The Effects of Capillarity
on Photonic Crystal Selective Emitters

by

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Abstract

Photonic crystals offer an unparalleled control over optical properties and are ideal candidates as high efficiency selective emitters. They are, however, known to degrade at elevated temperatures through a number of processes, with one of the most notable being surface evolution by capillary forces. By comprehensively simulating the morphological and optical effects of this phenomenon, in the form of surface diffusion, vapor transport, and grain boundary grooving, this thesis seeks to understand its consequences and attempts to pinpoint methodologies that may prevent it.

It was shown that while grain boundary grooves have a negligible effect on photonic crystal structures, vapor transport and surface diffusion may be significant. Indeed, vapor transport was found to progressively reduce the dimensions of photonic crystal cavities, and thus slightly alter their optical properties. Conversely, surface diffusion gradually closed off these cavities, thereby eliminating coupling into their resonant modes, and eradicating their selective emission capabilities.

Changes to the shape of these photonic crystal structures that decreased their curvature and removed discontinuities were found to be beneficial in inhibiting degradation by capillarity, and an optimized structure that displays both higher efficiency and greater stability over time was ultimately theorized.

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1 Introduction

1.1 Thermophotovoltaics

The direct transformation of thermal energy into electrical energy can be achieved using thermophotovoltaic (TPV) energy conversion. Behaving essentially as optical heat engines, TPV systems employ high temperature emitters to convert heat into radiated photons, which are subsequently absorbed by low temperature photovoltaic (PV) cells, and used to generate an electrical current; see Figure 1.1. Importantly, this energy conversion scheme offers significant advantages over comparable alternatives [1], including fuel source versatility (devices based on solar radiation [2,3], combustible fuels [4,5] and radioisotope decay [6,7] have been demonstrated), high efficiencies (exceeding the theoretical limits of PV cells [8]), high power densities, and the absence of moving parts.

![Figure 1.1: Standard design of a thermophotovoltaic system [1], which converts input heat into electrical output via thermally emitted photons.](image)

In conceiving a TPV system, the match between the spectrum of light radiated by the emitter and the bandgap of the PV cell is crucial. In fact, the efficiency of the system is primarily limited by either the emission of low energy photons that cannot overcome the bandgap and contribute only heat, as well as the radiation of overly energetic photons which also result in thermalization losses. Maximum energy conversion is therefore achieved by utilizing specially designed selective emitters that emit only at energies above, yet close to, their associated PV cell’s bandgap.
The improvement of current TPV technology through the development of emitters with high selectivity that are stable for long durations at elevated temperatures ultimately serves as the principal motivation behind this study.

1.2 Photonic Crystals

Photonic crystals (PhCs), theorized independently by Yablonovitch [9] and John [10], offer an unparalleled control over optical properties, and are thus perfectly suited for use as high efficiency selective emitters. These metamaterials are engineered to have periodic dielectric constants, allowing them to behave analogously to semiconductors [11,12], but with photons taking up the role of electrons. Indeed, just as the periodic potentials of atomic lattices generate electronic bandgaps, the periodic lattice of dielectric constants alters the photonic density of states and generates a wide array of unconventional optical properties.

Infrared selective emitters based on PhCs have been previously investigated, both theoretically and experimentally, using 1D [13–15], 2D [1,13,14,16–22], and 3D [23–25] periodic structures, and have been found to produce nearly ideal spectral emissivities. Moreover, fabrication procedures capable of reliably producing large area PhCs, with both fine features and high aspect ratios, have been recently outlined [1,26–28].

1.2.1 Refractory Metal Selective Emitters

The high temperature selective infrared emitters studied in this work consist of periodic arrangements of micron sized cavities (either one-dimensional series of rectangular trenches or two-dimensional arrays of cylindrical and square openings; see Figure 1.2). Their ability to selectively emit only at desired wavelengths is produced by enhancing their emissivity over a particular wavelength range through a variety of mechanisms, including cavity resonances [11, 15,17–19,29,30], diffraction peaks [13,15,18,20,31], and surface plasmon modes [13,15,18,32], with the cavity resonant modes being the most significant.

![Figure 1.2: Schematic representation of (a) 1D, (b) 2D cylindrical, and (c) 2D square PhCs.](image-url)
These structures are typically fabricated from refractory metals such as tungsten [13, 14, 16, 17, 19–21, 23–25, 27, 31, 33–37] and tantalum [1, 3, 22, 28, 38]. While this choice is partly validated by the high melting points of these materials, and therefore their ability to withstand the high temperatures necessary for efficient operation, it is primarily justified by their extremely high intrinsic infrared reflectivity [39], as exemplified by Figure 1.3. This signifies that undesired and unenhanced wavelengths will have low emissivity, and that the PhC’s ability to emit only at preferred wavelengths will be improved.

![Figure 1.3: Infrared reflectivity of selected refractory metals, adapted from [40].](image)

It is worth noting that special attention will be given to tantalum structures where applicable. This is due to the fact that tantalum not only shares the high temperature capabilities and low intrinsic reflectivity of comparable refractory metals, but can also be welded and machined, making it one of the most promising materials for high temperature photonic applications [1, 22, 28, 38].

### 1.2.2 Cavity Resonant Modes

The resonant wavelengths of a cavity, which denote frequencies at which an integer number of half-wavelengths fit inside the cavity, can be predicted by assuming that the cavity behaves as a closed box (i.e. as an infinite potential well) [41]. The emissivity is then enhanced at
peaks that lie above the diffraction limit (i.e. at wavelengths larger than the periodicity of the PhC structure), and below the dominant resonant peak (i.e. below the cutoff wavelength).

For 2D rectangular cavities (trenches found in 1D PhCs; see Fig. 1.2a) of width \( w \) and depth \( d \), the resonant frequencies for the transverse electric (TE) modes are given by

\[
\nu_{ij}^{2D} = \frac{c}{2\pi\sqrt{\mu_r\epsilon_r}} \sqrt{\left(\frac{i\pi}{w}\right)^2 + \left(\frac{j\pi}{d}\right)^2} \tag{1.1}
\]

in which \( i \) and \( j \) are integers, \( c \) denotes the speed of light, and \( \mu_r\epsilon_r \) is the product of the relative permeability and permittivity of the material filling the cavity.

Assuming that the cavity is unfilled (i.e. \( \mu_r\epsilon_r = 1 \)), the resonant wavelengths can then be calculated as

\[
\lambda_{ij}^{2D} = \frac{2}{\sqrt{\left(\frac{i}{w}\right)^2 + \left(\frac{j}{d}\right)^2}} \tag{1.2}
\]

The dominant resonance peak for such a cavity resonator is the \( \lambda_{11}^{2D} \) mode, and this can be used to estimate the location of the cutoff wavelength \( \lambda_c \) (the wavelength beyond which the emissivity abruptly drops down to unenhanced levels, and which must be engineered to coincide with the bandgap of the associated PV cell, i.e. \( E_{\text{bandgap}} \approx \frac{hc}{\lambda_c} \)).

Following a similar procedure, the resonant TE modes of a 3D rectangular cavity of width \( w \), length \( l \), and depth \( d \), and a 3D cylindrical cavity of radius \( r \) and depth \( d \) (both found in 2D PhCs), are given as

\[
\lambda_{ijk}^{3D,\text{rec}} = \frac{2}{\sqrt{\left(\frac{i}{w}\right)^2 + \left(\frac{j}{l}\right)^2 + \left(\frac{k}{d}\right)^2}} \tag{1.3}
\]

\[
\lambda_{ijk}^{3D,\text{cyl}} = \frac{2}{\sqrt{\left(\frac{\zeta_{ij}'}{r\pi}\right)^2 + \left(\frac{k}{d}\right)^2}} \tag{1.4}
\]

with \( i, j, \) and \( k \) denoting integers, and \( \zeta_{ij}' \) representing the \( j \)th root of the \( i \)th order Bessel function derivative \( J_i' \). The dominant peaks are \( \lambda_{101}^{3D,\text{rec}} \) and \( \lambda_{111}^{3D,\text{cyl}} \), respectively.

Note that these equations will tend to consistently underestimate the resonant wavelengths by approximately 5 to 10\% [19]. This is due to the fact that the cavity is open at one end, and that the walls do not act as perfect mirrors. As such, the effective dimensions of the cavity will be slightly larger than its nominal dimensions.
1.2.3 Operating Temperature

For a selective emitter, there exists an optimal operating temperature which promotes the production of radiative power at desired wavelengths. This optimum occurs at the temperature at which the emitter’s emissivity peaks coincide with the peak in the blackbody radiation curve $\lambda_{\text{max}}$ [42].

From Wien’s displacement law, the blackbody radiation peak can be determined according to $\lambda_{\text{max}} = \frac{b}{T}$, in which $b$ is Wien’s displacement constant. As the emissivity peaks will tend to be near the cutoff wavelength $\lambda_c$, the optimal temperature is then approximately given by

$$T_{\text{opt}} = \frac{b}{\lambda_c} \approx \frac{2897.8 \mu m \cdot K}{\lambda_c}$$  \hspace{1cm} (1.5)

As such, an emitter tuned to a cutoff wavelength of 2 $\mu$m (the arbitrary value used in this work, as it lies approximately midway in the near-infrared range) will have an optimal temperature of approximately 1450K, a value that will be used throughout this work. More precisely, however, this temperature represents a low estimate of the optimal point, as the emissivity peaks will be at slightly lower wavelengths than the cutoff. Nevertheless, this clearly indicates that the temperatures that near-infrared selective emitters must be capable of withstanding are substantial.

1.3 High Temperature Degradation

Despite their potential as high efficiency TPV emitters, the thermal stability of these PhC structures remains lacking, a fact that is especially troubling when considering the high operating temperatures required of them and their proposed lifetimes on the order of decades. In fact, these structures are known or suspected to degrade at elevated temperatures through a variety of different phenomena, including grain growth and surface diffusion, as well as chemical reactions and thermal stresses.

1.3.1 Grain Growth

One of the most commonly discussed degradation mechanisms is grain growth, a process which steadily increases the average grain size in order to reduce the total grain boundary area, and thus the grain boundary energy. This phenomenon is believed to affect the shape of PhC cavities if their dimensions are comparable to the grain size. Indeed, many high temperature studies [1, 14, 22, 28, 38] take steps aimed at preventing the occurrence of this process,
such as the use of single crystal substrates, and certain authors report differences between
the deterioration rates of small grained and large grained samples which are attributed to
grain growth.

For instance, the results of Sai et al. [16], shown in Figure 1.4, reveal that while 2D
tungsten PhCs built on single crystal substrates maintain the sharp angular shape of their
cavities after annealing, their polycrystalline counterparts experience significant rounding
and smoothing of the surface. Likewise, the findings of Lee et al. [36,37] (see Figure 1.5)
expose a slower degradation rate in large grained samples when compared to small grain
samples. Indeed, the annealed cavities in Fig. 1.5b are much more rounded than those in
Fig. 1.5c, and the deep grooves formed (see circled region in Fig. 1.5b) are taken as evidence
of pronounced grain growth. These results were also further confirmed by studies of more
complex 3D architectures [33–35], which once again observed a “coarsening” of the structure
with annealing, which was displayed as the smoothing of finer features and was attributed
to grain growth.

![Figure 1.4: Difference in degradation after annealing for 1 hour at 1400K between (a) single crystal, and (b) polycrystalline 2D rectangular tungsten PhCs; adapted from [16].](image1)

![Figure 1.5: Focused-ion-beam milled cavities in W, (a) as-fabricated, (b) after annealing for 40 hours at 1500K in a small grained sample, and (c) after annealing in a large grained sample; from [37].](image2)
That being said, these conclusions are problematic for a number of reasons. First, grain growth is known to come about through atomic “shuffles” across grain boundaries [43,44], which produce a net movement of these interfaces over time. These transfers of atoms occur over distances smaller than an atomic spacing, and thus do not require long-range diffusion, a fact that can be confirmed by measuring the activation energy for grain boundary motion and noting that it is consistently less than that for diffusion (for instance, the energy for grain boundary motion is 2.05 - 2.32 [45] and 1.51 - 1.87 eV/atom [46,47] for W and Ta, respectively, compared to self-diffusion energies of 5.39 - 6.08 [48–50] and 3.88 - 4.77 eV/atom [50–52]). Crucially, this form of diffusionless shuffling “does not produce a specimen shape change” [43], and should therefore have no effect on the PhC cavities.

Second, the investigations reviewed do not directly measure changes to grain sizes, and therefore only infer the occurrence of grain growth. It is therefore worth noting that studies of grain growth in both tungsten [45,53,54] and tantalum [55–59] do not reveal significant growth below temperatures of approximately 1500K and 1300K, respectively, which are comparable to the annealing conditions used in these studies. Furthermore, surface effects will tend to hinder or inhibit grain boundary motion [60–62], and the PhC cavities may produce a drag force on moving boundaries, not unlike conventional Zener drag [63]. As such, grain growth at PhC surfaces is expected to be rather negligible at typical operating temperatures, and might not have taken place during these studies.

Finally, the degradation observed (both the smoothing and rounding of sharp corners and rough surfaces, and the formation of grooves at grain boundaries) is not indicative of grain growth, but rather of surface evolution by capillary driving forces, which may occur at different rates in small grained and large grained samples due to seemingly minor differences in their chemical makeup. It therefore appears that there is significant doubt on the legitimacy of grain growth as a degradation mechanism for PhCs, and that previous results may have been caused by other processes.

1.3.2 Surface Diffusion

Surface evolution by capillarity involves the reshaping of an interface at elevated temperatures in an attempt to minimize its energy. Simply put, this phenomenon modifies portions of the interface that introduce an excess surface area, such as sharp edges and fine protrusions, and ultimately results in a smooth and stable surface. Importantly, the complex surface morphologies of photonic structures, which possess many abrupt corners that are necessary in generating periodic changes in dielectric constants, may render them especially prone to
this form of deterioration, as revealed by the previously discussed grain growth findings.

The effects on PhCs of one surface evolution mechanism, namely surface diffusion, have been previously investigated both experimentally and computationally by a few authors. For instance, Yeng et al. [21] simulated the degradation of 2D tungsten PhCs at 1200K, and found no evidence of surface diffusion after 10 hours. Additionally, simulations at 1100K for 3 years found at most a 2% change in the optical properties. Conversely, Lee et al. [36, 37] performed similar calculations at a higher temperature of 1473K and found that both the shape and the optical properties of the structure changed significantly after 48 to 96 hours. It is worth noting that no explanation of the resulting changes and no analysis of their effects on the efficiency of the PhC were reported.

These latter simulations are fairly consistent with the experimental findings of Schlemmer et al. [14], which reveal that annealing 1D W PhCs consisting of shallow trenches at 1473K for 99 hours generated a “near flat tiled surface”. This degradation was also found to produce a substantial decrease in the spectral emissivity of the selective emitter towards that of an unstructured surface. Similar investigations of 3D tungsten PhCs at 1273K by Arpin et al. [24,25] also revealed “severe structural degradation” that was attributed to a sintering of the initially fine structure by surface diffusion.

Furthermore, a number of studies [1,36–38] have also witnesses the formation of grooves on the surface, as was shown previously in Fig. 1.5, and plainly visible in Figure 1.6. While the effects of these grooves have never been directly addressed in the literature, their presence has occasionally been attributed to grain growth due to their position at intersections between grain boundaries and free surfaces. Instead, these represent clear indicators of surface evolution by capillary forces, as their formation occurs by the same energy reducing mechanisms, but with additional constraints imposed by the existence of a nearby grain boundary.

Altogether, these results undoubtedly show that surface evolution by capillarity not only occurs on PhC surfaces during annealing, but also has substantial effects on both their morphology and their optical properties. That being said, the details of these effects remain unexplored, and few strategies have been proposed to address their detrimental consequences. Moreover, previous investigations have exclusively focused on surface diffusion, and have given no attention to closely related mechanisms, such as vapor transport. As such, the effects of capillarity are the primary focus of this work.
1.3.3 Other Mechanisms

A number of other high temperature degradation mechanisms have also been noted in previous studies, with the most notable involving chemical reactions and thermal stresses. Indeed, the metallic surfaces used to construct PhC selective emitters are relatively reactive [64,65] and are thus prone to chemical changes that may alter both their chemistry and morphology. Likewise, differences between the thermal expansion coefficients of different components may generate large internal stresses. Controlling and preventing both reactions and mechanical failure is therefore crucial in ensuring the thermal stability of PhCs.

For instance, a few authors have noticed detrimental reactions between tungsten structures and oxygen. First, poor vacuum conditions containing trace amounts of water vapor were shown to cause the formation of volatile WO$_2$(OH)$_2$ needles [33,35] that completely destroyed the photonic properties of 3D W specimens. Likewise, the formation of a WO$_3$ surface oxide, which is permeable to oxygen and may allow prolonged oxide growth, has been noted as potentially damaging [14, 36, 37]. This was confirmed by annealing 2D samples in an oxidizing environment [36], which resulted in a substantial oxide layer and caused a significant roughening of the surface.

Alternatively, the formation of carbon-based protrusions has occasionally been observed on tantalum photonic crystals [22,38,66], as exemplified by Figure 1.7. These agglomerates were detrimental to the optical properties of the devices due to their increased surface roughness and enhanced long-wavelength emissivity. These occurrences were reported as tantalum carbides and were assumed to be caused by contamination from the vacuum chamber used.

On the other hand, certain analyses [24,25] on the effects of annealing in multicomponent
Figure 1.7: Tantalum 2D PhC (a) before and (b) after carbide formation at 1173K for 24 hours, from [38].

structures have observed the formation of cracks during prolonged testing, which may be related to the different thermal expansion coefficients of these constituents. These effects are not usually observed, but are likely to become more common as future studies explore the effects of cyclical temperature changes. Note, however, that both chemical reactions and the development of cracks, though significant, are beyond the scope of this work.

1.4 Research Objectives and Thesis Outline

From the previous discussion, it appears that the high temperature stability of complex PhC structures remains suspect, and that a thorough understanding of some of their most important failure mechanisms has not yet been attained. In particular, the review of both grain growth and surface diffusion results indicates that the effects of surface evolution by capillarity are both poorly comprehended and crucial in realizing the best possible stability. This gap in knowledge will be overcome by extensively simulating the effects of capillarity, taken here to include both surface diffusion and the entirely ignored phenomenon of vapor transport, on a variety of different photonic crystal structures, and rationalizing the trends that appear. Ultimately, an optimized structure, displaying both high efficiency selective emissivity and an inherent resistance to surface evolution, will be theorized.

More precisely, this work is organized as follows. First, Chapter 2 will provide a thorough analysis of the mathematics of surface evolution by capillary-driven motion, as well as the parametric equations used in the calculations. Chapter 3 will describe the details of the methodology employed, including the material constants considered, and the optimization procedure utilized. The results are then arranged based on the complexity of the simulated
structures. The simple case of grain boundary grooving on an initially flat surface is explored
Chapter 4, and used to confirm the validity of the simulations. Next, one-dimensional pho-
tonic crystals are comprehensively analyzed in Chapter 5, and their structures are optimized
in Chapter 6. Finally, Chapter 7 re-evaluates these findings for more realistic two-dimensional
photonic crystals in order to confirm the behaviors observed.
2 Surface Evolution by Capillarity

2.1 Surface Energetics

Due to the unfilled bonding of their atoms, surfaces (or, more generally, interfaces) introduce an excess energy in comparison to the bulk, which is quantified per unit area by the surface free energy $\gamma$. Each surface atom adds an area $\Omega \frac{dA}{dV}$, in which $\Omega$ denotes the atomic volume and the ratio $\frac{dA}{dV}$ represents the change in surface area with a change in volume. Since this ratio is equivalent to the mean curvature $\kappa$ \cite{43, 67, 68}, the excess energy per atom is given by $\gamma \Omega \kappa$ \cite{43, 60, 68}, and the local shape of the surface affects its energy.

As many photonic crystal structures consist of cavities with sharp edges, their curvature is nearly infinite in the as-fabricated state. They are therefore initially in an unstable high energy state, which drives the redistribution of their atoms from regions of high curvature, where the amount of surface area per atom is high, to regions of low curvature, where the amount of surface area per atom is low.

The evolution of such surfaces can occur through a number of different phenomena \cite{43, 60, 69–73}, including volume diffusion, surface diffusion, and vapor transport (also known as evaporation-condensation or surface-attachment-limited kinetics). While contributions from volume diffusion are expected to be negligible at the low homologous temperatures typically employed (0.3 to 0.4 $T_m$), surface diffusion and vapor transport can be significant under certain conditions. Moreover, these mechanisms represent two limiting kinetic regimes: either the movement of atoms along the surface, or their attachment to the surface, is rate-limiting.

2.2 Surface Diffusion

For a surface undergoing surface diffusion, evolution occurs by the flow of adatoms along the surface from region of high curvature to regions of low curvature \cite{43, 60}.

The starting point for the derivation of the surface diffusion velocity is the Teorell formula, which defines the flux $J$ of diffusing atoms as the product of their concentration $c$, their mobility $M$, and the gradient in energy $-\nabla \mu$. From the Einstein relation, the mobility can be rewritten in terms of a diffusion coefficient $D$ as $M = D/k_B T$, in which $k_B$ is the Boltzmann constant and $T$ is the temperature.

$$J = -\frac{cD}{k_B T} \nabla \mu \quad (2.1)$$
In the case of surface diffusion, the energy is given by \( \mu_s = \gamma \Omega \kappa \). Then, taking the concentration as equivalent to the inverse of the atomic volume, \( c = 1/\Omega \), the flux of atoms undergoing surface diffusion becomes

\[
J_{SD} = -\frac{1}{\Omega} \frac{D_s}{k_B T} \nabla_s (\gamma \Omega \kappa)
\]

(2.2)
in which \( D_s \) is the surface diffusivity, and \( \nabla_s \) denotes a gradient taken along the surface.

From Gauss’s theorem, the accumulation of atoms at a surface site is equal to the volume integral of the divergence of the flux, i.e. \( \dot{N} = -\int \nabla \cdot J dV \approx -\Omega \nabla \cdot J \), in which the negative sign indicates that a positive flux (flow out of the volume) decreases the amount of atoms. As each atom adds a height \( \delta \) in the direction of the normal to the surface \( \vec{n} \), the velocity of the surface is

\[
\vec{v}_{SD} = -\delta \Omega \left( \nabla \cdot J_{SD} \right) \vec{n} = \frac{\delta \Omega}{k_B T} \left( \nabla \cdot \frac{D_s}{\Omega} \nabla_s (\gamma \Omega \kappa) \right) \vec{n}
\]

(2.3)

In this work, the effects of faceting (see [72, 74], for instance) are ignored for simplicity. The surface is therefore assumed to be isotropic, and the atomic volume \( \Omega \), surface diffusivity \( D_s \), and surface free energy \( \gamma \) are assumed constant. The velocity is then

\[
\vec{v}_{SD} = \left[ \frac{\delta \Omega D_s \gamma}{k_B T} \right] \nabla_s^2 \kappa \vec{n} \equiv C_{SD} \nabla_s^2 \kappa \vec{n}
\]

(2.4)
in which \( \nabla_s^2 \) denotes the surface Laplacian of the mean curvature. The surface diffusion rate constant \( C_{SD} \) combines the material constants of the surface and has units of \( \text{nm}^4/\text{s} \).

### 2.3 Vapor Transport

During surface evolution by vapor transport, regions with high curvature experience enhanced evaporation, while regions with low curvature experience enhanced condensation, causing a net change to the shape of the surface [43, 60]. However, it is worth noting that this phenomenon is not limited to sublimation, but instead encompasses all mass transport through a surrounding medium with kinetics limited by the attachment of atoms to the surface [71, 72]. Among these mass transport processes are chemical reactions that generate volatile products at the surface. As such, despite the extremely low vapor pressures of the refractory metals used [75], their considerable reactivity [64, 65], even under high vacuum conditions, makes them likely candidates for surface evolution by attachment-limited transport.
From the kinetic theory of gases and the Hertz-Knudsen equation, the net flux $J_{VT}$ of gas atoms on a surface is given by the difference between the evaporating and condensing fluxes, and is therefore proportional to the difference between the ambient pressure $P_{amb}$ and the vapor pressure of the surface $P_{surf}$. After taking the coefficients of evaporation and condensation as unity, the proportionality constant $K$ depends solely on the temperature $T$ of the process, as well as the mass $m$ of the evaporating or condensing molecule.

$$J_{VT} = \frac{1}{\sqrt{2\pi mnk_B T}}(P_{amb} - P_{surf}) \equiv K(P_{amb} - P_{surf}) \quad (2.5)$$

The velocity of the surface $\vec{v}_{VT}$ is then obtained by the product of this flux and the atomic volume $\Omega$ (which accounts for both the height of an atomic site, and the atomic surface area), as well as the surface normal vector $\vec{n}$.

$$\vec{v}_{VT} = \Omega J_{VT} \vec{n} = \Omega K(P_{amb} - P_{surf}) \vec{n} \quad (2.6)$$

The equilibrium pressure for a surface of curvature $\kappa$ is related to the equilibrium pressure for a flat surface $P_0$ by the Kelvin equation.

$$P_\kappa = P_0 \exp \frac{\gamma \Omega \kappa}{k_B T} \quad (2.7)$$

In this work, the ambient pressure is taken as equivalent to the equilibrium pressure for a flat surface. This is due to fact that only evolution due to curvature is investigated (rather than from non-equilibrium evaporation, for instance), and that the ambient gas is well-mixed (i.e. the mean free path of the atoms in the vapor is taken as large compared to surface features). The velocity then becomes

$$\vec{v}_{VT} = \Omega K P_0 \left(1 - \exp \frac{\gamma \Omega \kappa}{k_B T}\right) \vec{n} \quad (2.8)$$

Finally, the exponential function is replaced by its Taylor series expansion in order to achieve a relation of the same general form as that obtained for surface diffusion.

$$\vec{v}_{VT} \approx -\left[\frac{\Omega^2 K P_0 \gamma}{k_B T}\right] \kappa \vec{n} = -\left[\frac{\Omega^2 P_0 \gamma}{\sqrt{2\pi mn(k_B T)^{3/2}}}\right] \kappa \vec{n} \equiv -C_{VT} \kappa \vec{n} \quad (2.9)$$

The vapor transport rate constant $C_{VT}$, which has units of nm$^2$/s, depends not only on the material constants of the surface, but also on the details of the reaction taking place and
the ambient conditions through $m$ and $P_0$.

### 2.4 Grain Boundary Grooving

A special case of surface evolution by capillarity occurs at the intersection between a grain boundary and a free surface. Indeed, such junctures will spontaneously form a groove in order to establish triple junction angles (i.e. balance the surface and grain boundary free energies) [43, 60, 61, 76, 77]. As this groove has a positive curvature, both surface diffusion and vapor transport will cause a net transfer of atoms away from its center, thereby causing it to deepen and widen over time.

The velocity of the surface during grooving follows the previously defined equations (Eq. 2.4 and 2.9), but the free energy balance introduces an additional boundary condition on the slope of the surface near the groove. If the surface and grain boundary energies are denoted by $\gamma$ and $\gamma_{GB}$, the dihedral angle $\psi$ between the two opposite surfaces of the groove is a constant given by

$$\psi = 2 \arccos \left( \frac{\gamma_{GB}}{2\gamma} \right)$$

(2.10)

It then follows that the slope of the surface slope at the groove (taken as $x = 0$) must have the following form at all times $t$.

$$\frac{dy}{dx} \bigg|_{x=0} = \tan \left( \frac{\pi - \psi}{2} \right)$$

(2.11)

### 2.5 Parametric Equations

Due to the complex nature of the structures considered in this work, the previous equations and terms, including the curvature $\kappa$, the Laplacian of the curvature $\nabla^2_s \kappa$, and the surface normal $\vec{n}$, must be used in parametric forms.

In two-dimensional space, a parametric surface is characterized by the variables $x(s)$ and $z(s)$, in which $s$ is a parameter that varies along the surface. The curvature of such a surface is then defined as the following, in which subscripts represent differentials [43, 78].

$$\kappa_{2D} = -\frac{z_{ss}x_s - x_{ss}z_s}{(x_s^2 + z_s^2)^{3/2}}$$

(2.12)

The surface Laplacian of the curvature is then equivalent to the 2nd derivative of this curvature in 2D. As such, after noting that the surface element $ds$ is equivalent to $(x_s^2 + z_s^2)^{1/2}$,
it can be rewritten as

\[ \nabla^2 s \kappa_{2D} = \frac{d}{ds} \left( \frac{d \kappa}{ds} \right) = -\frac{1}{(x_s^2 + z_s^2)^{1/2}} \left\{ \frac{1}{(x_s^2 + z_s^2)^{1/2}} \left[ \frac{z_{ss} x_s - x_{ss} z_s}{(x_s^2 + z_s^2)^{3/2}} \right] \right\} \]  

(2.13)

Similarly, the surface normal vector is related to derivatives of the variables \( x \) and \( z \), and is given by

\[ \vec{n}_{2D} = \left( -\frac{dz}{ds}, \frac{dx}{ds} \right) = \left( -\frac{z_s}{(x_s^2 + z_s^2)^{1/2}}, \frac{x_s}{(x_s^2 + z_s^2)^{1/2}} \right) \]  

(2.14)

On the other hand, a surface in three-dimensional space is characterized by three variables and two parameters (i.e. \( x(u, v) \), \( y(u, v) \), and \( z(u, v) \)). The curvature of this surface is then given by the following equation [43]

\[ \kappa_{3D} = -\left[ \frac{1}{(X^2 + Y^2 + Z^2)^{3/2}} \right] \left\{ \left( x_u^2 + y_u^2 + z_u^2 \right) (x_{uv} X + y_{uv} Y + z_{uv} Z) \right\} \]

\[ -2 \left( x_u y_v + z_u z_v \right) (x_{uv} X + y_{uv} Y + z_{uv} Z) \left( x_u^2 + y_u^2 + z_u^2 \right) \right\} \]

\[ \]  

in which the terms \( X \), \( Y \), and \( Z \) are defined as the components of the cross product \((x_u, y_u, z_u) \times (x_v, y_v, z_v)\), i.e.

\[ X \equiv y_u z_v - y_v z_u \]

\[ Y \equiv x_v z_u - x_u z_v \]

\[ Z \equiv x_u y_v - x_v y_u \]  

(2.16)

The surface Laplacian of the curvature is, in this case, equivalent to sum of the 2\( ^{nd} \) derivatives of the curvature with respect to the parameters \( u \) and \( v \).

\[ \nabla^2 s \kappa_{3D} = \frac{1}{(x_u^2 + y_u^2 + z_u^2)^{1/2}} \left\{ \frac{\kappa_u}{(x_u^2 + y_u^2 + z_u^2)^{1/2}} \right\} + \frac{1}{(x_v^2 + y_v^2 + z_v^2)^{1/2}} \left\{ \frac{\kappa_v}{(x_v^2 + y_v^2 + z_v^2)^{1/2}} \right\} \]  

(2.17)

Finally, the surface normal vector for a surface in three-dimensions is given as

\[ \vec{n}_{3D} = \frac{(x_u, y_u, z_u) \times (x_v, y_v, z_v)}{\|(x_u, y_u, z_u) \times (x_v, y_v, z_v)\|} = \frac{(X, Y, Z)}{(X^2 + Y^2 + Z^2)^{1/2}} \]  

(2.18)
3 Modeling Methodology

3.1 Morphological Simulations

Changes to the morphology caused by both surface diffusion and vapor transport were investigated using a finite-difference algorithm with adaptive step-size and controlled time-stepping implemented in Mathematica 9 (Wolfram). This computational tool employed the previously derived velocity equations (Eq. 2.4 and 2.9), but with the curvature $\kappa$, surface Laplacian of curvature $\nabla^2_s \kappa$, and surface normal vector $\vec{n}$ rewritten in their parametric forms (see Section 2.5).

More precisely, grain boundary grooving on a flat surface (essentially a one-dimensional system) is explored in Chapter 4, with the groove boundary condition (Eq. 2.11) introduced using a method of lines [77] and with 2nd order forward finite differences. Then, in Chapters 5, 6 and 7, the morphology of 1D PhCs (two-dimensional systems) and 2D PhCs (three-dimensional systems) are extensively simulated to understand and quantify the various changes that occur during surface evolution by capillary forces. In all cases, the simulated structures are chosen so as to produce emissivity cutoffs at a wavelength of approximately $\lambda_c = 2000$ nm, a value selected arbitrarily as approximately in middle of the near-infrared range.

In order to render the results independent of the material used, the operating temperature, and the reactions taking place, the rate constants $C_{SD}$ and $C_{VT}$ (in Eq. 2.4 and 2.9) were incorporated in the simulated time. For grain boundary grooves and two-dimensional structures, simulations were carried out until $t = 5 \times 10^{10} / C_{SD}$ s and $t = 10^5 / C_{VT}$ s for surface evolution by surface diffusion and vapor transport, respectively. These values were chosen so as to produce a relatively similar amount of degradation by both mechanisms. For three-dimensional cases, these simulated times were reduced to $t = 2 \times 10^9 / C_{SD}$ s and $t = 2 \times 10^4 / C_{VT}$ s, due to the additional computation time required, as well as the increased curvature of these structures.

3.2 Material Constants

While the calculations are made independent of the rate constants, estimates of these values can be obtained from material constants in the literature in order to assess the potential degradation speed. As tantalum and tungsten are the most commonly used materials for high temperature photonic crystal selective emitters, their parameters are listed in Table 3.1.
and 3.2 for reference. Also listed is the ratio of the grain boundary energy and the surface energy, which is used in grain boundary grooving simulations.

**Table 3.1: Material constants of tantalum**

<table>
<thead>
<tr>
<th>Material constant</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant $a_0$ (Å)</td>
<td>3.30276</td>
<td>[79–81]</td>
</tr>
<tr>
<td>Surface energy $\gamma$ (J/m$^2$)</td>
<td>2.902</td>
<td>[82–86]</td>
</tr>
<tr>
<td>Surface diffusivity $D_s$ (cm$^2$/s)</td>
<td>$18 \exp\left(-\frac{2.6}{k_B T}\right)$</td>
<td>[87–89]</td>
</tr>
<tr>
<td>GB energy ratio $\gamma_{GB}/\gamma$</td>
<td>0.28</td>
<td>[90]</td>
</tr>
</tbody>
</table>

**Table 3.2: Material constants of tungsten**

<table>
<thead>
<tr>
<th>Material constant</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant $a_0$ (Å)</td>
<td>3.16522</td>
<td>[80,91]</td>
</tr>
<tr>
<td>Surface energy $\gamma$ (J/m$^2$)</td>
<td>3.265</td>
<td>[82–86]</td>
</tr>
<tr>
<td>Surface diffusivity $D_s$ (cm$^2$/s)</td>
<td>$0.24 \exp\left(-\frac{2.85}{k_B T}\right)$</td>
<td>[92–94]</td>
</tr>
<tr>
<td>GB energy ratio $\gamma_{GB}/\gamma$</td>
<td>0.38</td>
<td>[90]</td>
</tr>
</tbody>
</table>

The approximated surface diffusion rate constants for Ta and W are plotted in Figure 3.1a as a function of temperature. This reveals that the rate increases exponentially with temperature. For instance, tantalum surfaces at 1200K and 1400K would degrade 5 times slower and 6 times faster than those at 1300K. Moreover, due primarily to its lower diffusivity, an increase in temperature of about 300 to 400K is necessary to produce the same deterioration in tungsten. However, it is worth noting that these rate constants are extremely sensitive to surface condition, and that small chemical changes have been shown to greatly influence surface diffusivity [95–97] as these impurities are located at step and kink sites that are vital for diffusion. As such, these estimates are only applicable to extremely pure surfaces, and may be taken as maximum values. Conversely, the vapor transport rate constants for Ta and W are shown in Fig. 3.1b as a function of the $P_0/\sqrt{m}$ ratio at 1450K (i.e. the optimal temperature for a 2 μm cutoff). Unlike the surface diffusion results, these are found to be practically identical due to the similarity between the lattice constants and the surface energies of tantalum and tungsten.
Figure 3.1: Surface evolution rate constants for Ta (solid blue line) and W (dashed red line); (a) \( C_{SD} \) as a function of temperature, and (b) \( C_{VT} \) as function of \( P_0/\sqrt{m} \) at 1450K.

### 3.3 Optical Simulations

Optical simulations were performed using the MIT Electromagnetic Equation Propagation (MEEP) software [98], a finite-difference time-domain (FDTD) [99] computational tool developed at MIT. This tool discretizes the structure in both space and time dimensions, and approximate derivatives by central finite differences. This allows Maxwell’s equations to be directly solved in a leapfrog manner (electric field components calculated at a given time \( t \), magnetic field components calculated at the subsequent time \( t + \delta t \), and so on).

The simulations were set up to measure the reflection of a light pulse off the surface, and the spectral emissivity is then calculated from the spectral reflectance according to Kirchhoff’s law using \( E(\lambda) = 1 - R(\lambda) \). The surface was modeled using the optical constants of tantalum at 298K. This choice is not expected to affect the conclusions of the study, which will apply to other relevant materials and to higher temperatures, as these materials are simply reflective at the wavelengths of interest; recall Fig. 1.3. The permittivity \( \epsilon(\omega) \) of tantalum at 298K was introduced using a Drude-Lorentz oscillator model, i.e.

\[
\epsilon(\omega) = \epsilon_0 + \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - i\omega \gamma_j} \tag{3.1}
\]

with the oscillator strengths \( f_j \), the resonant frequencies \( \omega_j \), and the damping constants \( \gamma_j \) fit to experimentally measured values, and tabulated in Table 3.3. The parameter \( \epsilon_0 \) is set to unity.
Table 3.3: Drude-Lorentz optical constants of tantalum at 298K

<table>
<thead>
<tr>
<th>j</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_j$</td>
<td>4.645081</td>
<td>5.230754</td>
<td>3.460918</td>
<td>4.242806</td>
</tr>
<tr>
<td>$\omega_j$</td>
<td>0.000087</td>
<td>2.172037</td>
<td>3.753765</td>
<td>7.900368</td>
</tr>
<tr>
<td>$\gamma_j$</td>
<td>0.125254</td>
<td>1.931860</td>
<td>1.499478</td>
<td>3.755287</td>
</tr>
</tbody>
</table>

3.4 Figures of Merit

In this work, two figures of merit are used to quantify, and ultimately optimize, the efficiency of a selective emitter. These are loosely based on previous optimization work [3, 100–103], but are selected such that they are independent from the efficiencies and properties of the other components of a typical TPV system, including the absorber and the PV cell.

First, the emission efficiency $\eta_e$ measures the amount of useful radiative power (i.e. with photon energies above the proposed band gap energy, or photon wavelengths below the cutoff wavelength $\lambda_c$) emitted relative to a blackbody. It is worth noting that the spectral radiance $I(\lambda, T)$ (i.e. the energy emitted per unit time at each wavelength $\lambda$ for a given temperature $T$) of a grey body with spectral emissivity $\varepsilon(\lambda)$ is given from Planck’s law as

$$I(\lambda, T) = \frac{2hc^2\varepsilon(\lambda)}{\lambda^5 \left( \exp \left( \frac{hc}{\lambda k_B T} \right) - 1 \right)}$$

in which $h$, $c$, and $k_B$ denote the Planck constant, the speed of light, and the Boltzmann constant, respectively. Moreover, the radiative power is calculated by integrating this spectral radiance over the wavelength range of interest (i.e. $P = \int I(\lambda, T) d\lambda$). The emission efficiency then takes the form

$$\eta_e = \frac{\int_0^{\lambda_c} \frac{\varepsilon(\lambda)d\lambda}{\lambda^5 \left( \exp \left( \frac{hc}{\lambda k_B T} \right) - 1 \right)}}{\int_0^{\lambda_c} \frac{d\lambda}{\lambda^5 \left( \exp \left( \frac{hc}{\lambda k_B T} \right) - 1 \right)}}$$

Second, the number of photons emitted per unit time at each wavelength is given by the spectral radiance $I(\lambda, T)$ divided by the energy per photon $E(\lambda) = hc/\lambda$, and the total
number of useful photons can then be calculated by integrating this ratio from \( \lambda = 0 \) to \( \lambda = \lambda_c \). For maximal electric power generation, each useful photon generates an electron of energy \( \frac{hc}{\lambda_c} \). The maximum electrical power is then

\[
P_{\text{max}} = \int_0^{\lambda_c} \frac{2hc^2 \varepsilon(\lambda) d\lambda}{\lambda_c \lambda^4 \left( \exp \left[ \frac{hc}{\lambda_c k_B T} \right] - 1 \right)}
\]  (3.4)

The conversion efficiency \( \eta_c \) then quantifies the quality of the energy radiated by an emitter of spectral emissivity \( \varepsilon(\lambda) \), by measuring the maximum amount of electric power it can generate relative the total amount of power it radiates.

\[
\eta_c = \frac{P_{\text{emitter max}}}{P_{\text{emitter total}}} = \frac{\int_0^{\lambda_c} \varepsilon(\lambda) d\lambda}{\int_0^{\infty} \varepsilon(\lambda) d\lambda} \frac{\lambda_c \lambda^4 \left( \exp \left[ \frac{hc}{\lambda_c k_B T} \right] - 1 \right)}{\lambda^5 \left( \exp \left[ \frac{hc}{\lambda k_B T} \right] - 1 \right)}
\]  (3.5)

Together, these two figures of merit reward high emissivity at wavelengths near the desired cutoff wavelength \( \lambda_c \), and penalize emissivity at wavelengths that stray from this cutoff. The temperature \( T \) used to calculate these efficiencies is taken as the optimal operating temperature for cutoff wavelengths of 2 \( \mu \text{m} \) (i.e. 1450K according to Eq. 1.5). While this value does affect the results obtained, it is not expected to change the general trends observed.
4 Grain Boundary Grooving

4.1 Morphological Changes

The morphologies of grain boundary grooves growing as a result of either surface diffusion or vapor transport are revealed in Figure 4.1. Note that the simulations shown were carried out using the ratio of grain boundary energy to surface energy $\gamma_{\text{GB}}/\gamma$ of tungsten, as it is larger than that of tantalum (cf. Table 3.1 and 3.2). This value then produces more rapid grooving (i.e. deeper grooves), and serves as a worst-case scenario. Moreover, both sides of the groove were assumed to be symmetric.

Figure 4.1: Morphological changes caused by grain boundary grooving as a result of (a) surface diffusion, and (b) vapor transport. The times are listed in terms of $10^7/C_{\text{SD}}$ s and $100/C_{\text{VT}}$ s, respectively, and the grain boundary is centered at $x = 0$.

In both cases, the center of the groove is found to drop to a depth of roughly 70 to 75 nm, while the width of the groove gradually increases to a size of approximately 1000 nm. Despite these similarities, significant discrepancies between the effects of the two mechanisms are also observed. Indeed, while the vapor transport results in Fig. 4.1b reveal only a deepening groove with no modification of the surrounding flat surfaces, the surface diffusion results in Fig. 4.1a show the development of oscillating bulges on either side of the groove, which generate slight modifications to the surface height that extend almost 4 $\mu$m in either direction.

This is due to a vital difference between these two limits of surface evolution by capillary forces. In fact, while vapor transport can directly transfer atoms from one region to another, evolution during surface diffusion must occur by the movement of atoms along the surface. This, in turn, signifies that a reduction in the curvature and energy of one region must be accompanied by a temporary increase in the curvature and energy of a neighbouring region as it experiences a net inflow of atoms. This characteristic difference has previously
been referred to as a “proximity effect” \[72, 73\]. Furthermore, notice that this distinction implies that while atoms cannot leave the surface during surface diffusion (i.e. it is a volume-conserving phenomenon), vapor transport can cause a net removal of atoms from the surface. This feature is also clearly portrayed in Fig. 4.1, as the volume is visibly diminished during vapor transport-based grooving.

It is worth mentioning that these grooving results can be used to validate the simulation methodology used. Indeed, as grain boundary grooving is a relatively simple case of surface evolution, analytical expressions for the dimensions of the grooves have been previously presented. For instance, Mullins’ seminal work on the subject \[60\] describes the depth of a groove undergoing surface diffusion and vapor transport using the following expressions.

\[
d_{\text{SD}} = 0.973 \tan \left( \frac{\pi - \psi}{2} \right) (C_{\text{SD}} t)^{1/4} \tag{4.1}
\]

\[
d_{\text{VT}} = 1.13 \tan \left( \frac{\pi - \psi}{2} \right) (C_{\text{VT}} t)^{1/2} \tag{4.2}
\]

A comparison between the simulated depth (black solid line) and the depth obtained from these analytical expressions (red dashed line) is shown in Figure 4.2. In both cases, a very good match is obtained, indicating the legitimacy of the modeling approach used.

\begin{figure}[h]
\centering
\begin{subfigure}[b]{0.45\textwidth}
\includegraphics[width=\textwidth]{groove_depth_surface_diffusion.png}
\caption{(a) Groove depth caused by surface diffusion.}
\end{subfigure}
\begin{subfigure}[b]{0.45\textwidth}
\includegraphics[width=\textwidth]{groove_depth_vapor_transport.png}
\caption{(b) Groove depth caused by vapor transport.}
\end{subfigure}
\caption{Comparison of the simulated (black solid line) and theorized (dashed red line) groove depth caused by (a) surface diffusion (time units of \(10^7/C_{\text{SD}}\) s), and (b) vapor transport (time units of \(100/C_{\text{VT}}\) s).}
\end{figure}

For a discussion of the rate constants, and an estimate of the annealing times necessary to produce this amount of grooving, the reader is directed to Sections 5.2 and 5.3 for evolution
by surface diffusion and vapor transport, respectively.

### 4.2 Optical Changes

The effects of the formation of a grain boundary groove on the near-infrared optical properties are shown in Figure 4.3. These were computed from the previous morphological changes at the maximal simulated times (i.e. $5 \times 10^{10}/C_{SD}$ s and $10^5/C_{VT}$ s) using the optical constants of tantalum at 298K (see Section 3.3), and by assuming that the grain structure is periodic and has a grain size of 10 µm. In both cases, no significant change in the spectral emissivity is observed. In fact, the maximum change is below 0.01%.

![Figure 4.3: Change in the emissivity of flat Ta (with a grain size of 10 µm) undergoing grain boundary grooving by either surface diffusion or vapor transport.](image)

It therefore appears that grain boundary grooves are far too shallow to have a substantial effect on the emissivity of unstructured refractory metals, and are therefore expected to have a negligible effect on the properties of high temperature PhC selective emitters. While the present results do not exclude the possibility that much smaller grain sizes might produce a significant modification to the optical behavior, such grain sizes ($\ll 10$ µm) are not encountered in the PhC literature.
5 Two-Dimensional Simulations

5.1 Simulated Structure

The initial two-dimensional structure considered, see Fig. 1.2a, is a one-dimensional photonic crystal consisting of periodic trenches of depth \(d = 5000\) nm, width \(w = 930\) nm, and period \(p = 1300\) nm. These dimensions are in line with previously investigated structures [1,21,22,28,38], and generate an emissivity cutoff at the desired wavelength of \(\lambda_c = 2000\) nm.

A comparison of the infrared spectral emissivity of this 1D PhC structure with that of a flat unstructured surface, both simulated with the optical properties of tantalum at 298K, is shown in Figure 5.1a. Unlike the flat surface, which is reflective throughout the entire near-infrared range, the structured surface comprises a series of emissivity peaks that lie between the diffraction limit \((\lambda = p)\) and the cutoff wavelength \((\lambda = \lambda_c)\). These maxima, marked \(a\) through \(f\), correspond to resonant cavity modes (see Section 1.2.2). This is confirmed by plotting the electric field of the simulated light pulse in Fig. 5.1b, which reveals that an integer number of half-wavelengths fit inside the cavity at those wavelengths. Additionally, the local minima between these peaks (with an example marked \(g\)) correspond to points at which a quarter-wavelength sticks out of the cavity. Finally, at wavelengths beyond the cutoff (marked \(h\)), the emissivity drops down abruptly to the level dictated by the average emissivity.

Figure 5.1: (a) Comparison of the infrared spectral emissivity of a 1D Ta PhC (solid blue line) and flat Ta (dashed black line); (b) electric field in the PhC at the wavelengths denoted in (a), with red and blue colors indicating positive and negative values, respectively.
dielectric constant, which depends on the volume fractions of the constituents (i.e. tantalum and free space, in this case). This is due to the fact that large wavelengths cannot discern the structuring and therefore cannot interact with it or be enhanced by it.

5.2 Surface Diffusion

The morphological changes produced by surface diffusion on the previously described 1D PhC trenches are shown in Figure 5.2. These results reveal the gradual smoothing of the structure, especially at the sharp corners where the curvature is initially unstable. This rounding progressively erodes the top of the structure as material is diffused away from it and unto the sidewalls, which then bulge outwards into the cavity. Conversely, the bottom of the cavity gradually rises as atoms are transferred to it from the nearby sidewalls, which retreat away from the center of the cavity. Both of these outcomes are caused by the previously discussed proximity effect: atoms cannot be directly relocated from regions of high curvature to regions of low curvature, but must instead flow along the surface, thus instigating temporary surges in curvature and energy in the surrounding regions in which they accumulate. This process results in nearly circular forms at the top and bottom of the cavity known as Wulff bulbs [72, 73], as they have the same shape as the material’s Wulff plot (circular in this case, as the surface energy was assumed constant). Moreover, these features steadily grow over time, thereby further decreasing their curvature.

In order to quantify the effects of surface diffusion, the evolution of the structure’s surface energy and dimensions was calculated. In Figure 5.3a, the surface energy, normalized to that of a flat surface $\gamma$, is plotted. The as-fabricated structure is found to possess nearly 9 times more surface energy than a flat surface of comparable area, due primarily to its deep cavities, as well as its rectangular shape. This amount decreases suddenly at short times as the sharp corners are abruptly rounded, and this rate of decrease steadily declines throughout the simulation.

The cavity depth, cavity width, and aperture width are plotted as a function of time in Figure 5.3b. The cavity depth is defined as the difference between the maximum $z$ value at which the width is within 10% of its initial value and the minimum $z$ value. This quantity decreases approximately linearly with time by more than 1000 nm during the entire simulation. Due to the non-uniformity in the spacing between the sidewalls, the cavity width is defined as the average spacing over the entire height of the cavity. This value changes slightly with time, from its initial value of 930 nm to its final value of 900 nm. Finally, the aperture width is defined as the minimum spacing between the sidewalls near the top of
the cavity. This measure decreases rapidly at first, and finishes up approximately 400 nm smaller than its initial value.

**Figure 5.2:** Change in morphology of a 1D PhC undergoing surface diffusion; (a) 2D cross-section (time in terms of $10^7/C_{SD}$ s), (b) 3D representation as-fabricated, and (c) after $10^{10}/C_{SD}$ s.

**Figure 5.3:** Changes caused by surface diffusion to a 1D PhC’s (a) surface energy as a multiple of the energy of a flat surface, and (b) dimensions. The time axis is in terms of $10^7/C_{SD}$ s.
The changes caused by surface diffusion to the infrared spectral emissivity of this structure are revealed in Figure 5.4a. Two major deviations from the as-fabricated emissivity (cf. Fig. 5.1a) are observed. First, the emissivity peaks are found to gradually shift towards smaller wavelengths, with the effect becoming more pronounced for higher order resonance modes (i.e. higher values of $j$ in Eq. 1.2, and thus lower wavelengths). For instance, while the 2nd order peak initially at 1874 nm moves by 19 nm, the 5th order peak at 1458 nm shifts by more than 100 nm. More importantly, however, a significant decline in the emissivity of most maxima and minima occurs as time progresses, which is most pronounced at wavelengths near the cutoff. Indeed, after $10^{10}/C_{SD}$ s, the rightmost peak is almost undetectable as its emissivity approaches that of unstructured tantalum.

This degradation of the structure’s near-infrared emissivity has noticeable consequences on its efficiency as a selective emitter, as shown in Fig. 5.4b. In fact, while the as-fabricated structure undeniably outperforms unstructured tantalum, surface diffusion causes both the emission and conversion efficiencies to decline sharply over time. At long durations, these figures of merit appear to asymptotically approach those of flat Ta, thereby indicating the complete suppression of the PhC’s ability to selectively emit at desired wavelengths.

![Figure 5.4](image)

**Figure 5.4:** (a) The infrared spectral emissivity of a 1D Ta PhC undergoing surface diffusion, and (b) a comparison of the emission (solid line) and conversion (dashed line) efficiencies of 1D Ta PhC and flat Ta over time (units of $10^7/C_{SD}$ s).

Finally, the time scale over which this degradation occurs can be estimated by assuming that the surface is free of any contaminants and using the parameters in Tables 3.1 and 3.2. For a tantalum surface, the maximal simulated degradation (i.e. $5 \times 10^{10}/C_{SD}$) would take over a year to occur at 1100K, but only 1230, 193, and 40 hours at 1200, 1300, and 1400K,
respectively. Conversely, a tungsten surface would require over a decade to achieve this level of deterioration at temperatures below 1320K. This lifetime reduces to 466 hours at 1700K. It is worth restating, however, that these times are extremely sensitive to surface condition, and could potentially be off by a few orders of magnitude.

5.3 Vapor Transport

The effects of vapor transport (or, more generally, surface-attachment-limited transport) on the shape of the 1D PhC trench are portrayed in Figure 5.5. Much like the previous results in Fig. 5.2, these findings show a rapid rounding of the structure, which focuses on the pointed corners, erodes the top of the sidewalls, and fills in the bottom of the cavity. However, unlike surface diffusion, vapor transport allows atoms to move directly from regions of high curvature to regions of low curvatures. This implies that no transfer of atoms occurs to or from the surrounding sidewalls, which then remain perfectly flat while their extremities are smoothed.

Figure 5.5: Change in morphology of a 1D PhC undergoing vapor transport; (a) 2D cross-section (time in terms of 100/$C_{VT}$ s), (b) 3D representation as-fabricated, and (c) after $5 \times 10^4/C_{VT}$ s.
The evolution caused by vapor transport is quantified by the surface energy (normalized to the energy of a flat surface), as well as the previously defined structure dimensions in Figure 5.6. The change in the surface energy follows a similar behavior as that observed for surface diffusion, with an initial rapid plunge followed by a slow but steady reduction. Interestingly, the energy varies linearly with time in this case, rather than with a gradually declining rate.

The dimensions of the cavity are shown as a function of time in Fig. 5.6b. The variation in the cavity depth is comparable to that observed during surface diffusion, with a nearly linear decrease towards a final value of under 4000 nm. On the other hand, both the cavity width and the aperture width remain relatively unchanged over time. Indeed, the aperture width, which measures the minimum distance between the two sidewalls near its opening, stays completely unmoved at 930 nm. The cavity width decreases slightly over time, as the bottom of the structure retreats further towards the cavity center than the top of the structure pulls away.

Figure 5.6: Changes caused by vapor transport to a 1D PhC’s (a) surface energy as a multiple of the energy of a flat surface, and (b) dimensions. The time axis is in terms of $100/C_{VT}$ s.

The consequences of this phenomenon on the infrared spectral emissivity are presented in Figure 5.7a. Like the surface diffusion results in Fig. 5.4a, the cavity modes are observed to shift slightly towards lower wavelengths, with the effect being more pronounced at lower wavelengths. However, the large drop in emissivity displayed by the surface diffusion results does not occur during vapor transport. In fact, while certain peaks decrease marginally, some portions of the spectrum are unchanged, and others are even enhanced (for instance, the dominant peak at 1967 nm).
These small alterations of the infrared emissivity result in minor adjustments to the efficiency of the structure as a selective infrared emitter. Indeed, both the emission and conversion efficiencies are found to stay relatively invariant, with drops from 0.56 to 0.52 and from 0.53 to 0.52, respectively, over the duration of the simulation. Moreover, both of these metrics do not decrease monotonically, but instead reach their peak at times between $t = 5000/C_{VT}$ and $t = 10000/C_{VT}$.

**Figure 5.7:** (a) The infrared spectral emissivity of a 1D Ta PhC undergoing vapor transport, and (b) a comparison of the emission (solid line) and conversion (dashed line) efficiencies of 1D Ta PhC and flat Ta over time (units of $100/C_{VT}$ s).

An estimate of the times required to reach these levels of degradation can be obtained from the tantalum and tungsten material constants tabulated in Tables 3.1 and 3.2. Assuming that the mass of the molecule being transported is on the order of $3 \times 10^{-25}$ kg (i.e. near the mass of either Ta or W), and a temperature of 1450K, equilibrium vapor pressures below $P_0 = 10^{-7}$ Pa will take more than a century to reach the maximal simulated degradation (i.e. $t = 10^5/C_{VT}$). As the rate varies linearly with the pressure, the necessary time decreases to over a decade at $10^{-6}$ Pa, to over a year at $10^{-5}$ Pa, and to about one tenth of a year at $10^{-4}$ Pa. Variations in the temperature, even on the order of $\pm 100$K, have a comparatively minor effect on this rate, and the rate is nearly identical for both tantalum and tungsten.
5.4 Effect of the Cavity Dimensions

Both surface evolution mechanisms were found to produce a characteristic shift in the position of the resonance peaks towards smaller wavelengths as time progressed (see Fig. 5.4a and 5.4a), which became more significant at lower wavelengths. From Eq. 1.2, this change can be largely attributed to a significant reduction (> 1000 nm) in the depth of the 1D PhC trenches. Indeed, as both the depth $d$ and the width $w$ decrease, the theoretical wavelength $\lambda_{ij}^{2D}$ of the cavity mode is also expected to decrease. However, while a decreasing width would produce a larger theoretical shift at lower order resonance peaks (i.e. lower $j$ values), a decreasing depth would generate the observed trend of a more significant shift at higher order resonance peaks.

To confirm this explanation, the optical properties and efficiencies of 1D PhC structures with depths ranging from 4000 to 5000 nm were simulated, as shown in Figure 5.8. As expected, a smaller cavity depth leads to a decrease in the wavelength of the cavity modes, especially at lower wavelengths. Moreover, the change from 5000 nm to 4000 nm (not shown) is very similar to the behavior observed during annealing. For example, the 3rd order peak goes from 1741 nm to 1642 nm as the depth is reduced, which is on the same order as the change during either surface diffusion or vapor transport (i.e. a decrease to 1663 or 1660 nm, respectively). It is worth noting, however, that this depth change is found to produce a relatively small drop in the efficiency of the PhC. Clearly, this effect is far from being the dominant source of declining efficiency.

![Figure 5.8](image)

**Figure 5.8**: (a) The infrared spectral emissivity, and (b) the efficiency of 1D Ta PhCs with varying cavity depths.
For the sake of completeness, the emissivity and efficiency variations caused by different cavity widths were also simulated, with the results given in Figure 5.9. The differences observed, which include a relatively significant shift in the dominant peak, are not found to correlate with the surface evolution results, despite similar decreases in the cavity width. It therefore appears that the behavior of a non-uniform cavity cannot be directly predicted from its average width.

![Graph](image)

**Figure 5.9:** (a) The infrared spectral emissivity, and (b) the efficiency of 1D Ta PhCs with varying cavity widths.

### 5.5 Effect of the Aperture Width

While both surface evolution mechanisms caused a similar reduction in the depth and width of the photonic crystal cavity, their effects on the aperture width (measured here as the minimum width near the top of the cavity) differed significantly. Indeed, while the direct transfer of atoms caused by vapor transport did not decrease this spacing (in fact, vapor transport generated a slightly larger opening due to its rounded nature), surface diffusion’s proximity effect caused the upper sidewalls to bulge inwards.

The effects of an aperture were analyzed by simulating rectangular trenches with small variations in the spacing between the top 100 nm of their cavities (see the inset cross-sections in Figure 5.10). The results indicate that the spectral emissivity is extremely sensitive to the width of the cavity opening. In fact, apertures smaller than the cavity width by as little as 100 nm produce a substantial drop in the emissivity of the peaks near the cutoff wavelength. This matches almost exactly the behavior observed during surface diffusion, but with no
change to the location of these peaks. It therefore appears that a smaller aperture does not alter the resonances, but simply reduces coupling of cavity modes into free space modes. In essence, the smaller opening allows for less interaction between the cavity and the incoming light pulse. This reduced emissivity subsequently produces a large decline in the emission and conversion efficiencies of the structure, especially when compared to the changes caused by the cavity depth or width (cf. Fig. 5.8b and 5.8b).

![Graphs showing emissivity and efficiency](image)

**Figure 5.10:** (a) The infrared spectral emissivity, and (b) the efficiency of 1D Ta PhCs with varying aperture widths.

Note, however, that an opening 100 nm larger than the width of the cavity (blue line in Fig. 5.10a) produces the opposite behavior: a slight enhancement in the emissivity by promoting better coupling into the lower order resonance modes (i.e. better interaction between the light pulse and the cavity). This, in turn, generates a slight increase in the efficiency of the structure (aperture of 1030 nm in Fig. 5.10b). Together, these observations provide an explanation for the increased emissivity of the dominant peak during vapor transport, as well as the efficiency peak observed between \( t = 5000/C_{VT} \) and \( t = 10000/C_{VT} \) (see Fig. 5.7). Indeed, it appears that the rounded opening behaves as a larger aperture, which causes a slight rise in the efficiency of the structure that is gradually overcome by the decreasing cavity depth.
6 Two-Dimensional Optimization

6.1 Size Effects

In order to achieve an optimized PhC structure that is resistant to surface diffusion and vapor transport, the effects of its dimensions (i.e. period $p$, width $w$, and depth $d$) on the rate of degradation must be determined. This was realised by simulating the morphological changes that occur during surface evolution by capillarity on a series of structures in which one of these dimensions is altered and the remaining two are kept constant.

First, the behavior of 1D PhC structures with different periods is revealed in Figure 6.1. Regardless of the surface evolution mechanism, the structures with smaller periods are found to degrade faster (a greater reduction in depth, for instance) than those with larger periods. Interestingly, this change is exclusively displayed at the top of the cavity, while the bottom remains unchanged.

![Figure 6.1](image)

Figure 6.1: Morphological changes in structures undergoing surface diffusion (a,b) and vapor transport (c,d) with width $w = 900$ nm, depth $d = 5000$ nm, and variable periods $p = 1250$ nm (a,c) and $p = 1500$ nm (b,d).

This behavior can be explained by evaluating the curvature of the structure. In fact, assuming that the structures are nearly circular once they are slightly rounded (a valid assumption as surface diffusion produces circular Wulff bulbs, and vapor transport will reduce...
the curvature and thus also produce circular shapes), the curvature of the top of the sidewalls can be approximated by $\kappa_{\text{top}} \approx 2/(p - w)$. On the other hand, the curvature of the bottom of the cavity approaches a value of $\kappa_{\text{bottom}} \approx 2/w$. As such, increasing the period with a constant cavity width causes the top curvature to decrease, but does not affect the bottom curvature.

Then, the behavior of 1D PhCs with different widths is shown in Figure 6.2. As expected from the previous analysis, an increasing width causes the curvature of the sidewalls to increase and the curvature of the bottom of the cavity to decrease. This is exactly the outcome observed, with the structures with larger widths (Fig. 6.2b and 6.2d) degrading faster near their top and slower near their bottom than comparable structures with smaller widths (Fig. 6.2a and 6.2c).

![Figure 6.2](image)

**Figure 6.2:** Morphological changes in structures undergoing surface diffusion (a,b) and vapor transport (c,d) with period $p = 1400$ nm, depth $d = 5000$ nm, and variable widths $w = 800$ nm (a,c) and $w = 1000$ nm (b,d).

Finally, the effect of a variable depth is explored in Figure 6.3. Unlike the period or the width, the depth does not affect the curvature of the structure and is therefore not expected to cause a change in the rate of degradation, and this is indeed the behavior observed. That being said, a smaller depth will however reduce the time required for the top and bottom of the cavities to interact. This is made obvious in Fig. 6.3a, where the top and bottom Wulff
bulbs are in very close proximity after $t = 5 \times 10^{10}/C_{SD}$ s.

Figure 6.3: Morphological changes in structures undergoing surface diffusion (a,b) and vapor transport (c,d) with period $p = 1300$ nm, width $w = 900$ nm, and variable depths $d = 4000$ nm (a,c) and $d = 6000$ nm (b,d).

Additionally, it is worth noting that due to the formation of bulbs during surface diffusion, the dimensions of the cavity also affect the behavior at infinite time. This is reminiscent of a Rayleigh instability [43]: shallow and wide cavities, whose bulbs will be small in comparison to their width, will tend to flatten out. Conversely, deep and narrow cavities, whose bulbs will be large compared to their width, will ultimately form a subsurface pore.

6.2 Optimized Rectangular Structure

From an understanding of these size effects, an optimized structure which has a high efficiency that is stable over time can be determined. As the cavity width and depth determine the cutoff wavelength, and as the effects of the cavity depth on the degradation rate are relatively negligible, these two values are kept constant at 930 and 5000 nm for the sake of consistency and to allow comparisons with the results of Chapter 5. The only remaining degree of freedom is then the period $p$ of the structure, which decreases the surface evolution rate as it is increased.
However, it is worth noting that an increase in the periodicity results in a decrease in the emissivity and the efficiency of the PhC structure. This is due to the fact that the emissivity enhancement occurs primarily between the cutoff wavelength, which depends on the cavity dimensions, and the diffraction limit, which is equal to the period. As such, a larger period decreases the wavelength range over which emission is enhanced, which in turn causes the emission efficiency to drop.

To determine the optimal period which improves the stability without significantly altering the optical properties, the total efficiency over the entire time span is calculated according to

$$\eta_{\text{tot}} = \frac{1}{t_f} \int_0^{t_f} \eta_e \eta_c dt$$

(6.1)

This quantity is plotted as a function of the period for both surface evolution mechanisms in Figure 6.4. In either case, the total efficiency peaks at intermediate periods, and decreases as the period approaches either the cavity width (causing rapid degradation) or the cutoff wavelength (resulting in negligible emission enhancement).

![Figure 6.4: Total integrated efficiency (with $t_f = 5 \times 10^{10}/C_{SD}$ for surface diffusion, and $t_f = 10^5/C_{VT}$ for vapor transport) as a function of the structure period.](image)

For surface diffusion, the drop in efficiency over time is large (recall Fig. 5.4b), and the benefits of an improved stability outweigh the detriments of reduced emissivity enhancement. The maximal total efficiency then occurs at a relatively large period value of $p = 1800$ nm.
Conversely, the efficiency decline during vapor transport is small (see Fig. 5.7b). As such, a smaller period that results in greater emissivity enhancement is favored, and the maximum efficiency occurs at approximately $p = 1550$ nm.

In order to balance these two contributions, a value of 1700 nm is selected as the optimal periodicity for a 1D PhC with a cutoff wavelength of 2000 nm. The morphological changes that befall such a structure during surface evolution are illustrated in Figure 6.5. For either mechanism, this deterioration is found to be far less than that observed for the initial structure (cf. Fig. 5.2 and 5.5).

![Figure 6.5: Morphology changes for an optimized rectangular structure undergoing (a) surface diffusion, and (b) vapor transport. The times are listed in terms of $10^7/C_{SD}$ s and $100/C_{VT}$ s, respectively.](image)

### 6.3 Optimized Rounded Structure

The rectangular shapes studied thus far are discontinuous at their corners, which causes their curvature, as well its derivatives, to be unstable. This, in turn, produces a high initial surface evolution rate which rapidly deteriorates the emissivity and the efficiency of the structure.
As such, further improvements to the stability of PhC selective emitters can be achieved by considering rounded structures which possess fewer discontinuities.

To study this effect, a series of structures were constructed from linear segments, as well as curved segments based on parametric functions with a generalized Fresnel integral form, i.e.

\[
(x(s), z(s)) = B \left( \int_0^s \sin \frac{\pi}{2} u^n du, \int_0^s \cos \frac{\pi}{2} u^n du \right)
\]

in which \( B \) is a coefficient selected to match the size of the structure, and the exponent \( n \) determines the order of the integral. These equations define spirals that allow for the right-angle bends necessary for photonic crystal cavities, with \( s = 0 \) at 0° and \( s = 1 \) at 90°. More importantly, however, these functions have a convenient curvature \( \kappa \), gradient of curvature \( \kappa_s \), and Laplacian of curvature \( \nabla_s^2 \kappa \) behavior. Indeed, these depend on the Fresnel integral order according to

\[
\kappa = \frac{\pi}{2} \frac{n}{B} s^{n-1}
\]

(6.3)

\[
\kappa_s = \frac{\pi}{2} \frac{n(n-1)}{B^2} s^{n-2}
\]

(6.4)

\[
\nabla_s^2 \kappa = \frac{\pi}{2} \frac{n(n-1)(n-2)}{B^3} s^{n-3}
\]

(6.5)

The properties of the different structures are then summarized as follows

1. Rectangular structures can be expressed as 0\textsuperscript{th} order Fresnel integrals, and thus have \( \kappa = \kappa_s = \nabla_s^2 \kappa = 0 \). That being said, the discontinuities at their corners render their curvature unstable at those sites.

2. 1\textsuperscript{st} order Fresnel integrals define circular sections that are continuous throughout the structure, including across the junction between linear and curved segments. However, their curvature is discontinuous at this junction, where it abruptly shifts from \( \kappa = 0 \) to \( \kappa = \pi/2B \). Their gradient of curvature is therefore unstable.

3. 2\textsuperscript{nd} order Fresnel integrals, known typically as clothoids, Euler spirals, or Cornu spirals, have a linearly increasing curvature which is continuous throughout the structure. However, abrupt changes in the gradient of curvature cause \( \nabla_s^2 \kappa \) to be unstable at junctions between different linear and curved segments.

4. Finally, 3\textsuperscript{rd} order generalized Fresnel integrals have curvature proportional to \( s^2 \), gradient of curvature proportional to \( s \), and a constant nonzero Laplacian of curvature. This

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signifies that the junction between the linear and curved segments has a continuous \( \kappa_s \), and a stable \( \nabla^2 \kappa_s \).

As they would not result in fewer discontinuities, Fresnel integral orders higher than 3 are not considered here. The four remaining shapes \((n = 0 \text{ to } n = 3)\) are then plotted in Figure 6.6, with the previously established optimal dimensions (i.e. \( d = 5000, w = 930, \) and \( p = 1700 \) nm). Notice that unstable sites are marked by black circles, and that the curvature is illustrated by inscribed green circles, which become progressively smaller, thereby signifying a larger curvature, as the structure becomes less discontinuous. Additionally, the aperture width increases slightly with increasing Fresnel integral order.

![Figure 6.6](image)

**Figure 6.6:** PhC structures constructed from linear segments and generalized Fresnel integrals of order (a) \( n = 0 \), (b) \( n = 1 \), (c) \( n = 2 \), and (d) \( n = 3 \). Black circle denote unstable locations, and green circles illustrate local curvature.

As the differences between the morphological deterioration of these generalized Fresnel integral structures are rather subtle, they are best portrayed by plotting the reduction in the cavity dimensions over time, as exemplified by Figure 6.7. In all cases, increasing the Fresnel integral order slightly reduces (by up to 30 nm) the amount of degradation that the structures experience. For surface diffusion (Fig. 6.7a), this improvement gradually decreases with time as the structures tend towards similar final shapes. Conversely, evolution by vapor transport (Fig. 6.7b) appears to cause a widening gap between the different shapes over time.
Figure 6.7: Reduction in (a) the aperture width during surface diffusion, and (b) the effective depth during vapor transport, for optimized Fresnel integral structures. Times are given in terms of $10^7/C_{SD}$ s and $100/C_{VT}$ s, respectively.

The emission and conversion efficiencies of these optimized structures are compared to those of the initial rectangular structure discussed in Chapter 5 in Figure 6.8. The results for optimized $n = 1$ and $n = 2$ structures are not shown for simplicity, but were consistently found to be between those of their $n = 0$ and $n = 3$ counterparts.

In the case of surface diffusion, all optimized structures are found to have an improved stability when compared to the initial structure, which is displayed by the more gradual decline in the efficiency. For instance, a reduction in the emission efficiency to a value of 0.3 requires about $1.7 \times 10^{10}/C_{SD}$ for the initial structure but approximately twice as long for the optimized structures. That being said, the $0^{th}$ order Fresnel integral structure balances this enhanced stability with a reduction in the as-fabricated (i.e $t = 0$) emission efficiency $\eta_e$, as discussed in Section 6.2. Indeed, this metric drops from 0.56 for the initial shape to 0.50 for the optimized one. On the other hand, the rounded $3^{rd}$ order structure not only boosts the stability of selective emitter, but actually increases the efficiencies at all times, including $t = 0$, when compared to either the initial or optimized rectangular PhCs. This can be rationalized by considering the enlarged aperture of the rounded structures, which, as explained in Section 5.5, allows for better coupling to the long wavelength cavity modes and therefore results in a rising spectral emissivity.

The effects of optimization are less obvious in the vapor transport results, but follow the same trends. For example, while the optimized $n = 0$ structure experiences a seemingly significant drop in emission efficiency, its amplified conversion efficiency and stability nev-
ertheless produce a slight increase in its total integrated efficiency. Moreover, the 3rd order Fresnel structure is once again a clear winner, due to its higher emission efficiency and higher conversion efficiency than the optimized and initial rectangular structures, respectively.

Figure 6.8: Comparison of the emission (solid line) and conversion (dashed line) efficiencies of the initial and optimized structures undergoing (a) surface diffusion (units of 10⁷/CSD s) and (b) vapor transport (units of 100/CVT s). The ηc results for vapor transport are shifted by -0.1 for clarity.
7 Three-Dimensional Simulations

7.1 Simulated Structures

The initial structures studied in this Chapter are two-dimensional photonic crystals consisting of periodic arrays of either cylindrical or rectangular cavities (recall Fig. 1.2b and 1.2c). For consistency, the cavity dimensions were once again selected to generate an emissivity cutoff at the desired wavelength of $\lambda_c = 2000$ nm. This entailed a radius $r = 540$ nm and a width $w = 920$ nm, for the cylindrical and rectangular cases, respectively. The depth of the cavity was kept constant at the previously used value of $d = 5000$ nm, while the period was increased slightly to $p = 1400$ nm in order to accommodate the much larger diameter of the cylindrical cavity (its maximal width is 1080 nm, as opposed to 930 and 920 nm, for the 2D and 3D rectangular cavities). Once again, these dimensions are almost identical to those used in recent investigations of PhC selective emitters [1,21,22,28,38].

7.2 Morphological Changes

The morphological evolution of a 2D cylindrical PhC by surface diffusion and vapor transport are shown in Figures 7.1 and 7.2, respectively. The surface diffusion results reveal a behavior that is analogous to that obtained in 1D PhCs in Chapter 5. Indeed, the degradation begins with the rapid rounding of the initially sharp edges (see Fig. 7.1b), and proceeds with the formation of Wulff bulbs (see top of cavity in Fig. 7.1c) that gradually decrease the aperture radius from 540 to 475 – 480 nm with only minor modifications to the cavity radius and depth.

In the case of vapor transport, the degradation is again similar to that previously observed in two-dimensional space, with a smoothing of the corners of the cavity that comes about without any bulging. However, whereas 1D PhCs have zero curvature at all positions away from these sharp edges, the sidewalls of this cylindrical cavity have a constant nonzero negative curvature throughout. This leads to a gradual movement of the sidewalls towards the cavity center which progressively decreases the radius of the entire cavity from 540 to 500 nm.

Additionally, one noteworthy feature present for both surface evolution mechanisms is an angular dependence on the degradation. Indeed, positions at which the separation between the cavities is at a minimum will tend to have rapidly decreasing depths, while positions shifted by $45^\circ$ from these (at which the separation is at a maximum) will bulge upwards.
slightly. This ultimately generates an undulating surface topology.

These 2D cylindrical results are contrasted with those of 2D rectangular PhCs in Figures 7.3 for surface diffusion and 7.4 for vapor transport. In these cases, the evolution of the surface rapidly erodes not only the top and bottom of the cavity, where the curvature is initially unstable, but also the edges of the sidewalls. Interestingly, despite the starkly
different initial structures, both surface diffusion and vapor transport steadily reshape the initially rectangular cavities into cylindrical ones (for instance, compare Fig. 7.1c and 7.3c). However, their initially smaller dimensions cause them to be slightly narrower than their purely cylindrical counterparts.

**Figure 7.3:** Morphology of a 2D rectangular PhC undergoing surface diffusion, (a) as-fabricated, (b) after $2.5 \times 10^8/C_{SD}$ s, and (c) after $2 \times 10^9/C_{SD}$ s.

**Figure 7.4:** Morphology of a 2D rectangular PhC undergoing vapor transport, (a) as-fabricated, (b) after $2.5 \times 10^3/C_{VT}$ s, and (c) after $2 \times 10^4/C_{VT}$ s.
Finally, it is worth noting certain striking similarities between the present simulated results and the experimental findings of Sai et al. [16] previously shown in Fig. 1.4. In fact, not only do both sets of results reveal a smoothing and rounding of the initially sharp features, they both also reveal the evolution of initially rectangular cavities into nearly cylindrical ones, as well as the bulging of positions at which the cavity separation is largest, thereby producing a characteristic undulating surface shape.

### 7.3 Optical Changes

As was the case for 1D PhCs, the morphological changes caused by capillarity have a significant effect on the optical properties of more complex 3D structures. This is portrayed in Figure 7.5 which plots the infrared spectral emissivity of 2D tantalum PhCs with cylindrical and rectangular cavities both before and after evolution by surface diffusion.

![Figure 7.5](image.png)

**Figure 7.5:** The effects of surface diffusion on the infrared spectral emissivity of 2D Ta PhCs with (a) cylindrical, and (b) rectangular cavities. The time is listed in terms of $10^7/C_{SD}$ s.

Regardless of the cavity shape, the initial emissivity spectra consist of numerous peaks that once again represent cavity resonances (dictated by either Eq. 1.3 or 1.4, depending on the cavity shape). However, surface diffusion causes the aperture of the cavities to close off, which was previously shown to reduce coupling into low order resonances (recall Section 5.5). This is exhibited in both Fig. 7.5a and 7.5b as a reduction in the emissivity of the maxima and minima near the cutoff wavelength, and is in agreement with previous 1D PhC results.
One noteworthy difference in the behavior of the two types of structures during surface diffusion is a pronounced shift in the cutoff wavelength for PhCs with rectangular cavities. This is due to the fact that the cavity is progressively reshaped into a cylindrical form, which possesses a smaller radius and thus displays a smaller cutoff wavelength.

The effect of vapor transport of the optical properties of 2D tantalum PhCs is revealed in Figure 7.6. In contrast to the surface diffusion results, no drop in emissivity is experienced in this case. In fact, the spectral emissivity of the dominant peak (i.e. the peak immediately preceding the cutoff) actually increases slightly, a feature that can be attributed to the rounded nature of the cavity which then serves as a larger aperture (see Section 5.5). That being said, a gradual shift in the position of the peaks, as well as a displacement of the cutoff wavelength, occurs for both cylindrical and rectangular cavities, with the effect more pronounced at larger wavelengths and for the rectangular structures. This change can be traced back to the reduction in the cavity radius during vapor transport in 3D. Indeed, following the discussion of Section 5.4, this would generate the observed trend of a larger shift at lower order resonances (i.e. lower values of \( k \) in Eq. 1.3 and 1.4, and larger wavelengths), and would be more significant for rectangular cavities due to their smaller final radii.

Figure 7.6: The effects of vapor transport on the infrared spectral emissivity of 2D Ta PhCs with (a) cylindrical, and (b) rectangular cavities. The time is listed in terms of \( 100/C_{VT} \) s.

In all cases, the modification of the spectral emissivity is found to have a negative impact on the structure’s ability to perform as a selective emitter. This declining performance is especially important for rectangular structures, due to the greater reduction in the dimensions of their cavities. For instance, the emission efficiency of a 2D Ta PhC with cylindrical cavities decreases from a value of 0.68 in its as-fabricated state to values of 0.64 and 0.66
after degradation by surface diffusion and vapor transport, respectively. On the other hand, the emission efficiency of a similar PhC with rectangular cavities drops from 0.72 to either 0.60 after surface diffusion or 0.63 after vapor transport.

7.4 Optimization

In order to assess the potential for optimization of these 2D PhCs, the effects of their dimensions on the degradation rates were determined. In order to maintain the same cutoff wavelength, the cavity radius and depth were kept constant for consistency, as was the case in Chapter 6. The only remaining variable is then the periodicity of the structure, which, much like the previous 1D PhC results (see Section 6.1), was found to improve resistance to capillarity as it is increased. Indeed, while the average aperture radius was reduced by up to 62 nm for the initial cylindrical structure (with \( p = 1400 \) nm) during surface diffusion, this amount decreased to 46 nm and 42 nm for periods of 1600 and 1800 nm, respectively. Likewise, the drop in cavity depth during vapor transport decreased from 117 nm to as little as 10 nm as the periodicity was enlarged from 1400 to 1800 nm.

These findings are exemplified by Figures 7.7 and 7.8, in which the morphologies of 2D cylindrical PhCs with periods ranging from 1400 to 1800 nm are shown at the maximum simulated times (i.e. \( 2 \times 10^9 / C_{\text{SD}} \) and \( 2 \times 10^4 / C_{\text{VT}} \) s). The most visible feature is a reduction in the undulating surface topography with increasing periodicity for either surface evolution mechanism, which is caused by the reduced curvature of the structure. Additionally, a slight decrease in the tapering of the cavity during surface diffusion can also be discerned (see Fig. 7.7). It is worth noting, however, that the diameters of the cavities undergoing vapor transport are all identical (see Fig. 7.8), as their gradual diminution depends solely on the initial radius.

Moreover, regardless of the PhC’s period, additional improvements of up to 25% (in terms of the amount of aperture radius or cavity depth change during annealing) could be made by employing rounded (\( n = 1 \) in the generalized Fresnel integral formulation of Eq. 6.2) cavities. Together, these outcomes reveal that realistic two-dimensional photonic crystal selective emitters are amenable to the same optimization procedures detailed in Chapter 6, which involved the maximization of the total efficiency (Eq. 6.1) over a given time range by varying the structure’s period, and reducing the number of curvature discontinuities.
Figure 7.7: Morphology after degradation by surface diffusion for $2 \times 10^9/C_{SD}$ of 2D cylindrical PhCs with varying periods (a) $p = 1400$ nm, (b) $p = 1600$ nm, and (c) $p = 1800$ nm.

Figure 7.8: Morphology after degradation by vapor transport for $2 \times 10^4/C_{VT}$ of 2D cylindrical PhCs with varying periods (a) $p = 1400$ nm, (b) $p = 1600$ nm, and (c) $p = 1800$ nm.
8 Conclusion

Photonic crystals are known to degrade through a wide range of mechanisms, with one of the most notable being surface evolution due to capillary forces, in the form of either surface diffusion or vapor transport. In order to extensively probe the effects of these phenomena on the morphology and the optical properties of photonic crystals, as well as their ability to behave as selective emitters, a comprehensive computational study was undertaken. It was concluded that

- Surface evolution initiated the formation of wide grooves at the intersections between free surfaces and grain boundaries. However, these features were far too shallow to produce any changes to the optical properties of the surface.

- Conversely, these same processes were found to greatly alter the shape of one-dimensional photonic crystals in order to reduce their surface energies, which, in turn, resulted in substantial modifications to their optical properties.

- Indeed, smoothing by surface diffusion caused the photonic crystal cavities to gradually close off. This was due to a “proximity effect”, which requires atoms to flow along the surface from high energy regions to low energy ones, thereby resulting in temporary bulges in the surrounding areas. This phenomenon reduced coupling into cavity resonance modes, and thus significantly reduced the emissivity and efficiency of the structure.

- Alternatively, while vapor transport also produced a rounding of the structure, its ability to directly transfer atoms from high curvature to low curvature regions prevented any changes to the width of the cavity. This smoothing then generated a comparatively small variation in the optical properties of the photonic crystal.

- These forms of degradation were found to be sensitive to the dimensions of the structure, with larger periods and smaller cavity widths reducing the deterioration rate. Additionally, rounded structures with fewer discontinuities in their curvature, also achieved slightly better stability over time.

- By considering these size and shape dependencies, optimized one-dimensional photonic crystal structures were presented, which possessed higher efficiencies that were stable with respect to surface evolution. The best results were obtained with structures made up of 3rd order generalized Fresnel integrals.
• Finally, cursory verifications were performed on more realistic, but more complex, three-dimensional structures (2D photonic crystals with square arrays of cylindrical or rectangular cavities). Despite a few notable differences, such as the reduction of the cavity radius during vapor transport, the effects described, as well as the solutions proposed to inhibit them, were nevertheless found to be valid.


9 References


