugs [3] bio-sensing [4] and detecting cancer in its infant stages [5,6], and has been the goal of researchers in several different fields. Single molecular detection has been achieved using a variety of methods, from surface enhanced raman spectroscopy (SERS) [7], to micro-mechanical sensing [8], to high Q optical cavity resonators [9], and each of these requires labels or tags as well as surface functionalization in order for the target molecule to be detected. And of these techniques only SERS has the capability to accurately identify molecules but because the fundamental interaction is so weak it is difficult to achieve, compounding this issue is the challenge of trapping a molecule at a hotspot without functionalization of either the surface or the analytes. And so the goal is to not just detect a molecule, but to identify it without the need for labels or tags or surface modifications.

Many important bio-molecules have natural fingerprint vibrational spectra in the THz, which for optical excitation corresponds to a wavelength between 2 – 10 microns. Researchers have been using this spectral band to probe and characterize analytes for many years by using FTIRs. Unfortunately this measurement is not sensitive and often requires quite a lot of material to make any accurate identification. Surface enhanced infrared absorption or SEIRA [10,11] combines the light squeezing ability of plasmonic hot spots with the specificity of an FTIR to try and solve this sensitivity challenge. Compared to raman cross-sections, IR absorption cross-sections are 10 orders of magnitude greater. The problem is that the interaction strength between light on the order of microns and molecules on the order of nanometers is quite small. So we propose a device that can squeeze light by using a combination of a photonic crystal and a metal-dielectric-metal (MDM) sandwich [12].

Photonic crystals [13] have received much attention for their ability to control light, and in particular for their ability to squeeze light in a cavity. This type of metamaterial, an array of periodically arranged holes, on the order of the wavelength, forming an artificial crystal has a photonic band structure so that there are states of allowed modes and a bandgap of forbidden modes. The geometry can be designed so that a point defect (one removed hole) built into the crystal will trap modes found in the bandgap. This trapped mode will spend a much longer time in the cavity because every time it tries to escape it will be reflected back, thus building up energy. The quality or Q-factor is the measure of

\*hmohseni@northwestern.edu; phone 1 847-491-7108; bisol.northwestern.edu

how much energy is stored inside to the amount of energy that leaks out. Since the Q-factor is inversely proportional to the linewidth of the cavity mode, in order to capture a broad enough spectral resonance wide enough for multiple peak detection, one cannot design a device with a high Q-factor. This becomes important because for direct IR absorption you want the interaction strength to be as large as possible inside the cavity defect. But relying on a high Q-factor underscores the need for very narrow spectral linewidth, which in turn reduces the robustness of the device and makes it impossible to obtain enough of a molecules spectral fingerprint; preventing reliable detection and high specificity. Also, due to nanometer limited geometrical tolerances, it is hard to reproduce PCs that match the spectral feature of interest. Similarly tight tolerances to ambient (temperature, concentration, humidity, etc.) changes render these devices difficult to use in the field.

A photonic crystal cavity can squeeze the mode in the planar direction, but to further squeeze the mode it can be coupled into a gap plasmon mode by coupling the optical mode into a plasmonic mode and then squeezing down to the volume needed. Our simulations have shown that this possible by using an MDM sandwich to squeeze the mode in the electric field direction and a photonic crystal cavity defect to squeeze the mode in the planar direction. Furthermore the effective index of the MDM or gap mode is quite high and so it is very slow, in this way the mode is not only squeezed by many orders of magnitude but also lasts more time in the cavity. In this way we can attain an electromagnetic mode that resonates in the THz but can be trapped to a volume on the order of a single molecule without having to rely on a high Q structure.

For any optical detection technique to be practical for single molecule detection, the interaction time between the light and the target molecule needs to be long and the spectral line width needs to be broad enough to allow for detection of the spectral signatures of the molecules being detected. By exploiting the properties of nanoscale cavities, we have been able to design and simulate a device that can squeeze light in all three dimensions into a small volume facilitating a larger interaction with single molecules. This interaction strength between the light and the cavity can be characterized by Purcell's constant,

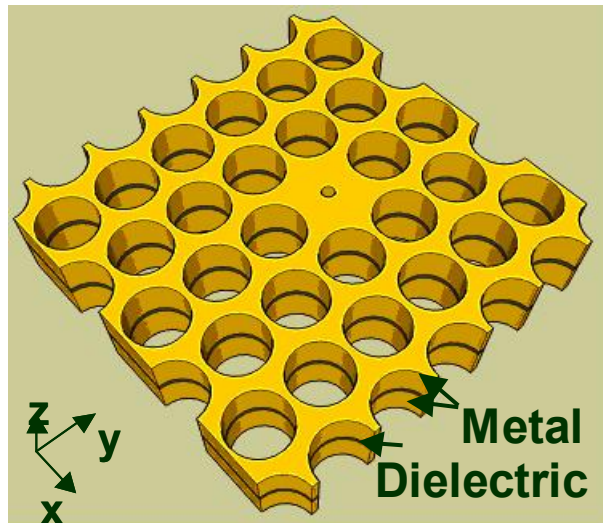
$$p = \frac{3}{4\pi^2} \frac{Q}{V} * \lambda^3 \quad (1)$$

where Q is the quality factor of the cavity, V is its volume, and  $\lambda$  is its resonant mode.

A high p, implying an intense interaction between the light inside the cavity and electronic states of the molecules, would be required for any efficient optical sensor [14]. One needs to increase Purcell's constant without relying on extremely high Q factors to build a practical sensor. In order to meet these two conditions, V the volume of the cavity must be as small as possible.

The presented device combines an MDM structures and a two-dimensional cavity to produce a practical structure that addresses many issues plaguing the aforementioned sensors. We show that our new structure can squeeze light a million times volumetrically, leading to a high Purcell constant comparable to the best reported values by conventional photonic crystals. However, the small Q-factor of the proposed structure leads to a very wide spectral bandwidth producing robustness and better specificity as a photonic molecular sensor while at the same time we can keep the interaction volume small and thus the Purcell factor high. We also show that the main plasmonic mode of the proposed structure has a good coupling to the far-field, and hence can be excited by conventional optical devices (e.g. an optical microscope).

By combining an MDM with a PC, two structures into one, we can build a nanocavity resonator with the mode squeezed vertically by very closely spaced (10s of nm) cladding layers and laterally by a plasmonic polaritonic crystal (PPC) surrounding the interaction point (Figure 1). This cavity will have a low Q factor and therefore be able to support a broad spectral response though with a zeptoliter volume the Purcell constant would still be large. Molecules could be escorted either in gas or liquid to the interaction point by a microfluidic channel running the length of the device through the cavity defect. The cavity can be coupled to from the far field by an FTIR microscope. The optical mode would travel through the crystal and out into a detector that would measure its spectrum. As a molecule passes into the cavity and interacts with the squeezed mode, its unique spectral fingerprint will be recorded at the detector site.



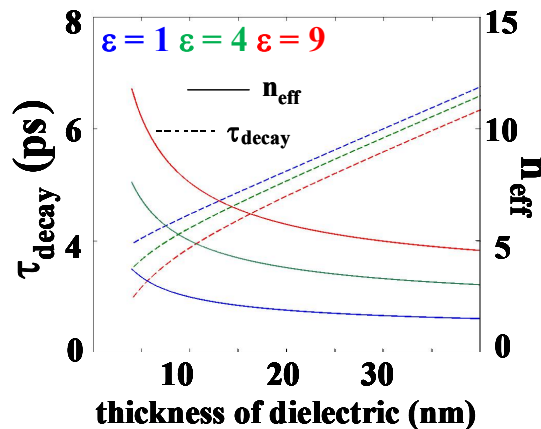
**Figure 1 - Plasmon Polariton Crystal (PPC) with metal cladding layers sandwiching a dielectric layer pierced with an hexagonal lattice of holes. A defect hole is placed within the crystal to create a nanocavity resonator and an interaction point.**

## 2. SIMULATION RESULTS

Full 3D Finite Difference Time Domain (FDTD) simulations were run to analyze the nanocavity device. For the design of the structure, we started by choosing a fixed wavelength for the first Brioullin zone boundary (i.e., at  $\beta_{\text{gap}}(\lambda) \approx \pi/a_0$ , with  $a_0$  as period). Gold was chosen as the metal because it has excellent plasmonic properties and also doesn't oxidize as readily as silver. The next step was to settle on the remaining parameters, i.e., thickness and dielectric constant. A basic relation was noted by looking at the loss and dispersion plots in Figure 2: The decay length decreased for either thinner layers or higher dielectric constants. On the other hand, the effective index showed an inverse behavior, with shrinking thickness and higher dielectric constant it increased. The metric of the decay length as a decay time can be seen as a normalized decay length for the periodic structure. Since, for a fixed wavelength of the Brioullin zone edge the period is inversely proportional to the effective index. A gap mode sees a number of cells proportional to  $n_{\text{eff}} \times L_{\text{decay}}$  during its lifetime. This figure also demonstrates that this measure is not sensitive to the choice of dielectric constant in the observed wavelength range, but sensitive to the thickness. Therefore, in order to maximize this normalized decay length, the thickness should be minimal. At the same time this would decrease  $n_{\text{eff}}$ , requiring the dielectric constant be chosen as high as possible. In this case, amorphous silicon with an index of 3 was chosen, though for the experiment silicon nitride was used as it has a relatively high index of 2 and it is smooth and easy to process. In this structure, the gap height was 12 nm, because this would provide a very high effective index between 5 and 6. Then the period  $a_0$  was set to 500 nm, so that  $\beta_{\text{gap}}(\lambda) \approx \pi/a_0$  was satisfied for mid-infrared wavelengths. The holes were made large ( $r = 225$  nm), because otherwise in a normal photonic crystal of this type there would be no TM bandgap [13]. The height of the structure is 600 nm.

Bloch-boundaries were introduced in each lateral direction and PML and anti-symmetric boundaries in the vertical direction. The anti-symmetric boundary was chosen because the anti-symmetric gap mode is longer lived for the TM polarized case and by placing the boundary at the center of the gap in the z-direction saved simulation memory and time. The upper PML boundary was placed far enough away from the structure so that there is no distortion in the simulation from back reflections or artificial absorbing effects. In and around the gap a small grid size of 3 nm was imposed. In the metal cladding, this grid size was gradually increased toward the top. The construction of the unit cell and the placement of the sources was equivalent to the simulation of photonic crystals. After exciting the structure with a few short point source (i.e., with the correct TM polarization of the gap mode), the time response of the vertical electric field component was recorded in different locations in the structure. The placement of the point sources and the monitors is very important. As a first rule they should not lie on a symmetry axis (zero of a mode). This restriction is alleviated by using 2 sources per unit cell and 6 field monitors. On top of this, an FDTD script iterated through the desired values of the

crystal-momentum  $k$  and saved the recorded signals for each iteration into a file. Eventually, these files were processed by a Matlab script. For each  $k$ -value the recorded time signals are read out and spectrally analyzed with the Padé approximation method. A simple peak detection method then reads out the resonances in the time signals. These resonances, correspond to modes of the periodic gap structure. But not each time signal can record all the resonances (i.e., the modes). Therefore, a flexible bin system is used that collect the peaks found in each time signal and then choose the ones that appeared more in multiple signals. Eventually, the peaks from all the  $k$ -iterations are assembled into a band plot. The band plot for this structure is shown in Figure 3 and was obtained with the Padé approximation method. From the plot there is a clear band gap between 115 THz and 135 THz. Also shown in Figure 3 is a band plot calculated using a bandsolver eigenmode calculator. The relevant constants used were taken for the gap mode, such as the effective index and the hole size and period. The shape of the graph matches, unfortunately because the bandsolver does not take loss into consideration the band plot and the band gap were shifted down quite a bit and only after artificially inflated the effective index do we arrive back at our real band plot.



**Figure 2 - Graph of the decay time and effective index at 87 THz for various starting permittivities as a function of dielectric thickness. As the thickness of the material decreases the effective index increases however the decay time is nearly independent of thickness, so we can choose a thin layer high dielectric material to optimize our device with minimal sacrifice to the lifetime of the photons.**

We have focused at a wavelength of 87 THz which is far from the plasma frequency and because it is in the mid-infrared is located in area with a flat dispersion. This is important because this center frequency has a linewidth of 7 THz and we want to be certain that the optical response of the device is flat over the region of its operation. As one moves even lower in energy the properties of the device do not change, they scale accordingly. And so by doubling the period we can double the center frequency of the cavity mode. In designing the device we first realized that by squeezing light we could increase the effective index of the material, thus slowing it down [15]. However by decreasing the thickness of the dielectric layer, the percent of field energy in the metal increases, thus increasing the loss and decreasing the lifetime. Therefore, higher index dielectrics can increase effective index without a significant reduction of the lifetime (Figure 2). So we chose a dielectric thickness of 12 nm, although layers as thin as 3 nm have been shown [16], and a high dielectric constant of 9. The effective index of the gap mode increases with decreasing gap thickness which effectively causes the mode to have a very slow velocity. This property is desired because it helps increase the Purcell factor for the cavity, for if the mode travels slowly through the gap, it will last for a long time in the cavity and have a higher chance to interact with a molecule there. The gold metal cladding layers were each 200 nm thick, many times larger than the skin depth, so as to minimize the energy loss to the upper surface.

For our plasmon polariton crystal (PPC) with a defect, a 3D FDTD simulation was used to calculate the wavelength of the resonant modes and the cavity's Q-factor. First we simulated and calculated the bandgap for the crystal (Figure 3). Bloch boundary conditions were used around a unit cell consisting of 2 holes with one hole in the center and a quarter hole at each of the corners. Then we built our cavity by placing a 40 nm defect hole in PPC with a hexagonal array of 450 nm holes and a period of 500 nm. The time evolution of the field is analyzed by first plotting the log of the  $E_z$  field versus time (Figure 4). The peaks are detected and a line is fitted with decay time  $\tau = -1/\text{slope}$ . The quality factor is the angular frequency multiplied by the decay time,  $Q = \omega * \tau$ .

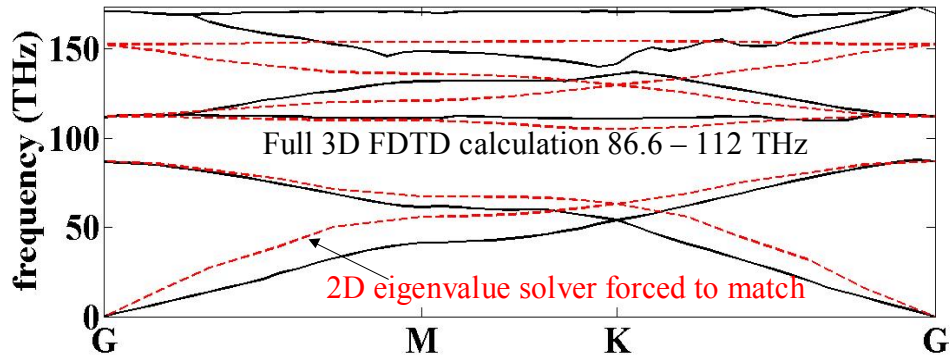


Figure 3 - 3D FDTD band plot simulation of the PPC, hole diameter of 450 nm, period of 500 nm, shows a clear bandgap between 86.6 - 112 THz.

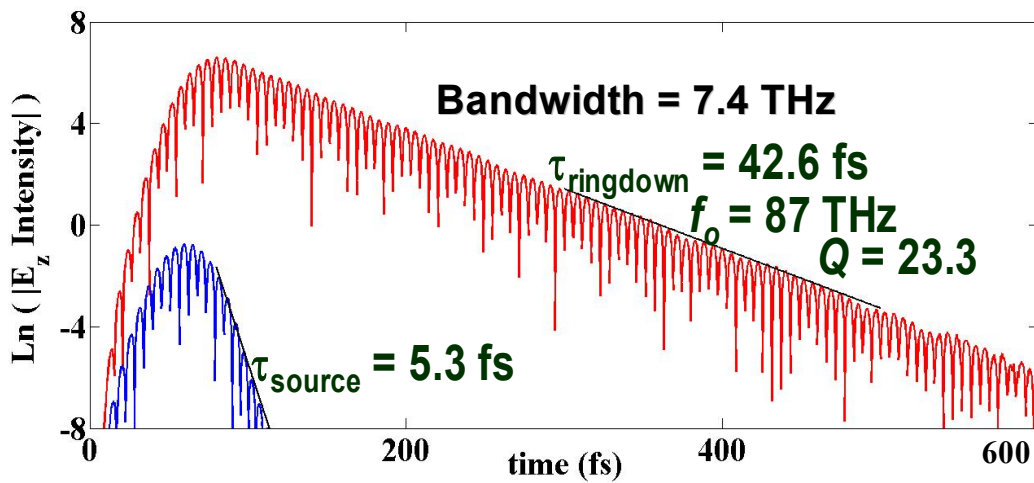


Figure 4 - Cavity ringdown plot for the fundamental mode, 87 THz, of the crystal showing both the source decay and the mode decay. With a decay time of 42.6 fs the quality factor for the cavity is 23.3 with a spectral line width of 7.4 THz.

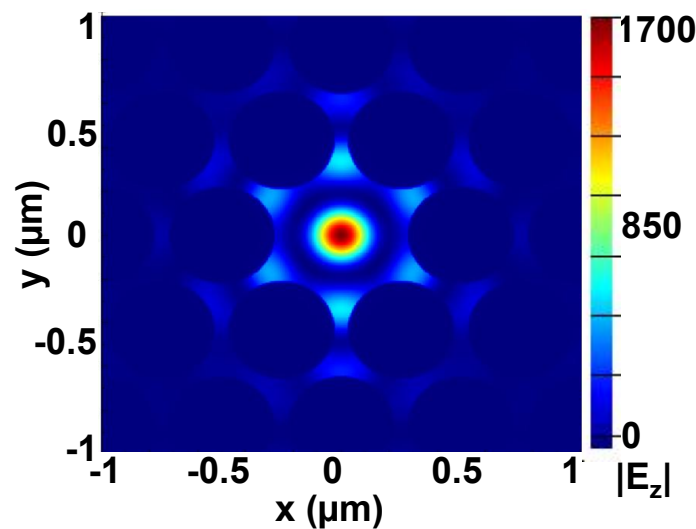


Figure 5 -  $E_z$  mode profile (87 THz) of the center of the cavity at  $z = 0$  nm, the mode is intensely squeezed in the cavity (one hole missing), with a maximum intensity inside the cavity approaching 1700 times the incident field.

Our simulation shows a Q-factor of 23.3 with the fundamental resonant frequency of 87 THz. The best photonic crystals at a wavelength of 1.575  $\mu\text{m}$  experimentally produce p values of  $1.9 \times 10^5$  with a Q of  $4.5 \times 10^4$  [17]. Theoretical maximums are on the order of  $10^6 - 10^7$  for ultra high Q structures with a tight linewidth of hundreds of MHz [18]. Our device at a wavelength of 3.45  $\mu\text{m}$  shows a Purcell value of  $4.8 \times 10^6$  with a  $\Delta f$  of 7.4 THz showing that we can squeeze a lot of light, with a broad spectral range, into a small volume. The simulation shows a mode confinement in a 20 nm radius disc in the cavity. The electric field enhancement is  $\sim 10^3$  so the intensity of light in the cavity reaches  $\sim 10^6$  (Figure 5).

Analogously to the sensor this high Purcell constant cavity could be used as a laser if the medium inside can compensate for the high loss introduced by the proximity of the metal cladding layers to the dielectric layer. Simulation shows that a gain material with a gain value of 5500  $\text{cm}^{-1}$  satisfies lasing condition, and a coherent stabilization of the electromagnetic radiation inside the cavity. Similar to surface plasmon [19] lasers this device would emit light in the Terahertz frequency.

Another critical feature of this device is that it can be easily coupled to from the outside; a property most useful for building a sensor or a laser. The cavity not only exhibits very intense energy density inside, it also shows a column of energy emanating from the center up through the 40 nm diameter defect hole and stays sub-diffraction at least 500 nm above the top of the crystal (Figure 6). So, theoretically it would be possible to optically pump the micro-cavity by coupling back through the column thus enabling energy to build up inside. Since the column runs the full length of the device, one could pump from one side and the cavity could emit through the other. This column also allows the passage of media either gaseous or liquid to be passed through the cavity with its contents scanned for certain molecules.

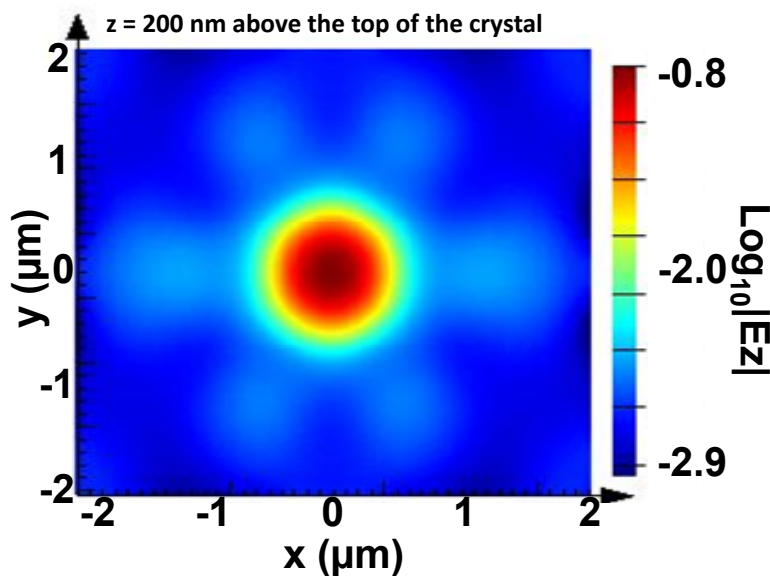
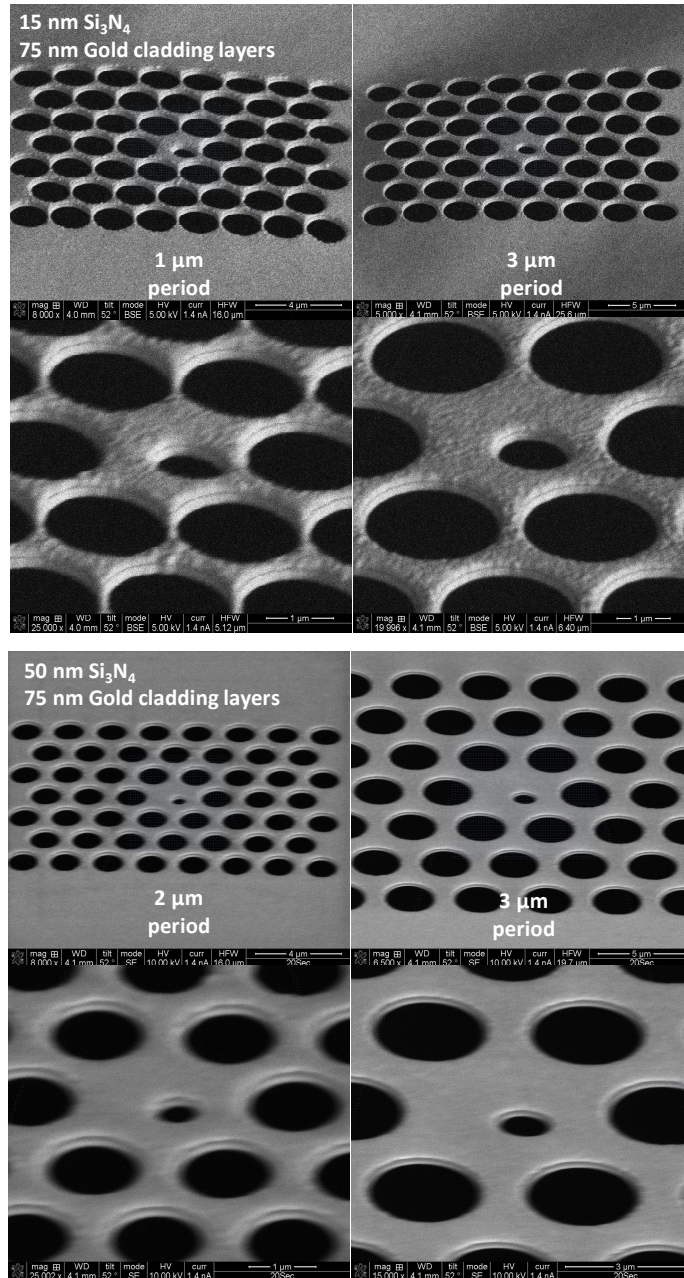


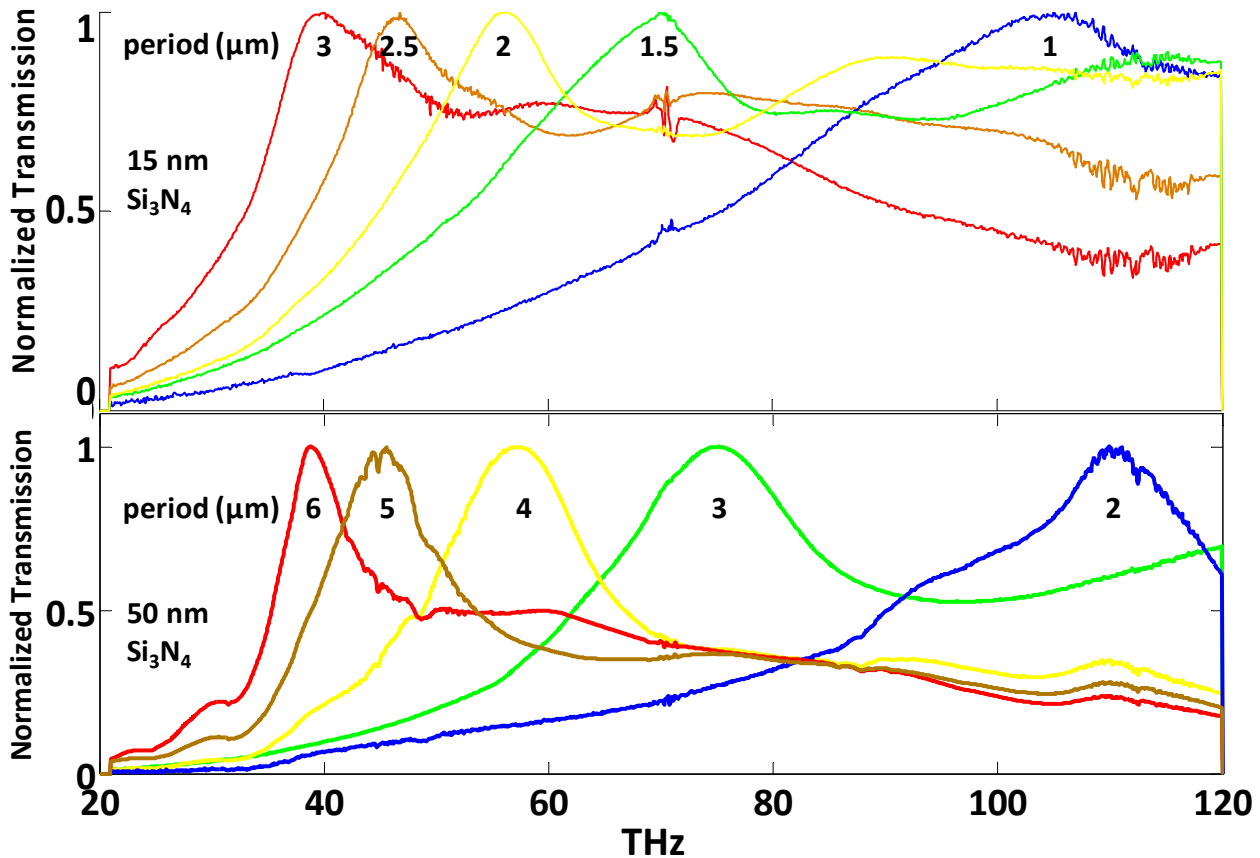
Figure 6 - The  $E_z$  intensity of an x-y slice 200 nm above the crystal, there is a column of energy that emits from the cavity defect into the far field. Because the cavity couples well to the far field it will also be possible to couple back into the cavity.

### 3. FABRICATION AND CHARACTERIZATION

In order to fabricate these devices we started with commercial silicon nitride ( $\text{Si}_3\text{N}_4$ ) membrane (15 nm and 50 nm) TEM grids from Kurt Lesker. After adequate cleaning, 75 nm of gold is deposited on either side of the membranes and a focused ion beam (FIB) is then used to make the patterns through the free standing MDM membranes. The photonic crystal hole sizes and the cavity defect hole scale approximately with the period such that the linear geometric ratios remain constant. The difference in hole size to period ratio from period to period are a result of different etchant rates of the FIB for the different size scales.



**Figure 7 – SEM images of representative of free standing Plasmonic Photonic Crystal devices of both 15 and 50 nm  $\text{Si}_3\text{N}_4$  dielectric thickness. The gold cladding layers are 75 nm thick each and the hole diameters and cavity defect diameter scale with the period.**



**Figure 8 – Transmission measurements taken with an FTIR microscope for devices with 15 nm and 50 nm dielectric thickness. The period for the 15 nm device ranges from 1 to 3 μm and for the 50 nm device from 2 to 6 μm. Both sets of devices show a characteristic red shift and linewidth change for change in period.**

The devices were then characterized using an FTIR microscope so that only one device was illuminated at a time. Spectra were taken and the averaged over 128 scans in transmission mode for each period and the results were plotted and compared in figure 8.

The FTIR microscope illuminates with normal incidence focused onto the sample with a diffraction limited spot size. The aperture of the microscope was set to 100 μm by 100 μm so that maximum intensity would reach the samples. The light is then collected through the other side in transmission mode and measured with a cooled MCT detector that is integrated with the FTIR. In this way isolated devices can be characterized without any cross talk or interference from neighboring devices.

First the microscope is calibrated to collect the maximum amount of energy through the sample, then a background is collected and finally the spectra of the PPC structures are taken. The source is a hot wire that emits in the infrared and passes through the microscope and back into the FTIR to be detected. The devices clearly have a resonance that depends both on the crystal period and the thickness of the dielectric. Free standing membranes were used to minimize the loss due to the presence of a substrate. Because the devices with smaller periods also have smaller holes the energy penetrating them will be less, and so the data is normalized to the peak maximum to show their location more accurately on the same scale.

The devices show a characteristic red shift for an increase in period, such that by doubling the period one can double the center frequency of the resonance. Moreover by decreasing the dielectric thickness in the MDM one can further squeeze



the mode such that longer wavelength excitation energy can be squeezed to an even smaller volume. The center frequency of the resonance has been further red shifted by the decrease in dielectric thickness.

#### 4. CONCLUSIONS

These metal-dielectric-metal (MDM) sandwich structures with a photonic crystal cavity defect have been shown to theoretically squeeze mid-infrared light down to the order of nm with a field enhancement approaching 10,000. Because of the low Q factor of the cavity the linewidth of the resonance is broad enough (THz) to sufficiently capture enough of a molecule's absorption spectra to make an accurate identification without the need for tags, labels, functionalization, or surface modifications. Even though the quality of the cavity is low, because the volume is also small, the Purcell constant (interaction strength between the cavity and the molecule) is still high enough for single molecule sensitivity.

The devices were fabricated using free standing  $\text{Si}_3\text{N}_4$  membranes which were then coated on both sides with gold. An FIB was used to make the patterns and an FTIR microscope was used to characterize the devices. The resonance peak is red-shifted with increasing period and also with a thinner inner dielectric membrane. The optical mode is indeed further squeezed by the thinner dielectric core where long wavelength light can have a very strong interaction with a molecule. As we move into the future these devices will help us gain insight at the fundamental limits of analytical chemistry, by understanding and better characterizing the behavior and vibration modes of single molecules.

#### REFERENCES

- [1] Federici J. F., et. al., "THz imaging and sensing for security applications—explosives, weapons and drugs," *Semicond. Sci. Technol.* **20**, S266 (2005).
- [2] Ferguson B. and Zhang X. C., "Materials for terahertz science and technology," *Nat. Mater.* **1**, 26 (2002).
- [3] Ho L., Pepper M., Taday P. F., "Terahertz Spectroscopy Signatures and fingerprints," *Nat. Photonics* **20**, 541 – 543 (2008).
- [4] Tonouchi M., "Cutting-edge terahertz technology," *Nat. Photonics* **1**, 97 (2007).
- [5] Woodward R. M., et. al., "Terahertz pulse imaging in reflection geometry of human skin cancer and skin tissue," *Physics in Med. And Bio.* **47**, 3853-3863 (2002).
- [6] Nakajima S., et.al., "Terahertz imaging diagnostics of cancer tissues with a chemometrics technique," *Appl. Phys. Lett.* **90**, 041102 (2007).
- [7] Dong-Kwon Lim, et. al., "Nanogap-engineerable Raman-active nanodumbbells for single-molecule detection," *Nature Materials* **9**, 60 - 67 (2010).
- [8] Singh-Zocchi M., et. al., "Single molecule detection of DNA hybridization," *PNAS* **100**, 13 (2007).
- [9] Armani A. M., et. al., "Label-Free, single-molecule detection with optical microcavities," *Science* **317**, 783 – 787 (2007).
- [10] Enders D. and Pucci A., "Surface enhanced infrared absorption of octadecanethiol on wet-chemically prepared Au nanoparticle films," *Appl. Phys. Lett.* **88**, 184104 (2006).
- [11] Adato R., et. al., "Ultra-sensitive vibrational spectroscopy of protein monolayers with plasmonic nanoantenna arrays," *PNAS*, **106**, 46, (2009).
- [12] Gelfand R. M., Bruderer L., and Mohseni H., "Nanocavity plasmonic device for ultrabroadband single molecule sensing," *Optics Letters* **34**, 1087, (2009).
- [13] Krauss T. F., "Photonic crystals: Cavities without leaks," *Nat. Mater* **2**, 777 - 778 (2003).
- [14] Joannopoulos J. D., Johnson S. G., Winn J. N., and Meade R. D., [Photonic Crystals: Molding the Flow of Light (Second Edition)]. Princeton University Press, February 2008.
- [15] Hibbins A. P., et. al., "Squeezing Millimeter Waves into Microns," *Phys. Rev. Lett.* **92**, 143904 (2004).
- [16] Miyazaki H. T., Kurokawa Y., "Squeezing visible light waves into a 3-nm-thick and 55-nm-long plasmon cavity," *Phys. Rev. Lett.* **96**, 067401 (2006).
- [17] Akahane Y., et. al., "High-Q photonic nanocavity in a two-dimensional photonic crystal," *Nature* **425**, 944-947 (2003).
- [18] Song B., et. al., "Ultra-high-Q photonic double-heterostructure nanocavity," *Nat. Mater* **4**, 207 - 210 (2005).
- [19] Zheludev N. I., et.al., "Lasing Spaser," *Nature Photonics* **2**, 351 - 354 (2008).