Full paper

Thermodynamic loss mechanisms and strategies for efficient hot-electron photoconversion

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A R T I C L E   I N F O

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A B S T R A C T

There are currently extensive interests on the hot-electron-mediated photoconversion. However, the device quantum yield is fundamentally low due to the existences of various hot-electron loss channels; moreover, the nanostructured plasmonic/metamaterial are generally required, which bring challenges to the low-cost and large-scale fabrication. In this study, we focus on distinguishing the thermodynamic losses in hot-electron devices and presenting the possible route-maps for performance improvement. It is shown that a number of optical, electrical, and material factors, which lead to the substantial losses of hot electrons during the generation, transport, and emission processes. These loss mechanisms involve extensively the photon absorption, resistive dissipation, electron/electron or electron/phonon thermalization, carrier diffusion, Schottky barrier, and electron-momentum conservation. We further exemplify several planar hot-electron systems to show the possibilities of breaking these limitations for high efficiency. The planar hot-electron devices are based on Tamm plasmons, microcavity with double barriers, and optimized system by controlling the barrier and electron density of state, respectively. Results indicate that these designs can significantly improve the efficiencies of hot-electron generation, transport, and collection. It reveals that the external quantum efficiency of the system after the multi-domain optimization can be up to 60% in the near-infrared band. This study will motivate deeper understanding on the physical mechanisms, which restrict the performance of hot-electron device, and provide the solutions to improve the performance of hot-electron devices.

1. Introduction

The generation of hot electrons in metal through nonradiative decay of plasmons offers new and exciting opportunities in directly converting light into electricity by forming a metal-semiconductor (M/S) Schottky junction [1–4], which enables the below-bandgap infrared photo-detection with many advantages (such as convenient fabrication, room-temperature operation without electric bias, and high tunabilities of the working wavelength, etc.) [5–7]. To promote the hot-electron generation, metallic nanostructures that excite surface plasmons to concentrate the light within a subwavelength volume have been extensively demonstrated [8–12]. With plasmonic gratings, the photon energy can be strongly coupled into surface plasmons, resulting in a strong/narrowband absorption and intensive hot-electron generation proximal to the interfacial region. Such a system exhibits a photo-responsivity of 0.6 mA/W and an internal quantum efficiency (IQE) of ~0.2%, which is indeed not very high, but has already been improved by 20 times over the nanoantenna-based devices [6]. Further performance improvement can be realized by using metamaterial, where the hot electrons are efficiently generated within (for example) the 15 nm gold film, which is thin enough to ensure an effective electron transport to the interface and the resultant high responsivity up to 3.37 mA/W [7]. Besides the widely discussed surface plasmons, other photonic mechanisms have also been considered recently for hot-
electron photoconversion. For example, microcavity resonance [13,14] and Tamm plasmons [15] have been found highly beneficial for this kind of application under planar and low-cost system scenarios compared to conventional plasmonic systems with high-dimensional and subwavelength nanopatterns.

Despite the enormous efforts, the photoconversion efficiencies of hot-electron devices are still low, preventing from their practical applications [16-18]. The previous studies primarily focused on the optical modulation for a higher-efficiency of hot-electron generation. However, the hot-electron devices involve complex optoelectronic process, where the device performance relies on both the optical and electrical properties. Particularly, some fundamental mechanisms during the generation, transport, and collection processes of hot-electron set the key limitations on the performance improvement of hot-electron devices, which cannot be solved by solely the optical methods.

Therefore, a complete exploitation on the lossy mechanisms in hot-electron devices from the optical and electrical perspectives is highly beneficial from both fundamental science and the advanced optoelectronic applications.

To explore the possible ways to realize high-efficiency hot-electron photoconversion, we systematically address in this study the thermodynamic losses of hot electrons during the generation, transport, and collection processes. We suggest that 1) the lack of absorption, 2) the resistive dissipation from collective oscillation of electrons, 3) the nearly uniform hot-electron energy distribution, 4) the rapid thermalization due to electron-electron/phonon scattering, and 5) the momentum conservation in interfacial electron transfer are the primary and fundamental reasons for the extremely low hot-electron photoconversion efficiency. These mechanisms are discussed in detail with the exemplified strategies to break these limitations. For example, we indicate that the advances in the manipulation of light in metallic nanostructures, the modification of the Schottky interfaces, and the engineering of electron density of state (EDOS) in metallic materials can minimize the thermodynamic losses to obtain ultrahigh-efficiency hot-electron devices. Taking Au/Si barrier as an example, the external quantum efficiencies (EQE) of the thick-film single-barrier, thin-film single-barrier, and thin-film double-barrier configurations in the near-infrared region show extremely high EQE up to ~60%. Two planar hot-electron devices based on Tamm plasmons and microcavity are proposed to approach the efficiency limits. We show how the limiting factors such as the electron-momentum conservation, barrier height, and thermalization loss can be controlled by managing the light and hot electrons. This study is beneficial for deeply understanding the inherent science of hot-electron devices as well as motivating advanced solutions to overcome the fundamental limitations to obtain unprecedentedly high hot-electron photoconversion efficiency.

2. Result and discussion

2.1. Thermodynamics in hot-electron conversion

The approach addressing the various loss mechanisms for the hot-electron photoconversion as well as the opportunities for efficiency improvement is under the assumption that each plasmon by photon excitation decays into one energetic electron-hole pair, i.e., high-order processes such as multiple electron-hole pair generation are forbidden [19,20]. Hot electrons are generated by an event of photon absorption (A), and each absorbed photon with energy $E_{\text{ph}}$ raises only one electron from the occupied energy level below the Fermi level to the unoccupied high-energy level in the conduction band. Apart from the hot-electron generation via single-particle excitation, another source of the plasmon loss in metal is the classical resistive dissipation, as shown in Fig. 1a, where the $ab$ initio predicted efficiency ($\eta$) of plasmons decay into hot electrons ($\eta_{\text{eh}}$) or dissipate thermally ($\eta_{\text{th}}$) in bulk gold as a function of plasmon energy is illustrated [19]. It is shown that the proportion of the resistive dissipation is increased under low-energy (long-wavelength) photon excitation.

After excitation, hot electrons are thermalized by the electron-electron and electron-phonon scatterings in tens of femtoseconds (10–100 fs), subsequently cooled by the energy transfer to the lattice in around 100 fs to 1 ps via electron-phonon scattering, and ultimately the lattice phonons are equilibrated with the surrounding bath on the timescale of 100 ps [21]. Under room temperature, the lifetimes of the electron-electron scattering, electron-phonon scattering, and phonon-phonon/bath thermalization are ~40 fs, 800 fs, and 86 ps, respectively (please see details for the effect of the temperature in the section S5 of Supporting Information). Only the electrons generated within the region defined by the mean free path ($l_{\text{MFP}}$) from the Schottky interface can participate effectively in interfacial electron transfer without encountering essential relaxation [22]. Fig. 1b shows the electron lifetime ($\tau$) and $l_{\text{MFP}}$ as a function of the electron excess energy above Fermi level ($E_{\text{ex}}$) in gold. The low-energy electrons have a long $\tau$ and a large $l_{\text{MFP}}$ because the electron-phonon scattering dominates and the electron-electron scattering is negligible. Typically, in gold, hot electrons with $E_{\text{ex}} \sim 0.75$ eV have $l_{\text{MFP}} \sim 25$ nm and are thermalized within 14 fs.

For hot electrons arriving at the Schottky interface, only those with kinetic energy with the normal momentum component higher than the barrier height ($\phi_{SB}$) can be injected into semiconductors [23]. However, even for the electrons diffusing perpendicularly to the interface, the proportion of the injected electrons with $E_{\text{ex}} > \phi_{SB}$ is still low. For example, it is ~23% for incident photons with $\lambda = 1300$ nm in the Au/Si contact ($\phi_{SB} = 0.75$ eV), calculated from the initial energy distribution, $D(E)$, of the excited hot electrons in the bottom panel of Fig. 1b. Due to the conservation of electron momentum component parallel to the Au/Si interface as shown in Fig. 1c, only a small fraction ($\eta_{\text{inj}}$) of electrons can accomplish the interfacial electron transfer process. Further considering the possible electron reflection at the interface due to the impedance mismatch, the proportion ($\eta_{\text{inj}}$) tends to be less [24], e.g., $\eta_{\text{inj}} = 0.12$ even when $E_{\text{ex}} = 2\phi_{SB}$.

From the above thermodynamic analysis of the hot-electron conversion process based on the three-step phenomenological model proposed by C. Scales and P. Berini by further adding additional physics to model the resistive dissipation in the hot-electron generation process, the thermalization loss in the hot-electron transport process, and the electron reflections at the M/S interface in the hot-electron collection process [23], the EQE of the hot-electron devices can be calculated by:

$$\text{EQE}(\lambda) = A \eta_{\text{eh}}(\lambda) \times \int_{\text{SB}} D(\lambda, E) \eta_{\text{inj}}(E) \times \eta_{\text{eh}}(E) dE$$

where $\lambda$ is the wavelength, $A$ the light absorption efficiency, $\eta_{\text{eh}}$ the efficiency of plasmons decay into hot electrons, $D$ the initial energy distribution, and $\eta_{\text{inj}}$ (or $\eta_{\text{inj}}(E)$) hot-electron transport (injection) efficiency to Schottky interface (into semiconductors). It is obvious that the EQE value is determined by the five terms on the right under distinguished physical origins.

2.2. Categorized hot-electron losses

Based on the above analysis, we can categorize the mechanisms of hot-electron energy losses into three kinds occurring in the hot-electron generation, transport, and emission processes, respectively, and accordingly present the inherent physical limiting factors as well as provide the potential solutions (see Fig. 2).

2.2.1. Limitation 1: optical loss and resistive dissipation in hot-electron generation (I and II in Fig. 2)

Due to the significant impedance-mismatch between metal and air, there is a high reflectance by the planar metal surface, leading to very poor hot-electron generation. Therefore, the outstanding light-trapping strategy is of prominent importance to enhance the photoemission of hot electrons. This has been paid by the most past attention in the hot-electron photoconversion field. Considering that the plasmonic or metamaterial nanostructures have large absorption cross-sections and...
strongly enhanced electric fields in resonance, these artificially de-
nosized nanosystems have been discussed extensively as the efficient
light-management strategies to improve the optical absorption for ef-
ficient hot-electron generation [25]. Apart from the optical loss, the
short-lived electronic states comprising the collective oscillation leads
to the classic resistive loss with energies converted into heat. The re-
sistive contribution to plasmon loss in metal is expected to reduce with
lowering the temperature. Below the interband threshold, resistive loss
competes with phonon-assisted excitations and accounts for
~30%–50% of the absorbed energy [19]. Fortunately, the proportion of
resistive loss ($\eta_{res}$) in the metallic absorption can be reduced by using
smaller gold nanoparticles [19], e.g., $\eta_{eh}$ is improved to ~90% in a
10 nm-diameter sphere from 60% in bulk gold with $E_{ph} = 1$ eV [19].

2.2.2. Limitation 2: thermalization loss in hot-electron transport (III and IV
in Fig. 2)

The first step for hot-electron transport is the diffusion from the
position of hot-electron generation to the M/S interface, which is
mostly determined by the mean free path of hot electrons and the dif-
fusion angle (see Equation S5 of the Supporting information). However,
this has been indicated that only a small fraction of hot electrons can
reach the interface due to the rapid relaxation [23]. To improve the hot-
electron transport efficiency, concentrating the electric field near M/S
interface or employing a metal film with a thickness smaller than
$l_{MFP}$ are promising ways [26, 27]. For the conventional single-barrier
Schottky device, half of hot electrons will transport toward the M/S
interface based on the assumption of isotropic initial momentum dis-
tribution [23]. Technically, this can be solved by modifying the initial
momentum distribution of hot electrons by engineering the surface
plasmon mode since hot electrons are preferentially generated with a
momentum parallel to the electric field [20]. By the excitation of sur-
faccle plasmon under TM illumination, more electric fields lie in the di-
rection normal to M/S interface compared to that under TE case (purely
tangential to M/S interface). The hot electrons are initially generated
with a $k_z$-vector matching the plasmon mode by the Landau damping
and preferentially directed along the surface plasmon momentum di-
rection [24]. For example, applying an external electric bias facilitates
the unidirectional hot-electron transport toward the interface [28].
Furthermore, employing double Schottky barriers is an effective strategy since all of the hot electrons will diffuse toward the M/S interfaces now.

2.2.3. Limitation 3: low collection efficiency in hot-electron emission process (V and VI in Fig. 2)

The other fundamental restriction for the efficient hot-electron collection is the Schottky barrier height, which hinders the low-energy electrons from emission into semiconductors. Thus, a low barrier height is generally preferred. Recent studies have shown that the barrier height can be strongly affected by the details of the interface, which may vary significantly with the fabrication method and surface treatment [16,18]. Another strategy is to engineer the EDOS with the band edge just below the Fermi level, which results in a narrow energy distribution with a single peak above the barrier height [12,18,29]. Since only the electrons within the escape cone of momentum space have a relatively high probability to transport across the interface, the injection probability is expected to be boosted with a thin metal film due to multiple electron reflections between the internal metal surfaces [23]. Another approach to overcome the momentum limitation of electron emission over the barrier is to form a three dimensional (3D) Schottky barrier by embedding the plasmonic nanostructure within the semiconductor [30]. The Schottky barriers formed on the vertical sides of the metal in addition to the planar Schottky interface increase the momentum space for hot-electron emission. Moreover, the electric field is strongly localized in the metallic grating edges, where more hot electrons are generated. The abrupt boundaries provide the necessary momentum for electrons to inject into semiconductor and relax the requirement of the parallel momentum conservation [24]. Besides, roughening the M/S surface can relieve the momentum restriction by providing the necessary tangential momentum for the carrier injection [24,31,32]. This analysis could be highly desirable for understanding the limiting factors and providing potential solutions for the efficient conversion of hot electrons. In the following sections, we will show the role of light and carrier management in improving the efficiency using Au/Si barrier as an example. It is noted that the discussed strategies are universal and applicable to other hot-electron systems.

2.3. Solutions for improved efficiency

Above analyses indicate that there are various loss mechanisms during the generation, transport, and collection processes, resulting in the low hot-electron photoconversion efficiency. Our categorized investigation allows exploring the corresponding solution for each limiting factor so that the device performance can be improved step-by-step. In the following, we will introduce three kinds of designs, each of which solves a specific problem in the hot-electron generation, transport, or collection process. It is noted that the methods/strategies presented here are general and applicable for the systems with other metals and semiconductors.
2.4. **Hot-electron generation engineering**

The first example is shown to obtain the significantly improved optical absorption by the planar multilayer design. The system (i.e., Device I) is composed of three pairs of alternating SiO₂/Si (each with the quarter-wavelength thickness) on an Au layer with the thickness \(d_{Au} = 200\) nm, as shown in Fig. 3a. The refractive index of Si is taken as 3.5 for the design of distributed Bragg reflector (DBR) with the central wavelength \(\lambda_{DBR} = 1100\) nm. The Si layer in contact with Au is n-type doped, forming a single Schottky barrier. Tamm plasmons (TPs) are excited in the system with light propagating along the DBR/Au boundary [15], thus the electric field is highly confined in the region and decays exponentially toward the Au layer (see Fig. 3a), resulting in a narrow reflection dip and perfect absorption on resonance (see the inset of Fig. 3b). As a result, most hot electrons are generated close to the upper surface of the metal film with \(\delta_G = 13\) nm, which is defined as the distance where the generation rate drops to 1/e of the maximum (see Fig. 3b). Even for the excited highest-energy electrons, \(\delta_G\) is smaller than \(\lambda_{gap} = 18\) nm, which implies a favorable hot-electron spatial distribution with a relatively large probability to reach the interface (see the top panel of Fig. 3c). Most hot electrons reaching the interface come from that generated in the region close to the upper surface of Au due to the high generation rate and transport probability there (see the bottom panel of Fig. 3c). The overall hot-electron transport efficiency \(\eta_{trans}\) (defined by Equation S8 in the Supporting information) is 28%, which is 11.6 times larger than the value of 2.4% for plasmonic nanostripe-based device [24].

The angular distribution of ballistic electrons reaching the interface is quite anisotropic since under a larger diffusing angle, the propagation path is increased and more electrons will be thermalized (see Fig. 3d). With the injection efficiency of electrons reaching the interface (see Fig. 3e), the EQE and the responsivity of the device are obtained as 0.2% and 2.07 mA/W, respectively, which are more than 3 times of those based on plasmonic nanograting [6]. Besides, the IQE ~ 0.2% (under \(A \sim 1\)) of the device is the same as that of the grating nanostructure, which further demonstrates that an efficient optical absorption is vital to the high-performance hot-electron device. For a further insight into the energy losses, we compare the various contributions of the energy losses by examining the hot-electron flux at each stage in Fig. 3f. It is found that the resistive dissipation and thermalization
losses dominate the energy losses in the device. In contrary, the collected energy in the system is negligible, showing the great chance for the development of ultrahigh-efficiency hot-electron device. The barrier loss is higher than the sum of the optical reflection and momentum loss.

2.5. Hot-electron transport engineering

In hot-electron devices, the electron diffusion is normally uncontrolled if not any external means employed; therefore, only half of the hot electrons diffuse toward the Schottky interface in the single-barrier systems. To conquer this limitation, an ultrathin-film double-barrier system (Device II) is proposed in this study (see Fig. 4a). The double Schottky junctions can be formed by burying the 1 nm Au film into a Si layer, which are covered by two DBRs. We performed the optical optimization on the top and bottom DBRs in order to obtain the highest optical absorption. Specifically, the top DBR is consisted of 3.5 pairs of SiO$_2$/Si (thickness of 150/113 nm) on top of a 330 nm Si buffer layer and the bottom DBR has 10 pairs of SiO$_2$/Si (thickness of 71.4/170 nm). The special design enables a perfect absorption (see Fig. 4b) and ~30-fold enhancement of the local electric field in Au film (see Fig. 4c) at the same resonance of Device I under normal incidence. The ultrathin metal film leads to an extremely high hot-electron transport probability (see the top panel of Fig. 4d), uniform spatial distribution of electrons reaching the interface (see the bottom panel of Fig. 4d), and nearly isotropic momentum distribution of electrons at the interface (not shown here). Fig. 4e indicates that the injection efficiency of the electrons into the semiconductor is more than twice of that in Device I, due to the emission over two barriers and multiple electron reflections between the double Au/Si interfaces. As a result, the responsivity (EQE) of Device II is 19.29 mA/W (1.85%), which is the highest value reported in the hot-electron systems. However, it is still much lower than that in the hot-hole device with PtSi/p-Si arising from the smaller Schottky barrier height [33,34]. It is clear from Fig. 4f that the thermalization loss is decreased dramatically, while the barrier and momentum losses are increased since there are more electrons reaching the interface.

2.6. Hot-electron collection engineering

With the above improvements on the optical absorption and electrical diffusion, the further strategy to promote the system performance is to optimize the hot-electron collection by controlling the barrier configuration or the hot-electron momentum direction. Here we examine the opportunity to further improve the photoresponsivity of Device II by promoting the ratio ($R_{\text{high-energy}}$) of over-barrier hot electrons within the overall excitation. Figs. 5a and 5b show the parabolic EDOS and the resulting hot-electron distribution with raising the effective Fermi level ($E_{\text{ef}}$) from 0.15 to 5.5 eV ($E_{\text{ef}}$: the effective conduction bandedge below the Fermi level of the metal [12,18,29]). With a lower $E_{\text{ef}}$, more electrons are concentrated within an extremely narrow energy range below Fermi level at thermal equilibrium. The excited hot
electrons are distributed in a higher and narrower energy range, which results in an increased $R_{\text{high-energy}}$ (see the inset of Fig. 5c), e.g., all excited electrons have enough energy to overcome the barrier ($R_{\text{high-energy}} = 100\%$) at $E_{\text{ef}} = 0.15\,$eV. On contrary, with a high $E_{\text{ef}}$, a number of electrons are located away from the Fermi level and the hot-electron distribution is broad and nearly uniform (i.e., the significantly decreased $R_{\text{high-energy}}$), which is detrimental to hot-electron collection. As a result, the responsivity is increased from 27.7 to 152.9 mA/W with lowering $E_{\text{ef}}$ from 1 to 0.1 $\,$eV (see Fig. 5c). Moreover, the responsivity of the hot-electron device can also be improved by using a lower barrier height, which directly leads to an increased $R_{\text{high-energy}}$ and allows more electrons to accomplish the interfacial electron transfer process (see Fig. 5d). However, it is worth to note that the lower barrier height dramatically increases the thermal emission and results in a higher dark current, so the tradeoff must be considered to maximize the overall photocurrent.

2.7. Efficiency limit of hot-electron devices

We now show the potential route-maps for the hot-electron device to improve the efficiency. The limiting EQEs of the planar hot-electron devices under various configurations, including thick-film, thin-film, single-barrier, and double-barrier, are examined and compared. Here, we list the strategies to enhance the device performance step-by-step. 1) For thick-film single-barrier device, the perfect hot-electron transport denotes the limiting $\eta_{\text{trans}} = 0.5$ (i.e., all of the hot electrons are distributed in the region very close to the interface), allowing to obtain the corresponding limiting EQE. 2) With a thin-film configuration, the hot-electron collection efficiency $\eta_{\text{inj}}$ can be further improved. Ideally, for the over-barrier hot electrons, we have $\eta_{\text{inj}} = 1$ if $E_{\text{ex}} > \phi_{\text{SB}}$; therefore, the corresponding EQE limit of thin-film single-barrier device can be achieved. 3) Actually, the highest $\eta_{\text{trans}} = 0.5$ in single-barrier system can be further improved up to 1 by employing the double-barrier, leading to the doubled limiting EQE compared to the single-barrier system. 4) In addition, if all excited hot electrons can be collected by engineering the EDOS of the metal, the barrier loss can be completely suppressed, enabling even higher EQE. 5) Finally, neglecting the resistive loss of the absorbed energy in the small metallic nanoparticles, the perfect conversion with EQE = 100% can be obtained in principle, i.e., all incident energy can be converted into photocurrent.

Figure 6a–c plot the spectra of limiting EQE of the planar hot-electron devices under thick-film single-barrier, thin-film single-barrier, and thin-film double-barrier configurations. Moreover, the possible EQE spectra with eliminating the barrier and resistive losses are introduced into the optimized system in order to examine the upper-limit of the EQE. In these three figures, the distinguished electrical parameters are also considered, i.e., (a) $E_{\text{ef}} = 5.5\,$eV and $\phi_{SB} = 0.75\,$eV, (b) $E_{\text{ef}} = 0.15\,$eV and $\phi_{SB} = 0.75\,$eV, and (c) $E_{\text{ef}} = 5.5\,$eV and $\phi_{SB} = 0.5\,$eV. The contribution of the wavelength-dependent resistive loss to absorption in metal is taken from Ref. [19]. It is found that, even for the ideal planar thick-film/single-barrier hot-electron device, the EQE is extremely low, leaving a great room for improvement by increasing the
interfacial electron injection efficiency with a thin-film metal and collecting more electrons with double Schottky junctions. With a very low $E_{sd} = 0.15$ eV (Fig. 6b), the barrier loss is eliminated when $\lambda < 1377$ nm because all excited hot electrons have energies higher than $\phi_{SB}$. In this case, the momentum and thermalization losses are the main limiting factors, so the thin-film double-barrier setup can be used for a high conversion efficiency. With a low barrier height (Fig. 6c), the barrier loss is slightly relieved and the sum of thermalization and the momentum losses tends to compete with that of the barrier loss.

The corresponding responsivity spectra of the thick-film single-barrier, thin-film single-barrier, and thin-film double-barrier hot-electron devices shown in Fig. 6a are plotted in Fig. 6d, where the responsivity spectra of i) an actual system (Device II) with $E_{sd}$ and $\phi_{SB}$ corresponding to Figure 6a–c and ii) a metamaterial system are included. It is shown that the responsivity of Device II with $E_{sd} = 5.5$ eV and $\phi_{SB} = 0.75$ eV can be even one-magnitude larger than the highest reported value in the hot-electron device by integrating the metamaterial perfect absorber as marked by the white circles [7]. The engineering of EDOS (redline with star-marker) and barrier height (blackline with sphere marker) can make the responsivity higher than the limiting values. It is noted that the responsivity of Device I is close to the theoretical limit of the thick-film single-barrier device, especially at long-wavelength band (see the inset of Fig. 6d). With the optimized optoelectronic design and properly modulating the values of $E_{sd}$ and $\phi_{SB}$, the responsivity of Device II exhibits the significantly increased responsivity, revealing the way to realize high-efficiency planar hot-electron devices.

It is noted that the EQE itself cannot reveal enough information of the device performance, so we discuss the effect of dark current here. The dark current density can be obtained from the thermionic emission theory [26]:

$$J_{dark}(T, V) = A^* \frac{T^2}{e^{qV/kT} - 1}$$

where $A^*$ is the effective Richardson constant, $T$ is the operation temperature, $k_B$ is the Boltzmann's constant, and $V$ is the voltage across the device. With a low barrier height, the EQE is high, while the resulting large dark current may lead to a low conversion efficiency. Although the dark current is small for a high barrier height, the conversion efficiency may be low as well due to the decreased EQE. Reducing the operation temperature is an effective way to obtain a low dark current and a high conversion efficiency. However, cooling needs more energy consumption and is inconvenient, especially for an extremely low temperature. Thus, choosing a reasonable barrier height to balance the dark current and EQE is essential to obtain a high conversion efficiency. It is noted that the high EQE and responsivity of the hot-electron devices can be obtained without applying an external bias.

3. Conclusions

In summary, we systematically investigate the fundamental thermodynamic losses in the hot-electron generation, transport, and emission processes, elucidate the inherent physical limitations to the photoconversion efficiency, and highlight the opportunities for solving/relieving the problems. The low optical absorption, resistive dissipation, nearly uniform hot-electron energy distribution, rapid hot-electron thermalization, and momentum conservation in interfacial electron transfer are found to be the key reasons leading to the extremely low hot-electron photoconversion efficiency. Based on the analysis, we present a planar multilayer system composed of three pairs of DBR on metal with the excitation of TPs, which enables the perfect absorption and efficient hot-electron transport to the M/S interface. It is found that the responsivity can be as high as 2.07 mA/W, which is close to the theoretical limit of the thick-film single-barrier hot-electron devices. We further design an ultrathin-film double-barrier system which shows the perfect optical absorption, dramatically decreased thermalization loss, and improved injection probability, leading to an extremely high responsivity up to 19.29 mA/W (one-magnitude larger than the highest reported using metamaterial perfect absorber). Further, the low effective Fermi level can promote $R_{high-energy}$, allowing more electrons to accomplish the interfacial electron transfer process, and results in a high responsivity up to 152.9 mA/W. By simulation, the optimized planar hot-electron devices under thin-film double-barrier design exhibits an EQE as high as 60% in the near-infrared region. The thermodynamic analysis on the fundamental science, the proposed potential solutions, and the planar devices with extremely high performance provide the communities the opportunities to realize high-efficiency and low-cost hot-electron devices.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.10.051.

References

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