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Heat to electricity conversion by cold carrier emissive energy harvesters

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This paper suggests a method to convert heat to electricity by the use of devices called cold carrier emissive energy harvesters (cold carrier EEHs). The working principle of such converters is explained and theoretical power densities and efficiencies are calculated for ideal devices. Cold carrier EEHs are based on the same device structure as hot carrier solar cells, but works in an opposite way. Whereas a hot carrier solar cell receives net radiation from the sun and converts some of this radiative heat flow into electricity, a cold carrier EEH sustains a net outflux of radiation to the surroundings while converting some of the energy supplied to it into electricity. It is shown that the most basic type of cold carrier EEHs have the same theoretical efficiency as the ideal emissive energy harvesters described earlier by Byrnes et al. In the present work, it is also shown that if the emission from the cold carrier EEH originates from electron transitions across an energy gap where a difference in the chemical potential of the electrons above and below the energy gap is sustained, power densities slightly higher than those given by Byrnes et al. can be achieved. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4936614]

I. INTRODUCTION

Emissive energy harvesters (EEHs) are devices that radiate heat to cooler surroundings while converting part of the heat supplied to the device into work. Such energy harvesters have the potential to utilize low temperature heat, for example from the mid-infrared radiation emitted by the earth into space.1 A sketch of the energy flows involved during the operation of an EEH is shown in Fig. 1. The EEH emits a radiative heat flux $Q_{em}$ to the surroundings and absorbs a radiative heat flux $Q_{abs} < Q_{em}$. To maintain a constant temperature, the EEH receives a heat flux $Q_i$ from a heat source. Part of the heat supplied to the EEH is converted to work Byrnes et al. suggested rectennas, p-n junction diodes, and devices based on intersubband transitions as possible optoelectronical implementations of emissive energy harvesters.1 The p-n junction implementation has obvious parallels to photo voltaics. In ideal photovoltaic cells, a photocurrent is produced due to an imbalance between the number of photons absorbed and emitted by the cell. A p-n junction used as an emissive energy harvester radiates more photons than it absorbs, which allows it to generate a current with opposite direction of that generated in photovoltaic mode. Although theoretical efficiency limits of p-n junction EEHs can be established,2 practical implementations of the concept is likely to meet some challenges. The p-n junction will either have to be made from a material with a very small band gap, which makes it vulnerable to non-radiative processes, or it has to be operated at elevated temperatures, which is likely to introduce issues related to material stability and durability.

The present paper suggests and analyses a type of EEH based on the same physical principles as the hot-carrier solar cell. The absorber of an ideal hot-carrier solar cell is made from a material where the cooling of the charge carriers, upon photon absorption, is suppressed. This allows the temperature of the charge carriers in the absorber to be much larger than the lattice temperature. Charge carriers are then extracted from these hot populations through narrow energy bands or discrete states. This operation principle allows a more efficient conversion of solar energy into electric energy, than what is possible with conventional p-n junction solar cells.

Slowed carrier cooling has been observed in some III-V semiconductors like InP and InN where there is a large difference in atomic mass between the two elements that constitutes the compound. 3,4 Conibeer et al. suggested a number of other materials that might show similar properties.5 In these materials there is a large phononic band gap that prevents optical phonons to undergo Klemens decay; that is, decaying into two acoustic phonons with equal energy, but opposite momenta.6 If the material has a narrow optical phonon energy dispersion, as in materials with high symmetry, Ridley decay can also be minimized. An optical phonon undergoes Ridley decay when decaying into a low energy longitudinal acoustic phonon and a transversal optical phonon with a little less energy than the original phonon.7 When decay of optical phonons into acoustic phonons is suppressed, so is the transport of heat from the charge carriers to the surroundings since this relies on emission of acoustic phonons. A population of hot carriers and hot optical phonons can thus be contained in the hot-carrier material.

Nanostructured quantum wells have also shown reduced carrier cooling.8,9 The mechanisms causing this are not yet fully understood, but one or more of the following are believed to play a role:5 (1) Pile-up of hot carriers in the quantum wells create a phonon bottleneck effect. (2) Limited overlap between the optical phonon energies in the well and barrier material confines the phonons to the quantum wells. (3) Bragg reflection of phonon modes perpendicular to the wells creates one-dimensional phonon energy gaps.

The purpose of the present paper is to suggest and analyse a new type of EEH, which, for reasons that will become
clear in the following, is called a cold carrier EEH or a cold carrier cell. Like hot carrier solar cells, the active region in cold carrier EEHs must be made from materials in which the charge carriers are thermally insulated from the rest of the device. In cold carrier EEHs, however, the purpose of the de-coupling between the carrier temperature and the lattice temperature or device temperature is not to avoid carrier cooling, but to avoid carrier heating. In Section II it is explained how a device with cool carriers can convert heat to electricity. After the description of the working principle, expressions for the theoretical power density and efficiency of ideal cold carrier EEHs are derived. Finally, numerical values of these quantities are calculated for a selection of cases.

II. WORKING PRINCIPLE

In a cold carrier EEH the active material, with suppressed electron-phonon interactions, is optically coupled to surroundings with a lower temperature than the cell. This gives a net emission of photons from the cell to the surroundings which reduces the temperature of the electrons in this emitter. The population of cold electrons can be connected to metallic contacts via energy selective contacts, which allows transport of electrons to and from the emitter in narrow energy bands or at discrete energy levels. Resonant tunnelling through confined states in quantum dots is a possible mechanism to utilize. Two types of energy selective contacts are needed. One should be connected to the emitter at an upper energy \( E_{c,u} \), while the other should be connected at a lower energy \( E_{c,l} \), as shown in Fig. 2. The difference between these two energies is defined as the contact energy \( E_c \).

Ideally, the electrons can be transported without loss within the emitter and between the emitter and the metallic contacts. With these criteria fulfilled, the occupation factor for electrons must be the same on both sides of the energy selective contacts. In thermal equilibrium, the temperature of the metallic contacts, \( T_c \), the surroundings, \( T_s \), and the electrons \( T_e \) are all equal. The metallic contacts and the emitter then share a common Fermi level, as shown in the upper part of Fig. 2. If there is a net influx of photons, the electrons in the active layer will be heated. To maintain equal occupation factors on both sides of the energy selective contacts, a difference in the chemical potential, \( \Delta \mu_c \), must arise between the two metal contacts. \( \Delta \mu_c \) is related to a voltage \( V \) between the metal contacts through \( \Delta \mu_c = qV \). If a load is connected to the metal contacts, the device is now operated as a hot-carrier solar cell. This is sketched in the middle section of Fig. 2. If, on the other hand, there is a net outflux of photons from the active layer to the surroundings, the electrons in the emitter will cool down. This will also induce a voltage between the two metal contacts, but of the opposite polarity, as shown in the lower part of Fig. 2. The device can now be operated as a cold carrier EEH. To avoid heating the cold electron population by thermal radiation from the metal contacts or the heat source that is maintaining the temperature of the contacts, the energy selective contacts should either be reflective to thermal radiation or they should be point contacts, as small as possible, surrounded by a reflector that covers most of the area between the heat source and the active layer. The reflector could, for example, be an omnidirectional di-electric reflector. A possible structure of the cold-carrier energy converter is sketched in Fig. 3.

When a load is connected to a cell operating in EEH-mode, electrons will be extracted through the energy selective contact at \( E_{c,l} \). The electron is thermalized at the respective metallic contact whose chemical potential is higher than at the opposite metallic contact. A current will therefore flow between the contacts. Electrons are re-inserted to the emitter at the energy \( E_{c,u} \) where they thermalize with the cold-electron population. Since the metal contacts are constantly transporting energy to the emitter, heat must be supplied to maintain a constant temperature in the metallic contacts.

III. MATHEMATICAL MODEL

The modeling of the cold carrier EEH is divided into two parts. In the first part a derivation of central performance
parameters such as power density and conversion efficiency is made assuming that the radiation emitted by the cold carriers has zero chemical potential. This is analogous to Würfel’s treatment of the hot carrier solar cell with impact ionization. This model applies to cases where rapid non-radiative processes prevent a chemical potential different from zero in the cold carrier emitter. In such cases the net number of photons emitted from the cold carrier EEH does, in general, not equal the number of electrons passing through the device. Therefore, this is called “the model without particle balance.” In the second part, particle balance is taken into account, following in the footsteps of Ross and Nozik. The latter model applies when non-radiative processes are so slow compared to radiative processes that they can be neglected. The net number of photons emitted by the cold carrier EEH will then equal the net number of electrons passing through the energy selective contacts. When modelling a device with particle balance, the light emitted by the cold carriers will in general have a non-zero chemical potential.

A. Model without particle balance

As described above, the emitter receives electrons at the energy $E_{c,u}$ and releases electrons at the energy $E_{c,l}$. Assuming both the emitter and the ambient to radiate as black bodies, the energy balance for an emitter in steady-state then becomes

$$E_c = J_q \frac{q}{q} - q_{em} = \sigma (T_a^4 - T_c^4),$$

(1)

where $J_q$ is the current density delivered by the device and $\sigma$ is Stefan-Boltzmann’s constant. Using Fermi-Dirac statistics and equalling the occupation factors at the contact energies $E_{c,u}$ and $E_{c,l}$ gives

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**FIG. 2. Diagrams with energy levels and occupation factors for three different cases.** Upper: Thermal equilibrium. The Fermi levels of the active material and the metallic contacts are aligned and the electron temperatures are equal in all three parts of the cell. Middle: Operation as a hot-carrier solar cell. The electrons in the active layer are heated. This raises the position of the Fermi level in the metallic contact connected at $E_{c,u}$ relative to that connected at $E_{c,l}$. Lower: Operation as a cold-carrier EEH. The electrons in the active material are cooled, which rises the Fermi level of the contact connected at $E_{c,l}$ relative to that connected at $E_{c,u}$. The nine curves illustrate the occupation factor in the metallic contacts and the active material. The occupation factor has to be equal on both sides of the energy selective contacts, as indicated by the orange dashed lines going through the energy levels of these contacts.
Eqs. (1) and (2) allow us to obtain the complete current-voltage characteristic of the cold carrier EEH. Note that the electron temperature varies with the cell voltage. Setting \( J = 0 \) and solving for \( T_e \) shows that the electron temperature equals \( T_a \) when the cell is in open circuit. Setting \( V = 0 \) gives \( T_e = T_c \), i.e., the electron temperature equals the contact temperature when the cell is short circuited. The short circuit-current and the open-circuit voltage are thus given by

\[
J_{sc} = \frac{q \sigma}{E_c} \left( T_a^4 - T_e^4 \right),
\]

and

\[
V_{oc} = \frac{E_c}{q} \left( 1 - \frac{T_c}{T_a} \right),
\]

respectively. In hot-carrier cells, the current is defined as positive when electrons are extracted through the contact at \( E_c \). This definition of positive direction is maintained in the present work. Both open circuit voltage and short circuit current are therefore negative when the device is operated in EEH mode.

The power density delivered by the cell is given by

\[
P = JV = \sigma (T_a^4 - T_e^4) \left( 1 - \frac{T_c}{T_e} \right),
\]

Note that this equation is of the form expected for an ideal emissive energy harvester (Eq. (3A) in Ref. 1) and that it is equivalent to the equation for the power extracted from a hot carrier solar cell that receives black body radiation over a hemisphere (Eq. (22) in Ref. 13). The power density is independent on the contact energy \( E_c \), which can be set arbitrarily. A large contact energy gives a small current and high voltage, while a small contact energy gives a large current and a low voltage.

The hot carrier solar cell and cold carrier EEH must be treated a bit differently when it comes to efficiency. For an emissive energy harvester, the efficiency should be defined as the ratio of the produced work to the heat supplied to keep the device at a constant temperature, that is

\[
\eta = \frac{W}{Q_s} = \frac{P}{\dot{Q}_{em} - \dot{Q}_{abs} + W},
\]

where the right hand side is found by applying the energy balance \( \dot{Q}_s + \dot{Q}_{abs} = \dot{Q}_{em} + W \), which is justified by inspection of Fig. 1. Applying Stefan-Boltzmanns law to substitute for the radiative energy fluxes emitted and absorbed by the device, and using the expression in Eq. (5) for the power, gives

\[
\eta = \frac{1}{1 - \frac{E_c}{qV}},
\]

after some straightforward algebraic manipulation. The voltage can take values between the open circuit voltage (which is negative) and zero. It was found above that \( T_e \) approaches \( T_a \) when the voltage approaches the open circuit voltage. Therefore, the net emission from the emitter to the surroundings goes towards zero and so does the power delivered by the cold carrier EEH. Inserting Eq. (4) into Eq. (7) also shows that when the voltage approaches the open circuit voltage, the efficiency approaches the Carnot efficiency.

If the reflector between the active material and the heat source is removed, radiative heat transfer between these two parts must be taken into account. Assuming the heat source to be a black body holding the cell temperature \( T_c \), the energy balance of the cold-carrier device gives

![Diagram](image-url)
The efficiency is still given by Eq. (6). A cell without a reflector will produce less power than a cell with a reflector as long as \( T_e < T_c \), because the factor in the first brackets should be as negative as possible.

As proposed and discussed by Byrnes et al., an EEH can be radiatively coupled to outer space through the infrared atmospheric window where the atmosphere is close to transparent. This window transmits radiation with wavelengths between 8 and 13 \( \mu \)m. The power density emitted by a black body of temperature \( T \) in a wavelength interval with a lower limit \( \lambda_1 \) and a higher limit \( \lambda_2 \) is given by

\[
P = \sigma \left( T^4_e + T^4_c - 2T^4_e \right) \left( 1 - \frac{T_c}{T_e} \right), \tag{8}
\]

where \( h \) is Planck’s constant, \( c \) is the speed of light, \( \Delta \mu \) is the chemical potential of the emitted radiation and \( k \) is Boltzmann’s constant. When the exchange of radiative energy between the EEHs and the surroundings is restricted to certain energy ranges, the various terms of the form \( \sigma T^4 \) in Eqs. (1), (3), (5) and (8) can be replaced with \( \tilde{Q}(T,0) \) as given by Eq. (9).

\[
\tilde{Q}(T, \Delta \mu) = \int_{\lambda_1}^{\lambda_2} \frac{2\pi \hbar c^2}{\lambda^2} \frac{d\tilde{\lambda}}{\epsilon(\hbar c/\lambda - \Delta \mu)/kT - 1}, \tag{9}
\]

where \( \hbar \) is Planck’s constant, \( c \) is the speed of light, \( \Delta \mu \) is the difference between the quasi-Fermi levels in the emitting region, and \( \lambda \) is the wavelength. The conversion efficiency is still given by Eq. (7). With particle balance, the contact energy \( E_c \) becomes a parameter to optimize, because the number of carriers entering and leaving the cell depends on it.

Non-radiative excitation mechanisms such as impact ionization and Auger recombination will reduce the separation between the quasi-Fermi levels. If the energy gap is of the order of \( kT_e \) or smaller, such processes are unavoidable and will drive the quasi-Fermi level splitting towards zero.

IV. RESULTS AND DISCUSSION

In the first part of this section only EEHs without particle balance, that is, with \( \Delta \mu_e = 0 \) are considered. Devices with carrier balance are discussed in the second part.

A. Results without particle balance

For reference, a plot showing the power density of an ideal EEH, emitting in the atmospheric window, is shown in Fig. 4. This figure is equivalent to the power density map published by Byrnes et al. The power density of an EEH which is exchanging radiation with the sky can be enhanced if the exchange is extended to include the full spectrum—as long as the sky temperature for wavelengths outside the atmospheric window is lower than the temperature of the cold carriers. A plot showing the power density of an ideal

\[
P = \left( \tilde{Q}(T_e,0) - \tilde{Q}(T_e, \Delta \mu_e) \right) \left[ 1 + \frac{T_c}{T_e} \left( \frac{\Delta \mu_e}{E_c} - 1 \right) \right]. \tag{13}
\]

This figure is equivalent to the power density map published by Byrnes et al. The power density of an EEH which is exchanging radiation with the sky can be enhanced if the exchange is extended to include the full spectrum—as long as the sky temperature for wavelengths outside the atmospheric window is lower than the temperature of the cold carriers. A plot showing the power density of an ideal...
device exchanging radiation with surroundings at a temperature of 300 K outside the atmospheric window, and varying temperatures in the atmospheric window, is found in Fig. 5. For cell temperatures close to 300 K, the electron temperature is below 300 K, which causes a net inflow of energy from the surroundings to the cell outside the atmospheric window. This reduces the maximum power density of a full-spectrum EEH compared to one confined to the atmospheric window. For the higher device temperatures shown in Figs. 4 and 5, including wavelengths outside the atmospheric window, increases the maximum power density because there is now a net outflux of energy from the cell to the surroundings also outside the window. The increase can be as large as 50% when the device temperature approaches 500 K.

Allowing the EEH to exchange radiation with surroundings that are colder over the full spectrum causes a further increase in the power density. This is shown in the power density map in Fig. 6. Such a situation is relevant for space applications. A vessel in outer space can be covered by a full-spectrum EEH that absorbs the 3 K background radiation. If this vessel holds room temperature, the EEH can deliver a power density of up to 50 W/m². This happens at a conversion efficiency of slightly below 25%. The conversion efficiency at the maximum power point is shown in Fig. 7 for a variety of temperature combinations for full spectrum EEHs. Heating the EEH of the space vessel to 350 K, increases the maximum power density to around 90 W/m². Even higher device temperatures, and higher power densities, might be obtainable if the EEH is separated from the part of the vessel that contains electronics or other components that should not be subject to elevated temperatures.

B. Devices with particle balance

A comparison between the maximum power density of devices with and without particle balance is shown in Fig. 8. The devices are holding a temperature of 400 K while exchanging radiation with surroundings holding 200 K. Both device types are assumed to have an energy gap which is

![Fig. 5. Power density (W/m²) of full-spectrum ideal cold-carrier EEH without particle balance placed in surroundings radiating as a black body with temperature of 300 K for all wavelengths except those between 8 and 13 μm, where the temperature of the radiation is given by the vertical axis.](image)

![Fig. 6. Power density (W/m²) of full-spectrum ideal cold-carrier EEHs without particle balance as a function of the cell temperature (horizontal axis) and the temperature of the surroundings (vertical axis).](image)

![Fig. 7. Efficiency (%) at the maximum power point for a full-spectrum ideal cold-carrier EEH without particle balance as a function of the cell temperature (horizontal axis) and the temperature of the surroundings (horizontal axis).](image)

![Fig. 8. The power density of devices with and without particle balance as a function of the size of the energy gap. Values are shown for the maximum power point. The device temperature is set to 400 K and the temperature of the surroundings is set to 200 K.](image)
varied according to the horizontal axis of the plot. The integrals are calculated with zero as the lower integration limit, and the higher integration limit set to the wavelength corresponding to the size of the energy gap. Like for hot-carrier solar cells, it turns out that devices with particle balance have a slightly higher theoretical efficiency than devices without. The difference is small and will only give a slight adjustment to plots like those shown in Figs. 4–6. For the case shown in Fig. 8, there is a difference in power density of up to 4.9 W/m², which is found for an energy gap of 30 meV. While devices without particle balance can achieve a maximum power density of 126.2 W/m² for an energy gap equal to zero, devices with particle balance can achieve a maximum power density of 130.1 W/m² for an energy gap of 12 meV. A map of the power density for devices emitting in the atmospheric window, like that in Fig. 4, can be computed for devices with particle balance as well. The difference between the resulting plot and that in Fig. 4, will, however, be so small that any differences will hardly appear. Such a map is therefore not shown.

The temperatures of the cold electrons at the maximum power point are shown in Fig. 9. In devices with particle balance the optimal temperature of the cold carriers is higher than in devices without. A higher electron temperature allows particle balance to be maintained with a more negative \( \Delta \mu_e \), which, according to the term in square brackets in Eq. (13), is beneficial for the power density. As mentioned earlier, particle balance can only be achieved if the energy gap in the active material is larger than \( kT_e \). For the cases with particle balance plotted in Figs. 8–10, the value of \( kT_e \) is between 29 and 34 meV. For the lowest values of the energy gap shown in the plots, it will thus be impossible to avoid non-radiative transitions across the energy gap. If non-radiative transitions dominate, the cold carrier EEH will emit radiation with zero chemical potential and be described by the model for devices without particle balance. With a mix of radiative and non-radiative transitions, the power density will be somewhere between the two curves in Fig. 8. The lower energy of photons passing through the atmospheric window is around 90 meV, which is approximately three times the value of \( kT_e \), meaning particle balance can in principle be achieved.

Note that Eq. (13) allows the cold carrier EEH with particle balance to deliver power even when \( T_e \) is equal to or higher than \( T_e \). \( qV \) will then be equal to or larger (less negative) than \( \Delta \mu_e \). It is still crucial that the carriers in the active material are thermally isolated from the rest of the device, because the current delivered by it is limited by the number of electrons entering via the energy selective contacts. To get a large current, as much as possible of the energy supplied to the carriers in the active material should come from electrons that are passing through these contacts. It becomes a bit awkward to talk about a cold carrier EEH in cases where the carriers in the active material are warmer than the device temperature. However, since the maximum power density is achieved when the carrier temperature is lower than the device temperature, it is the opinion of the author that even a device with particle balance is aptly named as a cold carrier EEH.

The increased power density of devices with particle balance comes at a price, because it is accompanied by a slightly lower conversion efficiency at the maximum power point. This is shown in Fig. 10 for conditions identical to those of Fig. 8. The higher temperature of the cold carriers in devices with particle balance leads to a larger emission, which enhances the power density, but also reduces the conversion efficiency.

V. CONCLUSIONS

Ideal cold carrier EEHs without particle balance are shown to behave as ideal emissive energy harvesters as described by Byrnes et al.\(^1\). Radiative interaction with the surroundings in the long infrared range can be cancelled by choosing an emitter material with an energy gap of an appropriate size. Possible applications for such devices include utilization of waste heat, power sources for space vessels
and, as suggested in Ref. 1, utilization of the earth's mid-infrared radiation into space. If a cold carrier EEH has an energy gap it is possible to model a device in which the number of electrons entering and leaving the emitter equals the net number of photons emitted by the device. Devices operated with such a balance of particles are shown to be able to achieve slightly higher power densities than devices without this particle balance, but at a slightly lower conversion efficiency. The difference in power density is small, and for practical devices the ability or disability of a cold carrier EEH to achieve particle balance is not likely to be important.

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