Plasmonic nanostructures for absorption enhancement
in organic solar cells

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Aimi Abass

30th May 2010
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Abstract

We studied the possibility of combining various optical phenomena to enhance thin organic solar cells through metallic grating nanostructures. These phenomena include Fabry-Perot effects, surface plasmon resonances, slab waveguide modes, and scattering. The strategies to look for the optimum usage of all these phenomena are discussed and the effects of the grating geometry are numerically investigated. We show how we can achieve an increase of 15% in integrated absorption of the am1.5g solar spectrum in the 300 to 800 nm wavelength range using a simple periodic 1D grating and reach up to 20 % using a multiperiodic structure. Calculations for 3D pyramids also indicate promising absorption boosts, opening up the possibility to have enhancement independent of polarization. The optimization in this work is done for the polymer P3HT:PCBM but it can be adapted to the needs of other materials as the strategies remain the same.

Keywords: Surface plasmon polariton, localized surface plasmon resonance, Fabry-Perot, Bloch modes, exciton, thin film organic solar cell.
Increasing polymer solar cell efficiency with triangular silver gratings

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Abstract: We investigate strongly enhanced light absorption in a thin P3HT:PCBM solar cell with a triangular silver grating back contact. The correlation between grating and plasmonic absorption spectrum features are identified and studied with rigorous numerics.

Keywords: Surface plasmon polariton, localized surface plasmon resonance, thin film organic solar cell

1. Introduction

The control of plasmonic mode excitation by incoming light via periodic metallic gratings was shown to be a powerful tool for increasing solar cell absorption. In some cases, the gratings are present in order to avoid the excitation of these modes and to increase the reflection from the metallic back contact, e.g. for fairly thick inorganic solar cells [1]. In other cases, the gratings allow to actually utilize the plasmonic modes, e.g. for thin film polymer solar cells with a thickness on the order of 100nm [2]. Recently, our group studied the increase of absorption efficiency by incorporating silver nanoparticles inside a thin polymer solar cell [3]. These works show that the subwavelength confinement of plasmonic modes can help for organic solar cell enhancement, as thin cells are required in order to maintain an efficient charge collection.

Here we numerically study the performance of a triangular silver grating with 1D periodicity, as a back contact of a P3HT:PCBM bulk heterojunction solar cell. A geometrically similar solar cell structure with different metal and polymer was presented earlier in [2] without an in-depth analysis of the structural effects, which we offer here. With triangular gratings, we demonstrate an integrated absorption efficiency increase of 15.6% for the active layer throughout the 300-800nm spectral region (weighted with the AM1.5G spectrum). This is mainly achieved by extending the absorption edge (around 650nm for P3HT:PCBM) to significantly higher wavelengths. A recent publication indicated that the internal quantum efficiency (IQE) in the region of 600-650nm is still close to 70% [4] and there is a report that charge generation is still possible even at 800nm [5].

The rigorous simulations were performed in 2D using the frequency domain finite element software COMSOL. We studied the system for a wide range of parameters: polymer thickness, grating period, fill factor and height. Here we focus on results for an active layer of 150nm thickness.

Fig. 1. (a) The simulated system, a plane wave incoming at normal incidence to the solar cell structure. (b) Polymer absorption spectrum for the planar and patterned device, respectively. The patterned device has a period of 400nm with fill factor 0.5 and triangle height 120nm. (c) Plot of the norm of the magnetic field profile for the TM polarization input at 640nm wavelength.
2. Results

First, we consider an infinitely periodic grating structure, excited with a plane wave, as depicted in Fig. 1(a). Figure 1(b) shows an example of enhancement in the absorption spectrum that can be achieved by the introduction of a triangular grating (grating periodicity 400nm, fill factor 0.5 and triangle height 120nm). The peak at 640nm (for TM) is due to excitation of a plasmonic mode. The plot of the field profile at this wavelength is shown in figure 1(c). The field is distributed mostly in the polymer, leading to a huge enhancement at this wavelength. The integrated absorption efficiency for a planar unpatterned structure is 48% while for a patterned structure it is 63.6% for TM polarization and 56% for the TE Polarization. The absorption enhancement for the TE polarization is due to scattering and better Fabry-Perot conditions induced by the grating profile. We aimed to put resonances mainly in the wavelength range of 600 to 690nm and put secondary priority to the wavelength region above it.

As already mentioned, the peak appearing in figure 1(b) stems from a surface plasmon effect. More specifically, it comes from a Surface Plasmon Polariton (SPP) mode associated with a flat polymer-silver interface. We see this by examining the ‘folding’ of the dispersion relation of the SPP mode induced by the 400nm periodicity, which is shown in figure 2(a). We are interested in the crossings at k=0 because this corresponds to modes that can be excited by perpendicularly incident waves. Besides imposing periodicity, the grating will induce a perturbation and thus split the k=0 degenerate modes in figure 2(a). As we make the grating more pronounced by increasing the height or fill factor, the splitting of the crossings becomes larger.

Figure 2(b) shows a plot of the integrated efficiency as a function of grating fill factor and triangle height at 400nm period. As indicated in the figure, there is an optimum combination for the fill factor and height which is due to the complex interaction of the SPP peak position and strength, and the grating scattering capability.

Figure 2(c) shows the absorption spectrum at different points in figure 2(b). We see in figure 2(c), as we go from graph A, B, to C (corresponding to triangle heights 10 nm, 60nm, and 120nm), that the peak position stems from the flat SPP mode at 800nm which gets blue shifted. Indeed, as the triangle height increases, a stronger perturbation splitting effect is observed.

We improve the absorption even further by having more resonances. We show here a structure as a proof of principle in which we utilize coupled localized surface plasmon resonances (LSPR). We add triangular groove defects with a small period on our main triangular grating. We show the result of employing this multiperiodic grating structure in figure 3 and 4. When we introduce additional small periodic defect grooves on top of our main grating, a single plasmonic resonance peak in figure 3(a) is replaced by four weaker LSPR resonances (C,D,E,F in 3(b)) that overlaps with each other and fills up a large wavelength range as we can see in figure 3(b). The integrated absorption in the polymer of the multiperiodic structure reaches to 68.7% which gives us a total increase of 20.7% as compared to the flat structure. The new resonances have a flat dispersion as can be seen in figure 3(c) and their field profile is shown in figure 4. This is an expected behaviour of coupled LSPR modes. Further optimization needs to be done in introducing the second additional periodicity to make the field less confined to the metal interface to reduce exciton quenching by the metal interface.

![Fig. 2. (a) Dispersion diagram of SPP mode at a flat polymer-silver interface folded with 400nm grating period, where G is the reciprocal lattice vector. (b) Dependence of integrated absorption efficiency in the 300-800nm region. (c) TM polarization absorption spectrum at different points in (b).](image-url)
Fig. 3 Results on double grating period with main period 390nm and small period 30nm, main triangle height of 120nm, defect groove depth of 15nm on average, and FF for the main grating is 0.5 and for the defects it is 1/3. Absorption spectrum in the polymer (a) for the main grating case (period P-1) only. (b) multiperiodic case. (c) Complete absorption spectrum of the multiperiodic geometry in (b).

Fig. 4 Norm of magnetic field profile at the resonances of figure 3(a) and (b). The field profile is normalized with the same scale shown on the left. 8 in the color bar means 8 times the incoming plane wave amplitude. The white area in the profile shows amplitude values beyond this range.

3. Conclusions

We performed detailed numerical studies of the potential of 1D triangular silver gratings as a back contact for P3HT:PCBM bulk heterojunction solar cells to increase the absorption efficiency. We show a 15.6% increase of integrated absorption efficiency in the 300-800nm wavelength range. Moreover, most of the increase of efficiency occurs in the region for which the internal quantum efficiency can still be optimal. The correspondence between the plasmon peak positions and the grating geometric parameters was studied. We also showed a proof of principle of the usage of multiperiodic grating structures to get more resonances that will give the integrated absorption up to a 20.7% increase.

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References


# Abbreviations and acronyms

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<tr>
<td>SPP</td>
<td>Surface Plasmon Polariton</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized Surface Plasmon Resonance</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse Magnetic</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse Electric</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl C61 Butyric Acid Methyl Ester</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene),</td>
</tr>
<tr>
<td>p</td>
<td>Periodicity</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
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<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
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<td>EQE</td>
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Chapter 1 Introduction

As mankind progresses, electronics and photonics become more and more integrated with our lives. Along with that, our necessity for power also increases. Solar cells may never be able to replace the capacity of a nuclear power plant, but they are still essential in fulfilling mankind’s need for a clean power source. Quite a big portion of mankind’s attention is directed to optimizing our harnessing the sun’s freely given power. Throughout the years, solar based energy solutions have already been introduced commercially and have already quite a stable market. It can be said that they already have a firm role in supplying energy to humanity. However, to keep up with the ever growing demand for energy, it is still of great importance that we keep improving our ability to harness the sun even more. Monocrystalline GaAs solar cells could already achieve 26% efficiency in harnessing the broad solar spectrum with devices based quite close to the theoretically predicted maximum efficiency at 31% for monojunctions [1]. Multijunction solar cells which consist of different type of semiconductor thin films stacked together can even go to 40% efficiency[1]. The organic material solutions on the other hand, are quite far behind in terms of efficiency which is currently around 6.8% for state of the art cells [2].

Although solar cell solutions based on inorganic material can be said to be more technologically mature and are already able to produce such high efficiency, it is still worth while to look into organic materials. One reason not to rely so much on these inorganic materials is the fact that some of them are quite limited in quantity and they are also of great importance in other applications while not being abundant in nature. For example, GaAs, which is a rather expensive material, is also used for lasers and modulators. Indium, a material used in CuInSe based solar cells, is quite rare and is used in the flat screen monitor industry quite heavily. It is a different matter for silicon which is a very abundant material on earth. Furthermore, its production technology is already mature and very efficient. However, even with silicon’s advanced production technology, organic materials have the possibility to be cheaper when the fabrication process is industrialized. The organic solar cells are capable to be a cheaper solution for a lot of applications that do not require huge voltages. Some of the organic solar cell materials also have good mechanical properties compared to silicon, enabling us to integrate these solar cells to equipments more easily.
Figure 1.1 shows the development of the solar cell technology over the years. There are many possible technologies for solar cells already that are competing with each other. It is not always the one that provides the highest efficiency that wins. The competition also depends on the target consumer. These technologies are separated again to groups of different market share due to their different costs and intended application. We see that the organic solar cell development is starting to catch up in efficiency with the cheap and robust solar cell technology based on amorphous silicon, although the organic solar cell technology has just started its development around 2001. If the efficiency of the organic solar cells can grow even closer to the efficiency of amorphous silicon cells, they will surely start to be a strong competition in the market share for low voltage applications, which are now dominated by those amorphous silicon cells.

The main problem of organic solar cells can be said to stem from its charge collection properties [3]. When a photon is absorbed in these organic solar cell materials, it does not form a free electron and hole pair, but rather an exciton. These excitons have to dissociate somehow. For effective dissociation, they need more electric field which could be provided by a heterojunction structure. However, upon creation, these excitons still have to find their
way to that junction. After that, the free electron and hole have to go through transport processes in order to generate current that are prone to recombination. These things greatly limit the thickness of these organic solar cells. For optimal charge collection, typical bulk heterojunction polymer solar cells are currently limited to thicknesses below 200nm for good IQE quality [4]. Compared to typical inorganic solar cells which are in the range of several to hundreds of micrometers, it is really not much. Although it is far thinner than conventional inorganic solar cells, absorption in a certain wavelength range can be already high, reaching to above 70%, but there are still wavelength regions in which the organic material could use some help. From the economical point of view, we can say that we try to use even less material, and thus it has the potential to cost less.

One photonic solution to this extra thin requirement is by utilizing surface plasmon polariton modes to increase the absorption efficiency of these solar cells. These Surface Plasmon Polariton (SPP) modes are essentially photons that are coupled to plasmons in metals and they are highly confined to a dielectric metal interface. So the idea is trapping incoming free photons in SPP modes to increase the absorption in our organic solar cells due to increased dwell time of photons in our solar cell structure before it escapes. Of course, we have to ensure that the absorption happens mostly in our solar cell material instead of the metal. Successful attempts in utilizing plasmonic modes via metal nanostructures to increase absorption efficiency of organic solar cells have already been reported. However, a thorough study still needs to be done in order to fully exploit the metal nanostructure.

A lot of structures have been considered and studied thus far. Basically the metal nanostructure approaches that have been done can be categorized in three main approaches: upper electrode patterning, putting something in the active layer, and back contact patterning as shown in figure 1.1. In some applications for inorganic solar cells, introducing a grating structure on the back contact is actually done with the purpose of inhibiting the excitation of plasmonic modes that will cause reduced back reflection to the active layer [5]. This is done because the active layer in the nonorganic solar cell case can be very thick and thus very efficient in absorbing photons and collecting current, and if there are plasmonic mode excitation that would mean losing a few of the photons to absorption in the metal.

In this work, we focus on studying polymer solar cells with a nanostructured metallic back contact. Effects of the nanostructures’ geometry on the allowed plasmonic modes, scattering and diffraction properties, and absorption in the polymer are studied. The simulation work
was done using COMSOL multiphysics. We studied various optimization routes that we can take to improve the absorption efficiency. We wish to gather the necessary knowledge to be able to do optimization for other solar cell materials, since it is very likely that we will have better materials with different needs in the future. Results of fabrication attempts are also discussed.

Figure 1.2: Different approaches in using metallic structure to improve absorption in solar cell. (a) Nanoparticles in the middle of the active layer [6] (b) Grated Back Contact. Example field profile plot of the norm of electric field is given along with each sketch. (c) Grated upper electrode with norm of magnetic field plot [7].
Chapter 2 Theoretical Background

2.1 Charge Generation in Polymer Solar Cells

Unlike the case of non-organic solar cells, photon absorption doesn’t directly generate an electron hole pair in organic solar cells. When photons are absorbed, they generate excitons first. To be able to get a current out of our cell, the excitons need to disassociate into separate electrons and holes. Inducing disassociation of excitons naturally and effectively would require a system that energetically favours separated electron and hole instead of an exciton. Such a system can be found in junctions of two different materials of different electron affinity and ionization energy. At such a junction, there exists an electric field and we can choose the material such that the built in electric field combined with the external applied voltage, is strong enough to split excitons into electron hole pairs.

![Energy band diagram at a heterojunction](image)

Figure 2.1.1 Energy band diagram at a heterojunction

It is of the utmost importance that excitons reach these junctions but unfortunately, there’s a complication. The exciton diffusion length is typically on the order of 10nm. Several types of solar cell structures have been developed to circumvent this exciton dissociation problem. One solution is by stacking thin layers of different materials to have multiple planar heterojunctions as in figure 2.1.2 (a), and another is by having the heterojunctions all over the bulk of the active material, see figure 2.1.2 (b). If engineered correctly this obviously provides more chance for generated excitons to meet a heterojunction. The latter structure is called the bulk heterojunction structure. The active absorbing layer considered in this work is the bulk heterojunction P3HT:PCBM. Photons absorbed in the PCBM part of the blend do not really contribute to the power generation of the solar cell. This is because the exciton diffusion length in PCBM (~5nm) [8] is smaller than in P3HT (~10nm)[9].
2.2 Surface Plasmon Polariton (SPP)

Surface Plasmon Polariton(SPP) is a photonic mode of propagation in which photons are coupled to plasmons or electron cloud. These modes exist mainly at the interface of two different materials at which one of the materials has a negative real part of the permittivity. The SPP mode needs a relatively free electron cloud which can be moved easily by an electromagnetic wave to sustain a coupled propagation of plasmons and photons. For optical wavelengths, such conditions can readily be found in metals. An SPP mode has the novel characteristic of having the electromagnetic field highly confined to the interface [12]. Subwavelength confinement of the electromagnetic field is possible in this SPP mode. Surface Plasmon Polariton modes can be categorized into propagating and non propagating type. The non propagating type is often called localized SPP modes.
The simplest propagating SPP mode that we can describe is in the case of planar dielectric-metal interface as depicted in figure 2.2.1 (a). This SPP mode is a valid solution of the Maxwell equation at the interface of two different materials when one of the materials has a negative real part of the permittivity. This propagating SPP mode has the peculiar characteristic of having momentum greater than the momentum of free propagating photons in either of the two materials that make the interface [12]. The intuitive reasoning to explain this bigger momentum of the SPP mode is the fact that the photons are coupled to oscillating plasmons and thus, when an SPP mode is propagating, the plasmons and the photons copropagate which means the total momentum of the mode would be the momentum of the photon plus the momentum of the plasmons. Thus free incoming photons may need more “kick” to excite a propagating SPP mode in order to conserve momentum.

Figure 2.2.1 (b) shows what the charge distribution of a propagating SPP mode on a flat interface looks like. We see that the electric field corresponding to the mode’s charge configuration would have a Transverse Magnetic (TM) polarization and thus can only be excited with incoming light of such polarization. In this case, the TM polarization means there are only y and x direction components of the electric field since we are dealing with a planar structure that is symmetric in the z direction. Transverse Electric (TE) polarization means that the electric field is perpendicular to the plane of propagation which is the z direction in this case. Again further examining the charge distribution we see that in order for the charge to be confined at the surface, we will need an electric field that changes sign at different sides of the interface. Seeing also that the electric displacement vector $\mathbf{D} = \varepsilon \mathbf{E}$ has to be continuous at
the interface, we see that the permittivity of the two materials should have opposite signs and thus one of them has to have a negative real component. As mentioned before, example materials with negative real components of the permittivity in the optical wavelength region are metals. Note that some semiconductors have negative permittivity in the terahertz region.

By solving the Maxwell equation in the case of an infinite flat interface in figure 3 above for a mode that propagate in the interface and thus is exponentially decaying in the vertical direction, we will get

\[
k_x = \frac{\omega}{c} \left( \frac{\mathcal{E}_d \mathcal{E}_m}{\mathcal{E}_d + \mathcal{E}_m} \right)^{1/2}
\]

\[
k_y^2 = k_{\text{medium}}^2 - k_x^2
\]

The field solution is of the form:

\[
\mathbf{E}(y > 0) = (E_z \hat{x} + E_z \hat{z}) \exp(jk_x x + jk_y y)
\]

\[
\mathbf{H}(y > 0) = (H_z \hat{y}) \exp(jk_x x + jk_y y)
\]

\[
\mathbf{E}(y < 0) = (E_z' \hat{x} + E_z' \hat{z}) \exp(jk_x x + jk_y' y)
\]

\[
\mathbf{H}(y < 0) = (H_z' \hat{y}) \exp(jk_x x + jk_y' y)
\]

Looking more closely at equation (2.1), we see that the SPP mode on a flat surface always has a bigger k-vector than that in the homogeneous dielectric. The dispersion relation of an SPP mode on a flat air metal interface is plotted in figure 2.2.2. A disparity in the k-vector physically means that there is a momentum mismatch. Modes that have no momentum mismatch have the possibility of coupling from one to another, provided that their field profile is not antisymmetric with respect to one another. Modes that have smaller k-vector value cannot couple automatically to modes of larger k vector because it does not have the necessary momentum to excite modes with larger k vector. The fact that the SPP mode in this case always has a bigger k-vector than that of air means that light incoming from air can never couple to the SPP mode. In general, even for interfaces with different material combinations, free propagating photons impinging upon a flat dielectric metal interface can never couple to a propagating SPP mode if nothing special is done.
Figure 2.2.2 The red line is the dispersion relation of the SPP mode on a flat interface with field plots of the mode at two different k values. The blue line is the dispersion relation for waves propagating in air. Modes with large propagating k vector will be more tightly confined to the interface.

A technique that can be used to bridge the momentum mismatch is utilizing evanescent modes which occur in total internal reflection (TIR), e.g. with the help of a prism. The evanescent wave in TIR has the possibility to couple to a propagating SPP mode on a different interface as they may have the necessary momentum to excite one. A technique that is based on this principle in which a prism is utilized is shown in Figure 2.2.3 [13]. By taking into account the refractive indices of the prism and the k vector of the SPP mode we wish to excite, we can thus find the necessary incidence angle $\theta$.

Figure 2.2.3 Excitation of SPP mode via evanescent field produced in Total Internal Reflection[14]

Non propagating SPP is found when we are dealing with relatively isolated nanoparticles which size is comparable to the decay length of the field inside the material comprising those particles. Basically, the nanoparticle object in question needs to be small enough that there can be charge build up at its interface due to the presence of electric field from the incoming EM wave which moves the electrons inside the nanoparticle [14]. One can therefore
intuitively imagine that this resonant effect depends on the shape of the nanoparticle object. The charge build up at the interface leads to great near field enhancement. These non propagating SPP is more commonly called Localized Surface Plasmon Resonance (LSPR). Unlike the case of propagating SPP modes, there is no momentum mismatch problem when it comes to LSPR modes. The physical phenomenon is different. Since we are not dealing with a propagating mode, there is no need to describe an effective momentum of the whole mode. This does not mean that any wave can excite an LSPR mode. The wave still needs to have the right frequency.

If we put nanoparticles close together without having them touching each other, the LSPR mode of the particles begin to couple to other nanoparticles and thus it can start propagating from one particle to another. This coupled LSPR modes have a defining very flat dispersion characteristic [15]. The flat dispersion characteristic stems from the fact that the mode propagates via near field coupling.

2.3 SPP modes on Periodic Grating Interface

![SPP modes on Periodic Grating Interface](image)

Figure 2.3.1 Plasmonic excitation in a grated interface

Coupling free photons to propagating SPP modes can be done directly if the interface in question is geometrically periodic as depicted in figure 2.3.1. Having a periodic structure means that any fundamental mode that exist in this structure is Bloch-periodic [16]. Any wave mode in a periodic system can be written in the form:

\[
\varphi_k (\vec{r}) = \tilde{\varphi}_k (\vec{r}) e^{i \vec{k} \cdot \vec{r}} \quad (2.3)
\]
which is a Bloch wave function. $\tilde{\varphi}_k(\vec{r})$ is a periodic function with periodicity that of the grating and thus can be expressed as a summation of plane waves $\sum_G a(\vec{k} - \vec{G}) e^{-i\vec{G}\cdot\vec{r}}$ where G is the grating lattice vector which have the expression $G = \frac{2\pi}{P}$ where P is the periodicity of the grating.

Physically, the Bloch wave function means that the wave comprises of a periodic amplitude term that have the same periodicity as the grating and that if we move to a different cell we should have the same amplitude but the phase can be different. Such a wave function has the property of $\varphi_k(\vec{r}) = \varphi_{k+G}(\vec{r})$. This means that modes at $k=0$ are identical twins to modes at $k=G$. We can show this by writing

$$\varphi_k(\vec{r}) = \sum_{G'} a\left(\vec{k} - \vec{G}'\right) e^{-i\vec{G}'\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}$$

$$\varphi_{k+G}(\vec{r}) = \sum_{G'} a\left(\vec{k} + \vec{G} - \vec{G}'\right) e^{-i\vec{G}'\cdot\vec{r}} e^{i\vec{k} + \vec{G}\cdot\vec{r}}$$

$$\varphi_{k+G}(\vec{r}) = \sum_{G'} a\left(\vec{k} + \vec{G} - \vec{G}'\right) e^{i\vec{G}'\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}$$

Rewriting the summation by using $\vec{G}'' = \vec{G}' - \vec{G}$ and noting that the $G'$ originally run only through values of integer multiples of $G$ in the range of $-\infty$ to $\infty$, we see that we end up with

$$\varphi_{k+G}(\vec{r}) = \sum_{G''} a\left(\vec{k} - \vec{G}''\right) e^{-i\vec{G}''\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}}$$

with $G''$ as the running index that runs through also all the value of integer multiples of $G$ which means that

$$\varphi_k(\vec{r}) = \varphi_{k+G}(\vec{r})$$

The previous statement is general and holds also for

$$\varphi_k(\vec{r}) = \varphi_{k+nG}(\vec{r})$$

Thus, modes with a certain $k$ have identical twins to modes at $k+nG$ where $n$ is an integer.
To illustrate what is the impact of this property to the dispersion relation, we consider the SPP dispersion relation of a flat interface. Then, if we consider there’s a shallow periodic disturbance that does not affect the propagating modes of this system too much and apply the conditions above, what will happen is an effective flipping of the dispersion diagram as illustrated in figure 2.3.2. Another way to view it is to say that the periodicity on the interface provides the necessary momentum for the incoming photons to couple into the propagating SPP modes.

![Figure 2.3.2](image)

Figure 2.3.2 Effect of periodicity on the dispersion diagram. Blue curve, dispersion of propagating SPP modes on a flat interface of silver-P3HT:PCBM. Red and green curve are lines dispersion mode induced by the grating periodicity.

The grating structure also induces more effects than just the folding of the dispersion diagram. It does not only give a periodic nature, but also a perturbation. As we make the grating structure more pronounced, the more the modes deviate from those of a flat structure. In effect, the crossings that we see when we flip the dispersion curve will be split into two [12]. The more pronounced the grating, the more difference in energy the two field profiles can have. Such a phenomenon is common for waves in any system that suffers from periodic disturbance. The splitting is illustrated in figure 2.3.3. We see such similar traits in quantum mechanics particularly the electron’s wave equation as they propagate through periodic potentials.
Figure 2.3.3 Splitting of the degenerate modes

The splitting signifies that modes that are once indistinguishable or degenerate in energy can change such that the energy of those modes is no longer the same. The field profile of one mode now holds more energy than the other. Typically we can see why the two modes have different energy from their field distribution and charge distribution. For example, one mode may be more concentrated in the higher refractive index media than the other and also the separation of charges in one mode may be much larger.

When the periodic grating system under consideration contains more than one periodicity components that is non negligible, the flipping effects that might occur may be even more complicated. In effect, we may have more modes which incoming plane waves can couple to. A non sinusoidal grating structure like triangles or square can be decomposed to its Fourier series components which reveal its higher order components.
2.4 Diffraction Grating Effects

The grated metal back contact structure that is of interest in this work obviously also functions as a diffraction grating like that shown in figure 2.4.1 [17]. The arising diffraction orders play an important role in the absorption of the polymer film. Peaks in the spectrum of photon absorption in the polymer may arise due to diffraction effects but they can also be quite costly for our plasmonic resonances. The diffraction orders that can occur is defined by the grating equation

\[ AB-CD = P \left( \sin(\theta_m) - \sin(\theta_i) \right) \]

Figure 2.4.1 A reflection grating type of the diffraction grating structure [17].

Since basically we are dealing with a reflection grating with a very thin sub wavelength thickness layer on top of the grating, we can still use the refractive index of the top layer where the wave is coming from for the grating equation.

\[ P(\sin \theta_m - \sin \theta_i) = m(n\lambda) \]  

(2.4)

Where \( \theta_m \) is the angle of the diffracted order, \( \theta_i \) is the angle of incidence, \( \lambda \) is the wavelength, \( n \) is the refractive index of the top surrounding material, and \( m \) is an integer.

 Incoming waves with wavelength and k vector that satisfies one or several diffraction mode will have a harder time coupling to a plasmonic resonance at that wavelength because it can also couple to those diffraction modes aside from the normal specular reflection. It will be then be a sort of competition. The power of the incoming wave need not be evenly distributed
to all the possible modes that it can couple to but it is clear, the more the diffraction modes possible, there is a high chance that less power will be given to the target plasmonic mode. This also limits our choice of the periodicity. One would be tempted to think that we just pick a large periodicity so that we will have a lot of higher order resonances to boost our absorption, but among many other reasons, the amount of competing diffraction modes also limits the performance of those peaks.

2.5 Dark and Bright Field Profile

As mentioned before, each crossing in the flipped dispersion diagram in figure 2.3.2 will be split into two. One mode correspond to symmetric and the other to an antisymmetric solution. The first order crossing at k=0 have field distributions shown in figure 2.5.1.

![Figure 2.5.1](image)

Figure 2.5.1 The color plot is the Hz field distribution of 2 propagating SPP modes from the first order crossing at k=0 while the white arrows are the electric field. (a) Symmetric mode, (b) Antisymmetric mode

The first order antisymmetric mode cannot be excited with normal incident plane waves because the overlap integral of that mode with the normal incident incoming plane wave is 0. An intuitive physical reasoning to this is the fact that in such an antisymmetric mode the total dipole moment of the mode is 0 where as in the symmetric mode there is a non zero total dipole moment. The band that has this antisymmetric feature at k=0 is not always unexcitable by incoming plane waves. Modes that cannot be excited by normal incident light are called
“dark” modes. “Bright” modes, on the other hand, can be excited perpendicularly [18]. However, non-perpendicular plane waves (thus incoming at an angle from the normal) can excite modes on the dark mode band. Note that the mode profile of that band changes also when we move to other k values. Most importantly, note that the mode in this band can only be effectively coupled to a plane wave incoming at an angle. The angle of incidence with which an incoming plane wave can couple the best to this dark mode band depends on the geometric structure of the triangle. Additional care needs to be taken if we wish to use the dark mode also to enhance absorption near normal incidence angle.

An important question to be addressed for the solar cell design is “Which mode has the higher energy?”. This question is not so simple to answer however. It all depends on the structure in question. We will show that at some instances the antisymmetric mode can have a lower energy than the symmetric mode but at larger film thickness, the situation can be the other way around.

Higher order crossings also split into antisymmetric and symmetric pattern as shown in figure 2.5.2.

![Figure 2.5.2 The Hz field distribution of 2 propagating SPP modes from the second order crossing at k=0. (a) Symmetric mode, (b) Antisymmetric mode](image-url)
2.6 Numerical methods

At most part of the cell except at the edges, the incoming waves will see an infinite structure compared to its wavelength. Thus, the main effects of interest in our solar cell structure are well represented also in an infinite periodic grating system. Simulating a structure that is infinitely periodic gives a lot of simplifications since, due to symmetry, all the information is contained in the Bloch propagation constant and the field profile in a single cell. This is essentially the Bloch theorem which governs the modes in a periodic system. Figure 2.6.1 (a) shows the absolute value of the amplitude of a plane wave impinging at an angle on a triangular grating structure. The amplitude profile repeats itself for every cell just as stated in the Bloch theorem, but from cell to cell, in general the phase may be different as we see in figure 2.6.1 (b).

(a)       (b)

Figure 2.6.1 Field amplitude profile of a wave coming at an angled incidence on an infinite grating structure. (a) Absolute amplitude profile (b) Real part of the field at a certain phase

To model an infinitely periodic structure by just simulating one cell of that structure, we need the appropriate boundary conditions on the edge of each cell. When we simulate plane waves impinging at a grating structure, how the wave is incident is also important in determining the appropriate boundary conditions. The wave’s angle of incidence will determine the phase difference of the fields at different cells. In this thesis, we will take the frequency domain approach where we simulate waves at different frequencies one at a time. This enables us to utilize easily Bloch periodic conditions on the left and right end of the cell. The Bloch periodic condition is essentially forcing the field amplitude at the left end of the cell to be equal to the field amplitude on the right end of the cell, multiplied by a certain phase factor. The condition can be written as

\[ E_R = E_L e^{i k_f r_p} \]
Where $E_L$ and $E_R$ is the field on the left side and the right side at the same height $y$, $r_p$ is the period of the structure and $k_f$ is the Bloch wave vector. In the case of incoming plane waves at arbitrary angle, the Bloch wave vector has to be, see appendix.

$$k_f = k_{in} \sin(\theta)$$ \hfill (2.5)$$

Where $k_{in}$ is the magnitude of the incoming plane wave $k$ vector and $\theta$ is the angle with respect to the direction perpendicular to the grating structure.

The simulation is done using comsol’s scattered field RF module in which we define an input field throughout the whole domain. We use Perfectly Matched Layer (PML) for the top and bottom computational domain termination. The sketch of the computational domain that we simulate is given below in figure 2.6.2

Figure 2.6.2 Sketch of the simulated computational domain

In the special case of normal incidence, we can make use of symmetry arguments and use perfect electric conductor walls for the left and right end of the computational boundary when we simulate for TM polarized light. In the 2D case of figure 2.6.2, TM polarization is when the $H$ is perpendicular to the plane. This stems from the inherent symmetry of the problem. We consider such perfect conductor boundary conditions because we will use it in our 3D simulations in which we only consider a normal incident field. We make use of the symmetry so that we only need to simulate a quarter of a cell.
Chapter 3 Result and Discussion

3.1 The Studied System

Figure 3.1.1 Simulated structure

The structure under study is a triangular grating structure depicted in figure 3.1.1. There are four geometrical parameters in the structure in question that we should take into consideration:

- Periodicity (p)
- Grating fill factor (FF)
- Grating height (h)
- Maximum film thickness (t)

The structure is optimized for the irradiation condition of the am1.5g solar spectrum as seen in figure 3.1.2. The am1.5g spectrum is the irradiation spectrum from the sun that arrives at the sea level of earth when the sun is 41.81° above the horizon. Basically, the goal is to absorb as much as possible of the irradiation spectrum from 300 to 800 nm. At first, it was well accepted that the bandgap of the main absorbing material P3HT is around 1.9 eV (653 nm) [19]. But studies done by Cunningham, show that charge creation and effective charge transport is still possible even at wavelength of 800 nm and it is suspected that this is due to the existence of long lived triplet exciton states which can also dissociate to generate electrons and holes [20]. However, the optical transitions to this state tend to be weak. It is also reported that the version of P3HT nowadays can have a bandgap 1.74 eV (which is at 712.5 nm) for the first polaronic absorption [20]. Note that the energy gap of the P3HT:PCBM can still be tuned without changing its chemical components. This is done by
changing the arrangement of its chemical chains or simply by changing the ratio of P3HT and PCBM in the blend.

![Graph of Power Spectrum vs Wavelength](image)

Figure 3.1.2  The am1.5g solar spectrum

The active layer in this work is bulk heterojunction P3HT:PCBM solar cell. We use silver as the material for the grated back contact. Silver is chosen for several reasons. First, we know from experience and trial calculations that good absorption enhancement due to Fabry-Perot effects is achieved in the wavelength region of interest when we use silver. In enhancing optical absorption in the polymer through this effect, it seems to perform better than aluminium. Second, the cut off wavelength at which silver stops behaving as a metal is below 400nm. At the wavelength range below this, the am1.5g solar power spectrum is still low. Gold is out of the question because it has its cut off wavelength around 500nm, the wavelength region where the am1.5g is at its maximum and also the wavelength at which the polymer absorbs the best. The main problem with silver is the fact that it is not stable. The silver atoms of the back contact can escape the surface and penetrate inside the polymer and thus gradually damage the active layer as more and more atoms penetrate in time if there is no additional protective layer on top of the grating. In this work, we did not simulate an additional blocking layer between the silver metal and the active layer to prevent diffusion of and exciton quenching by the metal [21]. nor did we consider any cladding or anode layer on top of the polymer.
Refractive index data of the P3HT:PCBM layer was taken from measurements done at imec, see figure 3.1.3. We see that the imaginary part of the refractive index has a large peak at 500nm. Though the main transition is thought to start around 712.5 nm, we can see in the data that the imaginary part of the refractive index, and hence the absorption, still has a non-zero tail above that even until 800nm as noted by Cunningham [20].

![Refractive index data](image)

Figure 3.1.3 The refractive index data of the P3HT:PCBM polymer. (a) Imaginary part, (b) real part.
3.2 Engineering the grating

The goal that we wish to accomplish is basically to get absorption enhancement that leads to increase of current generation. We therefore aim for as low as possible average thickness of our cell so that charge transport is still effective. To ensure that we will be increasing the current generation in an optimum way, we mainly focus to place resonances in the 600-690nm region where we are definitely sure the absorption mechanism can lead to excitons, and also because the absorption in this region can already use some help. Charge carriers can be still be generated in the wavelength region above 690nm, but we put secondary priority in improving the absorption in this range. We would also have to make sure that the absorption enhancement due to the plasmonic resonances occur in the polymer, and that the field is not too concentrated near the metal, but fairly spread throughout the polymer. A fairly distributed enhancement is more favourable than a highly localized one because of possible exciton quenching near metallic surfaces [22]. The radiative decay rate can be enhanced near a metal interface due to an increased photon density of states. Besides enabling SPP mode excitation, we also aim for a structure that will scatter waves with non-resonant wavelengths efficiently throughout the polymer, such that the absorption at these wavelengths is also increased. Furthermore, the structure should have a good angular response, meaning the absorption enhancement is not abruptly lost by a slight change in angle of incidence. In addition, the resonance wavelengths should not change so much with different angles so that the SPP resonances do not shift easily from the wavelength region where they can help. If they are placed in the wrong wavelength region, e.g. where exciton creation is possible, the plasmonic resonances will be useless. In worst case scenario, the plasmonic resonance may actually be situated at a wavelength at which the polymer is already absorbing optimally. Additional plasmonic mode excitation can actually ruin this because we will be increasing the absorption in the metal back contact by having an SPP mode there. It is important therefore that the plasmonic resonances have a flat dispersion characteristic. That is to say that the resonances do not shift much as the angle of incidence changes.
Figure 3.2.1 Absorption spectrum in the polymer for flat structures.

Figure 3.2.1 Shows the calculated absorption spectrum in the P3HT:PCBM for flat structures of several polymer films with varying thicknesses and a silver back contact. The absorption spectrum inside the polymer was obtained by integrating the divergence of the poynting vector ($\nabla \cdot \mathbf{S}$) throughout the polymer volume. We see in figure 3.2.1 that even at 60 nm thickness, the polymer is already able to absorb above 70% in the 450-575nm wavelength region. However, this is not yet the complete picture that will show us the performance of our solar cell. To get an idea of how well our solar cell generates electrical power, we also need information on the Internal Quantum Efficiency (IQE) of our structure. The IQE corresponds to the percentage of absorbed photons (for a given energy) that actually contributes to generating charge carriers that reach the electrodes. Another quantity of interest is the External Quantum Efficiency (EQE) which is a ratio of the number of generated charge carriers with the number of the incoming photons. So for EQE, optical effects are already accounted for. The expression for EQE is written as:

$$EQE(\lambda) = IQE(\lambda) \cdot A(\lambda)$$

where A is the absorption in the absorbing film.
Burkhard, et al. [4] published measurements of the IQE in P3HT:PCBM, see figure 3.2.2. The IQE is observed to change with different thickness of the polymer material. This is to be expected because of the charge transport problem discussed earlier in section 2.1. For normal planar structures, wavelengths that are highly absorbed by the polymer will mostly be absorbed at the front surface of the cell. One of the generated charge carriers will thus have to travel through a lot of polymer and we know that charge transport in polymer is still full of problems. Furthermore, there are effects of exciton quenching by the anode and other surface recombination traps that makes the charge generation near the front surface ineffective. These are the origin of the decrease of the IQE at lower wavelengths and its significant negative dependence to thickness at this lower wavelength range. The measurement data does not completely cover our whole wavelength region of interest which is from 300-800nm but we see that more than 50% of the absorbed photons from 375nm to 625nm will contribute to current generation in the cell. At 74 nm polymer thickness, the efficiency can go to nearly 70% on average throughout the whole measured wavelength range. There is no trend in the IQE data that it will go down to 0 at around 650nm, and since we know that the bandgap is approximately at 690nm, we use extrapolation of the IQE to calculate the EQE up to 650nm.

Now the question now is: “In what wavelength region should we put the plasmonic resonances?” The main idea is to place plasmonic resonances in regions where the absorption is low and in addition, we prioritize wavelength regions in which the absorption cannot be
increased effectively by other effects. Coming back to figure 3.2.1 we see that the optical absorption for 150nm film thickness is already good for wavelengths below 550nm. Also, examining the IQE performance in figure 3.2.2 for several thickness values, we can be sure that the average IQE throughout 375-625 nm is more than 60% for film thickness below 234 nm. Therefore, we can get good optical absorption for wavelengths below 550nm by using polymer films with effective thickness of 150nm and above without sacrificing too much the IQE. We thus mainly target the plasmonic resonances to be between 600 and 650 nm where the optical absorption is still low at film thickness below 250 nm. In this wavelength range, we are still quite sure that the internal quantum efficiency of P3HT:PCBM is significant.

We define a weighted integrated power spectrum IP which we refer to as integrated absorption from now on. It is the am1.5g sun spectrum weighted with the absorption spectrum $A(\lambda)$ like that in figure 3.2.1 and integrated throughout the whole wavelength range of interest.

$$IP = \int P_{am1.5g}(\lambda) \cdot A(\lambda) d\lambda$$

Figure 3.2.3 shows the integrated absorption for flat structures as a function of polymer film thickness normalized with the total power in the am-1.5 g spectrum in the wavelength region of interest. The oscillation in the graph is due Fabry-Perot effects. We are particularly interested at the Fabry-Perot maxima around 50 and 200 nm thickness. We can use this graph as a rule of thumb to check whether our structure is working near the optimum Fabry-Perot condition or not. Roughly speaking, when we put a grating structure on top of a flat back contact surface, the “effective” thickness of the active region changes. The idea is to make a rough estimate of the effective thickness of the film and to see approximately how far we are with regards to a Fabry-Perot maximum point.
3.3 Flattening the SPP dispersion

As mentioned in previous sections, we aim for plasmonic resonances with a flat dispersion, meaning that the resonance position does not change rapidly with a change in angle of incidence. First we examine the kind of SPP mode that we will be generating. Figure 2.2 in the previous chapter shows the dispersion relation for a propagating SPP mode on a flat interface. We see that there are regions where the SPP mode dispersion is already flat but unfortunately, as we aim to have our plasmonic resonances in the 600-650nm region, we will not be able to utilize such modes to begin with, because they only exist close to the plasmon frequency which in our case in metal is around the wavelength of 300nm. Furthermore, we actually do not wish to use SPP modes that are too tightly confined to the metal interface like those which frequencies are near to the plasmon frequency as mentioned before. We want it to be spread out through the polymer. It is therefore quite desirable to use SPP modes with frequency away from the plasmon frequency so that the modes are not highly confined. The problem is, at this frequency range, the dispersion of the SPP mode is quite far from flat.

To emphasize how dispersive a propagating SPP mode can be, we show the simulation results for silver-polymer interface grating structure at 300 nm periodicity with a shallow grating height of 10nm with waves impinging at different angles. Figure 3.3.1(a) shows the dispersion
relation of a propagating SPP mode on a flat silver-P3HT:PCBM interface flipped with 300nm periodicity in the brillouin zone. We compare that with Figure 3.3.1(b) which shows the absorption spectrum in the silver metal at different angles of incidence.

Figure 3.3.1 (a) Propagating SPP mode on silver-P3HT:PCBM interface, flipped with 300 nm grating periodicity, plotted inside the first brillouin zone. (b) Absorption spectrum in the metal for a triangle grating structure of 300 nm period, 0.5 Fill Factor (FF), and triangle height of 10nm, with maximum polymer thickness of 150nm.

The first order plasmonic resonances occur near the wavelength 650 nm as predicted in the flipped dispersion curve in figure 3.3.1(a). We see that the resonances can shift around 25 nm with just a change in the angle of incidence on the order of 10°. The small splitting we see between the modes at 650 nm arises due to the breaking of degeneracy as mentioned in chapter 2. This is further discussed in the next section. The bright mode that shifts to lower wavelengths seems to disappear just after 10° angle of incidence but this is just because the SPP mode is shifted to the wavelength region where the polymer is strongly absorbing.

A solution to this non-flat dispersion problem of the plasmonic mode is by using a more pronounced grating structure. As mentioned before in chapter 2, coupled LSPR modes have a very flat dispersion relation. As the grating structure deviates away from a flat interface geometry, the modes have a harder time running along the interface. At a certain point when we make the grating more and more pronounced, for example by increasing the height of the triangular gratings, the grating profile system would resemble big particles stacked close together, see figure 3.3.2. In such a heavily corrugated grating interface, the system is
effectively closer to a coupled LSPR system rather than a propagating SPP mode. Figure 3.3.3 shows the simulated absorption spectrum of a grating system similar to that in figure 3.3.1(b) but for bigger triangles. It shows that larger triangles indeed lead to a more flat dispersion.

Figure 3.3.2 (a) Shallow Grating system. (b) Heavily corrugated grating.

Figure 3.3.3 Absorption spectrum of triangular cell grating structure with FF=0.5, period=300nm, triangle height 100nm, maximum polymer film thickness=150nm. (a) Absorption in the metal. (b) Absorption in the polymer.

Care must be taken, however, in the effective thickness of the solar cell structure in the case of heavily corrugated gratings. We still wish to have good enhancement due to Fabry-Perot effects for the other wavelength region where we do not have plasmonic resonance.
3.4 Engineering the plasmon resonance

Notice also that even though the system in figure 3.3.3 has deviated far from that of a flat surface for SPP modes, the position of the plasmonic resonances can still be predicted quite well from the dispersion band flipping like what we did for figure 3.3.1. Even though there is a splitting of energy between the first order dark and bright mode, the central wavelength at \( k = 0 \) between the two is still close to the first order crossing at 650 nm at \( k = 0 \) in the flipped dispersion curve we see in figure 3.3.1(a). The physical intuition for the closeness of the two results at \( k = 0 \) stems from the fact those modes are actually standing waves at that \( k \) vector. The main difference between a propagating SPP mode and a coupled LSPR mode is how they propagate. The latter relies on near field interaction to excite a new LSPR mode on the neighbouring particles in order to transport energy from one particle to another. However, in the case at \( k = 0 \), both modes can be said to effectively not propagate from one period cell to another. They are just “standing” inside one period. The main characteristic that sets the difference between a coupled LSPR mode and a propagating SPP mode is therefore playing a little role when \( k \) is 0 and thus you can expect prediction made by flipping the flat-interface-propagating SPP mode’s dispersion curve can give us a good guess for the actual resonant wavelengths at this \( k \) value. Of course, for non zero \( k \) values, we should not expect a good agreement. Nonetheless, figure 3.4.1 shows that some higher order modes’ position at \( k = 0 \) can also be predicted with good accuracy by the same flipping.

![Figure 3.4.1](image-url)

Figure 3.4.1 (a) Flipped flat interface of silver-polymer dispersion diagram with flipping period of 550 nm, (b) Calculated absorption spectrum for maximum polymer thickness 150 nm, Period 550nm, FF=0.5 height 60 nm,
The splitting in energy between the antisymmetric and symmetric mode is basically due to the different field profile and charge distribution between the two. The field profile and the charge distribution are directly dependent on the geometrical structure of the grating. Thus, we can expect that by tuning the geometrical structure of the grating we can further control the difference of energy between the antisymmetric and symmetric modes.

Comparing the resonance positions in figure 3.4.2 for different triangular heights, we see that the splitting between the dark and bright mode becomes larger when we move to larger heights. We observed that this effect is fairly monotonous in the height range of interest from 0 to around 150nm. The higher the triangles the bigger the energy gap between the two modes. There is another thing worth noticing also in figure 3.4.2 regarding the resonance wavelength positions. We observe that the lower energy mode is shifted more than the higher energy mode. This is connected to the fact that the higher energy mode can only shift down in wavelength to asymptotically approach the wood anomaly wavelength associated to diffraction edge[23]. Similar behaviour of SPP modes is also shown in theoretical calculations made by Barnes in the case of sinusoidal gratings which indicate that the field for the higher frequency solution is less confined to the interface. This is connected with the fact that the higher energy solution mode is shifted closer to the light line in the dispersion diagram by the grating component that causes the splitting while the lower frequency solution is shifted away from it, see figure 3.4.3 [24]. In this figure we show the effect of a single sinusoidal grating with a grating lattice vector of 2K on the propagating SPP mode’s dispersion diagram which produces a bandgap at K and –K. The calculations by Barnes show that the highest frequency solution of the SPP mode occurs when the field is extended to the dielectric without decaying. Thus the higher frequency solution branch of the SPP mode can only approach the light line. In the case of our polymer-metal system, the higher energy solution branch can only approach the light line in the polymer as well. There is no upper wavelength bound at which the lower energy mode must not pass and thus it can shift more freely to higher wavelengths.
Figure 3.4.2 Absorption spectrum in the metal of triangular cell grating structure with FF=0.5, period=300nm, maximum polymer film thickness=150nm and triangle height (a) 10nm. (b) 25nm. (c) 60nm. (d) 100nm.

Figure 3.4.3 Gap induced by a shallow grating structure
We show the effect of the grating fill factor in figure 3.4.4. We see for FF=1, the splitting of energy between the dark and bright mode can be diminished to such an extent that the two appear to be degenerate again in energy. We may not be able to immediately predict what happens in the intermediate values of FF, but at FF=1 there is a direct physical intuition. This phenomenon of energy gap diminishing can be understood by looking at the Fourier components of the grating geometry [25].

We Fourier expand a simple periodic triangle function shown in figure 3.4.5 for a single cell:

\[
    f(x) = \sum_{n=-\infty}^{\infty} a_n \cos\left( n \frac{2\pi x}{P} \right) + \sum_{n=-\infty}^{\infty} b_n \sin\left( n \frac{2\pi x}{P} \right)
\]

(3.1)

We see that when we calculate the Fourier coefficients we get \( b_n = 0 \) for all fill factor (FF) and height (h) of the grating. So we pay our full attention only to the \( a_n \) components. In the case of FF=1 we see that we get \( a_2 = a_4 = a_6 = \ldots = 0 \). The reason why the gap between the two SPP modes in figure 3.4.5 diminishes at FF=1 lies in the fact that there are no Fourier component with reciprocal lattice vector \( k_g = \frac{4\pi}{P} \) in the grating function. This component also plays a role in creating the gap at the crossing that is flipped back to 0 again by the Fourier component with \( k_g = \frac{2\pi}{P} \) which amplitude is \( a_2 \). At other FF values, this Fourier component is non-zero because \( a_2 \) is non-zero. If \( a_2 \) is 0, than that means there is one less component that is opening the gap we are interested in, and thus the gap can be smaller.
Figure 3.4.4 Grating Structure with 150 nm maximum polymer thickness, height 60 nm. (a) absorption spectrum in the metal. (b) absorption spectrum in the polymer for FF = 0.5. (c) absorption spectrum in the metal. (d) absorption spectrum in the polymer for FF = 1.

Figure 3.4.5 A triangular function in one periodic cell.
Unfortunately unlike the effects of changing triangle height, the grating fill factor does not affect the energy split between the dark and bright modes in a monotonous way. At some other combination of geometric parameters of period and height, we find that increasing the fill factor of the grating could actually make the energy difference between the two modes larger. A rigorous analytical analysis to explain these behaviour completely can be done and has been represented in the paper by Barnes (1996)[…] using a mathematical method developed by Chandezon et al. Basically it involves a coordinate transformation to a system in which the grating structure is flat. We would then solve the Maxwell equation in this coordinate system for modes that are bound to the interface. Once we have obtained the possible modes, we can calculate their energy from the charge distribution and the field profile. In the Barnes paper, the grating they considered was comprised of two sinusoidal functions.

\[ f(x) = A_1 \sin(Kx) + A_2 \sin(2Kx + \phi) \]  

(3.2)

Where \( \phi \) is the phase difference between the two sines. They calculated the relation for the first order gap width and found that it is mainly a function of the amplitude of the dominant sinusoidal function of the grating which is \( A_2 \). In their result, the gap width \( \delta \omega \) comes with the expression:

\[
\frac{\delta \omega}{\omega_0} = \frac{2KA_2}{\sqrt{-\varepsilon_1 \varepsilon_2}} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \left( 1 - 2(KA_2)^2 + \frac{(KA_2)^2}{2(-\varepsilon_1 \varepsilon_2)} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \right)^2 \right) + O(KA_2)^4 \]  

(3.3)

We see that it is also not a monotonous function of \( A_2 \) from the higher order terms of \( KA_2 \). However, there is an approximation that could be made. By taking the grating perturbation to be shallow compared to its period, \( KA_2 \) can be considered to be small and its higher orders can be neglected. We see in the case of shallow gratings, the gap width expression would have a linear dependence on \( A_2 \). It is easy to see that by increasing the height of the triangle we will be increasing also the dominant amplitude term in the Fourier expansion of our grating. Thus, our result follows the trend in the expression of the gap width given by Barnes. The observed increase in central wavelength of the two modes when the grating height is increased also follows the expression given by Barnes [24]. Note that the shifting of the central wavelength is not so big in the range of grating height of interest, such that the
prediction by finding the first order crossing point in the flipped dispersion curve (like that in figure 3.7(a)) is good.

3.5 Using first order SPP Modes

Before we go on to show results for the optimized structures, we would like to discuss the physical intuition behind choosing the polymer thickness. As we saw before, we will need a pronounced grating structure to get the flat dispersion that we want. We should not choose a thickness value that corresponds to a Fabry-Perot maximum on the flat structures because the gratings we introduce change the effective thickness felt by the light wave, moving the structure away from the Fabry-Perot maximum. In the wavelength region where there is no diffraction, the grating structure roughly only acts to reduce the effective thickness of our polymer film. Thus, we should choose the maximum thickness value of our film to be larger than the targeted Fabry-Perot maximum in figure 3.2.3 that we want to be close with. In this work, we choose two thickness values of interest. The first is 150 nm which is chosen so that with the pronounced grating structure, it can be pushed down close an optimum point in the Fabry Perot condition which happens around 60nm thickness. We choose also another thickness of 250 nm so that the grating is in the neighbourhood of the Fabry-Perot maximum at 200 nm. At this polymer thickness, slab guided modes also comes into play and can be used to boost absorption in the wavelength region of interest. We do not choose thickness larger than this because the IQE becomes unfavourable.

3.5.1 Below 200 nm polymer film thickness

Figure 3.5.1 shows an example of an optimized structure that uses both first order dark and bright modes to boost the absorption in the 600-690 nm wavelength region. The maximum integrated absorption occurs when the angle of incidence is 18° from normal incidence due to the dark mode’s angled excitation condition. The structure has FF = 1 so that the two dark and bright modes are close together. The height of the grating is 100 nm which is large enough to make the dispersion of the SPP mode to be flat. Comparing to figure 3.4.4(d), we see that we also increased our absorption efficiency at other wavelengths where there are no plasmonic resonances. For normal incidence, diffraction does not occur for wavelengths larger than the periodicity of the grating, thus the absorption improvement cannot stem from that. We attribute this to better Fabry-Perot conditions. There is a decrease of absorption strength in the 400-450nm range with respect to the flat structure but the irradiance of the
am1.5g is lower than in the region of the plasmonic resonances around 600-650nm. Thus, the decrease of absorption in the polymer in the 400-450nm range is minimally felt, and overall, the structure still gives a decent increase of absorption.

![Absorption spectra and field plots](image)

**Figure 3.5.1** (a) Absorption spectrum in the polymer for maximum polymer thickness 150nm, period 300nm, height 100nm, FF=1. (b) a cut of the absorption spectrum in (a) for 18° degree angle of incidence compared with normal incidence spectrum of a planar structure. Insets: Hz field plots at the two SPP resonances A and B.

For the set of materials that we use, it turns out that we can get better absorption improvement by using the bright mode only with the device operating optimally for normal incident waves. Figure 3.5.2 shows the simulation result for a grating period of 400 nm and maximum film thickness of 150 nm for various fill factors and heights. Figure 3.5.2(a) shows the flipped flat dispersion diagram for flipping period of 400nm. At this periodicity, the first order crossing appears just a few nm above 800 nm. In this case we use a fill factor less than 1 so that we can push the first order bright mode to the 600-650 nm wavelength region by increasing height. Figure 3.5.2(b) shows a plot of the integrated absorption IP, as defined in section 3.2, as a function of grating fill factor and triangle height. As indicated in the figure, there is an optimum combination for the fill factor and height which is due to the complex interaction of the SPP peak position and strength, and the grating scattering capability as already discussed. The optimum configuration at point C in figure 3.5.2(b) gives the best absorption enhancement (for first order mode usage only) for normal incidence applications. Figure 3.5.2(c) shows the absorption spectrum at different points in figure 3.5.2(b). We see as we go from points A, B to C (corresponding to triangle heights 10 nm, 60 nm, and 120 nm), that the peak position stems from the flat SPP mode at 800nm which gets blue shifted. Indeed, as the
triangle height increases, a stronger perturbation splitting effect is observed as discussed previously.

Fig. 3.5.2 (a) Dispersion diagram of SPP mode at a flat polymer-silver interface folded with 400nm grating period, where G is the reciprocal lattice vector. (b) Dependence of integrated absorption efficiency in the 300-800nm region. (c) TM polarization absorption spectrum at different points in (b).

For the most optimum set of parameters in figure 3.5.2(b), we show a comparison of absorption spectrum for TE and TM polarization and also with a planar structure of thickness 150nm in figure 3.5.3(a). We see that the absorption for the TE polarization is also improved due to better Fabry-Perot conditions. The norm of the magnetic field profile is shown in figure 3.5.3(b). The field profile shows a spatially distributed enhancement of the field, which is favourable for efficient charge generation. The integrated absorption efficiency for a planar unpatterned structure is 48% while for a patterned structure it is 63.6% for TM polarization and 56% for the TE polarization. We therefore see an additional 15.6% increase in integrated absorption for the TM case.

Fig. 3.5.3. (a) Polymer absorption spectrum for the planar and patterned device, respectively. The patterned device has a period of 400nm with fill factor 0.5 and triangle height 120nm. (b) Plot of the norm of the magnetic field profile for the TM polarization input at 640nm wavelength.
3.5.2 Beyond 200 nm polymer film thickness

Now we consider polymer film thicknesses larger than of 200 nm, more specifically we choose 250nm for the calculations. In such a relatively thick film system, the opportunity to utilize waveguide modes in the polymer film arises. We mentioned that we were aiming to be close to the Fabry-Perot maximum point at 200 nm in figure 3.2.3. We therefore employ triangular gratings that are not so pronounced, as opposed to the previous section. With a triangular grating height of just around 50 nm, the waveguide modes in the polymer film can still exist in this system. To confirm and predict where the waveguide modes will be when we introduce a grating profile we calculated the dispersion diagram of these modes using the eigenmode solver in comsol to solve for a planar system of air-polymer-metal as shown in figure 3.5.4. The red line in the figure corresponds to the light line in air. The blue line corresponds to the theoretically calculated propagating SPP mode on a flat interface between infinite half planes of polymer and metal. The “*” are the modes obtained through calculation in the eigenmode solver for an air-polymer-metal interface for a 250 nm thick polymer film. The film is already thick enough such that the propagating SPP mode in this 3-layer system has similar characteristics with the propagating SPP mode on an interface of infinite half planes of polymer and metal. We see that, in figure 3.5.4, we have one more guided mode with lesser momentum than the SPP mode which signifies that the mode is confined mainly in the polymer. This mode corresponds to the “*” that is not followed by a blue line.

![Dispersion relation for waveguide modes](image)

Figure 3.5.4 Dispersion relation for waveguide modes. The red line indicates the light line for air.
To demonstrate the effects of having waveguide modes in the system we show results for a solar cell grating system of thickness 250 nm, period 400nm, fill factor 0.5, and triangle height 50nm in figure 3.5.5. We see that through flipping the dispersion diagram in figure 3.5.5(c), we predict an additional resonance possible in the structure through waveguide mode excitation around 600 nm at k=0. The mode that starts around 750nm, at point A in figure 3.5.5(a), is the bright first order mode. The mode that comes in the middle around 650nm, at point C, stems from a waveguide mode. We observe that there can be an interaction between the waveguide mode and the plasmonic mode that ruins the coupling efficiency of incident light to both modes’ when their dispersion crosses each other. The physical intuition behind this is the fact that, at the cross point, we have two modes with the same k-vector, frequency and are of the same polarization and therefore will produce a steady interference pattern with each other and in this case the interference is effectively destructive. We have to take care about this interaction when we place our resonances when we design our solar cell. Figure 3.5.5 (d) shows the field profile at different points indicated in 3.5.5(a) to further elucidate the nature of the modes, which one is an SPP mode and which one is a waveguide mode. Near the crossing point it is expected that the mode profile is a bit mixed as we can see in picture D. The field profile in figure E indicates that the resonance there is also a waveguide mode since the field is not confined to the metal interface, thus the branch in figure 3.5.5(a) and (b) that goes down above 40° incidence is the waveguide mode branch.
Figure 3.5.5 Results for solar cell grating system of maximum thickness 250 nm, period 400 nm, fill factor 0.5, and triangle height 50 nm. (a) Absorption spectrum in the polymer. (b) Absorption spectrum in the metal. (c) Flipped dispersion diagram with 400 nm periodicity. The blue line is the theoretically calculated SPP mode on polymer-metal interface. (d) Unnormalized profile of the norm of magnetic field at the points indicated in (a).

Figure 3.5.6 shows the absorption spectrum of an optimized structure for this thicker polymer film system. The structure has optimum integrated absorption at 13.5° angle of incidence when the coupling efficiency of the dark mode is maximum. For the wavelength range of 300-800 nm, the integrated absorption (IP) in the polymer 71.4 % for the TM polarization and 60.3% for the TE polarization. For a simple planar structure of 250 nm thick polymer film in an air-polymer-metal system, it is 56%. It is interesting to see that the dark and bright first order SPP modes switch places in energy. Now the antisymmetric, “dark” mode has a higher energy than the bright mode and thus it is placed at a smaller wavelength than the bright mode. We see this by noticing that the peak B in figure 3.5.6(b) only appears after a change in angle, see figure 3.5.6(c) for normal incidence absorption spectrum. We suspect this is due to the more polymer space available such that the bright mode field is less confined and thus the charge distribution can have smaller energy.
Figure 3.5.6 Results for solar cell structure with 250nm maximum polymer thickness, Period 290nm, triangle height = 60nm, FF = 1. (a) Absorption spectrum. (b) Cut of absorption spectrum of a grated solar cell at 13.5° angle of incidence compared with spectrum for a planar structure of 250nm polymer film at normal incidence. (c) Absorption spectrum at normal incidence. (d) Unnormalized field profile of the norm of magnetic field at the three peaks shown in (b).

We give the integrated EQE in the 350-650 nm wavelength range as a function of incident angle for several structures as a comparison of the performance in figure 3.5.7. Grating 1 represents the grating structure in figure 3.5.3 (for maximum polymer thickness of 150nm). Grating 2 represents the grating structure in figure 3.5.6 (for maximum polymer thickness of 250nm). We see that both gratings out-perform the second Fabry-Perot maximum in terms of integrated EQE (see figure 3.2.3) by about 4% at certain angles. The enhancement for grating 2 should be more, since the absorption enhancement is still extended to beyond 700nm, but
we did not take into account the enhancement effect above 650 nm to calculate the integrated EQE due to lack of IQE data.

Figure 3.5.7. Integrated EQE in the 350-650nm wavelength range for planar structures and for 2 grating profile structures that incorporate only first order modes. Grating 1 represent the grating structure in figure 3.5.3 (for maximum polymer thickness of 150nm). Grating 2 represent the grating structure in figure 3.5.6 (for maximum polymer thickness of 250nm).

3.6 Larger period gratings

Until now we considered the usage of only the first order crossing at k=0, but we can also opt to use modes that stems from higher order crossings. We can do that by using larger periods for our gratings. We cannot just use an arbitrarily large period because we do not wish the diffraction edge to be at a wavelength larger than where we intend to place our plasmonic and waveguide mode resonances, as we explained before. We show the absorption spectrum of a grating structure of 150 nm maximum film thickness, 450nm in period with fill factor = 0.5 and height 120nm in figure 3.6.1. The peak appearing at 670 nm at k=0 stems from the first order bright mode that we push down using tall grating height and fill factor =0.5. The second peak of the higher order mode only begins to show itself clearly at 20° angle of
incidence from 640nm. We see that the higher order mode still has a non-flat dispersion even though we already used pronounced triangular gratings with height of 120nm. It can even pass through the first order bright mode band. We will need to use even heavier corrugation (taller triangles in our case), to make it flat. This is quite unfavourable in our current applications since we still need our film to be quite thin and we do not wish the triangular tip to be even closer to the upper surface of the polymer film since there might arise short circuit problems. However, in the future, when the organic solar cell material has better charge transport properties such that we can opt to use thicker films, we may be able to use even taller grating structures without too much trouble.

![Diagram](image)

(a) (b)

(c) (d)

Figure 3.6.1 Solar cell gratings structure. Maximum thickness= 150nm, triangle height 120 nm, Fill Factor 0.5 (a) absorption spectrum in the metal, (b) absorption spectrum in the polymer, (c) Magnetic field profile plot of point A and (d) Magnetic field profile plot of point B from (b).

Diffraction is not always something that we wish to avoid. We can also use the Wood anomaly peak in the absorption spectrum related to the diffraction edge to boost absorption.
The plasmonic resonances, however, still have bigger linewidths and can boost absorption more than these diffraction peaks. Figure 3.6.2(a) shows the absorption spectrum at 550nm grating periodicity. The absorption peak due to diffraction is clearly seen also at 550nm in the graph. Figure 3.6.2(b) shows the norm of the magnetic field profile at the two peaks indicated in (a). We see that the peak of the absorption at 550nm indeed does not stem from a plasmonic mode since the fields are not confined to the interface. For our structure and material it is not beneficial to employ the diffraction peak to boost absorption in the 600-690 nm. If we use the diffraction peak to boost absorption in that wavelength region, we would be pushing our plasmonic resonances away from the region of interest and then we can only opt to use higher order plasmonic modes. This is due the permittivity characteristics of the materials we are using.

![Figure 3.6.2](image)

Figure 3.6.2 (a) absorption spectrum of a structure with period 550nm, t=150nm, h=120nm, FF=0.5 at normal incidence. (b) the norm of the magnetic field profile at the diffraction peak and at the second order peak.

Notice also the field profile in figure 3.6.2(b) of the second order mode is more confined to the interface than the first order ones. It is expected therefore that exciton quenching problems will be stronger with the higher order modes.
3.7 Multiperiod gratings

Figure 3.7.1 More complicated grating structure to get more plasmonic modes.

Until now we only considered relatively simple grating structures to utilize propagating SPP mode. In the case of very pronounced triangle gratings, it could be said that we also considered using coupled LSPR phenomena. The idea in this section, is to get additional resonances to fill up the absorption spectrum through more coupled LSPR modes. We can enable such modes to exist by having periodic defects with much smaller period introduced in our grating structure. The defects’ period should be small enough such that they can interact with each other via their near field. In this work, we use small triangular grooves as the defects. A sketch of the structure is given in figure 3.7.1.

The corrugation that we introduce is relatively weak in the hope not to destroy the modes given by the previous periodicity. The introduction of the secondary grating is not optimized here, but we wish to demonstrate a proof of principle. Figure 3.7.2 shows the absorption spectrum in the polymer for normal incidence for a geometry with single main periodicity (with only period P-1 in figure 3.7.2 (a) ), a geometry with a smaller periodicity (with only
period P-2 in figure 3.7.2 (b), and a multiperiodic geometry (with both period P-1 and P-2 in figure 3.7.2(c)). The new resonances in the combined structure seemed to stem from the interaction between both gratings since we see that individually these gratings do not produce the same resonances. We see that the new resonances arise and fill in the entire region from 650-770 nm. The new modes have flat dispersion characteristics as expected for coupled LSPR modes, see figure 3.7.2(d).

We proceed to examine the field profile of these resonant modes. Figure 3.7.3 shows the norm of the magnetic field profile of the resonances in both systems. Although the modes in the multiperiodic geometry are mostly confined in the grooves, they still can lead to an effective increase of absorption in the polymer up to 5 times at the resonant wavelengths. It is interesting to see that these new resonances boost the absorption in the polymer even for wavelengths above 700 nm where the polymer’s absorption capability is very small. One would tend to think that at this region, if the mode is highly confined inside the grooves and given the fact that the absorption of the polymer is already so low, that a major part of the absorption occurs in the metal. However, our calculation shows that the absorption in the polymer due to the coupled LSPR can still go up to around 50%. This again shows the promising capabilities of plasmonics to increase absorption in nanostructures. The integrated absorption for the TM polarization in the wavelength region from 300-800 nm for the case of the multiperiodic grating in figure 3.7.2(c) is 68.7%. In the single main grating in figure 3.7.2(a), it is 63.5% and in the flat planar structure it is only 48%. We have an additional 5.2% increase of integrated absorption in the case of multiperiodic gratings as compared to the single periodic one. A similar field profile like that in resonance A in figure 3.7.3 is not observed in the resonances for the multiperiodic geometry. This shows that the additional new corrugation, albeit supposedly weak compared to the main one, changes the eigenmodes of the structure strongly. The peak B in figure 3.7.2(c) seems to stem from Fabry-Perot effects. Its corresponding field profile in figure 3.7.3 does not seem to indicate that the field is confined to the metal interface.
Figure 3.7.2 Results on double grating period with main period 390nm and small period 30nm, main triangle height of 120nm, defect groove depth of 15nm on average, and FF for the main grating is 0.5 and for the defects it is 1/3. Absorption spectrum in the polymer (a) for the main grating case (period P-1) only. (b) for the secondary grating case only(period P-2). (c) multiperiodic case. (d) Complete absorption spectrum of the multiperiodic geometry in(c).
Figure 3.7.3 Norm of magnetic field profile at the resonances of figure 3.7.2(a) and (c). The field profile is normalized with the same scale shown on the left. 8 in the color bar means 8 times the incoming plane wave amplitude. The white area in the profile shows amplitude values beyond this range.

We can actually obtain flat coupled LSPR modes without having a big main triangle height. Figure 3.7.4 shows multiperiodic grating geometry but with a much less pronounced main geometry (triangle height of the main geometry is only 60nm). Although optical absorption in the polymer is improved significantly, there is a concern that most of the generated excitons will be quenched by the metal and thus we may not achieve the effective increase of charge carrier generation as we expected. More investigation of the geometry is needed to optimize the field profile of the new structure such that it spreads more into the polymer.
Figure 3.7.4 Results on double grating period with main period 340nm and small period 25nm, main triangle height of 60nm, groove depth of 25nm on average, FF for the main grating is 0.5 and for the defects it is 0.8. (a) absorption spectrum in the polymer at different angles. (b) absorption spectrum in the polymer at normal incidence. (c) unnormalized norm of magnetic field profiles of the absorption peaks in (b).

3.8 Pyramidal 2D gratings

We simulated a 2D pyramidal grating system to see whether our resonances would behave the same and whether our initial prediction tools could still work in a 3D case. We simulated for normal incident light for various pyramidal gratings with maximum polymer film thickness of 150nm. Because we are only considering normal incidence light, we can reduce the computational domain to a quarter of a cell and use perfect electric and magnetic conductor boundary condition on the sides, see figure 3.8.1.

Figure 3.8.1 The simulated domain for pyramidal 2D grating structures.
In figure 3.8.2 we show the absorption spectrum in the wavelength region from 500-800 nm. In each case, the pyramid height is 120 nm and the fill factor is 1. We found that the positions of the SPP peaks can still be predicted by following the analysis we did for the 1D gratings before. We basically see the first order and second modes appearing around the point we determine by band flipping as before. We see similar effects on the resonances for different geometries. For example when FF=1, at 300nm the dark mode and bright mode is relatively close together even at big grating heights. In addition, when the grating height is large for periods 400nm and above, the separation between the first order dark mode and bright mode gets larger even for FF =1 (as in the 1D grating case). We notice that in this normal incidence case, our calculation shows the peaks stemming from first order crossings is excited considerably weaker than the second order peaks for this structure. We can see that the dominant peaks in the graph occur at larger grating periods of 500 and 550nm. The peaks around 600nm wavelength in these grating structures are related to second order peaks. The other peaks are related to first order peaks. We also do not see a clear peak related to the diffraction edge in this 3D case for the 550nm grating period.

Figure 3.8.2 Absorption spectrum at normal incidence for 2D pyramidal gratings with FF=1, maximum thickness=150nm and height 120nm, for several different periods.

Now we show some initial results that seems to indicate the coupling strength of modes from a first order crossing is better at smaller fill factors for the 2D pyramidal grating case. The two peaks we see in figure 3.8.3(b) for both cases of grating fill factor stems from a first order crossing at k =0. We also see that, unlike in the case of figure 3.4.4 where with fill factor 1 we get a minimum separation between the two modes , the grating with smaller fill factor
value has a smaller separation of the modes from the first order crossings. We predict a first order crossing around 680nm for the grating period that we used for figure 3.8.3(b) using simple band flipping shown in figure 3.8.3(a). However, the result is quite off from the center of the two peaks in the 3D numerical calculations which is around 640 nm seen in figure 3.8.3(b). Through these calculations we also see that both modes from one crossing can be bright.

![Figure 3.8.3](image)

Figure 3.8.3 (a) Flipped dispersion curve of SPP modes on flat polymer-silver interface with 320nm period (b) Absorption spectrum at normal incidence for 2D pyramidal gratings with maximum thickness=150nm and height 120nm, and period of 320nm for FF =1 and FF =0.5

### 3.9 Proposed fabrication method

The triangle gratings of interest have periodic dimensions of 300 to 500 nm, and the height of these triangles goes up to about 100 nm. The fabrication route that we propose is by first patterning a silicon substrate to be a master copy. The pattern is then copied to a polymer mold first so that we can have several copies of the grating structure. This technique is a form of nano-imprinting. Afterwards, we can deposit the silver atoms on top of this polymer mold to get our metallic triangular pattern, see figure 3.9.1. We can simply deposit the solar cell polymer afterwards on top of the metal film. The metal film has to be quite thick for good electrical contact since we wish to use this as a back contact cathode for a solar cell. The plasmonic modes are quite confined to the interface of the metal structure and do not penetrate the metal much. In effect we do no need to worry so much about the additional polymer mold beneath the metal.
Figure 3.9.1. Pattern copying process to get metallic triangular structure. (1) Prepare the silicon substrate with the triangular grooves. (2) Copy nanostructure pattern to a polymer mold. (3) Deposit metal to make a film on top of the polymer mold.

In doing the lithography, we can either pattern the silicon substrate directly (by Focused Ion Beam (FIB) for example) or by patterning a mask or resist first and then use wet etching. Wet etching is a material removal process using a liquid-phase etchants. There are chemical solutions that etch away preferentially along a certain plane of orientation in a material. Such etching processes are called anisotropic etching and are of interest because they enable us to create pyramids or triangular groove structures in the substrate. Because the anisotropic etching process is specific to a certain plane of orientation of the substrate, the geometry of the produced triangle structure will be limited to this condition. In our case, we will be limited to making triangular grooves that pertains to a specific plane of orientation of the silicon crystal that reacts to the wet etchant that we use. We planned to use KOH as the wet etchant which have preferential selectivity between the $<100>$ and $<111>$ plane, and thus we can only make triangular grooves with angles of 52.47°, see figure 3.10.3 [26]. Once the two $<111>$ planes in figure 3.9.2 meets, the etching process have the property to stop and not etch anymore.

If we choose to shoot ions to etch away silicon directly, we will have more freedom in our triangular structure. The problem is the process will be quite slow since the ion columns have to be controlled precisely in order to produce the intended triangular groove nanostructure. Figure 3.9.3 shows an example that we attempted to do in making a triangle groove on silicon by shooting FIB directly. The platina in the figure is just deposited after the direct ion etching
so that we can make a cross section to image it. A good recipe for the beam current, voltage and of the dwell times of the FIB beam to create the triangular structure in figure 3.9.3 takes us about 2 minutes to create one triangle groove that is only about 1 µm in length. The beam current and the voltage quantify how many ions are sent each second and their individual energy. The dwell time indicates how long the beam is focused on a certain area. For our purpose of creating a semi-infinite periodic grating structure this is a bit unacceptable since it would require a very long time to complete the intended structure. For this reason of time constraint we suggest the usage of wet etching.

Figure 3.9.2 KOH wet etching preferences in silicon [27]

![Figure 3.9.2 KOH wet etching preferences in silicon](image)

In order to do wet etching, we will need a mask that is resistant to the wet etchant that we plan to use. At least the mask needed to be resistant long enough such that we can finish making the triangular grooves before the mask is completely gone. We were considering the

Figure 3.9.3 SEM cross-section view of a triangle groove created by shooting ion columns on a silicon substrate.

![Figure 3.9.3 SEM cross-section view of a triangle groove created by shooting ion columns on a silicon substrate](image)
possibility of using simply photo-resist or e-beam resist for the mask. But even if these two fail, we can still first transfer the pattern we need from the e-beam or photo-resist to a silicon nitride (SiN) which is known to be resistant to wet etchants like KOH. We can do this by first depositing SiN on top of our silicon. We will then do an intermediate step of dry etching to transfer a pattern from a developed resist that we put on top of the SiN. After the pattern is transferred to the SiN, it will function as mask and we can continue with the wet etching.

We propose to utilize e-beam lithography in making the mask for the wet etching. This time we do not suffer the time consuming problem like that in the direct FIB writing on silicon substrate. This is because we do not need special and complicated settings for the beam current, voltage, and dwell time. Unlike in direct writing where we try to create a prism structure, we only need to give exposure on rectangular areas on the resist that we deposit on top of the substrate, see figure 3.9.4 for the lithography process steps. In the figure, we give the example in the case of negative e-beam resist, meaning the exposed area remains while the rest are etched away.
Another possibility that we can employ to produce our gratings on silicon is by interference lithography. To produce the interference pattern, we can split the beam from a laser into two sub-beams that we bring together again under an angle to interfere and pattern a resist.
Chapter 4 Conclusions

Throughout this thesis work, we discussed mainly what characteristics are desired from the plasmonic modes and other phenomena (such as diffraction and slab guided modes) to boost absorption in organic polymer solar cells and how to realize them using triangular grating structures. The initial prediction tools (such as the dispersion band flipping) and optimizing strategy (such as and the integrated absorption calculation for planar structures to locate optimum maximum thickness) to do the design of the grating were outlined.

We discussed how the geometric parameters of the grating affect the behaviour of the plasmonic resonances of the system, what it takes to make the dispersion flat and what determines the resonance position. The behaviour of the antisymmetric and symmetric (bright and dark) modes was investigated and then put to use in the solar cell design. We demonstrated control of the separation between those two modes in frequency using the fill factor and the height of the grating structure. The energy of the two modes is indeed very closely related to the grating geometry and we found that, by playing with the polymer film thickness, we can choose which mode has the higher energy. In addition, we examined the usage of more complicated multiperiodic structures to gain more resonances that join and fill up a significant wavelength span.

In the 1D triangular grating case with a single period we demonstrated an increase of integrated absorption in the wavelength range of 300-800nm of 15.6% for the TM polarization and 8% for the TE polarization compared to the planar structure. Most of the enhancement occurs in the wavelength region below 690 nm. With the multiperiodic gratings, we demonstrated an increase of 20.7% for the TM polarization as compared to the flat planar structure. 3D simulation results for several pyramidal grating structures show that the resonance frequencies for SPP modes can also be roughly predicted by simple band flipping as demonstrated in the 1D grating case. The plasmonic resonances in the pyramidal grating case also show promising capabilities in boosting absorption in the polymer. In addition, we proposed a fabrication method and the steps to produce the gratings using electron beam lithography.

The designs that we show combine several physical phenomena such as propagating SPP modes, coupled LSPR modes, Fabry-Perot, diffraction, and slab waveguide modes together in order to boost the absorption capability of the polymer film and indeed the boost in
absorbance is evident in our numerical calculations. The proposed optimization route and usage strategies of the resonances are applicable for other materials. We can simply adapt to the needs of the new solar cell materials as the main strategy of resonance placements remains the same.

There are still a lot of possibilities and future works that can be done regarding the coupling strength of the incident light to the guided modes, interaction of waveguide modes and SPP modes, the optimization of the multiperiodic and 3D structures.
APPENDIX

The Bloch Boundary condition derivation

To see what phase factor, or more specifically Bloch wave vector, we actually need, first we examine the Helmholtz wave equations in terms of incoming and scattered fields.

$$\nabla^2 \vec{E} + k_0^2 \varepsilon_r (\vec{r}) \vec{E} = 0$$

$$\varepsilon_r (\vec{r}) = \varepsilon_{r0} + \Delta \varepsilon (\vec{r})$$

$$\vec{E} = \vec{E}_{in} + \vec{E}_s$$

$$\nabla^2 \vec{E}_s + k_0^2 \varepsilon_r (\vec{r}) \vec{E}_s = -k_0^2 \Delta \varepsilon_r (\vec{r}) \vec{E}_{in}$$

Where $\Delta \varepsilon (r)$ is the relative permittivity change with respect to a background permittivity. $\vec{E}_s$ is the scattered wave and $\vec{E}_{in}$ is the input wave which fulfils the Helmholtz wave equation without a source for a uniform medium with the dielectric permittivity of $\varepsilon_{r0}$.

$$\nabla^2 \vec{E}_{in} + k_0^2 \varepsilon_{r0} \vec{E}_{in} = 0$$

The incoming field in our case would be plane waves which have the form

$$\vec{E}_{in} (\vec{r}) = \vec{E}_0 e^{iK \cdot \vec{r}}$$

We express the scattered field in a general way to be a superposition of bloch functions

$$\vec{E}_s (\vec{r}) = \sum_k \vec{E}_{sk} (\vec{r}) e^{iK \cdot \vec{r}}$$

Inputting these terms in to Helmholtz equation for the scattered field we get

$$\nabla^2 \sum_k \vec{E}_{sk} (\vec{r}) e^{iK \cdot \vec{r}} + k_0^2 \varepsilon_r (r) \sum_k \vec{E}_{sk} (\vec{r}) e^{iK \cdot \vec{r}} = -k_0^2 \Delta \varepsilon_r (\vec{r}) \vec{E}_{in}$$

Since $\vec{E}_{sk} (\vec{r})$, $\varepsilon_r (\vec{r})$, $\Delta \varepsilon_r (\vec{r})$ are periodic and have the same periodicity, we can expand them as
\[ E_{sk}(\vec{r}) = \sum_{G} \tilde{E}(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}} \]
\[ \Delta \varepsilon(\vec{r}) = \sum_{G} \Delta \varepsilon_{G} e^{-i\vec{G} \cdot \vec{r}} \]
\[ \varepsilon(\vec{r}) = \sum_{G'} \varepsilon_{G'} (\vec{G}') e^{-i\vec{G}' \cdot \vec{r}} \]

and using this in the Helmholtz equation to get:

\[
\nabla^2 \sum_{k} \sum_{G} \tilde{E}_{G}(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}} + k_0^2 \left( \sum_{G'} \varepsilon_{G'} (\vec{G}') e^{-i\vec{G}' \cdot \vec{r}} \right) \sum_{k} \sum_{G} \tilde{E}_{G}(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}} \\
= -k_0^2 \sum_{G} \Delta \varepsilon_{G} e^{-i\vec{G} \cdot \vec{r}} \tilde{E}_{0} e^{i\vec{k}_{m} \cdot \vec{r}} \]

We can rewrite the second term on the left hand side to be in the form

\[
\nabla^2 \sum_{k} \sum_{G} \tilde{E}_{G}(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}} + k_0^2 \sum_{k} \sum_{G} A_{G}(\vec{k} - \vec{G}) e^{-i\vec{G} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{r}} \\
= -k_0^2 \sum_{G} \Delta \varepsilon_{G} e^{-i\vec{G} \cdot \vec{r}} \tilde{E}_{0} e^{i\vec{k}_{m} \cdot \vec{r}} \]

The scattered waves should solely come from the source term \( -k_0^2 \sum_{G} \Delta \varepsilon_{G} e^{-i\vec{G} \cdot \vec{r}} \tilde{E}_{0} e^{i\vec{k}_{m} \cdot \vec{r}} \). We see therefore, for this equation to hold, only terms on the left hand side with \( \vec{k} = \vec{k}_{m} \) should have non-zero coefficients. Therefore the scattered field will be of the form:

\[ \tilde{E}_{s}(\vec{r}) = \tilde{E}_{sk_{m}}(\vec{r}) e^{i\vec{k}_{m} \cdot \vec{r}} \]

Thus, since the scattered field will have a bloch wave vector of \( \vec{k}_{m} \) which is the k vector of the input field, the total field will also have the same form as the scattered field:

\[ \tilde{E}_{tot}(\vec{r}) = \tilde{E}_{tot_{k_{m}}}(\vec{r}) e^{i\vec{k}_{m} \cdot \vec{r}} \]

Therefore, now we know that the phase factor that connects the field amplitude on the left end of the cell to the field amplitude at the right end of the cell. The Bloch wave vector is thus

\[ k_{f} = k_{m} \sin(\theta) \]

Where \( \theta \) is the angle with respect to the direction perpendicular to the grating structure.
Bibliography


