A generalized “cut and projection” algorithm for the generation of quasiperiodic plasmonic concentrators for high efficiency ultra-thin film photovoltaics

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Abstract: This report will present a generalized two-dimensional quasiperiodic (QP) tiling algorithm based on de Bruijn’s “cut and projection” method for use in plasmonic concentrator (PC) / photovoltaic hybrid devices to produce wide-angle, polarization-insensitive, and broadband light absorption enhancement. This algorithm can be employed with any PC consisting of point-like scattering objects, and can be fine-tuned to achieve a high spatial density of points and high orders of local and long-range rotational symmetry. Simulations and experimental data demonstrate this enhancement in ultra-thin layers of organic photovoltaic materials resting on metallic films etched with arrays of shallow subwavelength nanoholes. These devices work by coupling the incident light to surface plasmon polariton (SPP) modes that propagate along the dielectric / metal interface. This effectively increases the scale of light-matter interaction, and can also result in constructive interference between propagating SPP waves. By comparing PCs made with random, periodic, and QP arrangements, it is clear that QP is superior in intensifying the local fields and enhancing absorption in the active layer.

OCIS codes: (350.6050) Solar energy; (240.6680) Surface plasmons; (310.6628) Subwavelength structures, nanostructures; (160.4890) Organic materials.

References and links

Thin film solar cells offer several advantages over traditional thick film devices—such as better electron transport properties and higher open circuit voltages [1]—but thicker films have the inherent advantage of being better absorbers of sunlight. To compensate for this, recently there has been a push to incorporate plasmonic concentrators (PCs) into thin film solar cells to improve the absorption properties of such devices, and thus improve the overall power conversion efficiency [2,3]. There are numerous examples of this unification of the fields of plasmonics and photovoltaics with researchers using various arrays (e.g., periodic, random, or spiral) and nanoscale scatterers (e.g., disks, spheres, ridges, grooves, or holes) [4–10] as a means of improving optical absorption. The authors have recently demonstrated a particularly successful example of PCs arranged in two-dimensional quasiperiodic (QP) layouts [11]. These deterministic aperiodic patterns were originally developed to tessellate planes with...
This report introduces a novel algorithm for generating QP patterns across a wide spectrum of point densities and orders of rotational symmetry (both local and long-range), and can also be used to reproduce certain periodic arrays. The results of this algorithm can be employed with PCs comprised of any type of symmetric scattering object (e.g., holes, spheres, or disks) to produce spectrally broad and angle- and polarization-insensitive enhancement. The scatterers used in this report are shallow holes with sub-wavelength diameters etched on the back metal contact, underneath the active layer. This particular type of PC is also known as a nanohole array (NHA). Nanoholes have two advantages in this context: in addition to having a relatively simple fabrication process – typically either via Nanoimprint Lithography (NIL), or Focused Ion Beam (FIB) milling, neither of which requires depositing extra material–nanoholes will not reflect or transmit a significant fraction of the incident light. It should also be noted that there have been studies on aperiodic NHAs for extraordinary transmission [12–14]. However, those structures employ through-holes, which are not compatible with solar cells – the nanoholes of this paper are very shallow compared to the thickness of the metal substrate to prevent light from being transmitted. Further, those papers only consider a small handful of aperiodic patterns, and in some cases the patterns were not truly QP, in that they maintained translational symmetry through the use of repeating unit cells; this report will cover a wide variety of purely QP geometries.

When employed in a solar cell, an NHA works as follows: the holes scatter the incident light field and reradiate a fraction of it along the dielectric / metal interfacial plane in the form of surface plasmon polaritons (SPPs). This structure enhances absorption in the active layer through two methods: (1) having the light redirected along the interfacial plane allows for increased light-matter interaction compared to single-pass absorption through the thin film; (2) if two or more holes are close to each other, the waves can constructively interfere and create strong EM fields, both locally and averaged over the entire array area. One of the goals of this report is to fine-tune the QP generation algorithm to see how the array’s properties (order of base polygon and inter-hole distance) affect absorption enhancement. Additionally, it will be argued that QP arrays are superior to comparable periodic and random arrays in absorption enhancement. It is believed that this concept should enhance absorption in any ultra-thin layer of absorbing material; an organic bulk heterojunction was chosen here as a proof of concept.

This report is broken into three sections. Section 1 will introduce the QP generation algorithm, provide a protocol on how to implement it, and explain some of the key properties as functions of its two tunable parameters. Section 2 delves into the underlying physics of plasmonic concentrators and thin film solar cells. In particular, the SPP propagation constants in a three layer system will be calculated, and are used to simulate the interference properties of several SPPs generated by an array of many nanoholes serving as localized sources of SPPs at various frequencies. In section 3, EM field enhancement and absorption enhancement are studied as functions of the two QP parameters using both simulations and experimental data.

1. Generalized construction algorithm for periodic and quasiperiodic arrays

To understand how quasiperiodic arrays were originally devised, imagine trying to tile a 2-D plane with regular N-sided polygons such that there are no empty spaces. This can be done easily with triangles \( (N = 3) \), squares \( (N = 4) \), and hexagons \( (N = 6) \), but there is a peculiar gap at \( N = 5 \). In 1974, Penrose developed a QP tiling method that employs two types of rhombi to tessellate the plane while maintaining five-fold rotational symmetry [15]. In 1981, de Bruijn proposed an algebraic theory for the generation of Penrose’s non-periodic tiling of
the plane. His algorithm, known as the “cut and projection” method, involves taking a 5-D hyperspace, dividing it into unit cubes whose vertices are at integer coordinates, intersecting the hyperspace with a 2-D plane, then projecting the centers of the bisected unit cubes orthogonally onto the plane. De Bruijn demonstrated that the ensemble of the projected points can be turned by a similarity transformation into the full set of vertices of Penrose’s tessellation [16].

This report introduces a generalization of the cut and projection method that can be used with a hypercube of any dimension (N). What follows is a step-by-step description of the algorithm for creating such patterns:

1. First, select a dimension number for the hypercube, \( N \geq 3 \). The axes of the hypercube are also called grids. A system made with five grids is called “penta-grid” (also called “Penrose-grid”), one made with seven grids is called “hepta-grid,” and so on. The grids exist in a complex space (“grid space”) defined by \( z = u + iv \), where \( u \) and \( v \) are real numbers. If \( N = 3, 4 \) or 6, the resulting array will be periodic; for all other values, the array is quasiperiodic.

2. Define a set of \( N \) real irrational numbers \( \{ \gamma_j \} \), where \( j \) is the integer grid index (with \( 1 \leq j \leq N \)). \( \gamma_j \) is the point on the \( j \)th grid where it is intersected by the 2-D plane. The user is free to pick any values for the set \( \{ \gamma_j \} \), but in addition to being real and irrational, there are other conditions: the set must sum to zero, and must be selected such that every point in the complex plane belongs to no more than two of the \( N \) grids (in practice, this can be achieved by making each \( \gamma_j \) value within a particular set unique). Different sets of \( \{ \gamma_j \} \) can produce slightly different real space arrays, but the reciprocal spaces will be identical.

3. The 2-D real space that contains the points of the tiling is called “array space,” with real coordinates \( x \) and \( y \). The function \( f(z): \mathbb{C} \rightarrow \mathbb{R}^2 \) maps the location of a vertex (i.e., a point of the QP array) from the \( N \)-hypercube onto a 2-D plane. It is defined by

\[
f(z) = \sum_{j=1}^{N} \kappa_j(z) \zeta^{j-1}, \tag{1a}
\]

Where

\[
\kappa_j = \left\lfloor \text{Re}[z \zeta^{j-1} + \gamma_j] \right\rfloor \tag{1b}
\]

\( \zeta = \exp[2\pi i / N] \), and \( \left\lfloor q \right\rfloor \) is the “roof” of \( q \), defined as the smallest integer \( n \) such that \( n \geq q \).

4. Set a scaling factor \( a \) (this can be understood as an equivalent lattice constant) to define the characteristic hole-to-hole separation. For simple periodic arrays (like square and hexagonal), this is identical to the array “pitch” or “lattice constant” (the distance between nearest neighbors). Depending on the context, \( a \) can be expressed in terms of pixels or meters; for this report, \( a \) will be on the order of \( \sim 10^2 \) nm.

5. For a given value of \( z \), the corresponding point (i.e., the location of the scatterer) in the real space array is located at \( (x, y) = \left( \text{Re}[f(z) a], \text{Im}[f(z) a] \right) \).

6. The process is repeated by rasterizing \( u \) and \( v \) in order to pick up every possible point in the array space (for the best results, the raster should be repeated multiple times, with the step size decreasing each time until a convergence in the number of points is observed). Typically, there are regions of neighboring points in grid space that are...
mapped to the same point in array space, so some array points will be found multiple times. These regions are called domains.

Fig. 1. Visual representation of the generalized cut and projection algorithm, starting in complex “grid space”, then moving to the real “array space” (which contains the actual pattern), then ending in reciprocal space (for analytical purposes). The algorithm works by mapping – via the function $f(z)$ – domains in the complex plane to points in real space, thus determining the position of points in the array. Corresponding domain-hole pairs are identified by the same color (colors are based on the distance from the central point of symmetry; 18 shown here). The examples of planar tilings provided have the same scaling factor ($a$) and hole diameter ($D$), but are made with different grid numbers ($N$). The top two examples are periodic: tri-grid ($N = 3$, a.k.a. honeycomb) and quad-grid ($N = 4$, a.k.a. square). The bottom two examples are quasiperiodic: penta-grid ($N = 5$, a.k.a. Penrose) and octo-grid ($N = 8$). The figures in the right column were obtained by performing a 2-D discrete fast Fourier transform (DFFT) on the real space array; the scale bar in those figures is $2\pi / a$. The insets in the right column show the first Brillouin zones of the Fourier power spectrum of each pattern; the scale bar in those inset figures is $\pi / a$. 
The resultant arrays can be identified by just two tunable parameters: the scaling factor $a$, and the grid number $N$. Although the set $\{\gamma_j\}$ can be altered (within the rules laid out in step #2), that is not considered a tunable parameter because changing $\{\gamma_j\}$ usually does not produce significant differences in key properties like planar density of points or in the reciprocal spaces.

Figure 1 shows the major steps of this process for several representative periodic and quasiperiodic arrays. For each pattern, the left column shows its grid space and the middle column shows its array space – each domain-point pair (as determined by the mapping function $f(z)$) is drawn in the same color in both columns. The colors are chosen based on the distance of the hole from the central point of symmetry in each array space; that is, every hole with the same color is equidistant from a central point (18 colors in all). The array of points is then transformed to reciprocal space (right column – note that this is not on the same color scheme as the other two columns) using a discrete fast Fourier transform (DFFT). This is often necessary when studying patterns with high $N$ values, as some of the relevant parameters (such as degree of rotational symmetry) are difficult to infer using the naked eye. For a given scaling factor, the area of the first Brillouin zone (FBZ) of every QP pattern is identical to the area of the FBZ of the corresponding tri-grid pattern. Since that quantity is well defined (a hexagon of area $6\sqrt{3}\pi^2 / a^2$), this can be used to define the scaling factor $a$ more concretely when discussing higher-order QP arrays.

One of the most important properties is the order of rotational symmetry, which is found by counting the number of points that circumscribe the FBZ in the reciprocal space images. For example, the penta-grid example in Fig. 1 (3rd row, right column) displays 10-fold symmetry about the center. The order of local rotational symmetry is closely related to the number of nearest neighbors that a typical hole will have. For instance, the square array in Fig. 1 (second row) is defined by four-fold rotational symmetry, which means that every hole in a square array has four nearest neighbors (ignoring holes at the boundary).
complicated QP patterns, it is not accurate to say that each point will be surrounded by the same number of nearest neighbors, but rotational symmetry is still important because it indicates that the points in the array are spread out evenly. As will be discussed below, it is essential in this device that each hole and the available space are being used as efficiently as possible in the light concentration process. For example, a highly asymmetric pattern may have regions with few or no holes, thus diminishing the beneficial effects of the plasmonic concentrator – quantifying the pattern’s rotational symmetry in such a manner helps the design process.

A quantitative overview of the predominant trends in these QP arrays is provided in Fig. 2. Figure 2(a) indicates that when \( N \) is even, the rotational symmetry of the array—determined by analyzing its Fourier power spectrum—equals \( N \), but when \( N \) is odd, the rotational symmetry of the array equals \( 2N \). Figure 2(b) plots the density of holes as a function of grid number for certain \( a = 400 \) nm patterns. All QP arrays (open diamonds) have higher hole densities than the periodic arrays (full diamonds), which further supports the hypothesis that QP arrays are better than periodic ones; indeed, if rotational symmetry was of no concern, QP arrays would still be better than periodic arrays due to this fact. Finally, note that the density of holes increases as the scaling factor decreases (see Fig. 2(c), which reports data for a heptadeca-grid pattern, with \( N = 17 \) and varying \( a \); the insets show the array and reciprocal space images for an \( N = 17, a = 250 \) nm QP pattern). As will be shown below, it is possible to create patterns that will produce much stronger absorption enhancement than a basic periodic array using only the two tunable parameters. For example, the data from Fig. 2 allows for a direct comparison of \( a = 400 \) nm heptadeca-grid and tri-grid patterns: although their FBZs are identical in size, the former has an order of rotational symmetry 5.67x greater than the latter (34 vs. 6), and a spatial density of points that is 1.66x greater (7.91 holes / \( \mu \)m\(^2\) vs. 4.76 holes / \( \mu \)m\(^2\)).

2. The physics of plasmonic concentrators & thin film solar cells

Consider a semi-infinite dielectric / metal interface; when light (free space wavelength \( \lambda \)) is normally incident on this interface, most of the radiation will be reflected back in the direction it came (Fig. 3(a)). Now imagine that there is a shallow circular hole (diameter \( D \ll \lambda \); this is known as the sub-wavelength regime) etched on the metallic surface (Fig. 3(b)). When light hits the hole, the incident radiation is coupled to the electron plasma in the metal to form a surface plasmon polariton (SPP). SPP modes can only form if some sort of corrugation or prism is present on the interface to compensate for the mismatch in the incident wave’s momentum and the SPP’s momentum. Since an SPP is an electromagnetic wave, Maxwell’s equations can be used to describe its propagation behavior. For the case of a semi-infinite dielectric / metal system, the parallel component of the wavevector is given by

\[
k_{\parallel}(\omega) = \frac{\omega}{c} \sqrt{\varepsilon_1 \varepsilon_2} = \frac{\omega}{c} n_{\text{SPP}}
\]

while the perpendicular component on the dielectric (\( i = 1 \)) or metal (\( i = 2 \)) side is

\[
k_{\perp,i}(\omega) = \sqrt{\varepsilon_i \left( \frac{\omega}{c} \right)^2 - k_s^2}
\]

where \( \omega = 2\pi c / \lambda \) is the angular frequency, \( c \) is the speed of light, \( n_{\text{SPP}} \) is the effective index of refraction of an SPP mode, and \( \varepsilon_1 = \varepsilon_1(\omega) \) and \( \varepsilon_2 = \varepsilon_2(\omega) \) are the dimensionless frequency-dependent complex dielectric functions of the dielectric and metal materials, respectively [17]. Other useful SPP parameters include the wavelength \( \lambda_{\text{SPP}} = \lambda / \text{Re}[n_{\text{SPP}}] \),
propagation length $\Lambda_{\text{spp}} = 1/(2\text{Im}[k_x])$, and skin depth $\delta = 1/\text{Im}[k_z]$. In the case of a three-layer system (vacuum / dielectric / metal), the dispersion relation will be calculated following the calculations developed by Dionne, et al. [18]. When generalizing to a 2-D interface, the in-plane SPP wavevector will be referred to as $k_{\text{spp}}$.

Fig. 3. Schematic detailing the process of absorption enhancement in a plasmonic concentrator (PC) realized using a nanohole array (NHA). (a) Light normally incident on a flat metal surface is mostly reflected back. (b) If light is normally incident on a nanocorrugated metal / dielectric interface, some fraction of the incident radiation can be converted to a propagating SPP mode (with amplitude scattering efficiency $\beta$). Constructive interference between SPP modes originating from neighboring holes can significantly increase the light intensity at the metal / dielectric interface, thus contributing to enhanced light absorption if the dielectric material is an optical absorber.

Although Fig. 3(b) shows only two holes, the figure does help demonstrate how the nanohole array (NHA) plasmonic concentrator works when scaled up to hundreds or thousands of holes, in which case the two tunable parameters of the QP array generator can profoundly affect the absorption enhancement process. Recall that the scaling factor ($a$) is directly related to the density of holes (Fig. 2(c)). Generally speaking, a smaller value for $a$ is better, as it means there are more locations where the incident light has a chance to scatter into SPP modes, and having the holes closer together means that the SPP waves do not have to travel as far to meet a counter-propagating wave and constructively interfere with it. The grid number ($N$) is related to the rotational symmetry of the array, and thus how many nearest neighbors a typical hole will have. As the incident sunlight is randomly polarized, it is expected that, on average, the SPP modes will emerge from the holes omnidirectionally, so having as many nearest neighbors as possible should lead to better constructive interference patterns.

It has been shown experimentally that SPP modes do propagate on the interfacial plane [19] and can exhibit bulk-like absorption within an optically-thin superstrate dielectric material (e.g., by a 20nm-thick layer of CdSe quantum dots [20]). The absorbing dielectric material here will be the organic bulk heterojunction formed by the polymer poly(3-hexylthiophene) (P3HT) and the fullerene (6,6)-phenyl C$_{61}$ butyric acid methyl ester (PCBM); the metal will be silver. P3HT:PCBM is one of the most widely studied active layers in organic thin film photovoltaics [21]; its highest recorded power conversion efficiency is 5% [22,23]. By comparison, the current state of the art for all single-junction organic solar cells is 10% [24]. One of the main setbacks hindering effective photovoltaic conversion in organic materials is the low exciton diffusion length (e.g., 4-12 nm in P3HT:PCBM [25,26]). Making the film thickness comparable to the diffusion length provides a way of avoiding this issue; incorporating a PC (such as an NHA) into such a device can enhance absorption in an
otherwise optically thin layer. In this manner, the benefits of a thin film solar cell (improved carrier transport behavior) are merged with the benefits of a thick film solar cell (improved light absorption) to create a high-efficiency device.

Figure 4 plots the SPP dispersion relation (the real part of $k_x$ vs. incident wavelength) and SPP propagation length in four different configurations parameterized by $d$, the thickness of the middle P3HT:PCBM layer in a three-layer vacuum / P3HT:PCBM / Ag system. The dispersion relations have been numerically calculated using the experimentally determined complex dielectric constants of Ag and P3HT:PCBM [27]. The $d = 0$ (no organic layer) and $d = \infty$ (no vacuum layer) cases were modeled as two-layer systems; the $d = 24$ nm and $d = 150$ nm cases were modeled as three-layer systems. The SPP propagation length graph provides significant insight in how an NHA can enhance absorption in the active layer. First, $\Lambda_{SPP}$ defines the scale of the extra light-matter interaction that occurs when the incident light is redirected perpendicular to the direction of incidence. Second, note that local constructive interference cannot occur if the SPP modes die out shortly after leaving each hole. Generally
speaking, the device performs better when the SPP propagation length is as large as possible (this is why silver was chosen as the metallic substrate in this paper – its dielectric properties are such that Im[\(\gamma_{SPP}\)] is relatively low).

The inset in Fig. 4(b) shows normalized plots of the \(E_x\) component of the SPP wave parameterized by \(d\), with the incident light at \(\lambda = 700\) nm. This shows the transition of the SPP mode from vacuum, to ultra-thin, to thin, and to bulk. The fact that the field amplitude rapidly decays on the metal side of the interface (quantified by the skin depth, \(\delta_z\)) further demonstrates that Ag is an appropriate choice for the substrate material – with most of the SPP’s energy on the dielectric side, there is a better chance for absorption and photocurrent enhancement, whereas energy on the metal side is essentially unusable. Although the propagation length increases significantly at higher wavelengths, this should be tempered by the fact that the band gap of P3HT is 670 nm (\(=1.85\) eV), so absorption beyond that wavelength will probably not produce any significant amount of photocurrent.

It appears as though the system reaches the “bulk limit” before \(d = 150\) nm, as the data for \(d = 150\) nm and \(d = \infty\) look quite similar. Aside from the benefits inherent in using a 24-nm-thick layer vis-à-vis the low exciton diffusion length, there are several reasons why a plasmonic concentrator etched on the back contact will have a greater impact when the active layer is thinner:

i. The propagation length increases as \(d\) decreases, as seen in Fig. 4(b). This means that the plasmonic concentrator (PC) will be more effective if coated with a thinner absorbing layer.

ii. Having a thinner layer means that more of the incident light will reach the NHA in the first place; therefore, an increased fraction of the incident light is scattered and turned into usable SPP modes.

iii. SPP modes are confined to the dielectric / metal interface and have finite skin depths; thus, most of the SPP’s energy will not reach the upper parts of thicker layers.

All this information, combined with previous research on SPP generation and absorption, suggests that the NHA paradigm should work to help improve the efficiency of a solar cell.

Finally, note that the absorption properties of the devices discussed in this paper cannot be analyzed in terms of the well-known “ergodic limit,” which claims that the maximum absorption enhancement factor a thin film can exhibit is \(4n^2\), where \(n\) is the index of refraction of the material [28–30]. The ergodic limit applies to films with textured / inhomogeneous surfaces – in this model, light can be trapped in the thin film in a waveguide-like mode, but reflections off the corrugated surface will randomize the paths of the rays, thus increasing the effective path length by \(4n^2\) when averaged over all angles, and when the film is adjacent to a perfectly reflecting surface on its back side. The derivation assumes that bulk absorption is weak enough throughout the layer such that the internal light intensity is uniform (that is, \(\alpha d \ll 1\), where \(\alpha = 4\pi\kappa / \lambda\) is the absorption coefficient of the material, \(\kappa\) is the wavelength-dependent imaginary part of the index of refraction, and \(d\) is the thickness of the layer), while at the same time assuming that the layer is much thicker than the incident wavelength \(\lambda\) (that is, \(d \gg \lambda\)). The first assumption is needed to give the direction of the light rays a chance to be sufficiently randomized by the corrugated surface; the second assumption is required when employing classical ray tracing arguments. In ultra-thin films, constructive interference between reflected waves within the layer is key in understanding absorption phenomena; optical ray tracing does not account for that. The second assumption clearly does not apply in this case, where the layer thickness is typically \(d = 24\) nm, and the incident wavelength is on the order of \(\sim 10^3\) nm. When trying to apply both assumptions simultaneously, it requires that \(1 \ll d / \lambda \ll 1/(4\pi\kappa)\); since \(\kappa\) for most materials (including P3HT:PCBM) is large when \(\lambda\) is small, this can present a contradiction, or will only allow the approximation to work in a narrow wavelength range.
3. SPP interference behavior in quasiperiodic, periodic, and random arrays

3.1 Description of simulation program

One of the hypotheses of this section is that NHAs made with higher $N$ values will provide better absorption enhancement than ones with low $N$ values, as high $N$ patterns have higher orders of rotational symmetry (Fig. 2(a)) and higher densities of holes (Fig. 2(b)). The next set of simulations model the interference behavior of SPP modes in two different NHAs with the same scaling factor: one periodic (low $N$), and one quasiperiodic (high $N$). In theory, the latter should have stronger EM fields across the entire plane, which implies stronger absorption in the active layer.

Although there are commercially available programs to model such a system (e.g., Lumerical’s Finite Difference Time Domain Maxwell Solver), they tend to be slow and computationally intensive. The authors present a quicker and easier simulation code, where an inherently 3-D problem is reduced to a simpler 2-D problem by confining the problem to the P3HT:PCBM / Ag interface, then using knowledge of the vertical field profiles (see the inset of Fig. 4(b) for examples) and the skin depths to complete the picture. In this model, each hole is assumed to be a source of planar SPP modes described by the three-layer $k_{SPP}$ wavevector (which is understood to have been created by a monochromatic, normally incident wave of wavelength $\lambda$). It is also assumed that the incident light is randomly polarized, so the SPP modes will propagate omnidirectionally and radially outward from each hole. To express this quantitatively, the field at any point on the plane (located at $r$) due to the $j$th hole (located at $r_j$) is given by

$$H_j(r) = \frac{H_0 \beta_j}{|r - r_j|} \exp \left[ i (k_{SPP} \cdot (r - r_j) + \phi_j) \right]$$

where $H_0$ is the amplitude of the incident wave, $\beta_j$ is the scattering efficiency of the $j$th hole (defined as the fraction of incident light that is turned into an SPP, originally introduced in Fig. 3(b)), and $\phi_j$ is the relative phase between the incident wave and the SPP wave emanating from the $j$th hole. The program renormalizes at the location of the hole itself ($r = r_j$) to avoid singularities. Each field spreads out evenly in a circle on the planar interface, which accounts for the inverse square root dependence. Since SPPs are transverse magnetic (TM) and confined to the plane, this is the only component of the magnetic field present [17]. The fields due to every hole are summed together at every point in space to produce a single map (specific for each incident wavelength). A map can be identified by the function

$$I(r, \lambda) = \frac{1}{H_0^2} \left| \sum H_j(r) \right|^2,$$

where the total SPP field intensity is normalized against the incident field to produce a quantity in arbitrary units. To simplify things further, any map can be described with a single number using the spatial average integral $\langle I(\lambda) \rangle = \frac{1}{area} \int \int I(r, \lambda) dx dy$, also in arbitrary units. It is important to note that $I(r, \lambda)$ only includes the field intensity of the interfacial SPP modes; it does not include any information about EM fields present in the absorbing layer due to classical light reflection and transmission behavior.

In Eq. (3), the two parameters $\beta_j$ and $\phi_j$ can be altered as needed to account for different devices and conditions. In general, $\beta_j$ and $\phi_j$ can depend on the materials used, the incident wavelength, the angle of incidence, the size and shape of the hole, etc. In the current model, all the holes are identical in size and shape and are being illuminated by the same light, so it is not unreasonable to assume that $\beta_j$ and $\phi_j$ are constants here. To obtain usable values for these
parameters, data from an extraordinary transmission experiment was used, wherein light (\(\lambda = 514.5\) nm) was normally incident on two holes (\(D = 50\) nm) bored through a layer of Ag, with SiO\(_2\) on top [19]. It was found that the phase difference between the incident wave and the SPP wave was \(\pi/2\), so \(\phi_j\) is set accordingly here. The SPP wave amplitude was found to be 35% of the incident amplitude, so \(\beta_j\) is set to 0.35 \(\mu m^{1/2}\) in Eq. (3). There is reason to believe that the holes scatter SPP modes reasonably well at all of the relevant incident wavelengths – that is, \(\beta_j\) may not be exactly 35% in all cases, but it should not deviate by a large amount, either. A systematic study is still needed, but it is known from other experiments that the scattering coefficient of a 200nm-wide shallow groove at a vacuum / Ag interfaces varies between 17% and 27% for incident light in the visible range [31].

3.2 Absorption enhancement as a function of grid number

![Scaling factor \(a = 400\) nm](image)

Fig. 5. Simulations of the normalized field intensity \(I(\lambda, \lambda)\) in square (periodic, \(N = 4\)) and heptadeca-grid (QP, \(N = 17\)) NHAs at four different incident wavelengths. In all cases, the array scaling factor is \(a = 400\) nm and the organic layer is 24 nm thick. The scale bars seen in the square, \(\lambda = 500\) nm case (both in the main figure and the inset) apply to all other images. Note that the color bar has been rescaled from 0 to 10 for clarity; the color seen on the map does not necessarily correspond to the actual value of \(I(\lambda, \lambda)\) (the zero value stays the same after the rescale). The calculated SPP propagation length is included for each of the four wavelengths studied (obtained from Fig. 4(b)).

Figure 5 presents a set of simulations of \(I(\lambda, \lambda)\) at the P3HT:PCBM (\(d = 24\) nm) / Ag interface for the square (\(N = 4\)) and heptadeca-grid (\(N = 17\)) NHAs at certain wavelengths, all with scaling factor \(a = 400\) nm. The inset in each panel is a zoomed-in image from the same location. Table 1 lists the calculated values for \(\langle I(\lambda, \lambda)\rangle\) (the spatial average of the intensity) and \(\text{max}[I(\lambda, \lambda)]\) (the highest intensity value observed) for each map. In the low wavelength limit, it is expected that the relative advantages and disadvantages of the different patterns should not matter as much because the SPP propagation length is so low (see Fig. 4(b)), so the SPP’s energy will quickly dissipate and almost no constructive interference will occur. This is what is observed, but there still may be certain regions where two or more holes happen to be extremely close together by chance (this is more likely to happen in the heptadeca-grid case, due to its inherent non-periodicity), which will produce a large value for \(\text{max}[I(\lambda, \lambda)]\), even though the average intensity \(\langle I(\lambda, \lambda)\rangle\) will be roughly the same in the two patterns (see Table 1). As \(\lambda\) and \(\Lambda_{SPP}\) increase, constructive interference becomes more prominent, so it is
necessary to closely examine the mechanisms underlying this phenomenon. It was stated before that the heptadeca-grid pattern should produce higher SPP fields on average due to its higher density of holes (which implies more scattering centers and more chances for constructive interference), and because of its higher order of rotational symmetry. To better understand the importance of rotational symmetry, consider the fact that any given hole in the square array only has four directions along which other holes are spaced at distances that are integer multiples of \(a\). The existence of these favored angles is confirmed by looking at the reciprocal space image of the square pattern (or indeed any periodic pattern), which shows discrete points as opposed to diffuse rings. Along every other direction, the hole distance are not integer multiples of \(a\), which leads to the possibility of destructive interference. Indeed, that is what is observed in the top row of Fig. 5: as the wavelength increases, out of phase SPPs emanating from holes not along the preferred line of sight will reach this “test” hole. Ergo, the amount destructive interference increases, which in turn causes \(\langle I(\lambda) \rangle\) to decrease (see Table 1). Looking at the top row more closely (in particular, \(\lambda = 580\) nm), it is clear that the local maxima are stronger near the edges of the array than in the center – this could be explained by the fact that holes on the edge of the pattern are less likely to have an off-angle neighbor, so there is less destructive interference. On the other hand, there is no favored angle in a quasiperiodic array, as the diffuse rings surrounding the first Brillouin zone can attest to. The diffusiveness of this ring (or, equivalently, the average number of nearest neighbors a typical hole will have) is a function of \(N\). In practice, this means a typical hole in a QP pattern is more likely to have a nearest neighbor with the correct distance for constructive interference to occur, which is why increasing the wavelength (and increasing \(\Lambda_{SPP}\)) has a net positive effect, as seen in Table 1.

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>Square ((N = 4))</th>
<th>Heptadeca-grid ((N = 17))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(&lt;I&gt;) (a.u.)</td>
<td>max([I]) (a.u.)</td>
</tr>
<tr>
<td>500</td>
<td>0.90</td>
<td>6.53</td>
</tr>
<tr>
<td>580</td>
<td>0.66</td>
<td>5.99</td>
</tr>
<tr>
<td>650</td>
<td>0.41</td>
<td>4.15</td>
</tr>
<tr>
<td>700</td>
<td>0.50</td>
<td>4.44</td>
</tr>
</tbody>
</table>

This model can offer significant insight into SPP behavior in thin films, but it must first be tested against experimental data. Ostfeld and Pacifici studied absorption enhancement in layers of P3HT:PCBM resting on Ag films that had been etched with periodic and quasiperiodic NHAs [11]. Although the data from that report clearly demonstrated that having an NHA will enhance absorption in organic thin films across a wide wavelength range, it was not well understood why some patterns worked better than others. To prepare the samples, P3HT and PCBM (1:1 weight ratio) were dissolved in dichlorobenzene at 50°C, then spincoated (at 5000 rpm for 60 sec to create a 24-nm-thick P3HT:PCBM layer, or at 1000 rpm for 60 sec to create a 150-nm-thick layer) onto 300-nm-thick Ag films that had been etched (via Focused Ion Beam milling) with periodic or QP NHAs, all of which was followed by annealing at 110°C for 10 minutes. The nanoholes were 70 nm deep, which is shallow enough to assume that no light is transmitted though the Ag layer. Each NHA had a total area of 100 \(\mu\)m \(\times\) 100 \(\mu\)m, and the hole diameter was \(D = 80\) nm in all cases. The incident beam was sent through a 40x objective lens with a numerical aperture of \(NA = 0.6\), then collected by the same lens to record the combined specular and diffuse reflectance \(R\). The spectral absorptance \(A\) was obtained using the formula \(A = 1 - R\) (since transmittance \(T = 0\)). Note that this is in contrast to the simulations above, where the incident light is assumed to be normal.
Fig. 6. (a) Experimental spectral absorptance (A) in a P3HT:PCBM film for different thicknesses (d) and NHAs [11]. The d = 0 case refers to just a vacuum / Ag interface. The equivalent lattice constant is a = 400 nm in all cases. (b) Spectral absorption enhancement when comparing a corrugated structure to an uncorrugated structure. The curves shown here are found by taking the “corrugated” curves from part (a) and dividing by an “uncorrugated” curve of the same thickness. (c) Comparison of heptadeca-grid to square in two different contexts (both at d = 24 nm). Left axis (solid magenta line): ratio of experimental absorptance (from panel (a)). Right axis (orange spheres): ratio of simulated normalized spatially-averaged field intensities (from simulations similar to those reported in Fig. 5).

Figure 6(a) plots the spectral absorptance in the P3HT:PCBM layer in a variety of devices: different active layer thicknesses were used, and back metal surfaces could have square, heptadeca-grid, or no NHA present (if an NHA is present, the scaling factor is a = 400 nm). The case plotted with the thin dotted line (d = 0, no NHA) is identical to a piece of pure, uncorrugated silver. This figure shows that the gap in absorptance between a thin 150 nm layer and an ultra-thin 24 nm layer can be partially filled by incorporating an NHA into the
device. This means that a 24-nm-thick P3HT:PCBM solar cell can benefit from the high absorption of a bulk-like layer without sacrificing its higher internal quantum efficiency (IQE). Of the two NHAs considered from this graph, the heptadeca-grid NHA outperforms the square NHA across the entire recorded spectrum, further confirming the original hypothesis. In Fig. 6(b), the “corrugated” (with NHA) curves of Fig. 6(a) are divided by the corresponding “uncorrugated” (without NHA) curves of the same thickness. The data shows that the NHA has very little effect in the $d = 150$ nm case, as the enhancement level is close to one for the entire recorded spectrum. On the other hand, the ultra-thin $d = 24$ nm cases show very strong absorptance enhancement, peaking at a factor of 6 near the band gap for the $N = 17$ case. These results confirm the hypothesis laid out in the end of section 2, which argued that the NHA will have a stronger effect if placed under a thinner absorbing layer.

Figure 6(c) compares heptadeca-grid to square in terms of both simulated and experimental data (everything in Fig. 6(b) has $a = 400$ nm and $d = 24$ nm). The left axis (solid magenta line) plots the ratio the experimental absorptance curves (from panel (a)), while the right axis (orange spheres) plots the ratio of the $\langle I(\lambda) \rangle$ values (from Fig. 5 and Table 1).

Absorptance is proportional to the square of the electromagnetic field, which is exactly what $\langle I(\lambda) \rangle$ measures. Since the only difference between the corresponding $N = 4$ and $N = 17$ curves is the nature of the extra SPP field present on the P3HT:PCBM / Ag interface, it is expected that these quantities are directly proportional to each other. Indeed, that is what is seen here, as the data follow the same trend across the entire recorded spectrum. Notice that both curves are at $\sim 1$ (meaning no relative enhancement) up until about 580 nm, which is also where the $\Lambda_{SPP}$ curve starts to increase (see Fig. 4(b)). In the high $\Lambda_{SPP}$ regime, heptadeca-grid should dominate due to its higher density of holes and higher order of rotational symmetry, which is observed here. The fact that the experiments and simulations match up so well gives credence to the model developed above; further improvements to the model will be discussed in future reports.

### Table 2. Calculated short-circuit current density based on the measured absorptance spectra as reported in [11].

<table>
<thead>
<tr>
<th>Name</th>
<th>Order of rot. sym.</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Relative increase vs. uncorrugated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square</td>
<td>4</td>
<td>6.935</td>
<td>33.3</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6</td>
<td>7.151</td>
<td>37.4</td>
</tr>
<tr>
<td>Penta</td>
<td>10</td>
<td>7.162</td>
<td>37.6</td>
</tr>
<tr>
<td>Dodeca</td>
<td>12</td>
<td>7.433</td>
<td>42.8</td>
</tr>
<tr>
<td>Heptadeca</td>
<td>34</td>
<td>7.521</td>
<td>44.5</td>
</tr>
</tbody>
</table>

The rest of the data from [11] is summarized in Table 2. The experimental spectral absorptance was used to calculate the short circuit current density ($J_{sc}$) via the formula

$$J_{sc} = e \int \eta_{IQE}(\lambda) A(\lambda) \left( \frac{dJ}{d\lambda} \right) d\lambda$$

where $e$ is the charge of an electron, $\eta_{IQE}(\lambda)$ is the internal quantum efficiency, and $\frac{dJ}{d\lambda}$ is the standard AM1.5G solar intensity spectrum (in units of photons / (s m² nm)). As a conservative estimate, it will be assumed that no significant exciton generation occurs beyond the band edge; thus, the range of integration was 400 nm < $\lambda$ < 670 nm. As for the IQE, it is expected to be very close to 100% for a layer as thin as this one; one recent report put it at $\sim 95\%$ for a similar P3HT:PCBM device [32]; for simplicity, it will be assumed that IQE is not a function of wavelength. The data shows that not only does the presence of an NHA
enhance absorption in all cases (when compared to an uncorrugated device whose $J_{sc}$ is 5.204 mA / cm²), but also NHAs with higher values of $N$ work better than ones with low $N$ values.

3.3 Absorption enhancement as a function of array scaling factor

Although it is expected that a higher density of holes will produce better absorption in the active layer, there is limit on how dense the holes can be before the surface of the metal is completely etched away (at which point the plasmonic concentrator would essentially be a nanopillar array). There needs to be enough material surrounding the hole for the electron plasma to reside. Considering the chosen hole diameter ($D = 80$ nm) and the known surface plasmon polariton (SPP) propagation lengths (Fig. 4(b)), it is expected that the ideal scaling factor should be on the order of $10^2$ nm, which is why $a = 400$ nm was the primary value used in this report.

**Fig. 7.** Simulations of the normalized field intensity ($I(r, \lambda)$) in PCs consisting of various NHAs with $a = 200$ or 850 nm, at three different incident wavelengths. In all cases, the grid number is $N = 17$ and the organic layer is $d = 24$ nm. The scale bars seen in the $a = 200$ nm, $\lambda = 450$ nm case (both in the main figure and the inset) apply to all other images. As with Fig. 5, the color bar has been rescaled from 0 to 10, with the zero point same after rescale). The calculated SPP propagation length is included for each of the three wavelengths studied (obtained from Fig. 4(b)).
Table 3. Summary of simulated intensity maps from Fig. 7 (a comparison of \(a = 200\) nm vs. \(a = 850\) nm when \(N = 17\)): space-averaged SPP field \(\langle I(\lambda) \rangle\) and highest intensity that is observed on a given map \(\text{max}[I(r,\lambda)]\).

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>(a = 200) nm</th>
<th>(a = 850) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(&lt;I&gt;) (a.u.)</td>
<td>(\text{max}[I]) (a.u.)</td>
</tr>
<tr>
<td>450</td>
<td>0.79</td>
<td>16.95</td>
</tr>
<tr>
<td>580</td>
<td>1.63</td>
<td>24.51</td>
</tr>
<tr>
<td>650</td>
<td>4.85</td>
<td>91.30</td>
</tr>
</tbody>
</table>

The next data sets look at how the device performs when the grid number is held constant but the scaling factor changes. Figure 7 shows simulations of \(I(r,\lambda)\) at various wavelengths and scaling factors, with \(N = 17\) and \(d = 24\) nm. A summary of \(\langle I(\lambda) \rangle\) and \(\text{max}[I(r,\lambda)]\) for each map is provided in Table 3. As with Fig. 5, the results can largely be understood in terms of the SPP propagation length: when the wavelength is low, the SPP propagation length is also low, so the overall enhancement is weak. However, the 200 nm case produces better enhancement from the sheer volume of holes – there are more scattering centers, thus more SPPs mode present on the interface. There is only a moderate amount of constructive interference occurring, and is only visible in a few specific locations were there happen to be two or more holes very close together by chance. By the same token, the value of \(\text{max}[I(r,\lambda)]\) for the 850 nm case probably would have been even lower had it not been for one small region where two holes are very close together; ultimately, the value for \(\langle I(\lambda) \rangle\) in the 850 nm case is extremely small in the low wavelength regime, as expected. It is interesting to note that the 850 nm case is so sparse that increasing \(\Lambda_{\text{SPP}}\) by a factor of 2.5 (from \(\Lambda_{\text{SPP}}(\lambda = 450\,\text{nm}) = 0.2\,\mu\text{m}\) to \(\Lambda_{\text{SPP}}(\lambda = 580\,\text{nm}) = 0.5\,\mu\text{m}\)) produces a very small increase in \(\langle I(\lambda) \rangle\). It is not until the SPP propagation length exceeds the characteristic distance of 850 nm does any sort of constructive interference start to occur.

The experiments from section 3.2 were repeated for this group of devices, but the maximum incident wavelength was reduced to 650 nm. Figure 8(a) shows the experimental absorption spectrum as a function of scaling factor. It can be seen that the absorptance maximum redshifts as \(a\) increases – this is probably a combination of varying interference conditions by increasing the characteristic hole-hole spacing, and of longer propagation lengths needed as the holes move farther apart, which occurs if the wavelength increases. Figure 8(b) takes the ratio of the absorptance curve against that of an uncorrugated device (recall that the \(a = 200\) and 850 nm patterns were shown in Fig. 7; the 400 nm pattern was shown in Fig. 5, lower row). Throughout almost the entire reported spectrum, the absorptance in a corrugated device equals or exceeds the absorptance in an uncorrugated device, as evidenced by the fact that the three normalized curves in Fig. 8(b) are greater than or equal 1. Again, \(\Lambda_{\text{SPP}}\) provides the insight needed to understand this figure: at low wavelengths, the enhancement in the 400 nm and 850 nm cases is negligible, as the holes are too far apart and...
the propagation length is too low, but the 200 nm case is dense enough to see some enhancement. As $\Lambda_{\text{SPP}}$ increases, the enhancement factor starts to improve, but much more slowly for the very sparse 850 nm case.

Using Eq. (5), a plot of short-circuit current density versus scaling factor is presented in Fig. 9 for a heptadeca-grid and a random NHA; Scanning Electron Microscope images of the $a = 200$ nm and $a = 850$ nm heptadeca-grid NHAs (fabricated on Ag) are also provided. At each data point on the $a$ axis, the two curves have the same density of holes, but the former was made with the standard QP algorithm, and the latter was made by randomizing the location of the points (while still avoiding accidental overlap). In the available data, the QP pattern peaks at $\lambda = 300$ nm, while the random pattern peaks at 200 nm. In other words, the QP pattern does not work best when the hole density is as high as possible, but the random one does. The latter point can be more easily explained: because there is no symmetry to speak of, hole density is the only relevant parameter. There appears to be something akin to a $\sim a^{-2}$ relationship between $J_{sc}$ and $a$ for the random curve. This is not too surprising, as the density of holes is closely related to $a$, and the density of holes will have a strong effect on $J_{sc}$. In fact, the density of holes in a square array is precisely defined by this $a^{-2}$ expression, but more complicated patterns may have a slightly different relationship; this $a^{-2}$ trend was also present in Fig. 2(c).

![Figure 8](image-url)

**Fig. 8.** (a) Experimental spectral absorptance of a 24-nm-thick P3HT:PCBM film in the presence of several PCs consisting of various quasiperiodic NHAs with the same order of rotational symmetry (heptadeca-grid, $N = 17$) but different equivalent lattice constants ($a$, in nm), as well as an uncorrugated structure (to serve as a reference for the absorption enhancement). (b) Absorptance enhancement in the specific NHAs, defined as that device’s absorptance curve divided by the uncorrugated curve.
The other key point in Fig. 9—that the smallest studied value for $a$ does not produce the best enhancement—cannot be explained as easily. One phenomenon that has not yet been considered is the possibility of an SPP being scattered back up into the vacuum when it hits another hole. Although the odds of this happening are generally small (and only a fraction of the energy will be lost in such a process), it is more likely to occur in the very dense 200 nm case. This could help explain why a “compromise” value of $a = 300$ nm produces the best $J_{sc}$ for the heptadeca-grid case.

![Fig. 9. Calculated short-circuit current ($J_{sc}$) as a function of NHA scaling factor, as well as the percent increase with respect to an uncorrugated device ($J_{sc} = 4.09$ mA / cm$^2$), as calculated using the data in Fig. 8 and assuming AM1.5G illumination conditions. In all cases, $d = 24$ nm, and IQE = 95%. The two curves refer to patterns with the same planar density of holes, but one is QP ($N = 17$) and the other is purely random. Insets: Scanning Electron Microscope images of heptadeca-grid NHAs (one at $a = 200$ nm, the other at $a = 850$ nm) etched on a 300-nm-thick Ag film.](image)

Looking at the general trend, Fig. 9 shows that the calculated $J_{sc}$ in the presence of either a random or heptadeca-grid NHA will produce a higher short-circuit current density when compared to the same solar cell without a PC present on the back metal contact, no matter what the scaling factor is. It is interesting to note that in both the case of extremely small $a$ ($= 200$ nm) and the extremely large $a$ ($= 850$ nm), the two patterns produce roughly the same $J_{sc}$. The latter situation is easily explained, as the holes are so far apart that next to no constructive interference will occur at all, and any enhancement is purely due to increasing the scale of light-matter interaction. In the former case, it is possible that the density of points is so high that every hole will have a relatively close by neighbor along every line of sight, even in the random case. Thus, the otherwise beneficial effects of high rotational symmetry will be neutralized in this ultra-high density regime.

**Conclusion**

This report has introduced a generalized tiling algorithm that can generate 2-D quasiperiodic patterns; both the planar density of points and the orders of local and long-range rotational
symmetry can be fine-tuned across a wide range of values. While this may prove to be interesting and insightful from a purely mathematical point of view, this algorithm was developed specially for use with in nanoscale plasmonic concentrators, in particular with plasmonic concentrators that have been incorporated into thin film solar cells. This merging of the fields of plasmonics and photovoltaics is needed to compensate for the poor absorption properties of thin film photovoltaic materials. By corrugating the back metal contact with a quasiperiodic array of nanoscale holes, it was found that absorption enhancement is a function of the two tunable parameters used in the QP array generation algorithm \((N, a)\). This can be understood by examining the underlying physics of PCs, where incident light is coupled to surface plasmons in the metallic substrate then propagate along the interfacial plane, thus increasing the scale of light-matter interaction and increasing the chances of constructive interference. The layout of the nanoholes was found to be vital in determining the level of constructive interference—the level of enhancement was greater when the hole-hole spacing in the pattern is low, and when the order of local rotational symmetry was high. There are still numerous questions that need to be resolved in future research, such as how high the grid number can go before the enhancement level saturates, and if different arrays with the same symmetry behave similarly. Additionally, the simulations can be improved by further exploring the scattering mechanism of the nanoholes—specifically, extracting more information on the scattering efficiency \((\beta)\) and launching phase \((\phi)\) of a nanohole as functions of intrinsic and extrinsic parameters. In any case, this novel paradigm should significantly expand the fields of plamonics and thin film photovoltaics, as the generation algorithm presented here can be employed not only for hole arrays, but also with any other planar arrangement of sub-wavelength scatterers (such as disks, nanoparticles, and more).

**Acknowledgments**

The authors would like to acknowledge scientific and technical support from Vihang Mehta during his undergraduate work in the Pacifici laboratory. Funding from the National Science Foundation (grants DMR-1203186 and CBET-1159255) is gratefully acknowledged. This work was performed in part at the Brown University Micro-electronics Facility, a member of the Materials Research Facilities Network, which is supported by the National Science Foundation (Grant No. DMR-0520651).