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Final LDRD report: Enhanced spontaneous emission rate in Visible III-nitride LEDs using 3D photonic crystal cavities

Arthur J. Fischer, Ganapathi S. Subramania, Yun-Ju Lee, Daniel D. Koleske, Qiming Li, George T. Wang, Ting S. Luk, Kristine W. Fullmer, Anthony J. Coley.

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Arthur J. Fischer, Kristine W. Fullmer, Anthony J. Coley
Departments of Semiconductor Material and Device Sciences

Ganapathi S. Subramania, Ting S. Luk
Photonic Microsystem Technologies

Yun-Ju Lee
Electronic Materials and Nanostructures

Daniel D. Koleske, Qiming Li, and George T. Wang
Advanced Materials Sciences

Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS1086

Abstract

The fundamental spontaneous emission rate for a photon source can be modified by placing the emitter inside a periodic dielectric structure allowing the emission to be dramatically enhanced or suppressed depending on the intended application. We have investigated the relatively unexplored realm of interaction between semiconductor emitters and three dimensional photonic crystals in the visible spectrum. Although this interaction has been investigated at longer wavelengths, very little work has been done in the visible spectrum. During the course of this LDRD, we have fabricated TiO_2 logpile photonic crystal structures with the shortest wavelength band gap ever demonstrated. A variety of different emitters with emission between 365 nm and 700 nm were incorporated into photonic crystal structures. Time-integrated and time-resolved photoluminescence measurements were performed to measure changes to the spontaneous emission rate. Both enhanced and suppressed emission were demonstrated and attributed to changes to the photonic density of states.

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NOMENCLATURE

1D	one dimensional
3D	three dimensional
DBR	distributed Bragg reflector
DOE	Department of Energy
CdS	cadmium sulfide
CdSe	cadmium selenide
DOS	density of states
GaN	gallium nitride
LED	light emitting diode
MOCVD	metalorganic chemical vapor deposition
MOVPE	metalorganic vapor phase epitaxy
PC	photonic crystal
PDOS	photonic density of states
PL	photoluminescence
SNL	Sandia National Laboratories
TIPL	time-integrated photoluminescence
TRPL	time-resolved photoluminescence
Q	quality factor
QD	quantum dot
QW	quantum well

1. INTRODUCTION

For most light sources in use today, the photon emission rate is determined by the emitting material such that photons are emitted with a fixed and characteristic time constant, called the radiative recombination rate, which is often considered to be a fundamental property of the material. However, it has long been known that the radiative recombination rate can be changed by altering the electromagnetic environment around the emitter, for example by placing it into an optical cavity¹. Enhancement or suppression of spontaneous emission has been studied in the past but primarily for long wavelength emitters ($\lambda > 700$ nm) and typically in one-dimensional (1D) cavities. Although 1D and two-dimensional (2D) cavities can be easy to fabricate and test, they have severe problems with leakage of light in directions with no optical confinement. This problem can be overcome by using a three dimensional (3D) photonic crystal to control light emission in all directions such that total control of light emission is possible. The main goal of this LDRD was to investigate the spontaneous emission enhancement at visible wavelengths using three-dimensional photonic crystal cavities.

The enhancement or suppression of photon emission can be understood in terms of a Fermi's golden rule argument. Fermi's golden rule is given by the following equation:

$$\lambda_{if} = \frac{2\pi}{\eta} |M_{if}|^2 \rho_f$$

where λ_{if} is the transition probability for a particular transition, M_{if} is the matrix element and ρ_f is the density of final states. This means that the photon emission rate is proportional the final density of photon states. If we can increase or decrease the photonic density of states (PDOS), we can increase or decrease, respectively, the rate of photon emission. Figure 1 shows the

Figure 1 : Calculated photonic density of states for a face centered cubic structure (adapted from ref [2]).

calculated PDOS in 3D for a photonic crystal with a face centered cubic structure². In 3D, the PDOS has a complicated structure with many sharp dips and peaks. The dashed line shows the density of states for an emitter in free space. The arrows show the photonic bandgap and the pseudogap, which are regions with a reduced density of states where decreased photon emission is expected. Other regions, such as those at the edge of the photonic bandgap, have an enhanced PDOS and are expected to show enhanced photon emission. By designing the appropriate 3D photonic crystal structure, photon emission can be controlled by tailoring the PDOS for a particular application. For example, one can use the enhanced PDOS at the edge of the band gap to increase the radiative recombination rate such that it can better compete with non-radiative recombination to make a light source with higher efficiency.

A variety of materials were investigated for the fabrication of 3D photonic crystals for use in the visible spectrum. For photonic crystal fabrication, a material with a high index of refraction and high transparency is desirable. Although many materials such as silicon have a very high index ($n = 3.6$) in the infrared, the index of refraction for almost all materials is much lower at visible wavelengths. TiO_2 was selected as one of the most promising candidate for a variety of reasons. Figure 2 shows a plot of the index of refraction and the extinction coefficient of TiO_2 as a function of wavelength across the visible spectrum. It is evident that TiO_2 has an index as high as 2.6 and is also transparent from 400 nm to 700 nm. Although a small amount of absorption is present on the extreme blue end of the visible spectrum, we have shown through the course of this LDRD that TiO_2 -based photonic crystals can be used for wavelengths as short as 400 nm. TiO_2 can be deposited via sputtering or via sol-gel spin coating which allows flexibility during the fabrication process. For the reasons discussed here, the majority of our 3D photonic crystals were fabricated using TiO_2 .

Figure 2 : TiO_2 index of refraction and extinction coefficient plotted vs. wavelength.

2. ONE DIMENSIONAL PHOTONIC CRYSTAL CAVITIES

A great deal can be learned from studying the simpler case of one-dimensional (1D) photonic crystal cavities. As a part of this LDRD, we developed a method of fabricating one-dimensional GaN microcavity samples with dielectric distributed Bragg reflectors (DBR) formed from alternating quarter-wave layers of HfO_2 and SiO_2 . Although these types of 1D cavities are used routinely at longer wavelengths for vertical-cavity surface-emitting lasers, very little work has been done in the visible and, in particular, only a handful of papers report the incorporation of GaN into a 1D cavity³⁻⁵. Although 1D cavities are simpler to fabricate and allow us to study interesting cavity related changes to photon emission, these samples are limited by the fact that they confine light in only one dimension.

In order to fabricate GaN microcavities, very thin (150 – 400 nm) GaN epilayers are grown by metalorganic vapor phase epitaxy (MOVPE) on sapphire substrates. A $\text{HfO}_2/\text{SiO}_2$ DBR is then deposited using e-beam evaporation followed by a thick plated Au layer. This sample is then soldered to a metalized silicon host wafer. Laser lift-off⁶ is then used to remove the sapphire substrate from the GaN epilayers. Laser lift-off is a process where a high power laser is focused on the interface between the GaN and the sapphire such that the gallium-nitrogen bond is broken liberating nitrogen and leaving behind a very thin layer of gallium. This method allows the sapphire substrate to be removed in a controlled fashion. In order to create a cavity with the desired resonance, further etching of the GaN layer is often required to create the proper cavity thickness. A second $\text{HfO}_2/\text{SiO}_2$ DBR is then deposited to form the cavity. The left side of Fig. 3 shows a cross-sectional scanning electron microscope (SEM) image of a GaN microcavity fabricated using this procedure. The right side of Fig. 3 shows a schematic diagram together with the calculated electric field for the structure. This type of cavity effectively traps light inside the structure as shown by the peaked electric field inside the cavity.

Reflectivity measurements were performed for a GaN microcavity sample with two 8 pair dielectric DBR mirrors as shown in Fig. 4. The dashed line shows the calculated reflectivity spectrum while the red and blue curves show a high resolution (blue) and a low resolution scan

Figure 3 : Cross-sectional scanning electron microscope image of a GaN microcavity (left). Schematic diagram of the same cavity together with the calculated electric field (right).

Figure 4 : Experimental reflectivity spectra of an 8 pair GaN microcavity sample plotted together with the calculated reflectivity spectrum (dashed line).

of microcavity reflectivity. The dip in the spectrum shows the cavity resonance at 365 nm which is very close to the band gap of GaN. The linewidth of this resonance yields a cavity quality factor (Q) of about 150. We have also fabricated samples with higher reflectivity DBRs which showed a cavity resonance at 329 nm with a cavity Q of ~ 500 (data not shown).

Photoluminescence (PL) measurements were performed for these 1D cavity samples. Time-integrated photoluminescence (TIPL) shows emission primarily at a wavelength near the cavity resonance for each sample with an emission intensity much lower than that of a control GaN layer which was not incorporated into a cavity. Time-resolved photoluminescence (TRPL) was also performed to measure the luminescence decay time for microcavity samples compared to control samples with no cavity. For these experiments, femtosecond pulses with a wavelength of 325 nm from an optical parametric amplifier which was pumped by an amplified Ti:S were used to excite luminescence in the GaN semiconductor emitter. A streak camera system with a 15 ps resolution was used to measure the luminescence decay time. Figure 5 shows TRPL data for an 8 pair GaN microcavity sample (red curve) compared to a control GaN epilayer with no cavity (black curve). The PL decay time for the reference GaN layer is much faster than for the GaN microcavity sample. In this case the microcavity is reducing the radiative recombination rate and

suppressing the luminescence from the GaN emitter. This can be interpreted as a reduction in the PDOS due to the 1D cavity which acts to both reduce the overall emission as well as change the luminescence decay time.

This 1D example clearly shows that it is possible to dramatically alter the photon emission rate by placing an emitter inside a 1D photonic crystal cavity. These structures are also interesting in their own right since high Q cavities can lead to new physics studies such as cavity polariton dynamics^{7,8} and Bose-Einstein condensation of polaritons in a solid state system^{3,9}. For this LDRD, we targeted incorporation of emitters into 3D photonic crystals. Although the emission change in 1D is dramatic, we have measured PL normal to the DBRs layers in order to show these changes. Since this is a 1D structure, light clearly can leak out of this structure parallel to the DBR layers. In order to demonstrate photon emission control in all direction, we have fabricated 3D photonic crystal structures.

Figure 5 : Time-resolved photoluminescence data for a GaN microcavity sample (red curve) compared to a reference GaN layer with no cavity (black curve).

3. FABRICATION OF LOGPILE THREE DIMENSIONAL PHOTONIC CRYSTALS

Of the various types of 3D photonic crystal cavities, the logpile structure was chosen due to its capability for demonstrating a full 3D bandgap with only a moderate index of refraction. As mentioned in the introduction, we chose TiO_2 due to its transparency across the whole visible spectrum and its relatively high index which is in the range from 2.3 to 2.7 depending on wavelength and material density. If one considers the inverse opal structure, which has the advantage of much easier fabrication, this photonic crystal requires an index greater than $n = 2.9$ in order to open a band gap¹⁰ in all three dimensions. In contrast, the logpile structure allows one to create a full 3D bandgap with an index as low as $n = 1.9$ ¹¹. Since our goal was to demonstrate spontaneous emission control at visible wavelengths where the indices are typically less than $n = 2.7$, we chose to fabricate the logpile structure. Photonic bandstructure of a logpile photonic crystal composed of TiO_2 rods with a refractive index $n = 2.3$ shows a complete bandgap in the reduced frequency range of 0.43 to 0.446 as shown in Fig. 6.

Figure 6 : (a) Calculated photonic band diagram for a TiO_2 logpile structure. (b) Diagram showing 3D bandstructure direction labels. (c) Schematic of logpile structure.

Logpile 3D photonic crystals are fabricated using a layer-by-layer fabrication procedure. Although previous logpile structures have been demonstrated, the structures fabricated for this project are specific for use in the visible spectrum which means they have much smaller lattice constants. In order to fabricate a logpile 3D photonic crystal, TiO_2 is deposited either using sputtering, electron beam evaporation or via spin coating using a sol gel process. For the initial phases of this LDRD, sputtering and solgel technique was used. The sputtered TiO_2 has the advantage that the film has a higher density and thus a higher index of refraction. The ability to spin coat a sample with a thin layer of sol gel to form a TiO_2 layer greatly speeds up the processing. Electron beam lithography is used for patterning nanometer scale features and a dry plasma based etching is used to etch the TiO_2 . This process is repeated for each layer. In a layer-by-layer fabrication process, accurate planarization of each level is critical and is challenging at small dimensions. A new planarization process was developed for the fabrication of TiO_2 woodpile structures where the trenches are filled with SiO_2 prior to the application of the planarizing fluid¹². This process improves the global uniformity from around 25% to better than 90%. However, there were some challenges to this approach. Sputtered TiO_2 was difficult to process owing to long deposition times combined with low etch rate and selectivity to the resist etch mask (PMMA). On the other hand, nano and micro pinholes in the solgel film resulted in film delamination during subsequent processing. To address these issues we utilized electron beam evaporation technique. By evaporating a TiO_2 target obtained from Cerac in an O_2 flow maintaining a pressure of 2×10^{-5} Torr, we were able to deposit a film with good optical quality. This mitigated the problems of low etch selectivity of TiO_2 and also reduced the number of processing steps. In either case, the fabrication process is time consuming as each layer must be patterned separately. However, this does allow for a great deal of flexibility for writing complicated patterns which is particularly useful when fabricating photonic crystal cavities.

Figure 7 shows scanning electron microscope (SEM) images of a 9 layer TiO_2 3D logpile photonic crystal structure. The left SEM image shows a top view of the structure showing a lattice constant of 250 nm and features sizes as small as 70 nm. The right SEM image shows a cross-sectional cut through the layers where nine layers are visible. Figure 8 shows the reflectivity spectrum for a 9 layer 3D TiO_2 logpile photonic crystal sample at normal incidence to the sample surface. The reflectivity spectra changes slightly depending on whether the

Figure 7 : Scanning electron microscope images of a nine layer 3D logpile photonic crystal sample fabricated from TiO_2 .

electric field of the incident light is parallel or perpendicular to the direction of the logs in the top layer of the structure. The dependence is not large and for simplicity only one polarization is shown (E-field perpendicular to logs in top layer). The dashed line shows the theoretical reflectivity spectrum which was calculated using commercial finite-difference time-domain software. The overall agreement between experiment and theory is reasonably good but not perfect. The theory reproduces the general shape of the reflectivity spectrum, but not the exact magnitudes or all of the features. This difference is due to slight inhomogeneities in the structure as well as to the fact that the features in these structures came out a bit thinner than intended (70 nm rather than 100 nm). However, the fact that we see greater than 80% reflectivity indicates that the morphology of these samples is quite good since the spot size for our reflectivity measurements is on the order of 100 microns. This data also shows that TiO₂ 3D logpile structures can be used across the whole visible spectrum since the band gap extends from about 380 nm to 500 nm. Over the course of this LDRD we have improved our nanofabrication capability such that smaller features sizes are now possible allowing us to operate at much shorter wavelengths. These structures are the shortest wavelength logpile photonic crystals that have ever been demonstrated.

A variety of different photonic crystals with defect cavities were fabricated as a part of this project. Cavities were incorporated into nine layer samples by fabricating the first four layers and then leaving out part of the structure of the fifth layer to make a defect. Finally, we fabricate the remaining four layers to complete the cavity. Finite-difference time-domain calculations were performed to simulate the fields inside of defect cavities. Defect cavities were designed based on our simulations using a large cavity Q as one of the main metrics to determine if a cavity would be suitable for spontaneous emission enhancements. Cavity Q is important since it

Figure 8 : Reflectivity data for a 9 layer 3D TiO₂ logpile photonic crystal sample.

is directly proportional to the Purcell enhancement expected to the radiative decay rate such that higher Q cavities will give larger changes in the decay rate. The other important parameter is the mode volume since a smaller mode volume will give a larger spontaneous emission enhancement. We chose to use air defect cavities rather than high index defect cavities since this allows us to incorporate emitters into the resulting air space after the photonic crystal cavity is completely fabricated.

Figure 9 shows scanning electron microscope (SEM) images of three different defect cavities which were fabricated as a part of this project. The base lattice constant for these structures is 220 nm which will yield a photonic band gap in the visible (~ 500 nm wavelength) based on calculations. Fig. 9(a) shows a defect cavity with one whole rod removed where the Q of the cavity is expected to be about 30. The mode volume in a 5×5 supercell for this case is $\sim 2(\lambda/n)^3$. Mode volumes can be reduced by a factor of 5-10 with other defect cavity geometries as shown in figures 9(b) and 9(c) with calculated Qs (mode volumes) of 250($\sim 0.25(\lambda/n)^3$) and 300($\sim 0.4(\lambda/n)^3$), respectively. The underlying rods in the logpile structure are also visible in these SEM images as vertical lines which are dimmer with lower contrast since they are underneath the top layer. Subsequent processing steps cover these defect cavities so that SEM images can only be taken during processing of the specific layer containing the missing pieces forming the defect cavity.

Over the course of this three year LDRD we have dramatically improved our ability to fabricate 3D logpile photonic crystal structures. We have transferred our process such that we can fabricate structures from TiO_2 for use in the visible and we have reduced feature sizes such that we can demonstrate stop bands across the whole visible spectrum. Once we have incorporated emitters into these structures, we have the necessary tools to investigate spontaneous emission control in 3D and at visible wavelengths.

Figure 9 : Scanning electron microscope images of three different defect nanocavities in a TiO_2 3D logpile structure.

4. INCORPORATION OF EMITTERS INTO PHOTONIC CRYSTALS

Since the goal of this LDRD is to study spontaneous emission enhancement, we have incorporated a variety of emitters into 3D photonic crystal structures. Our original plan was to incorporate nanoscale InGaN post light emitting diodes (LEDs). Since GaN is an important material for high efficiency semiconductor based lighting, incorporation of InGaN emitters should allow one to demonstrate enhanced optical efficiency by increasing the radiative lifetime. We designed and fabricated very small, sub-micron InGaN post LEDs with diameters as small as 100 nm using electron beam lithography. Special LED epitaxial material with very thin p-GaN was developed for this purpose. The standard thickness of the p-GaN for our InGaN LEDs is about 250 nm. The material used for this work had a p-GaN thickness of 50 nm which positions the emitter much higher on the post allowing for easier incorporation into a 3D logpile structure. Unfortunately, thin p-GaN can cause shorting problems in LEDs and a significant amount of development work was done to produce LEDs with thin p-GaN for incorporation into defect cavities in order to avoid these shorting problems.

Figure 10(a) shows a SEM image of a close-packed array of InGaN post LEDs on a triangular lattice. The post diameter is about 200 nm for these devices and the lattice constant is 315 nm. Each of these post LEDs has a disk of Ni metal on top which forms an Ohmic contact the p-GaN layer. We have developed an etch mask process where Ni can be used both as a contact material and as an etch mask for the Cl-based reactive ion etching used to form the post LEDs. The n-type contact for these devices is outside of the image area. Figure 10(b) shows an optical microscope image of electroluminescence for one (or a small number) of InGaN post LEDs for a close-packed array of emitters in a triangular lattice. The electrical probe used to contact the p-metal on the nanopost LEDs is shown as a dark region on the bottom of the image. The electroluminescence image shows four lobes of radiation out of six total lobes where two are blocked by the probe. The light is emitted from under the probe and the lobes are formed from the interaction between the triangular arrays of posts, which form a photonic lattice of their own, and the light emitted from the InGaN quantum wells. The six fold symmetric emission pattern is a direct result of the triangular lattice of post LEDs. This image shows that nanoscale LEDs can emit strong blue light under electrical injection. Figure 10(c) shows another SEM image of a more loosely packed array of submicron InGaN post LEDs where each LED is spaced 10 lattice constants apart on a square grid. The square grid and lattice constant of 220 nm were chosen to

Figure 10 : (a) SEM image of a close packed array of InGaN post LEDs. (b) Optical microscope image of electroluminescence from the device shown in Fig 9(a). (c) SEM image of a loose packed array of InGaN post LEDs.

match up to the logpile structures currently be fabricated for this project. The etch depth for these LEDs is about 500 nm producing posts that are sufficiently tall to position the quantum well inside of a defect cavity in a visible 3D logpile structure fabricated from TiO_2 .

Incorporation of InGaN post emitters into 3D photonic crystals proved to be a very difficult challenge for a number of technical reasons. The original plan of fabricating a 3D photonic crystal around an existing array of post LEDs proved challenging since the photonic crystal processing steps rely on planarization of the surface to create smooth surfaces for e-beam patterning. During the course of this project we developed alternative methods of incorporating emitters. The most effective method developed was the incorporation of CdS and CdSe quantum dots (QD) which are available commercially for wavelengths from 450 nm to 700 nm. In order to incorporate QDs the TiO_2 surface is first coated with 3-mercaptopropyltrimethoxysilane and then baked to form a self-assembled monolayer^{13,14}. QDs with the appropriate emission wavelength can then be chemically attached to form a single monolayer of QD emitters. This method allows one to attach a single monolayer of QDs to all surfaces of a TiO_2 logpile photonic crystal. This method leads to modest luminescence enhancements which are limited by the exact placement of the emitters inside the photonic crystal.

In order to improve the placement of QD emitters inside the photonic crystal as well as to increase the total number of emitters a new process was developed. The TiO_2 photonic crystal is first filled with a silica-based aerogel and then the QDs are attached to the aerogel. During the aerogel infiltration process¹⁵, the aerogel is applied via spin coating such that it wets the surface and fills the entire air volume of the photonic crystal. The aerogel has a very large surface area which can be functionalized allowing QD emitters to be attached. This results in a much larger number of QDs and increases the probability that some of the emitters are in the proper location within the photonic crystal to see enhanced luminescence. The largest enhancement and suppression of luminescence was observed for samples prepared in this manner.

Although the aerogel index is very low and close to air, the index change from $n = 1.0$ to $n = 1.1$ results in a small change to the optical properties of the photonic crystal. Figure 11 shows reflectivity curves before and after infiltration of aerogel for a four layer logpile structure.

Figure 11 : Reflectivity spectra for a four layer TiO_2 logpile 3D photonic crystal before and after infiltration with aerogel.

The same basic features remain after infiltration, but there is a red shift of the spectrum by about 8 nm due to the change in the low index material of the photonic crystal. It is interesting to note that the incorporation of quantum dots also changes the reflectivity in a measurable way, but the effect is even smaller than that observed due to the aerogel. Figure 12 shows SEM images of a four layer TiO_2 logpile structure before (left image) and after (right image) infiltration with aerogel. Note that the aerogel fills the structure to the top of the third such that virtually all of the air space is now filled with aerogel. This aerogel now serves as a very low index structure to which QDs can be attached.

Quantum dot incorporation is a valuable method of adding emitters to 3D photonic crystal structures as it allows us to investigate spontaneous emission control at visible wavelengths. As detailed in the next section, significant changes to the spontaneous emission rate were observed using quantum dot emitters.

Figure 12 : (left) SEM image showing logpile structure before infiltration with aerogel; (right) SEM images showing structure after infiltration.

5. ENHANCED LUMINESCENCE FROM EMITTERS IN 3D LOGPILE STRUCTURES

Photoluminescence (PL) measurements were performed to investigate changes to spontaneous emission for quantum dot emitters inside photonic crystal structures. Figure 11 shows time-integrated PL data for a five layer TiO_2 3D logpile photonic crystal sample which has been infiltrated with aerogel and CdSe quantum dots with emission at 625 nm. PL measurements were performed using a 532 nm source to excite luminescence in the CdSe QDs. Figure 13(a) shows the PL spectra for two different photonic crystal lattice constants compared to a reference QD sample with no photonic crystal (red curve). The blue and green curves show data for samples with lattice constants of 350 nm and 400 nm, respectively. The dashed lines indicate the position of the photonic bandgap for each lattice constant as determined from reflectivity measurements. For example, for the 350 nm lattice constant sample, the blue dashed line shows the shorter wavelength edge of the photonic bandgap at ~ 590 nm with the bandgap region extending to longer wavelengths. Similarly, the green dashed line shows the shorter wavelength edge of the photonic bandgap region for the 400 nm lattice constant sample beginning at ~ 635 nm. The quantum dot emission wavelength was selected to be 625 nm so that the emitter is inside the photonic bandgap for the 350 nm sample and outside the bandgap for the 400 nm sample. Suppressed emission is expected for emitters inside the photonic bandgap region since the photonic density of states in this region is lower than the free space density of photonic states. For regions at the edge of the photonic bandgap, enhanced emission is expected since the photonic density of states typically becomes large in this region. Our experimental data shows this since we see enhanced emission at 625 nm for the 400 nm sample and reduced emission for the 350 nm sample. Since the volume of emitting material is different between the reference sample and the photonic crystal sample, the PL data was scaled by the volume in order to obtain an accurate comparison between samples. Figure 13(b) shows the enhancement factor

Figure 13 : (a) PL data for a quantum dot emitter inside a TiO_2 logpile 3D photonic crystal, (b) enhancement factor showing enhanced and suppressed luminescence for a photonic crystal sample.

obtained by simply dividing the photonic crystal PL spectra by the reference spectrum. Enhancements as large as 3 times have been observed while suppression of the order of four times has also been observed. This data shows that both suppression and enhancement of spontaneous emission is possible by using TiO_2 logpile photonic crystal structures.

Time-resolved PL data was also measured for these samples in order to look for changes to the PL decay time. One problem with the interpretation based on time-integrated PL measurements is that it is difficult to decouple the enhancement to due radiative lifetime change inside the PC from improved light extraction.. TRPL allows one to unequivocally measure changes to the luminescence decay thereby demonstrating changes to the spontaneous emission rate. For these experiments, picosecond pulses with a wavelength of 405 nm from the second harmonic of a Ti:S laser were used to excite luminescence in the QD emitter. A streak camera system with a 15 ps resolution was used to measure the luminescence decay time. Figure 14 shows the time-resolved PL data for a 5 layer sample with a 625 nm emitter identical to the one shown in Fig. 13. The lifetime for the reference sample (black curve) is longer than the lifetime for the photonic crystal sample (red curve). This shows that the photonic crystal is acting to increase the radiative recombination rate. The data was fit to a single exponential with a weighting that favors the fast component of the data. The lifetime is reduced from 14.4 ns for the emitter with no photonic crystal to 7.1 ns for the emitter in the cavity. For a fixed non-radiative recombination rate, a faster lifetime means a faster photon emission rate and more total luminescence. Since the PL lifetime includes both radiative and non-radiative components this data is consistent with the factor of 1.5 times increase in PL at 625 nm as shown in Fig. 13. Through the use of time-resolved PL we have demonstrated that the changes observed are due to changes to the spontaneous emission rate. These changes to luminescence show that we are beginning to learn how to control photon emission processes at visible wavelengths.

Figure 14 : Time-resolved PL data for a TiO_2 3D logpile photonic crystal sample compared to a reference sample.

6. LOGPILE PHOTONIC CRYSTAL FABRICATED FROM GAN MATERIAL

When this LDRD was originally written, we proposed to use GaN as a material for photonic crystal fabrication since the index of refraction is relatively high ($n = 2.5$) and it is transparent across the visible spectrum. GaN is also an important material for solid state lighting applications. However, GaN is a hard, chemically inert material that is difficult to process and very little progress was made on direct fabrication of GaN 3D photonic crystal structures. However, very recently, we have developed a new method to produce logpile 3D photonic crystal structures made entirely from GaN.

We start with a GaN substrate grown by metalorganic chemical vapor deposition (MOCVD) and fabricate an SiO₂ logpile 3D photonic crystal structure using the layer-by-layer e-beam direct write approach described above. This structure which is the inverse of the final desired structure, can then act as a template for further MOCVD growth of GaN. GaN is grown at very high temperatures near 1000 C and SiO₂ has been shown to be able to withstand this temperature without degrading. Furthermore, GaN likes to nucleate growth on other GaN but not on SiO₂. Thus, by selecting the proper growth conditions, it is possible to grow GaN through the SiO₂ logpile structure. The SiO₂ template can then be removed with a simple hydrogen fluoride wet chemical etch, leaving behind a 3D logpile photonic crystal composed entirely of GaN material. Figure 15 shows a GaN 3D logpile structure produced using this approach. The lattice constant for these structures ranged from 260 nm to 300 nm. Reflectivity data from a GaN 3D photonic crystal structure is shown in Fig. 16 for samples with lattice constants of 280 nm and 300 nm. A very wide and broad stop band is observed from about 550 nm out to almost 800 nm. The stop band also shifts to shorter wavelength for the smaller lattice constants as expected.

The most exciting aspect of this new method of making photonic crystals is the possibility of demonstrating electrically injected 3D logpile photonic crystal structures, something which has never been done before. Since GaN is a semiconductor it can be doped n-type using Si and p-

Figure 15 : Scanning electron microscope images of an all GaN 3D photonic crystal structure showing a top view (left) and a partially cut cross-sectional view (right) where individual layers are visible.

type by using Mg. This means that during the growth of the GaN through the SiO₂ template it should be possible to grow the first half with n-type doping and then switch to p-type doping half way through the photonic crystal growth such that one can grow a pn junction. If this could be demonstrated it would allow for a relatively straightforward way to position an emitter inside a 3D photonic crystal and electrically pump carriers into that emitter. Due to the very recent nature of this work we have not yet demonstrated an electrically injected 3D photonic crystal light source, but we consider this to be an extremely promising area for future research.

Figure 16 : Reflectivity data for two different all GaN 3D logpile photonic crystal samples with lattice constants of 280 nm and 300 nm.

7. SUMMARY AND FUTURE WORK

During the course of this 3 year LDRD spontaneous emission control was investigated at visible wavelengths using three dimensional (3D) photonic crystal structures. We have expanded our ability to fabricate 3D logpile photonic crystal structures such that we can now fabricate structures for use at wavelengths as short as 400 nm. This required a significant reduction in the features sizes for these structures such that we have now demonstrated logpile photonic crystals with lattice constants as small as 220 nm and with features sizes as small as 70 nm. New processing procedures were developed so that we could fabricate 3D photonic crystals from TiO_2 which was selected and utilized as the most suitable material for the fabrication of structures in the visible. One-dimensional (1D) dielectric DBR cavities were also fabricated with GaN emitters inside as a test case to show modifications to the spontaneous emission rate. This work in 1D has led to interesting fundamental physics studies including the research on cavity polariton and strong coupling in wide bandgap semiconductor materials. This work has also led to follow-on funding from Basic Energy Sciences (BES) as a part of the newly funded Energy Frontier Research Center (EFRC) at Sandia.

In order to study changes to spontaneous emission, emitters were incorporated into a variety of different photonic crystal structures. For DBR cavities in 1D, the cavity was built around GaN emitters with an emission wavelength of 365 nm. Changes to the total PL intensity as well as to the luminescence decay time were measured for these samples. For 3D samples, we incorporated quantum dot (QD) emitters as well as fabricating whole structures from GaN. A process was developed using aerogel to incorporate QDs such that emitters would be placed in suitable locations within the structure to see changes to the spontaneous emission. Samples with incorporated QDs showed luminescence enhancements as large as three times as well as suppression of emission by up to a factor of four. Time-resolved photoluminescence measurements were used to demonstrate that these changes are due to a change in the radiative recombination rate which is in turn caused by photonic crystal related changes to the photonic density of states.

This work has opened up a number of interesting future research directions. With regard to TiO_2 3D photonic crystal cavities, it is known that emitter placement inside the structure is important for spontaneous emission control. This work highlights the need for extremely accurate placement of emitters inside photonic crystal structures. This together with higher quality factor cavities should allow a higher level of control over spontaneous emission. The work presented here demonstrates that this control is possible for wavelengths in the visible, but better control would clearly open up new application areas. Finally, our demonstration of all GaN 3D logpile photonic crystal structures is extremely promising research since there is a relatively clear path towards an electrically injected 3D photonic crystal light source based on existing GaN LED technology.

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APPENDIX A: LIST OF PUBLICATIONS, PRESENTATIONS, AND TECHNICAL ADVANCES

Refereed Publications:

- 1.) G. Subramania, Y.J. Lee, A.J. Fischer, and D.D. Koleske, “*Optical properties of TiO₂ logpile visible photonic crystals nanocavities in the near-UV and visible regime*,” accepted for publication in *Advanced Materials* (2009).
- 2.) G. Subramania, Y.-J. Lee, A. J. Fischer, T. S. Luk, D. Dunphy, and C. J. Brinker, “*Emission modification of CdSe quantum dots by titanium dioxide visible logpile photonic crystal*,” under review with *Applied Physics Letters* (2009).
- 3.) A.J. Fischer, G. Subramania, Y.J. Lee, T.S. Luk, J.R. Wendt, and D.D. Koleske, “*Improved InGaN LED Efficiency Using Photonic Crystal Patterning and Surface Plasmon Enhanced Emission*,” *ECS trans.* **13**, 5 (2008).
- 4.) G. Subramania, Y.J. Lee, B.A. Hernandez-Sanchez, A.J. Fischer, T.S. Luk, I. Brener, P.G. Clem, and T.J. Boyle, “*CdSe infiltrated TiO₂ based omnidirectional photonic crystals for visible light control*,” *Photonics and Nanostructures: Fundamentals and Applications* **6**, 12 (2008).
- 5.) G. Subramania, “*Planarization for three-dimensional photonic crystals and other multi-level nanoscale structures*,” *Nanotechnology* **18**, 035303 (2007).

Presentations:

- 1.) G. Subramania, Invited presentation at the MRS spring symposium San Francisco, CA, April 2009, “*Three-dimensional nanostructures for light manipulation at optical frequencies: A prototyping approach based on electron-beam lithography*.”
- 2.) G. Subramania, Invited Seminar, Albuquerque, IEEE/LEOS chapter at Center for High Technology Materials, University of New Mexico, November 2008, “*Nanostructured Materials: An Engineered Electromagnetic Environment for New Regimes of Light-Matter Interaction*.”
- 3.) G. Subramania, Oral presentation at OSA Plasmonic and Metamaterials Conference, Rochester, NY, October 2008, “*Chemoselective metal nanohole arrays for compact multiplexed chemical sensors*.”
- 4.) G. Subramania, Invited presentation at the SPIE Optics and Photonics meeting, August 2008, “*Emission from nanoscale light sources in two and three dimensional photonic crystals*”
- 5.) A.J. Fischer, Invited presentation at the Electrochemical Society Meeting, May 2008, “*Improved InGaN LED Efficiency Using Photonic Crystal Patterning and Surface Plasmon Enhanced Emission*.”
- 6.) G. Subramania, Invited seminar in the Dept. of Material Science, University of Illinois-Urbana Champaign, November 2007, “*Complete three dimensional gap photonic crystals at optical frequencies for light emission control*.”

- 7.) G. Subramania, Invited seminar in the Dept. of Material Science, Boston College, Boston, November 2007, "*Complete three dimensional gap photonic crystals at optical frequencies for light emission control.*"
- 8.) G. Subramania, Oral presentation at Photonics and Electromagnetic Crystal Structures (PECS)- VII conference, Long Beach, CA, April 2007, "*Omnidirectional photonic crystals for visible light control.*"

Technical Advances:

- 1.) G. Subramania, Y. J. Lee, A. J. Fischer, T. S. Luk, "Photonic crystal enhanced plasma based light sources" April 2007. SD# 10702

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