Plasmonic hot carrier dynamics in directional conductors

Sushant Kumar,1 Christian Multunas,2 and Ravishankar Sundararaman1,2

1Department of Materials Science & Engineering, 110 8th St, Troy, NY 12180, USA
2 Department of Physics, Applied Physics, and Astronomy, 110 8th St, Troy, NY 12180, USA.

(Dated: May 11, 2022)

Realizing the potential of plasmonic hot carrier harvesting for energy conversion and photodetection requires new materials that resolve the bottleneck of extracting carriers prior to energy relaxation within the metal. Using first-principles calculations of optical response and carrier transport properties, we show that directional conductors with Fermi velocities restricted predominantly to one or two directions present significant advantages for efficient hot carrier harvesting. We show that the optical response of film-like conductors, PtCoO$_2$ and Cr$_2$AlC, resemble that of 2D metals, while that of wire-like conductors, CoSn and YCo$_3$B$_2$, resemble that of 1D metals, which can lead to high mode confinement and efficient light collection in small dimensions, while still working with 3D materials with high carrier densities. Carrier lifetimes and transport distances in these materials, especially in PtCoO$_2$ and CoSn, are competitive with noble metals. Most importantly, we predict that carrier injection efficiency from all of these materials into semiconductors can exceed 10% due to the small component of carrier velocity parallel to the metal surface, substantially improving upon the typical < 0.1% injection efficiency from noble metals into semiconductors.

I. INTRODUCTION

High-energy electrons and holes excited in metal nanostructures upon the decay of plasmons provide a pathway to leverage light collected efficiently at the nano scale for photochemistry, imaging, and photovoltaic energy conversion. A continuing challenge in plasmonic hot carrier applications is utilizing the excited carriers prior to energy relaxation in the metal, requiring nanostructures smaller than the mean free paths of carriers and material interfaces that are capable of extracting a large fraction of carriers from the metal.

The field of plasmonic hot carriers has made great strides in expanding the space of materials from noble metals to include refractory plasmonic materials such as transition metal nitrides, and low-dimensional materials such as MXenes. These materials remain stable at smaller dimensions than noble metals, making it possible to minimize energy losses during the transport of carriers across the nanostructure. Additionally, low-dimensional plasmonic materials can exhibit higher mode confinement than 3D metals, allowing efficient light capture at smaller length scales. However, the overall efficiency of extracting hot carriers from plasmonic metals into semiconductors for photovoltaic and photodetection applications remains low, primarily due to the mismatch between carrier velocities near the Fermi energy in metals and the band edges in semiconductors, requiring further advances in materials for plasmonic hot carriers.

Here, we propose that directional conductors – 3D materials that behave like lower-dimensional metals due to Fermi velocities restricted to one or two dimensions – have the potential to simultaneously absorb light efficiently at nanoscale dimensions and inject carriers with high probability into semiconductors. Using first-principles calculations of electronic structure, optical response, electron-phonon and electron-electron scattering, we show that the best directional conductors, including PtCoO$_2$ and CoSn, are competitive with noble metals in their frequency range of plasmonic response and carrier transport distances. We show that their optical response resembles lower-dimensional metals, which may allow the design of plasmonic nanostructures with more efficient light collection at small dimensions than their 3D counterparts. Finally, we show that the lower magnitude of Fermi velocities and the strong directional distribution can be leveraged to greatly enhance the probability of carrier injection into the semiconductor: from below 0.1% typical for noble metals to over 10% for the directional conductors as predicted by a modified Fowler model.

II. RESULTS AND DISCUSSION

A. Directional conductors

We recently identified several directional conductors that exhibit promise for conduction in nanoscale geometries using a high-throughput screening based on electronic structure calculations. These materials fall into two broad classes, film-like and wire-like conductors, which exhibit excellent transport in two perpendicular directions and along a single axis respectively. To investigate the potential of directionality to additionally enhance harvesting of hot carriers far from equilibrium, we select two representative materials from each class. In particular, for the film-like conductors, we select the del-saffosite oxide PtCoO$_2$ with the lowest resistivity and the well-studied MAX phase Cr$_2$AlC, while for the wire-like conductors, we select the two most conductive materials, CoSn and YCo$_3$B$_2$.

Figure 1 shows the unit cell structure and Fermi surfaces for all four materials. PtCoO$_2$ exhibits an almost perfect hexagonal-prism-shaped Fermi surface, which leads to all the Fermi velocities directed in the hexagonal
plane of the material. This leads to an in-plane resistivity, along the preferred transport direction \( \hat{j} \), that is \( \sim 3,000 \times \) smaller than the out-of-plane resistivity along the preferred surface normal direction \( \hat{n} \) (Table I). Such large anisotropies have been reported for transport properties of two-dimensional materials like graphene, attributed to the weak van der Waals coupling between layers. However, all directional materials we investigate here are 3D crystals with strong bonding in all directions (Fig. 1). Cr\(_2\)AlC also has similar Fermi surface orientations and preferred transport directions, but a much weaker anisotropy in the resistivity.

The remaining two materials, CoSn and YCo\(_3\)B\(_2\), have Fermi surface sheets parallel to the hexagonal plane (Fig. 1(c-d)), leading to Fermi velocities and conduction predominantly along the \( c \) axis (Table I). These materials therefore have a single preferred transport direction, with two preferred surface normal directions, making them suitable for conduction in nanoscale wires. To discuss these film-like and wire-like materials on a similar footing, we will henceforth refer to properties along preferred transport direction \( \hat{j} \) and along the preferred normal direction \( \hat{n} \), but note that the crystallographic orientation of these directions is different for the two classes of materials as specified in Table I. Finally, note that the \( \hat{j} \) resistivity for all these conductors, except for the Cr\(_2\)AlC max phase, is comparable to that for the most common plasmonic metals: 1.6, 1.7, 2.3 and 2.8 \( \mu \Omega \cdot \text{cm} \) for silver, copper, gold and aluminium, while the \( \hat{n} \) resistivity is much larger.

### B. Optical response

To investigate the suitability of these materials for plasmonic applications, we first consider their Drude response. Figure 2 shows the calculated transport Eishalberg spectral functions (Section IV B) and corresponding frequency-dependent Drude momentum relaxation times due to electron-phonon scattering. The electron-phonon coupling at the Fermi level is weakest for PtCoO\(_2\), as indicated by the lowest spectral function magnitude in Fig. 2(a), followed by CoSn, YCo\(_3\)B\(_2\) and finally Cr\(_2\)AlC. Correspondingly, the Drude relaxation time \( \tau_D \) at low frequencies drops from \( \sim 110 \) fs for PtCoO\(_2\) to \( \sim 15 \) fs for Cr\(_2\)AlC, in the same order.

With increasing frequency, Drude relaxation can access higher energy phonon modes that were inaccessible using thermal energy at room temperature alone, causing \( \tau_D \) to decrease. For PtCoO\(_2\), \( \tau_D \) decreases from 110 fs at low frequency to 36 fs at optical frequencies, remaining larger than the low-frequency relaxation time for most elemental metals! The largest proportional drop in \( \tau_D \) is from 15 fs to 3 fs for Cr\(_2\)AlC, which has the highest-energy phonon spectrum, while the smallest drop in \( \tau_D \) is from 29 fs to 13 fs for CoSn with the lowest-energy phonon spectrum.
The decrease in $\tau_D$ with frequency accounts for phonon-assisted transitions along with the Drude term,\cite{footnote} which we then combine with predictions of direct transitions (Section IV B) to compute the overall complex dielectric functions shown in Fig. 3. Note that the dielectric functions are highly anisotropic, with qualitative differences between the $\hat{j}$ and $\hat{n}$ directions for these directional conductors. In particular, the plasmonic window – the region with $\text{Re} \, \epsilon < 0$ is much larger along the $\hat{j}$ direction than the $\hat{n}$ direction. The plasmonic window of PtCoO$_2$, CoSn, and YCo$_3$B$_2$ each extend above 2.5 eV along $\hat{j}$, surpassing the plasmonic range of gold (2.6 eV) and approaching that of silver (3.4 eV).\cite{footnote} In contrast, the plasmonic window along $\hat{n}$ is below 0.5 eV for all four materials, with that of PtCoO$_2$ (the most anisotropic of the four) being virtually negligible.

Additionally, $\text{Im} \, \epsilon$ along the preferred transport directions are relatively low when $\text{Re} \, \epsilon$ crosses zero, indicating plasmonic response with quality factors comparable to noble metals, most notably for CoSn. In the plasmonic frequency range for $\hat{j}$, most of these materials exhibit dielectric-like behavior, $\text{Re} \, \epsilon \gg \text{Im} \, \epsilon > 0$, along the $\hat{n}$ direction. Consequently, these materials essentially behave like lower-dimensional materials optically – the film-like conductors like 2D materials and the wire-like conductors like 1D materials, but we emphasize again that these materials are 3D crystals bonded strongly in all directions. This opens up the possibility to reap the advantages of low-D plasmonics, such as high confinement,\cite{footnote} while working with easier-to-process 3D materials. See the SI for tables of predicted dielectric functions to facilitate design of plasmonic structures using these materials; we focus here instead on material properties including hot carrier distributions and transport next.

**C. Hot carrier generation**

Plasmon decay is captured by the imaginary part of the dielectric functions, $\text{Im} \, \epsilon(\omega)$, and the energy $\hbar \omega$ lost by the plasmon is deposited in an electron-hole pair. Figure 4 shows the energy distribution of hot carriers excited upon plasmon decay, calculated by resolving contributions to $\text{Im} \, \epsilon(\omega)$ by carrier energy $\epsilon$ (Section IV B).\cite{footnote} Unlike a clear separation between phonon-assisted transitions below an interband threshold and direct transition above it in typical plasmonic metals,\cite{footnote} these complex conductors exhibit direct transitions at almost all plasmon frequencies. Only PtCoO$_2$ and CoSn show a small frequency range ($\hbar \omega < 0.5$ eV) where indirect phonon-assisted transitions contribute significantly. Interestingly, the relative importance of phonon-assisted transitions in PtCoO$_2$ is enhanced along the $\hat{n}$ direction, indicating a selection rule that the lowest energy direct transitions are allowed only for in-plane electric fields in...
Figure 4. Hot carrier distribution, $P(\omega, \varepsilon)$, as a function of carrier energy $\varepsilon$ and plasmon frequency $\omega$ for directional conductors, with plasmon electric field polarized along their corresponding $\hat{j}$ directions (left panels) and $\hat{n}$ directions (right panels). The probability is normalized such that $P(\omega, \varepsilon) = 1$ for a uniform electron and hole energy distribution. Note that direct transitions dominate at almost all plasmon frequencies, except for $\hbar \omega \ll 1$ eV in PtCoO$_2$ and CoSn, leading to carrier distributions sensitive to electronic structure details.

Figure 5. Fraction of interband absorption (left column) and fraction of energy in hot electrons (right column) for the directional conductors for light polarized along (a) the preferred transport direction $\hat{j}$ and (b) the corresponding normal direction $\hat{n}$. Interband absorption is stronger along the $\hat{j}$ direction, but is dominated by direct absorption for photons with energy larger than 1 eV in all cases. Energy is evenly distributed between electrons and holes, except for low-energy intraband-dominated absorption of $\hat{n}$-polarized light in PtCoO$_2$.

D. Carrier transport

Efficient hot carrier harvesting requires extraction of the carriers from the metal prior to thermalization by electron-phonon and electron-electron scattering. Figures 6 and 7 respectively show the predicted lifetime and mean free path of hot carriers in the directional conductors, accounting for both these scattering mechanisms (Section IV C). Electron-phonon scattering dominates near the Fermi energy, while the phase-space for electron-electron scattering increases with increasing electron or hole energies and eventually dominates over electron-phonon scattering, exactly analogous to the case for other plasmonic metals including elemental metals and transition metal nitrides. The mean free paths drop off with energy more quickly than the life times in most of the materials, especially for the holes, indicating a reduc-
Figure 6. Lifetime of hot carriers as a function of carrier energy in directional conductors, with color indicating relative contributions of electron-phonon and electron-electron scattering. Carrier lifetimes are comparable in magnitude to noble metals, especially in PtCoO$_2$ and CoSn, but drop off with energy faster than for noble metals.$^{22}$

The peak carrier lifetimes and mean free paths in these materials are competitive with noble metals, especially in PtCoO$_2$ and CoSn. However, the drop-off with energy is faster in these materials compared to noble metals, with mean-free paths dropping below 10 nm for carriers with 1 eV energies for all four materials. This is partly because the directionality of electronic structure is a feature restricted to a narrow energy window surrounding the Fermi energy, with a marked increase in density of states away from the Fermi energy (Figure S1 in SI), leading to a corresponding increase in phase space for scattering for higher energy carriers. This indicates the need to carefully design plasmonic geometries to minimize the average distance between the location of carrier generation and the interfaces where carriers can be collected to below 10 nm.

**E. Carrier injection across interfaces**

The final step in hot carrier harvesting is transferring the carriers across an interface, such as a metal-semiconductor interface, prior to energy relaxation in the metal. This step is typically the largest limiting factor in hot carrier collection efficiency because most carriers in the metal encounter total internal reflection at the interface with the semiconductor, as captured by the semiclassical Fowler model of carrier injection.$^{6,15}$ In particular, the injection from noble metals into semiconductors at energies just above the Schottky barriers is typically $\sim 0.1\%$ or smaller due to the large mismatch between the Fermi velocity in the metal and velocities near the band edges of the semiconductor.$^{16}$ Injection from lower-velocity bands of the metal, such as $d$-bands in copper, can slightly increase these probabilities, but they remain at that small order of magnitude.$^{17}$

The directional conductors investigated here have the potential to remedy this issue in two ways. First, the Fermi velocity in these materials is lower than in noble metals, exhibiting a slightly better match to velocities near semiconductor band edges. Second, the directionality of the velocity makes it possible to substantially reduce the component parallel to the surface (that needs to match across the interface) by collecting in an interface whose normal is along $\hat{j}$.

Figure 8(a) shows that the component of carrier velocity direction $\hat{v}$ along $\hat{j}$ is close to 1 for wire-like conductors CoSn and YCo$_3$B$_2$, indicating that the remaining components must be much smaller. This projection is smaller for the film-like conductors, which have large velocity components along two orthogonal directions, and approaches the isotropic limit of 1/2 for a noble metal like gold. Figures 8(b-c) show that this directionality of the...

Figure 7. Mean-free path of hot carriers as a function of carrier energy in directional conductors, with behavior closely following those of the lifetimes shown in Fig. 6.
velocity indeed leads to a significantly larger injection probability than for the case of gold, as predicted using a modified Fowler model (Section IV D). Compared to $P_{\text{inj}} \sim 10^{-3}$ in gold, all directional conductors have the potential to inject with $> 10\%$ probability into a model semiconductor (assuming a typical electron and hole mass of 0.3 for simplicity), presenting significant opportunities for efficient plasmonic hot carrier harvesting.

III. CONCLUSIONS

Using first-principles calculations of optical response, carrier generation, transport and injection, we show the significant promise of directional conductors for plasmonic hot carrier applications. The strong anisotropy of Fermi velocity in these materials to one or two directions introduces 1D wire-like or 2D film-like behavior in a 3D-crystalline material. These materials exhibit plasmonic response over a range of frequencies comparable to noble metals along the preferred transport direction(s) $\hat{\mathbf{j}}$, while simultaneously exhibiting dielectric behavior in the preferred normal direction(s) $\hat{\mathbf{n}}$ at those frequencies, mimicking the optical response of a lower-dimensional metal. Hot carrier generation and transport are also similar to noble metals, but directionality in the velocity shows promise for orders of magnitude higher efficiency in extraction of hot carriers from these materials into semiconductors. The dielectric functions, carrier transport and injection models reported here can now be used to design plasmonic nanostructures with the potential for high-efficiency hot carrier harvesting.

IV. METHODS

A. Computational details

We perform electronic structure calculations using the open-source JDFTx software for density-functional theory in the plane wave basis.\textsuperscript{24} We use the Perdew-Burke-Ernzerhof generalized gradient approximation to the exchange correlation functional,\textsuperscript{25} with ultrasoft pseudopotentials at kinetic energy cutoffs of 20 Hartrees for the wavefunctions and 100 Hartrees for the charge density.\textsuperscript{26} We optimize lattice parameters and internal geometries self-consistently for each material, and calculate phonons and electron-phonon coupling from first principles. Table II lists the converged lattice parameters and meshes for Brillouin zone sampling.

We construct maximally localized Wannier functions for each material to accurately reproduce the electronic band structure up to at least 5 eV above the Fermi level.\textsuperscript{27} Using these, we interpolate electronic energies $\varepsilon_{kn}$ at wave vector $\mathbf{k}$ and band $n$, their band velocities $v_{kn}$ and velocity matrix elements $v_{kn'\alpha}$, phonon frequencies $\omega_{q\alpha}$ at wavevector $\mathbf{q}$ and polarization $\alpha$, and the electron-phonon matrix elements $g_{k'\alpha,k\beta}$ to significantly finer $\mathbf{k}$ and $\mathbf{q}$ meshes for integrals over the Brillouin Zone (BZ) in the calculation of optical and carrier transport properties described next.\textsuperscript{22}

B. Dielectric functions

We calculate the complex dielectric tensor,

$$\varepsilon(\omega) = 1 + \frac{4\pi i (\overline{\sigma_0}/\tau_D)}{\omega(\tau_D^{-1}(\omega) - i\omega)} + \varepsilon_d(\omega),$$

where $\varepsilon_d(\omega)$ is the dielectric function due to dipole transitions.
where the second term captures the Drude response including the effect of phonon-assisted intraband transitions, while the final term captures the effect of direct optical transitions. We evaluate the final term directly using Fermi’s golden rule for the real part,\textsuperscript{28}
\[
\Im \bar{\epsilon}_d(\omega) = \frac{4\pi^2 e^2}{\omega^2} \int_{BZ} \frac{g_s \, dk}{(2\pi)^3} \sum_{n'n} (f_{kn} - f_{kn'}) \times \delta(\varepsilon_{kn'} - \varepsilon_{kn} - \hbar\omega) (\mathbf{v}_{kn'n} \otimes \mathbf{v}_{kn'n'}), \tag{2}
\]
where \(g_s = 2\) is the spin degeneracy factor and \(f_{kn}\) are the Fermi occupations of each electronic state. We then evaluate \Re \bar{\epsilon}_d(\omega) from it using the Kramers-Kronig relation.

The energy-conserving \(\delta \varepsilon^2\) scattering linewidths, which we also calculate from first principles, are given by
\[
\tau^{-1}_\text{D}(\omega) = \frac{2\pi}{\hbar g(\varepsilon_F) b_T(\hbar\omega)} \sum_{\alpha} \int_{BZ} \frac{dq}{(2\pi)^d} \times G_{q\alpha}^{p} b_T(\hbar\omega - \hbar\omega_{q\alpha}), \tag{3}
\]
derived from the Eliashberg spectral function,\textsuperscript{29} and generalized to finite temperature.\textsuperscript{14} Here, \(g(\varepsilon_F)\) is the density of electronic states at the Fermi level, \(b_T(\varepsilon) \equiv \varepsilon/(1 - e^{-\varepsilon/k_BT})\) and
\[
G_{q\alpha}^{p} = \sum_{n'n} \int_{BZ} \frac{g_s \Omega \, dk}{(2\pi)^3} \left| g_{(k+q)n'n, kn}^{p} \right|^2 \delta(\varepsilon_{kn} - \varepsilon_{kn'}) 
\times \delta(\varepsilon_{(k+q)n'} - \varepsilon_F) \left( 1 - \frac{\mathbf{v}_{kn} \cdot \mathbf{v}_{(k+q)n'}}{|\mathbf{v}_{kn}| |\mathbf{v}_{(k+q)n'}|} \right), \tag{4}
\]
is the weight of each phonon mode in the ‘transport Eliashberg spectral function’. Above, \(\Omega\) is the unit cell volume. (The final factor dependent on velocities above accounts for scattering angle compared to the conventional Eliashberg spectral function.)\textsuperscript{29} Finally, the numerator in the first term of (1) is
\[
\bar{\sigma}_0/\tau D_0 = \int_{BZ} \frac{e^2 g_s \, dk}{(2\pi)^3} \sum_n \delta(\varepsilon_{kn} - \varepsilon_F) (\mathbf{v}_{kn} \otimes \mathbf{v}_{kn}), \tag{5}
\]
which is essentially the generalization of \(e^2 g(\varepsilon_F) \nu_T^2/3\) from a spherical Fermi surface to the general anisotropic case.

We apply Monte Carlo sampling with a typical density of \(\sim 10^7\) \(k\)-values to fully converge the Brillouin zone integrals above, leveraging the Wannier interpolation of matrix elements. Histogramming the integrands in the above expressions with respect to \(\varepsilon_{kn}\), we also evaluate the energy distributions of carriers generated upon absorption. See Ref. 22 for further details and demonstration of the quantitative accuracy of this method for conventional plasmonic metals, as well as for low-dimensional and refractory plasmonic materials.\textsuperscript{10,30}

C. Carrier lifetimes and mean free paths

The electron-phonon contribution to the inverse lifetime is given by Fermi’s golden rule as
\[
(\tau^{-1}_\text{e-ph})_{kn} = \frac{2\pi}{\hbar} \int_{BZ} \frac{\Omega dk'}{(2\pi)^3} \sum_{n'\pm \alpha} \delta(\varepsilon_{kn'} - \varepsilon_{kn} + \hbar\omega_{k' - k, \alpha}) \times \left( n_{k' - k, \alpha} + \frac{1}{2} + (1 - f_{kn'}) \right) \left| g_{kn', kn}^{p} \right|^2, \tag{6}
\]
where the factors in order correspond to energy conservation, occupation factors and the electron-phonon matrix elements. The sum over \(\pm\) counts phonon absorption and emission processes. See Ref. 22 and 30 for further details.

The electron-electron contribution is calculated using
\[
(\tau^{-1}_e)_{kn} = \frac{2\pi}{\hbar} \int_{BZ} \frac{dk'}{(2\pi)^3} \sum_{n'} \left( f_{kn'} + n_T(\varepsilon_{kn'} - \varepsilon_{kn}) \right) \times \left( \sum_{GG'} \frac{1}{\pi} \Im \frac{4\pi e^2}{\Omega (k' - k, G + G') \varepsilon_{GG'}(\varepsilon_{kn} - \varepsilon_{kn'})} \right) \times \hat{p}_{k'n', kn}^{\alpha}(G) \hat{p}_{k'n', kn}^{\alpha}(G'), \tag{7}
\]
where \(\hat{p}_{q'n'q}^{\alpha}\) are density matrices in the plane-wave basis with reciprocal lattice vectors \(G\), and \(\varepsilon_{GG'}\) is the inverse dielectric matrix calculated in the Random Phase Approximation. See Ref. 31 for a detailed introduction to this method and Ref. 22 for our specific implementation details. The only difference from Ref. 22 is the factor \(f_{kn'} + n_T(\varepsilon_{kn'} - \varepsilon_{kn})\), where \(n_T(\hbar\omega) \equiv \left( \exp \frac{\hbar\omega}{k_BT} - 1 \right)^{-1}\) is the Bose function, which generalizes the approach from \(T = 0\) to the finite-temperature GW formalism.\textsuperscript{32,33} In particular, this extension ensures a finite \(\tau^{-1}_ee \propto (\varepsilon - \varepsilon_F)^2 + (\pi k_BT)^2\) near the Fermi energy as expected for metals,\textsuperscript{23} while the conventional \(T = 0\) formalism for \(\tau^{-1}_ee\) diverges as \(\varepsilon \to \varepsilon_F.\textsuperscript{22}\)

The net carrier lifetime is \(\tau^{-1}_k = (\tau^{-1}_\text{e-ph})_{kn} + (\tau^{-1}_e)_{kn}\). We use this to calculate the carrier linewidths \(\Im \Sigma_{kn} = \hbar/(2\tau^{-1}_k)\) for the broadening of the energy conservation factors above, as well as for the mean free path \(\lambda_{kn} = |\mathbf{v}_{kn}|/\tau_{kn}\).

D. Interfacial injection probability

We estimate probability of injecting carriers into semiconductors using a modified Fowler model that accounts for the electronic structure of the metal by directly employing band moments \(P_{kn} = m_e \mathbf{v}_{kn}\) computed from DFT (and interpolated using Wannier functions).\textsuperscript{16,17,34} Specifically, for each electronic state in the metal, we decompose the momentum into a component along the interface normal direction (assumed to be the preferred transport direction \(\mathbf{j}\)), \(p_{kn}^\perp \equiv P_{kn} - \mathbf{j}\), and a component parallel to the interface, \(p_{kn}^\parallel \equiv (|P_{kn}|^2 - (p_{kn}^\perp)^2)^{1/2}\).
The modified Fowler model matches the parallel component, requiring $p^\perp_{SC}(P_{kn}) = p_{kn}$. Assuming a parabolic band structure for the semiconductor, the corresponding interface-normal component of the momentum is

$$p^{\perp}_{SC}(P_{kn}, \varepsilon_{kn}) = \begin{cases} \sqrt{2m^*_e(\varepsilon_{kn} - \varepsilon_F - \phi_B^e) - (P_{kn})^2}, & \varepsilon_{kn} > \varepsilon_F + \phi_B^e \\ \sqrt{2m^*_h(\varepsilon_F - \phi_B^h - \varepsilon_{kn}) - (P_{kn})^2}, & \varepsilon_{kn} < \varepsilon_F - \phi_B^h \\ 0, & \text{otherwise} \end{cases}$$  

where $\Theta(x)$ is the Heaviside step function, $m^*_e/h$ and $\phi_B^e/h$ are the effective masses and Schottky barrier heights of electrons/holes in the semiconductor. Note that states that are not allowed to enter the semiconductor lead to $p^{\perp}_{SC} = 0$.

Finally, the probability of injection in the modified Fowler model, accounting for a transmission matrix element due to momentum mismatch, is

$$P_{nk}^{inj} = \frac{4v^e_{kn}v^h_{SC}(v_{kn}, \varepsilon_{kn})}{(v^e_{kn} + v^h_{SC}(v_{kn}, \varepsilon_{kn}))^2}. \quad (9)$$

In our analysis in section II E, we report the average injection probability at each carrier energy,

$$P_{inj}(\varepsilon) = \frac{1}{g(\varepsilon)} \int_{BZ} \frac{g_0 d\varepsilon}{(2\pi)^3} \sum_n \delta(\varepsilon_{kn} - \varepsilon) P_{nk}^{inj}, \quad (10)$$

where $g(\varepsilon)$ is the electronic density of states.

**ACKNOWLEDGEMENTS**

The authors acknowledge funding from SRC under Task No. 2966. Calculations were carried out at the Center for Computational Innovations at Rensselaer Polytechnic Institute.

---

1. S. Linic, P. Christopher, and D. B. Ingram, Nature Mater. **10**, 911 (2011).
2. P. J. Schuck, Nature Nanotech. **8**, 799 (2013).
3. F. Wang and N. A. Melosh, Nano Lett. **11**, 5426 (2011).
4. M. Moskovits, Nature Nanotech. **10**, 6 (2015).
5. M. L. Brongersma, N. J. Halas, and P. Nordlander, Nature Nanotech. **10**, 25 (2015).
6. S. Kumar, A. Habib, and R. Sundararaman, Trends Chem. **3**, 902 (2021).
7. U. Guler, A. Boltasseva, and V. M. Shalaev, Science **344**, 263 (2014).
8. P. Patsalas, N. Kalfagiannis, S. Kassavetis, G. Abadías, D. V. Bellas, C. Lekka, and E. Lidorikis, Mater. Sci. Eng. R Rep. **123**, 1 (2018).
9. S. Ishii, S. L. Shimde, W. Jevasuwan, N. Fukata, and T. Nagao, ACS Photon. **3**, 1552 (2016).
10. A. Habib, F. Florio, and R. Sundararaman, J. Opt. **20**, 604001 (2018).
11. K. Hantansirisakul and Y. Gogotsi, Adv. Mater. **30**, 1804779 (2018).
12. D. B. Velusamy, J. K. El-Demellawi, A. M. El-Zohry, A. Giugni, S. Lopatin, M. N. Hedhili, A. E. Mansour, E. D. Fabrizio, O. F. Mohammed, and H. N. Alshareef, Adv. Mater. **31**, 1807658 (2019).
13. J. Jeon, H. Choi, S. Choi, J.-H. Park, B. H. Lee, E. Hwang, and S. Lee, Adv. Funct. Mater. **29**, 1905384 (2019).
14. R. Sundararaman, T. Christensen, Y. Ping, N. Rivera, J. D. Joannopoulos, M. Soljačić, and P. Narang, Phys. Rev. Mater. **4**, 074011 (2020).
15. H. Chalabi, D. Schoen, and M. L. Brongersma, Nano Lett. **14**, 1374 (2014).
16. G. Tagliabue, A. Jermyn, R. Sundararaman, A. Welch, J. DuChene, R. Pala, A. Davoyan, P. Narang, and H. Atwater, Nature Commun. **9**, 3398 (2018).
17. G. Tagliabue, J. S. DuChene, A. Habib, R. Sundararaman, and H. A. Atwater, ACS Nano **14**, 5788 (2020).
18. S. Kumar, C. Multunas, B. Defay, D. Gall, and R. Sundararaman, “Ultralow Electron-Surface Scattering in Nanoscale Metals Leveraging Fermi Surface Anisotropy,” (2022), arXiv:2204.13458.
19. V. Eyert, R. Fréard, and A. Maignan, Chemistry of Materials **20**, 2370 (2008).
20. E. Pop, V. Varshney, and A. K. Roy, MRS bulletin **37**, 1273 (2012).
21. M. Bugnet, M. Jaouen, V. Mauchamp, T. Cabioch, and G. Hug, Physical Review B **90**, 195116 (2014).
22. A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard III, and H. A. Atwater, ACS Nano **10**, 957 (2016).
23. A. M. Brown, R. Sundararaman, P. Narang, W. A. Goddard III, and H. A. Atwater, Phys. Rev. B **94**, 075120 (2016).
24. R. Sundararaman, K. Letchworth-Weaver, K. Schwarz, D. Gunelce, Y. Ozhaebes, and T. A. Arias, SoftwareX **6**, 278 (2017).
25. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
26. K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, Comput. Mater. Sci. **81**, 446 (2014).
27. I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B **65**, 035109 (2001).
28. R. Sundararaman, P. Narang, A. S. Jermyn, W. A. Goddard III, and H. A. Atwater, Nat. Commun. **5**, 5788 (2014).
29. B. Allen, Phys. Rev. B. **3**, 305 (1971).
30. P. Narang, L. Zhao, S. Claybrook, and R. Sundararaman, Adv. Opt. Mater. **5**, 1609014 (2017).
31. F. Ladstädter, U. Hohenester, P. Puschnig, and C. Ambrosch-Draxl, Phys. Rev. B **70**, 235125 (2004).
32. L. X. Benedict, C. D. Spataru, and S. G. Louie, Phys. Rev. B **66**, 085116 (2002).
33. J. J. Kas and J. J. Rehr, Phys. Rev. Lett. **119**, 176403 (2017).
G. Tagliabue, J. S. DuChene, M. Abdellah, A. Habib, D. J. Gosztola, Y. Hattori, W.-H. Cheng, K. Zheng, S. E. Cantón, R. Sundararaman, J. Sá, and H. A. Atwater, *Nature Mater.* **19**, 1312 (2020).