One-Dimensional and Three-Dimensional Photonic Crystals Created Using Atomic Layer Deposition

By

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Thesis directed by Professor Steven M. George

Abstract

Photonic crystals (PCs) manipulate the flow of light via Bragg reflections. Potential applications for such crystals include low threshold lasers, low loss waveguides, highly efficient light bulb filaments, and many other exciting products. While predictions for PC applications grow very rapidly, the realization of these structures has been relatively slow. This thesis explores ways in which atomic layer deposition (ALD) may be used to create, or modify PCs.

One-dimensional PCs can be constructed entirely from ALD films. Thin alternating layers of tungsten (W) and alumina (Al_2O_3) were deposited in a viscous flow reactor and studied using X-ray reflectivity, X-ray diffraction, quartz crystal microbalance, secondary ion mass spectrometry, and transmission electron microscopy. The optimization of thin film growth and nucleation presented in this thesis led to thin film stacks that displayed ultrahigh reflectivity in the hard X-ray regime, and very low thermal conductivity.

Three-dimensional PCs were modified with ALD. The first in depth investigation of intensity and position of a Bragg reflection as a function of high index fill fraction will be shown. This study investigated Al_2O_3 ALD growth rates inside of PCs, and allows for predictions of how all other ALD systems are expected to behave in a similar system. The extent of red-shift for the Bragg peak of this system also revealed the degree of disorder present in the PC prior to deposition.

Three-dimensional PCs were also coated with W metal. This system created a photonic band gap (PBG), which is a section photon energy that cannot propagate through the PC. The location of the PBG was adjusted by varying the lattice constant of the PC. This system was tuned to interact with infrared (IR) and ultraviolet (UV) light. This was the first demonstration of a 3-dimensional metal PBG in the UV region.

Modified 3-dimensional PCs were studied with scanning electron microscopy to examine the structure of the crystals. UV-visible-IR spectroscopy was used to track optical response changes of the crystal as it was coated with ALD. The reflectance spectra were compared with transfer matrix method numerical simulations to understand the rate and uniformity of ALD on the crystal.

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Table of Contents

Chapter 1

Introduction

I. Photonic Crystals

A photonic crystal (PC) is a periodic material that interacts with light to produce standing waves in the crystal. Natural PCs, such as peacock feathers, butterfly wings, and opals, have been the objects of attention throughout time. In recent years, the dreams of controlling light in modern optics have drawn such structures under the microscope. Synthetic PCs which utilize macroscopic period spacing can be easily created using common techniques, but scaling down to micrometer and nanometer length scales require sophisticated construction techniques.

Photonic crystals interact with light in accordance with the Bragg law:

Eqn. 1.1: $m*\lambda = 2*d*\sin\theta$

Where m is the reflection order, λ is the light wavelength, d is the period spacing, and θ is the angle of incidence. When m = 1, 2, 3, . . ., the light is constructively interfered as a reflection. It was first hypothesized through simulation [1, 2], and then shown with experiments [3], that the Bragg peaks of reflection can be broadened to give a gap in the wave energies that can propagate through the material. The section of the energy continuum that cannot propagate through a material as a wave is known as a photonic band gap (PBG). The gap is created in a photonic crystal with large optical constant contrast between the layers. A PBG was first proposed in 1987 by Yablonovitch [1] and John [2]. Great strides have been made in the scientific world since that time to create 1, 2, and 3-dimensional (D) structures to fit a plethora of applications. Figure 1.1 shows a generic picture of the sought after structures.

A PBG can be observed in a PC constructed of dielectric or metal materials. These systems interact with light in different manners, but can both create a PBG. The dielectric PBG structure can be realized with alternating high and low refractive index layers. A metal PBG depends on the negative real part of the dielectric constant of the metal contrasting the positive real part of the dielectric constant of the matrix in which the metal resides. In both systems, light will partially transmit and partially reflect at each interface. The layers may consist of a continuous film in the case of the 1-D PC, a row of columns in the 2-D PC, or a layer of spheres in the 3-D PC. Correct tuning of the structure period will allow the reflected light to interfere constructively.

A simple Bragg relationship predicts the position of a photonic band gap, but the broadening of a peak into a gap seems counter intuitive. To simplify the discussion, photonic band gaps will be related to the more familiar electronic band gaps. Due to the nature of the photonic crystal, the electronic system will be treated with the nearly free electron approximation instead of the more familiar tight binding electron approximation. Both band gaps manifest themselves when using the periodic Bloch wavefunctions to describe the photon/electron wave that is propagating through the crystal. The electrons interact with a crystal of atoms; i.e. the electron waves interfere with potentials from the ionic cores of each atom. Photons interact with dielectric or metal placed into a crystal structure. Waves confining themselves in the crystal lattice resemble the familiar quantum mechanical problem of a

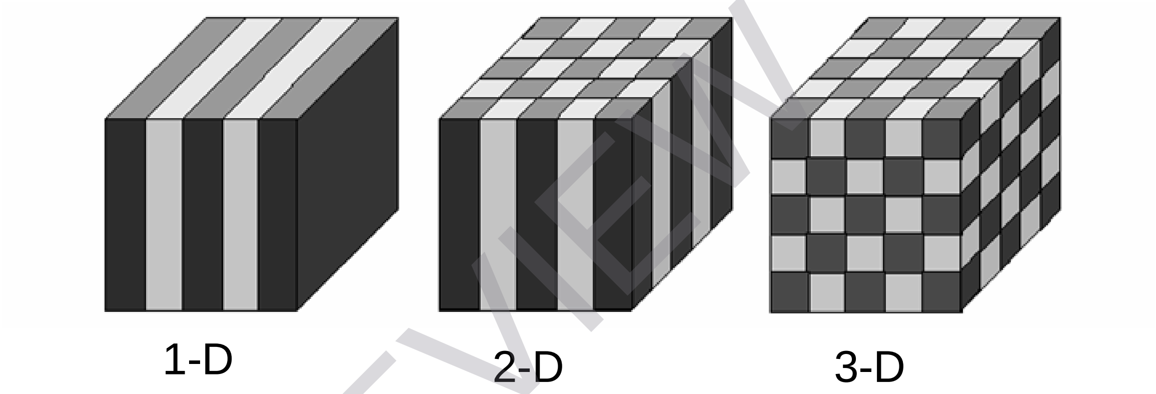

Figure 1.1

Illustration of photonic crystal structures in 1, 2 and 3 dimensions
Image from Joannopoulos[5]

particle above a square well potential. The periodic potential forms bands of allowed energy states. These allowed states are eigenmodes of the Schodinger equation for the electronic system, or harmonic modes which fulfill Maxwell's equations for the photonic system.

In both cases, the solution can be described using a combination of sine and cosine waves [4, 5]. In the crystal, the sine and cosine waves are pulled into two different energy bands as a result of wave's probability density location. One band in an electronic structure concentrates its probability density near the positive ion core. The other energy band is phase shifted by 90°, and is concentrated in the space between ion cores. The energy band with its probability density concentrated near the ion core is known as the valence band. The band with that has a concentration between the ion cores is called the conduction band. The positive core decreases the energy of the valence band via stabilization from the electron-nucleus attraction. This energy shift creates a gap in energies that can propagate as a wave through the system. In a dielectric PBG, a similar energy splitting around the standing wave will lead to a band gap. The electric field can again be described as a combination of sine and cosine wave. The lower energy band will localize its power inside of the high refractive index material. Because of the location of the power maximum for this band, it was given the title dielectric band. The band with power concentrated in the lower dielectric constant region (often air) is called the air band. A schematic of electric field and associated power modulation is shown in Figure 1.2 A and B. The light in high dielectric constant material will have lower energy than light with the

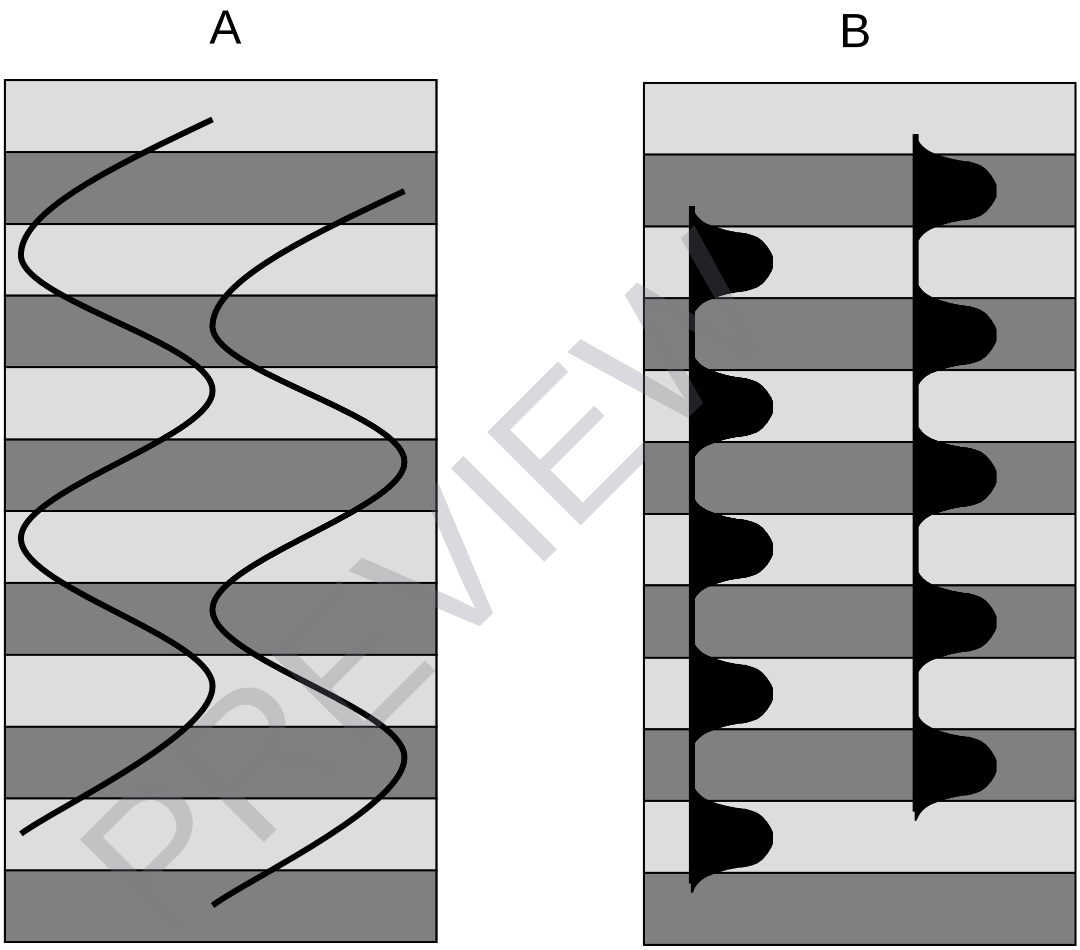

Figure 1.2

(A) Standing wave electric fields in a periodic dielectric materials and (B) the corresponding power distribution same wave vector in a low dielectric medium. The relationship between energy and the dielectric constant can be seen in the light line equation:

Eqn. 1.2: $\omega = \dfrac{ck}{\sqrt{\varepsilon}}$

Eqn. 1.3: $E = \hbar\omega$

Where c is the speed of light in a vacuum, k is the wavevector, ε is the dielectric constant, ω is the angular frequency, E is the energy, and ħ is Plank's constant times 2π.

How does the gap fit into the simple Bragg picture for photonic crystals? We can glance at epn. 1.1, and quickly see that the Bragg eqn. will need to be modified inside of the crystal because the wavelength and reflection angle are dependant on the index of refraction. This will be discussed in detail in Chapter 4. A larger refractive index, will red-shift a Bragg peak. Thus, if we think about a Bragg peak defined by the averaged index of refraction, we will have one Bragg peak which is red-shifted from the position of a Bragg peak created in an air crystal (Figure 1.3). We now refer back to a periodic wave that fulfills the Bragg condition as a combination of sine and cosine waves. Again, in the quarter wave stack configuration, these waves will be split so that one is concentrated in a high dielectric region, and one is concerntrated in the low. This will split the degeneracy of the Bragg solutions for an averaged refractive index medium, and will now give two solutions. One solution red-shifted, and one solution blue-shifted from the Bragg solution for the averaged refractive index. An image of this shift can be seen in Figure 1.4. The reflectance will remain high between the two peaks due to constructive interference. This gives a wide band gap, from the simple Bragg peak of a homogenous system.

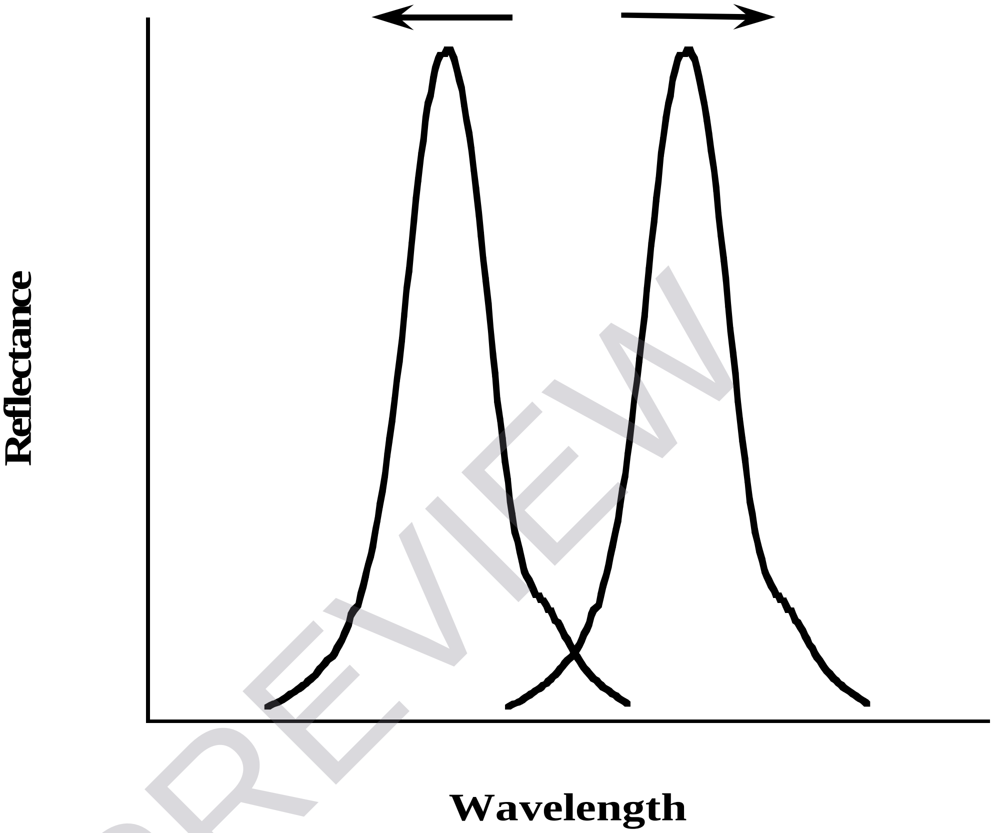

Figure 1.4

Splitting the degeneracy of the Bragg peak for an homogenous refractive index material

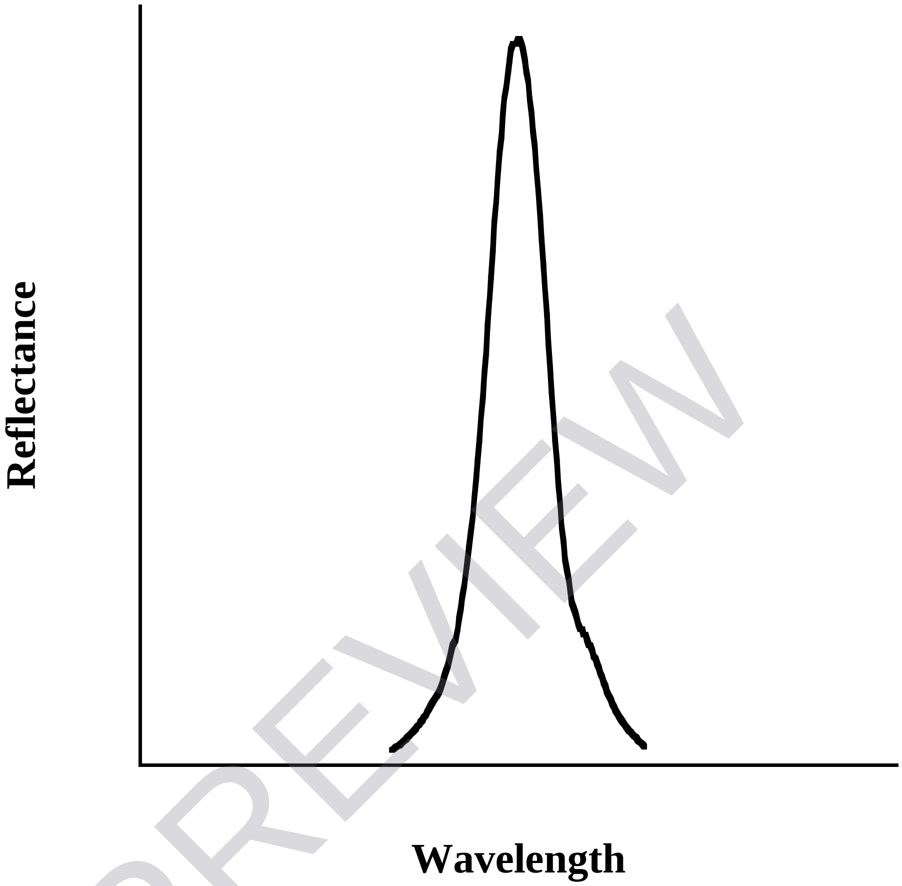

Figure 1.3

Bragg Peak of a material with
a homogenous refractive index

The energy gap in a metallic PBG was created in the same fashion as the dielectric PBG, but has added complications from the light-metal interaction. The light was quickly absorbed, and reemitted in a typical metal reflection. Therefore, the light only exists in the high dielectric constant of the metal on the length scale of the skin depth. Also the, metal has a large absorption coefficient in the wavelength range being investigated. Despite complications with metal PBG structures, previous theoretical studies have predicted that any metal in a high filling fraction crystal structure should produce a complete PBG [6].

In the past 19 years of study, photonic crystals have found use in low loss waveguides [7], LED enhancers [8], laser cavities [9-11], photovoltaics [12], thermo-photovoltaics [13], and antennas [14]. The field is exploding, and offers to change the way modern society uses light. Theoretical work is far more advanced than experimental demonstrations. The lag from experimentalist comes from the difficulties associated with creating structures with near perfect ordering and very small features. Atomic layer deposition (ALD) offers a solution to many of the structuring problems facing the PBG field.

II. 1-D System

In Chapter 3, I will discuss a 1-D PC created entirely using ALD thin Films. The 1-D PC structures were relatively simple structures of alternating materials. The PC structure was a stack of reflective and transmissive layers. The thicknesses of the bilayer period (one reflective and one transmissive layer) were tuned such that the reflected light from each interface constructively added to one another to produce large reflectances from the whole stack. Thicknesses of the layers needed to be deposited very accurately. A layer thickness inconsistent with the rest of the stack was a defect in the nanolaminate, and the optical properties quickly extinguish with structural defects. Due to the need for very precise thicknesses, ALD was an ideal deposition technique to create thin, layered structures.

1-D PCs were created with layers of alumina (Al_2O_3) and tungsten (W) ALD films. This structure will be discussed in great detail in Chapter 3. The stacked ALD films had thicknesses on the nanometer length scale, giving the structure the title nanolaminate. These 1-D systems interacted strongly with Cu Kα radiation (λ=1.54Å) when the period of the bilayer was 30Å. The high reflectivity peaks occur for near grazing incidence angles of 1.5° and 2.9°. Near grazing incidence is commonly used to test reflectance for highly penetrating light such as hard X-rays. These angles fulfill the Bragg condition for constructive interference with m=1 and 2 respectively.

The system showed high reflectivity, but no PBG can be found for the nanolaminates investigated in the X-ray region. Because the frequency of the electromagnetic radiations is too high for the electron to respond to, the real and imaginarty parts of the refractive index are similar optical constants. The refractive index (n) approaches 1 and extinction coefficient (k) approaches 0 for both materials. Without a significant difference in the optical constants, no gap formation was possible. The system did act as a well behaved Bragg mirror, and gave detailed information about the nucleation and growth of both W and Al_2O_3 ALD films.

The structure also performed as an excellent thermal barrier. In this capacity the nanolaminate did not use constructive interference to achieve a high reflectance, but utilized the high interface density of the structure to scatter heat waves (phonons) incoherently. The high number of interfaces in series with each other lead to the lowest measure thermal conductivity measured for a thin film[15]. Due to the mixing of metal and oxide physical properties, these films were expected not to spawl off of metal substrates. Spawling is currently the largest problem facing thermal barrier coatings. It is caused by difference in thermal expansion of the oxide thermal barrier coating and a metal substrate. The W/Al_2O_3 nanolaminate achieved record low thermal conductivity, but the structure which enabled this thermal impedance breaks down at relatively low temperatures. This makes any advantages that would have been realized against spawling effects moot.

III. 3-D System

Chapters 4 and 5 discuss 3-D PCs constructed of ALD coated synthetic opal. The opal was self assembling crystals of silica or polystyrene spheres. Chapter 4 discusses coating the opal with Al_2O_3, and Chapter 5 was written about W coated opal. 3-D PCs had the advantage of interacting with light from any direction, and any incident angle. Opals were PCs without any additional treatment, but a PBG was not possible using silica, or polystyrene spheres because of low refractive index contrast between the spheres and surrounding air. Previous investigations [16, 17] suggest that a minimum refractive index contrast of 2.8 is necessary for a PBG to appear in an air-dielectric PC. To realize a PBG, the opal was used as a template. The opal was coated with ALD films of high refractive index dielectric or metal, which may be able to create a PBG.

Al_2O_3 ALD films coated the opal template, and allowed for reflection peak position and intensity tuning. The refractive index of Al_2O_3 ALD (~1.65) did not allow for a complete PBG in opal. The deposition of Al_2O_3 ALD did elucidate facts about the opals template defects, and acted as a model system for W deposition. The Al_2O_3 could be monitored optically in the opal at various thicknesses to examine growth and saturation behavior. This information was then applied to W-opal systems which could not be monitored.

W ALD coated opals did produce a full PBG. The position of the gap was adjusted using various sphere sizes. The system was composed of W coated opals. These spheres were metellodielectric spheres in composition, but discussed as solid metal spheres. This assumption was based of theoretical work comparing the two systems [6]. Ultraviolet, visible, and IR PBGs were attempted, but visible PBGs could not be created using W ALD coated opal. The structure of the PBG formed by a metal coated opal is quit different from the gap seen in dielectric systems. In continuous metal PBGs, the gap extends from some cutoff frequency to zero frequency. The cutoff frequency can be found using the standing wave arguments, and can thus be tuned with the template geometry [18]. At wavelengths larger than the cutoff wavelength, the light sees a continuous (although less dense) metal film. The light is reflected off of this flat film , and remains highly reflected from the cutoff wavelength to infinite wavelength. Metal PBGs differ from traditional waveguides in that the metal PBG had greatly enhanced transmission and emission above the cutoff frequency. Because the bands inside of the gap were not allowed, there was a large shift in the photonic density of states. The photonic density of states under the gap was pushed to higher frequencies. This shift allows for a large number of allowed states to build up above the cutoff frequency, and facilitate large transmission and emission. This difference allows W-opals to potentially act as highly efficient light bulbs filaments, or thermal photovoltaics sources.

IV. Atomic Layer Deposition

Atomic layer deposition (ALD) deposited ultra thin layers of material with precise thickness control. ALD is a relatively new technique, being first explored in the 1960's and 70's [19, 20]. ALD is a surface reaction chemistry that utilizes reactive site switching to self limit thin film growth in each cycle. Gas phase precursors were exposed to activated surfaces independently of one another. The temporal separation between precursors avoided gas phase reactions. The first precursor (A) reacted with all sites available. After all sites were reacted, the surface was passivated with a new layer of the A precursor. This new layer prevented any additional precursor absorption, and prevented further reaction with that surface. The remaining precursor stayed in the gas phase, and could be pumped away with gas phase products. The surface was then a continuous layer of the A precursor ligands. The second precursor (B) could be exposed to this new surface, and react with the A ligands to deposit another layer of atoms. If the B precursor recreated the original surface, then a complete ALD reaction had occurred, and the process could start again. Each full reaction deposits one thin layer of ALD material. The A-B ALD sequence is shown in Figure 1.5.

The self limiting nature of ALD allowed the technique to deposit thin conformal films of very accurate thickness. The ALD technique grew a layer of set thickness

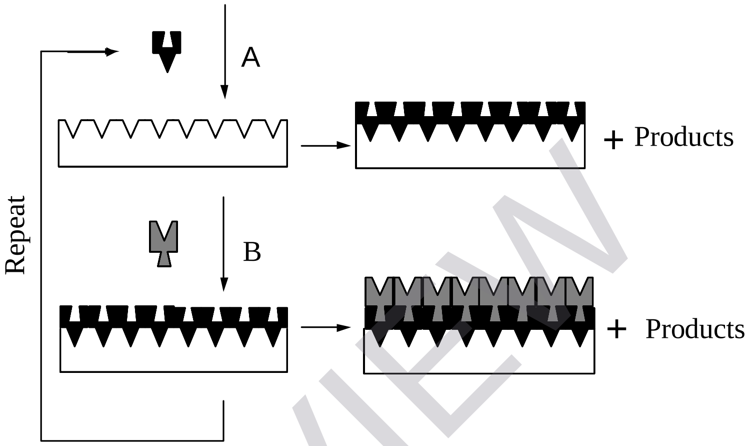

Figure 1.5

Cartoon showing the self-limiting nature of each
half reation during atomic layer deposition
Image from George[27]

deposited in each cycle. In the case of Al_2O_3 ALD, the thickness achieved was ~1Å/cycle. The W ALD film grew at ~4Å/cycle. The film thickness was defined by the number of cycles performed, assuming that the gas exposures were in saturation for the surface being coated. The well defined, slow growth rates allowed for the precise thicknesses needed for 1-D PC construction.

ALD did not need line of site connection between the sample and precursor. This allowed uniform growth on complicated geometries without shadowing, and the self limiting nature of the precursor adsorption prevented bottle necking of deposit. The conformal growth on complicated geometries with high aspect ratios made ALD the ideal choice for growth of thin films of opal templates. The opals had aspect ratios greater than 50, and structures that prevented line of sight deposition techniques from coating lower layers of the opal. ALD of dielectric and metal films on opal was performed in low and high filling fraction regimes. The films coated the structure with a conformal layer of material of precise thickness in a manner never before found with other deposition techniques.

V. Statement of Purpose

This project explored the ways in which ALD can enhance current PC construction. The photonics field is currently bottlenecked with slow, expensive, and complicated construction techniques. The progression in this field is dependant on a break-through technology which will allow PC samples to move out of the laboratory setting, and into public use. The studies presented here will introduce the current photonics community to ALD solutions to many of the problems in PC construction.