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Design Considerations for Enhancing Absorption in Semiconductors on Metals through Surface Plasmon Polaritons†

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Surface plasmon polaritons (SPPs) are collective oscillations of the electromagnetic field which propagate along an interface between a metal and a dielectric with complex relative permittivities, $\epsilon_m$ and $\epsilon_d$, respectively. The ability to spatially confine the electromagnetic field to an interface holds promise for a range of applications from nanoscale optical communications and switching to realizing negative index metamaterials for cloaking and microscopy. SPPs are important for energy applications, including photovoltaic or photoelectrochemical devices, because they can be used to enhance absorption through concentrating the electromagnetic field in the absorber, and thus boost device efficiency, particularly in thin films where the length scale for minority carrier diffusion is less than that for photon absorption. Recently, several papers have investigated the thermodynamic limit to nanophotonic enhancement of light absorption. These studies found that when nanophotonic strategies are employed, absorption enhancement - defined as the total absorption divided by the single pass absorption - can exceed $4n^2$ for illumination at normal incidence, where $n$ is the real part of the complex refractive index of the active layer. In ultrathin materials, single pass absorption is small, meaning that the denominator of the enhancement calculation is nearly zero and large values of enhancement can easily be obtained. A more appropriate figure of merit for energy applications is the total fraction of incoming light that can be captured in the dielectric using nanophotonic light trapping strategies, or equivalently the absolute attainable energetic efficiency. Here, we outline the fundamental physical requirements for absorption with SPPs by solving Maxwell’s equations for the simplest case, the interface between two semi-infinite materials. Our objective is to provide guidelines for selecting absorber materials and to determine which optical properties make materials good candidates for plasmonics. We demonstrate that optimum performance requires maximizing the imaginary part of the relative permittivity, $\text{Im} \{\epsilon_d\}$, while minimizing the real part of the relative permittivity, $\text{Re} \{\epsilon_d\}$. Interestingly, these considerations highlight the efficacy of using SPPs with organic PV materials as well as CdTe, but demonstrate the limitations of traditional absorbers including crystalline and amorphous Si, GaAs and oxides such as TiO$_2$ and $\alpha$-Fe$_2$O$_3$ for which the ratio of $\text{Re} \{\epsilon_d\}/\text{Im} \{\epsilon_d\}$ is not favorable.

The predominant experimental approach merging plasmonics and photovoltaics has been to coat existing cells with metallic nanoparticles that support localized surface plasmon modes and scatter light into guided modes of the underlying...
ing dielectric. This strategy was first pursued by Stuart and Hall, and has been applied to Si, GaAs, and organic photovoltaics among others. Because scattering is not the focus of the present article and because localized surface plasmon resonance occurs over a narrow frequency range for a single nanoparticle, compared to the broadband nature of surface plasmon polaritons, localized surface plasmon resonance will not be discussed further. Other light trapping strategies such as multilayer waveguides, dielectric slabs, photonic crystals, or other physical phenomena such as hot carrier transport which do not rely on SPPs will also not be considered. Strategies based on propagating SPPs have been most successful in organic materials. Using a P3HT:PCBM absorber, Morfa et al. increased photovoltaic efficiency from 1.3% in planar devices to 2.2% using a nanostructured thin film of Ag. Kang et al. developed a heterojunction organic cell containing a copper phthalocyanine electron donor and a C60 acceptor, and achieved absolute efficiency increase from 0.96% in a planar device to 1.32% in Ag nanowire plasmonic grating. These efficiencies, however, are still below the current record relating to the amplitude, $E_0$, and organic, $E_{\text{abs}}$. Solution of Maxwell's equations gives bound SPP modes for TM polarization only. Assume a bound SPP mode propagating along the interface in the positive $x$-direction as an idealized starting point. This assumption ignores (i) the finite thickness of both the metal and dielectric layers in real devices, (ii) the initial absorption owing to light propagating through the dielectric towards the interface and (iii) imperfect coupling of the incoming plane wave to SPPs at the interface. While coupling efficiencies of incoming light to SPPs of greater than 45% for TM polarized light have been reported, perfect coupling is unrealistic. Together these assumptions will therefore lead to an upper limit on the fraction of light which can be usefully absorbed using SPPs. For linear, isotropic media without external charge and current densities, the analytical solution for the electric field characterizing the SPP is given by the real component of the complex field (see Appendix A):

$$E_m = \left[ E_0, 0, -E_0 (E_d / E_m)^{1/2} \right] e^{i(k_x x + k_m z)}$$

$$E_d = \left[ E_0, 0, E_0 (E_m / E_d)^{1/2} \right] e^{i(k_x x - k_d z)}$$

where $E_m$ and $E_d$ are the complex electric fields in the metal and dielectric, respectively, $E_0$ relates to the amplitude, $k_0$ is the wavevector parallel to the interface and $k_{m,d}$ are the wavevectors perpendicular to the interface in the metal and dielectric, respectively.

Of primary interest is the power which can be usefully absorbed for energy generation. For linear media, the time-averaged dissipated power in the dielectric absorber owing to the SPP is given by:

$$P_{\text{abs,d}} = \frac{1}{2} \int_0^\infty \int_0^\infty \text{Re} \{ \sigma (E_d \cdot \cdot d) \} \, dx \, dz =$$

$$= \frac{1}{2} \int_0^\infty \int_0^\infty \omega \varepsilon_0 \text{Im} \{ E_d \} \left| E_d \right|^2 \, dx \, dz,$$

where the factor of 1/2 arises from time averaging, superscript $*$ denotes the complex conjugate, $\sigma (\omega ) = \omega \varepsilon_0 \text{Im} \{ E_d \}$ is the real-valued conductivity, and

$$\left| E_d \right|^2 = \left| E_0 \right|^2 \left( 1 + \left| \frac{E_m}{E_d} \right| \right) 2^{-i(k_z x + i(k_{d,m}))}.$$

Note that for the definite integral in Eq. (2) to be bounded and nontrivial, $\text{Im} \{ E_d \} > 0$ and $|\text{Im} \{ E_{d,m} \}| < 0$ are required. Overall, the power absorbed in the dielectric is calculated from Eqs. (2) and (3) to be:

$$P_{\text{abs}} = \frac{P_{\text{abs,d}}}{P_{\text{abs,m}}} \text{ gives:}$$

$$F_{\text{abs}} = \frac{\text{Im} \{ E_d \}}{\text{Im} \{ E_m \} \text{Im} \{ E_{d,m} \} \text{Im} \{ E_{d,d} \}},$$

The fractional power which is usefully captured by the absorber divided by the total power captured by both the metal and the dielectric absorber is $F_{\text{abs}} / (F_{\text{abs}} + 1)$. For plasmonic applications involving light absorption, maximizing the ratio $F_{\text{abs}}$ in Eq. (5) over the broadband solar spectrum is paramount. The relative power usefully absorbed can be considered the product of the field at the interface, the decay length of this field, and a material's ability to absorb. These quantities are represented in Eq. (5) by the terms $1/|E_d|$, $1/|\text{Im} \{ E_{d,m} \}|$ and $\text{Im} \{ E_d \}$, respectively. Assuming $\text{Re} \{ \varepsilon \} >> \text{Im} \{ \varepsilon \}$, which holds for typical materials, Eq. 5 can be simplified using Eqs. (14) to

$$F_{\text{abs}} \approx \frac{\text{Im} \{ E_d \} \text{Re} \{ E_m \}^2}{\text{Im} \{ E_m \} \text{Re} \{ E_d \}^2}.$$
The electromagnetic intensity and its decay are nearly identical for both cases, as shown by overlapping curves in the bottom half of Fig. 1. In the dielectric halfspace, $Re\{\epsilon_d\}$ is larger for Si than SiO$_2$ and both the interface value and the decay length of the electromagnetic field intensity is larger in SiO$_2$. The intensity at the interface is discontinuous and is given by $|E_d(z = 0^+)|^2/|E_m(z = 0^-)|^2 = |\epsilon_m|/|\epsilon_d|$, which is approximately $|Re\{\epsilon_m\}|/|Re\{\epsilon_d\}|$ when $|Re\{\epsilon\}| >> |Im\{\epsilon\}|$. Thus, for a fixed choice of metal, concentrating the intensity in the absorber at the interface requires minimizing its positive real permittivity. Next, to maximize the spatial extent of the field in the dielectric, we note that the ratio of decay lengths is given by $z_d/\delta_m = |Im\{\kappa_m\}|/|Im\{\kappa_d\}|$ from Eq. (14) for $|Re\{\epsilon\}| >> |Im\{\epsilon\}|$. On the absorber side, maximizing the integral of the exponentially decreasing intensity as in Eq. (2) requires maximizing its value at the interface as well as extending its decay length into the absorber, viz. minimizing the absorber’s real positive permittivity.

For energy applications, it is necessary to maximize the frequency range over which SPPs can be supported and to ensure optimal overlap between this range and the solar spectrum. Figure 2 plots the dispersion diagram showing the relationship between $Re\{k_z\}$ and $\omega$ for the interface between Ag and either (a) SiO$_2$ or (b) Si, along with (c) the solar irradiance. The dispersion diagrams each display a light line corresponding to $k_z = \sqrt{\epsilon_0 \omega/c}$. Additionally, material specific parameters such as the energy corresponding to the bulk plasma frequency of the metal, $\omega_p$, as well as the bandgap energy of...
the absorber, $E_g$, are labeled. From the dispersion diagrams, $Re\{k_x\}$ increases monotonically with $\omega$ up to a point termed the surface plasmon resonance frequency, $\omega_{\text{spp}}$. Beyond this point, bound surface plasmons can mathematically exist until $\omega_{\text{cutoff}}$, the frequency where one of the three necessary inequalities $Im\{k_{x,d}\} < 0$, $Im\{k_{z,m}\} < 0$ or $Im\{k_x\} > 0$ no longer holds. Thus, the parameters $\omega_{\text{spp}}$ and $\omega_{\text{cutoff}}$ depend on both materials comprising the interface. The appropriate energy range over which SPPs exist and can contribute to absorption is limited by the lower bound of $E_g$ and the upper bound of $E_{\text{cutoff}}$. SPPs with energy below $E_g$ are not absorbed; while above $E_{\text{cutoff}}$ SPPs do not exist as mathematically bound solutions. For optimal absorption, $E_g$ should lie below the energy of the least energetic photon and $E_{\text{cutoff}}$ should lie above the energy of the most energetic photon. For optimal efficiency, however, $E_g$ of the single bandgap device should lie closer to the energy of maximum solar irradiance, $1.1 \text{ eV-1.3 eV}$, and $E_{\text{cutoff}}$ should be maximized. We note that for the materials examined in this article, the cutoff energy typically coincides with the point where $Im\{k_{x,d}\} > 0$. Additionally, we note that in Fig. 2(a), the bandgap of SiO$_2$ of 9 eV lies outside the relevant frequency range for the solar spectrum and no cutoff frequency exists.

The previous sections demonstrated that minimizing the real permittivity of the dielectric increases the intensity of light in the absorber. Ultimately, however, the most important metric is the power that can be usefully absorbed in the dielectric. The ratio in Eq. (5) gives the power captured by the absorber divided by the power dissipated in the metallic support and, therefore, represents the objective function which must be maximized at each frequency to optimize absorption based on SPPs. Consider five independent variables: the frequency of incoming photons, the real and imaginary permittivity for the metal, and the real and imaginary permittivity for the dielectric absorber. Fixing the photon frequency and $\epsilon_m$, a contour plot of absorption as a function of the real and imaginary parts of $\epsilon_d$ is shown in Fig. 3. Various real materials are labeled by specific points in the plot. For Ag at a free space wavelength of 500 nm, corresponding to the peak solar irradiance from the sun, it is evident that maximizing absorption requires maximizing the imaginary part of the permittivity of the absorber. The black line designates the contour where $F_{\text{abs}} = 2$ specifying the threshold above which 67% of the incoming power is captured by the absorber. In Fig. 3(a), the optical parameters for $a$-Si lie to the upper right of the plotted range. From Fig. 3(a), favorable absorption can be obtained with both organic absorbers such as P3HT:PCBM and II-VI semiconductors like CdTe. Rutile TiO$_2$, on the other hand, does not absorb

* These inequalities arise from the restriction that the integral in Eq. (2) or its metallic counterpart must remain bounded. In general, several choices for the cutoff frequency exist including the surface plasmon frequency, $\omega_{\text{spp}}$, the intersection of $Re\{k_x\}$ and the light line, or the bulk plasma frequency, $\omega_p$. 

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**Fig. 3** Ratio of the power captured by the dielectric absorber divided by the power dissipated in the Ag support upon illumination by free space wavelengths of (a) 500 nm (2.5 eV) and (b) 830 nm (1.5 eV). The black line denotes the threshold where $F_{\text{abs}} = 2$ corresponding to power losses of 33% in the metal. The leftmost black stripe represents points where $Im\{k_{x,d}\} > 0$. 

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at 500 nm because this energy of 2.5 eV is below the limiting badgap cutoff of $E_g = 3.1$ eV.\textsuperscript{31} We note that Si does not have optimal real and imaginary permittivity for optical absorption enhancement using SPPs. The leftmost black stripe in the two plots shows regions where $\text{Im}\{k_z\} < 0$ is violated. At the longer wavelength of 830 nm, Fig. 3(b) again emphasizes the importance of maximizing $\text{Im}\{\varepsilon_z\}$ and minimizing $\text{Re}\{\varepsilon_z\}$ for increasing the power absorbed in the dielectric.

We next comment on the upper limits of power conversion efficiency from SPP enhanced absorption following the detailed balance method originally derived by Shockley and Queisser.\textsuperscript{32} The efficiency, $\eta_{\text{SQ}}$, is calculated by maximizing the power generated by incoming photons while taking radiative recombination into account, as shown by Eqs. (22)-(24) in Appendix B. Calculation of a modified efficiency, $\eta_{\text{SQ,SPP}}$, for the case of absorption through SPPs proceeds similarly. As always, there are losses associated with sub-bandgap excitations and the rapid thermalization of super-bandgap excitations. These result in a complete loss of the energy content of the solar spectrum below $E_g$, while harvesting only one $E_g$ worth of energy at all other frequencies. Additionally, there is some degree of absorption and subsequent loss in the metal layer, and surface plasmon polaritons are only supported over a finite range of energies, setting an upper bound on the absorbed energy. Including these losses reduces the maximum efficiency from the Shockley-Queisser limit. Table 1 gives values of the Shockley-Queisser efficiency, $\eta_{\text{SQ}}$, as well as the efficiency for purely plasmonic absorption with Ag as the chosen metal, $\eta_{\text{SQ,SPP}}$. Details for the calculation of $\eta_{\text{SQ,SPP}}$ are given in Appendix B. Efficiency is presented for a variety of semiconductor materials as well as for three hypothetical dielectric absorbers, D1, D2 and D3, whose complex permittivities are fixed with respect to frequency. Table 1 shows that absorbers such as CdTe and P3HT:PCBM, with small positive real permittivity and large positive imaginary permittivity, incur the least losses and display values of $\eta_{\text{SQ,SPP}}$ which are closest to the theoretical Shockley-Queisser limit. Comparing D3 to both D1 and D2 further supports this claim. The values for $\eta_{\text{SQ,SPP}}$ represent the upper efficiency limits for devices where absorption occurs purely through SPPs. Using a different energy cutoff, e.g. corresponding to $\omega_{\text{SPP}}$ rather than $\omega_{\text{cutoff}}$, will lead to lower values of $\eta_{\text{SQ,SPP}}$ since $\omega_{\text{cutoff}} > \omega_{\text{SPP}}$. Only for the case of a perfect electrical conductor is the calculated plasmonic efficiency exactly equal to the Shockley-Queisser limit, since the field is perfectly confined within the absorber. While the limiting efficiencies in Table 1 were derived for a 2D geometry where the incident light was linearly polarized (TM) to couple to SPPs, these presented efficiencies hold equally in 3D. For a 3D geometry, both TM and TE polarizations of incoming light can effectively couple to SPPs on the planar surface. The limiting efficiency derived for the 2D geometry with a single polarization will therefore be equivalent to that for the 3D geometry with a linear combination of two polarizations. Importantly then, the efficiency limits presented in Table 1 hold for both 2D and 3D geometries.

This article has demonstrated that minimizing positive real permittivity and maximizing positive imaginary permittivity of the dielectric are fundamental requirements for enhancing light absorption using surface plasmon polaritons. This guideline can be used to choose materials or to determine whether a particular material is a good candidate for plasmonic enhancement of optical absorption. Physically, these limitations suggest that plasmonic strategies hold promise for carbon-based nanomaterials including organic polymers, fullerenes, graphene and carbon nanotubes as well as for certain II-VI semiconductors like CdTe.\textsuperscript{33} For several oxides (TiO$_2$, Fe$_3$O$_4$) used in photoelectrochemical applications and for traditional absorber materials (c-Si, a-Si, GaAs), SPP enhancement does not appear promising for enhancing absorption over the broadband solar spectrum. While further improvements based on material combinations or patterning cannot be ruled out, these materials will likely be most useful in semiconductor sensing applications operating at a single, fixed frequency.\textsuperscript{34} Experiments support these conclusions. Considering photoelectrochemical applications\textsuperscript{35}, research on $\alpha$-Fe$_2$O$_3$ with Au plasmonic structures has resulted in either a decrease in absolute photocurrent\textsuperscript{36} or low measured enhancement which persists at photon energies below the bandgap where the semiconductor cannot absorb.\textsuperscript{37,38} These results support the theoretical difficulties identified in this article of improving absorption with SPPs in many real materials.

The previous analysis relied on several key assumptions: both the metal and the dielectric are semi-infinite, no power is absorbed as the incident light passes through the dielectric absorber on its way to the interface, and the incoming light perfectly couples to SPPs up to some cutoff energy, $E_{\text{cutoff}}$. Together these assumptions imply that $\eta_{\text{SQ,SPP}}$ is a true upper bound limit on the efficiency for a device where absorption occurs through surface plasmon polaritons, defined mathematically as bound electromagnetic waves. Our assumptions place certain limitations on the conclusions. Specifically, if other absorption pathways, such as absorption prior to coupling to SPPs, are considered, higher efficiencies could be achieved. Extension to more complex multilayer geometries with finite thickness of absorber, metal and even cladding materials is also possible, but the conclusions presented here for a single, semi-infinite interface will still provide valuable guidelines.

In conclusion, surface plasmon polaritons can be used to enhance absorption in materials with small positive real permittivity and large positive imaginary permittivity. The first requirement stems from considerations of maximizing the relative integrated intensity in the absorber, which for a semi-infinite interface requires maximizing the field intensity at the interface and the decay length of this field in the absorber.
Table 1 Table of the bandgap energy ($E_g$), cutoff energy for SPPs ($E_{cutoff}$), SPP energy corresponding to the local maximum in $Re\{k_x\}$ from the dispersion diagram ($E_{spp} = h\omega_{spp}/2\pi$), Shockley-Queisser efficiency ($\eta_{SQ}$) and the limiting efficiency calculated for cases where absorption proceeds entirely through SPPs ($\eta_{SQ,spp}$), for crystalline and amorphous Si, GaAs, CdTe, a P3HT:PCBM blend, $\alpha$-Fe$_2$O$_3$ and rutile TiO$_2$ as well as three fictitious materials with fixed, frequency-independent permittivities. References for the optical parameters of specific materials are listed. The parameters for Ag were taken from $^{39}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$ (eV)</th>
<th>$E_{cutoff}$ (eV)</th>
<th>$E_{spp}$ (eV)</th>
<th>$\eta_{SQ}$ (%)</th>
<th>$\eta_{SQ,spp}$ for Ag (%)</th>
<th>Ref / Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>1.12</td>
<td>2.88</td>
<td>2.03</td>
<td>31</td>
<td>7</td>
<td>$^{40}$</td>
</tr>
<tr>
<td>a-Si</td>
<td>1.12</td>
<td>2.38</td>
<td>1.83</td>
<td>31</td>
<td>12</td>
<td>$^{41}$</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>2.58</td>
<td>2.02</td>
<td>31</td>
<td>15</td>
<td>$^{40}$</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.45</td>
<td>2.89</td>
<td>2.26</td>
<td>30</td>
<td>22</td>
<td>$^{41}$</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>1.85</td>
<td>3.61</td>
<td>3.15</td>
<td>26</td>
<td>20</td>
<td>$^{42, 43}$</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>2.10</td>
<td>3.01</td>
<td>2.43</td>
<td>22</td>
<td>11</td>
<td>$^{44}$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.10</td>
<td>3.53</td>
<td>2.68</td>
<td>8</td>
<td>1</td>
<td>$^{45}$</td>
</tr>
<tr>
<td>D1</td>
<td>1.12</td>
<td>2.34</td>
<td>3.45</td>
<td>31</td>
<td>21</td>
<td>$Re{\varepsilon_2} = 10, Im{\varepsilon_2} = 1$</td>
</tr>
<tr>
<td>D2</td>
<td>1.12</td>
<td>2.16</td>
<td>2.98</td>
<td>31</td>
<td>25</td>
<td>$Re{\varepsilon_2} = 10, Im{\varepsilon_2} = 4$</td>
</tr>
<tr>
<td>D3</td>
<td>1.12</td>
<td>2.54</td>
<td>3.00</td>
<td>31</td>
<td>28</td>
<td>$Re{\varepsilon_2} = 2.5, Im{\varepsilon_2} = 4$</td>
</tr>
</tbody>
</table>

Small real permittivity also ensures a large frequency range over which SPPs can be supported and, in practical devices, will reduce reflections at the interface between the external medium such as air owing to the smaller index of refraction. The second requirement for large imaginary permittivity or large extinction coefficient is necessary for absorption. An extensive parameter space covering a broad range of permittivities for the absorber has been investigated with Ag as the choice of metal owing to low SPP losses. Several material systems including oxides (TiO$_2$, Fe$_2$O$_3$) and traditional semiconductors (c-Si, a-Si, GaAs) have real permittivities too large and imaginary permittivities too low to be usefully considered for enhancing absorption through SPPs. In contrast, select II-VI semiconductors including CdTe as well as organic materials such as polymers, fullerenes, graphene and carbon nanotubes hold promise. Our calculations support this assertion and show that an upper limit for the absolute photovoltaic efficiency of approximately 20 % can be achieved in CdTe or a P3HT:PCBM blend when absorption proceeds entirely through surface plasmon polaritons.
A Appendix A

For linear, isotropic media without external charge and current densities, Maxwell’s equations can be written as:

\[ \nabla \cdot \mathbf{E} = 0 \]  \hspace{1cm} (7a)

\[ \nabla \cdot \mathbf{H} = 0 \]  \hspace{1cm} (7b)

\[ \nabla \times \mathbf{E} = -\mu_0 \mu \frac{\partial \mathbf{H}}{\partial t} \]  \hspace{1cm} (7c)

\[ \nabla \times \mathbf{H} = \varepsilon_0 \varepsilon \frac{\partial \mathbf{E}}{\partial t}, \]  \hspace{1cm} (7d)

where \( \mu \) and \( \varepsilon \) are, respectively, the relative permeability and permittivity of a material, \( \mathbf{H} \) is the magnetic field, \( \mathbf{E} \) is the electric field, \( t \) denotes time and the subscript \( 0 \) signifies vacuum. The boundary conditions for continuity of the normal and tangential components are:

\[ \mathbf{n} \cdot (\varepsilon \mathbf{E}_d - \varepsilon_0 \mathbf{E}_m) = 0 \]  \hspace{1cm} (8a)

\[ \mathbf{n} \cdot (\mu_0 \mu \mathbf{H}_d - \mu_0 \mu_0 \mathbf{H}_m) = 0 \]  \hspace{1cm} (8b)

\[ \mathbf{n} \times (\mathbf{E}_d - \mathbf{E}_m) = 0 \]  \hspace{1cm} (8c)

\[ \mathbf{n} \times (\mathbf{H}_d - \mathbf{H}_m) = 0, \]  \hspace{1cm} (8d)

where the subscripted \( d \) and \( m \) refer to the dielectric and metal, respectively.

Assuming harmonic time dependence \( (\partial / \partial t = -i \omega) \), homogeneity in the \( y \)-direction \( (\partial / \partial y = 0) \) considering the geometry in the inset of Fig. 1 and propagation along \( x \) for SPPs \( (\partial / \partial x = ik) \), Eqs. (7c) and (7d) yield:

\[ -\frac{\partial E_y}{\partial z} = i \omega \mu_0 \mu H_x \]  \hspace{1cm} (9a)

\[ \frac{\partial E_x}{\partial z} - ik_x E_x = i \omega \mu_0 \mu H_y \]  \hspace{1cm} (9b)

\[ ik_x E_y = i \omega \mu_0 \mu H_z \]  \hspace{1cm} (9c)

\[ \frac{\partial H_x}{\partial z} = i \omega \varepsilon_0 \varepsilon E_x \]  \hspace{1cm} (10a)

\[ ik_x H_y - \frac{\partial H_y}{\partial z} = i \omega \varepsilon_0 \varepsilon E_y \]  \hspace{1cm} (10b)

\[-ik_x H_z = i \omega \varepsilon_0 \varepsilon E_z \]  \hspace{1cm} (10c)

Considering TM polarization with non-zero \( E_y \), \( E_z \) and \( H_y \) only and using \( \mu = 1 \) for non-magnetic materials, rearranging Eqs. (10a), (10c), and substituting these results into Eq. (9b) gives:

\[ E_x = -i \frac{1}{\varepsilon \varepsilon_0} \frac{\partial H_y}{\partial z} \]  \hspace{1cm} (11a)

\[ E_z = -\frac{k_x}{\omega \varepsilon_0} H_y \]  \hspace{1cm} (11b)

\[ 0 = \frac{\partial^2 H_y}{\partial z^2} + \left( \frac{\omega}{c} \right)^2 \varepsilon - k_x^2 H_y \]  \hspace{1cm} (11c)

where Eq. (11c) is recognized as the wave equation and \( 1/c^2 = \varepsilon_0 \mu_0 \) was used. Next, postulate that the solution for the magnetic field for this set of equations takes the form \( H_{y,j} = A_j \exp(i(k_{x,j} x + k_{z,j} z - \omega t)) \) where the plus and minus sign correspond to the metal and dielectric half-spaces \( j = \{ m, d \} \), respectively. Returning to the boundary conditions and considering the normal vector in the \( z \)-direction according to the geometry in the inset of Fig. 1, Eq. (8), for TM polarization, gives:

\[ \varepsilon_m E_{z,m} = \varepsilon_d E_{z,d} \]  \hspace{1cm} (12a)

\[ E_{x,m} = E_{x,d} \]  \hspace{1cm} (12b)

\[ H_{y,m} = H_{y,d}. \]  \hspace{1cm} (12c)

Thus, continuity of \( H_{y,j} \) requires that \( A_m = A_d \). Substitution into the wave equation (11c) yields, \( k_{z,m}^2 = (\omega/c)^2 \varepsilon_m - k_x^2 \) and \( k_{z,d}^2 = (\omega/c)^2 \varepsilon_d - k_x^2 \). From continuity of \( E_{x,j} \) and using Eq. (11a) then, \( k_{x,d}/k_{x,m} = -\varepsilon_d/\varepsilon_m \), so that the dispersion relation as an explicit function of \( \omega \) is obtained:

\[ k_x^2 = \left( \frac{\omega}{c} \right)^2 \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}. \]  \hspace{1cm} (13)

It follows that,

\[ k_{z,m}^2 = \left( \frac{\omega}{c} \right)^2 \frac{\varepsilon_m^2}{\varepsilon_m + \varepsilon_d}. \]  \hspace{1cm} (14a)

\[ k_{z,d}^2 = \left( \frac{\omega}{c} \right)^2 \frac{\varepsilon_d^2}{\varepsilon_m + \varepsilon_d}. \]  \hspace{1cm} (14b)

where the positive or negative root is chosen to ensure \( Im\{k_{z,j}\} < 0 \). Here, it is important to note that because the dielectric is an absorber, \( \varepsilon_d \) has an imaginary component which cannot be ignored in calculations. Using Eqs. (11a) and (11b), the final analytical solution for the electric field characterizing the SPP as a function of time and space is given by the real component of the complex field:

\[ E_m = [E_0, 0, E_0(-k_x/k_{z,m})] e^{i(k_x x + k_{z,m} z - \omega t)} \]  \hspace{1cm} (15a)

\[ E_d = [E_0, 0, E_0(k_x/k_{z,d})] e^{i(k_x x - k_{z,d} z - \omega t)}, \]  \hspace{1cm} (15b)

with \( k_x \) and \( k_{z,m} \) given explicitly by Eqs. (13) and (14), respectively. Substitution of \( (k_x/k_{z,m}) = (\varepsilon_d/\varepsilon_m)^{1/2} \) and \( (k_x/k_{z,d}) = (\varepsilon_m/\varepsilon_d)^{1/2} \) and omitting time-dependence gives Eq. (1) in the main text.

The previous calculations for the power absorbed in the dielectric, Eq. (4), can be verified by considering the Poynting vector and power flow. Using Eq. (15b), the magnetic field in the dielectric absorber is obtained from Eq. (11b) and is given by the real component of \( \mathbf{H}_d = [0, -E_0 \omega \varepsilon_0 \varepsilon_d / k_{z,d}, 0] \exp(i(k_x x - k_{z,d} z - \omega t)) \). The time-
averaged Poynting vector, $\langle S \rangle = Re\{E_d \times H_d\}/2$, is then:

$$\langle S \rangle = \begin{bmatrix}
Re\{\varepsilon_d\}Re\{k_x\} - Im\{\varepsilon_d\}Im\{k_x\} \\
0 \\
-Re\{\varepsilon_d\}Re\{k_{z,d}\} + Im\{\varepsilon_d\}Im\{k_{z,d}\}
\end{bmatrix} \frac{|E_0|^2 \omega \varepsilon_0}{2|k_{z,d}|^2} e^{2(-Im\{k_x\}x + Im\{k_{z,d}\}z)}.$$

Eq. (21).

The total power flowing through the surface surrounding the control volume, defined previously as the first quadrant of the Cartesian plane, is then,

$$P_{\text{flow},d} = -\int_{x=0}^{\infty} \langle S \rangle \cdot (\hat{x}) \, dz - \int_{z=0}^{\infty} \langle S \rangle \cdot (\hat{z}) \, dx - 0 - 0,$$  

where $\hat{x}$ and $\hat{z}$ are unit normal vectors. Note that zero power flows into the control volume at the limits where $x = \infty$ or $z = \infty$, as indicated by the final two zeros in Eq. (17). Separating terms based on the real and imaginary components of the permittivity gives,

$$P_{\text{flow},d} = -\frac{|E_0|^2 \omega \varepsilon_0}{8|k_{z,d}|^2} \left[ 2Re\{\varepsilon_d\}(Re\{k_x\}Im\{k_x\} + Re\{k_{z,d}\}Im\{k_{z,d}\}) + 2Im\{\varepsilon_d\}(Im\{k_x\}^2 + Im\{k_{z,d}\}^2) \right].$$

Noting that $\varepsilon_d(\omega/c)^2 = k_x^2 + k_{z,d}^2$, it can be shown that,

$$Re\{\varepsilon_d\} = \left( \frac{c}{\omega} \right)^2 \left[ Re\{k_x\}^2 + Re\{k_{z,d}\}^2 - Im\{k_x\}^2 - Im\{k_{z,d}\}^2 \right],$$  

(19a)

$$Im\{\varepsilon_d\} = 2 \left( \frac{c}{\omega} \right)^2 \left[ Re\{k_x\}Im\{k_x\} + Re\{k_{z,d}\}Im\{k_{z,d}\} \right].$$  

(19b)

Dividing Eq. (19a) by Eq. (19b) and rearranging to give an explicit function of $Re\{\varepsilon_d\}$, which is then substituted into Eq. (18), gives,

$$P_{\text{flow},d} = -\omega \varepsilon_0 |E_0|^2 \left( |k_x|^2 + |k_{z,d}|^2 \right) Im\{\varepsilon_d\} \frac{Re\{k_x\}Im\{k_x\}Im\{k_{z,d}\}}{8Im\{k_x\}Im\{k_{z,d}\}|k_{z,d}|^2}.$$

(20)

Further simplifying using $|k_x|^2/|k_{z,d}|^2 = |\varepsilon_m|/|\varepsilon_d|$, one obtains:

$$P_{\text{flow},d} = -\omega \varepsilon_0 Im\{\varepsilon_d\}|E_0|^2 \frac{|\varepsilon_m|}{8Im\{k_x\}Im\{k_{z,d}\}} \left( 1 + \frac{|\varepsilon_m|}{|\varepsilon_d|} \right),$$  

(21)

which confirms that the power absorbed in the dielectric calculated previously using Ohmic power dissipation in the dielectric, $P_{abs,d}$ in Eq. (4), is equivalent to the energy balance considering power flow entering and leaving through the surface, Eq. (21).

### B Appendix B

For photovoltaic energy conversion, the current density of the material specific information is required in addition to the cell is given by:

$$I(V) = \frac{q}{e^2} \frac{2\pi}{h^3} \left[ f \int_{E_{\text{g}}}^{E_{\text{cutoff}}} \left( \frac{F_{\text{abs}}(E)}{F_{\text{abs}}(E) + 1} \right) \frac{E^2 dE}{e^{E/kT_s} - 1} - \int_{E_{\text{cutoff}}}^{\infty} \frac{E^2 dE}{e^{E/kT_s} - 1} \right],$$  

(22)

where $q$ is the elementary charge, $e$ the speed of light in vacuo, $h$ Planck’s constant, $k$ is Boltzmann’s constant, $V$ is the applied potential, $f = R_{\text{sun}}^2/\sigma_{\text{sun}}^2$, where $R_{\text{sun}}$ is the radius of the sun and $\sigma_{\text{sun}}$ is the distance between the earth and sun, $T_s = 5780$ K is the temperature of the sun, and $T_e = 300$ K is the ambient temperature of earth. In equation (22), the first term accounts for radiation the cell receives form the sun over a small solid angle. The second term accounts for the cell, biased at potential $V$, radiating as a blackbody at $T_e$ over the hemisphere. Consistent with the original derivation, the blackbody radiation the cell receives at $T_e$ from its surroundings is negligible relative to the incoming radiation from the sun and has been ignored. The total power density incident on the cell from the sun is given by the Stefan-Boltzmann equation:

$$P_{\text{sun}} = \frac{2\pi^5 k^4}{15\varepsilon^2 h^3} T_s^4 f.$$  

(23)

Thus, the efficiency limit of Shockley and Queisser, defined as the power delivered to a matched load divided by the total incoming power, is given by:

$$\eta_{\text{Sh}} = \max \left[ \frac{I(V) V}{P_{\text{sun}}} \right].$$  

(24)

For plasmonics, only a fraction of the incoming power or, equivalently, only a fraction of the incoming solar photons at each frequency is absorbed by the dielectric and not lost to the metal. Additionally, SPPs can only be supported from the bandgap energy $E_g$ to some energy $E_{\text{cutoff}}$, corresponding to a cutoff frequency $\omega_{\text{cutoff}}$. When absorption proceeds strictly through SPPs, the current density is modified:

$$I_{\text{pp}}(V) = \frac{2\pi}{e^2 h^3} \left[ f \int_{E_{\text{g}}}^{E_{\text{cutoff}}} \left( \frac{F_{\text{abs}}(E)}{F_{\text{abs}}(E) + 1} \right) \frac{E^2 dE}{e^{E/kT_s} - 1} - \int_{E_{\text{cutoff}}}^{\infty} \frac{E^2 dE}{e^{E/kT_s} - 1} \right].$$  

(25)

Thus, the limiting efficiency when absorption proceeds entirely through SPPs is given by:

$$\eta_{\text{Sh},\text{PP}} = \max \left[ \frac{I_{\text{pp}}(V) V}{P_{\text{sun}}} \right].$$  

(26)

For example, for $E_g = 1.12$ eV corresponding to the bandgap of crystalline Si, $\eta_{\text{Sh}} = 30.6 \%$. To calculate the efficiency when absorption proceeds entirely through SPPs, further material specific information is required in addition to the bandgap energy. Calculation of $F_{\text{abs}}$ and $E_{\text{cutoff}}$ require the...
permittivity of both the metal and absorber to be known. The revised efficiency, which accounts for absorption losses in the metal as well as the frequency cutoff constraint for SPPs, is then given by \( \eta_{\text{SQ}} = \max \left[ \frac{J_{\text{spp}}(V)}{P_{\text{sun}}} \right] \). For example, for crystalline Si with \( E_{g} = 1.12 \) eV and \( E_{\text{cutoff}} = 2.88 \) eV, \( \eta_{\text{SQ}} = 6.9 \% \) as shown in Table 1.

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\[ \text{References} \]