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Hybrid photon-enhanced thermionic emission and photovoltaic converter with concentrated solar power



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ABSTRACT

Keywords: Photon-enhanced thermionic emission Photovoltaics Light-transparent anode Direct photoelectric emission Photon-enhanced thermionic emission (PETE) converter is a solid-state heat engine, in which hot electrons emit from a p-type semiconductor cathode to an anode across a vacuum gap. Photon-enhanced mechanism reflects in reducing the electron emission barrier by photo-induced quasi-Fermi level splitting. High photon-enhancement mode requires a thin cathode thickness to reduce the recombination of excited-electron during diffusion. Whereas, thin cathode causes huge photon penetration loss. In this work, we propose an original concept of hybrid photon-enhanced thermionic emission converter and photovoltaic (PETE-PV) solar cell. The penetrating solar photons are utilized by photovoltaic sub-devices to yield additional output power. The operating characteristics and superiority of a four-terminal PETE-PV solar cell were demonstrated by simulation. Results show that the solar cell gains a 4–8% point of power conversion efficiency boost thanks to the photovoltaic sub-device. In addition, we developed a PETE protype with light impinging through a transparent anode (i.e., indium-tinoxide film) to a cathode surface. Experimental results demonstrate that the cathode saturation current under illumination is ~300-fold larger than that of pure thermionic emission mode, and the cathode work function is reduced by 0.6 eV. This study lays a solid foundation for further development and application of PETE-PV solar cells.

1. Introduction

Solar energy utilization (especially for electricity generation) is a vital important issue of scientific research and engineering market, due to its abundance, sustainability and environmental friendliness. Current methods to harvest solar energy are generally based on thermodynamic cycle or photovoltaic (PV) effect. New technologies, e.g., hybrid concentrated photovoltaic-thermal, multi-junction PV cells, and spectral-splitting [1], were proposed trying to improve the conversion efficiency. However, they were not practically widespread due to system complexity or high cost.

Photon-enhanced thermionic emission (PETE) converter is a recently proposed concept that combines photo and thermal mechanisms into a single device for electricity generation [2]. A PETE converter consists of a hot p-type semiconductor cathode and a cooler anode separated by a vacuum gap. PETE converter utilizes over-bandgap photons to excite electrons from the valence band to the conduction band, (i.e., to overcome the bandgap). It utilizes thermal energy from sub-bandgap photons and thermalization loss of above-bandgap photons to overcome the electron affinity, which realizes a huge enhancement of emitted electrons. Thus, the effective barrier for electron emission is reduced by the difference between Fermi-level and photo-induced quasi Fermi-level. Theoretical efficiency can obtain ~40% for a PETE converter alone, and >50% for tandem with a thermal engine [2]. As a novel technology, previous research on PETE converters mainly focused on theoretical modeling, and system analysis (e.g., cathode materials, space charge effect, and near-filed radiative phenomenon) based on theoretical models [3,4]. Experimental studies on PETE converter were rarely reported, especially at high cathode temperatures. Schwede et al. [2] measured the emission current of a Cs-coated GaN cathode for 330–350 nm illumination at the cathode temperature of <220 °C. Later, they proposed a GaAs/AlGaAs heterostructure as the PETE cathode with low interface recombination, and measured the quantum efficiency by using a monochromatic laser at the cathode temperature of <120 °C [5].

Cathode thickness is a key parameter of PETE converters. The optimal cathode thickness is often derived by trading off in terms of photon absorption and recombination loss. Diffusion process of photoexcited electron to the emitting surface is accompanied by recombination loss. Meanwhile, non-radiative recombination loss heats the cathode, thus increasing the cathode temperature. For a larger thickness, PETE mode degenerates to pure thermionic mode, which deviates from

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Nomenclature		t	cathode thickness, m			
		q	elementary charge, C			
Α	Richardson constant, $A/(cm^2 \cdot K^2)$	h	Planck's constant, J.s			
D	carrier diffusion coefficient, m ² /s	ħ	Planck's constant over 2π , J·s			
$E_{ m F}$	Fermi level, eV	k	Boltzmann's constant, J/K			
E_{g}	semiconductor bandgap, eV	m_n^*	effective mass of electrons at the conduction band			
$E_{\rm A}$	impurity energy level, eV		minimum, kg			
$E_{\rm C}$	the conduction band minimum, eV	m_p^*	effective mass of holes at valence band maximum, kg			
$E_{\rm V}$	the valence band maximum, eV	$n_{\rm eq}$	equilibrium conduction-band electron concentration, 1/			
EQE	the external quantum efficiency of PV cell		m ³			
G	photogeneration rate of electron-hole pair, $1/(m^3 \cdot s)$	$p_{\rm eq}$	equilibrium valence-band hole concentration, $1/m^3$			
J	current density, A/m ²	$\Delta n (\Delta p)$	non-equilibrium electron (hole) concentration, $1/m^3$			
$N_{\rm A}$	impurity acceptor concentration, $1/m^3$	d	interelectrode gap size, m			
$N_{\rm C}$	$N_{\rm C}$ the effective density of states in the conduction band, $1/m^3$					
$N_{\rm V}$	the effective density of states in the valence band, $1/m^3$		Greek symbols			
Р	output power density, W/m ²	η	power conversion efficiency, %			
Q_{sun}	incident solar energy, W/m^2	Φ	work function, eV			
$Q_{\rm ele}$	heat transferred by emitted electrons, W/m ²	ψ	motive barrier in vacuum gap, eV			
$Q_{\rm rad C amb}$ radiative heat loss from the cathode to the ambient, W/		Ψ_{m}	the maximum motive barrier, eV			
m ²		χ	electron affinity, eV			
$Q_{\rm rad,C A}$	radiative heat loss between the two electrodes, W/m^2	ω	photon frequency, rad/s			
$Q_{\rm rad, recom}$ radiative energy of emitted blackbody photons above the		Subcerint	·			
bandgap, W/m ²		Λ	anodo			
$Q_{\text{unabsorbed}}$ solar energy not absorbed by the cathode, W/m ²		A C	anoue			
R	recombination rates of electron-hole pair, $1/(m^3 \cdot s)$, W/m^2	С "				
S	surface recombination rate, $1/(m^2 \cdot s)$	n	hele			
Т	temperature, K	р тт	note nhoneed thermionic emission			
U	output voltage, V		photon-childheed thermionic emission			
$U_{\rm MPP}$	voltage at the maximum power point, V	PV	photovoltaic			
C	speed of light, m/s					
	• • •					

the merits of PETE. For a smaller thickness, a lot of photons pass through the cathode and are absorbed by the anode, causing great photon loss. If the anode is light-transparent and in tandem with a PV cell, the PETE converter can operate at high photon-enhanced mode by optimizing the cathode thickness, and meanwhile the PV cell can utilize the transmitted solar photons. Here the concept converter is called hybrid photonenhanced thermionic emission and photovoltaic (PETE-PV) solar cells.

Hybrid thermionic-photovoltaic (TIPV) converter was previous proposed to synergistically use electrons and thermal photons emitted by the cathode of thermionic sub-device [6,7], and has been experimentally verified [8–11]. Structural arrangement of the PETE-PV converter is similar to that in the TIPV converter. However, PETE-PV differentiates from TIPV in principle. In PETE converters, the thermionic emission is photon-enhanced and the PV sub-device utilizes penetrating solar-photons rather than relying on cathode emitted thermal-photons. Therefore, near-field level spacing is not required and space charge effect can be eliminated by means such as cesium plasma.

In this work, we proposed an original concept of PETE-PV solar cells and clarified working principles of three types of PETE-PV solar cells (i. e., two-terminal, three-terminal and four-terminal). We demonstrated the superiority of a four-terminal PETE-PV solar cell by simulation. In addition, a PETE prototype converter was developed with light impinging through a transparent anode, i.e., indium-tin-oxide (ITO) film on borosilicate glass, to the cathode surface.

2. Theory and methods

2.1. Working principle

In a PETE-PV solar cell, a portion of solar-photons penetrate a thinfilm cathode and transparent anode of PETE sub-device, and impinges on PV sub-device, thus generates PV effect. PETE-PV solar cells can be divided into three types, i.e., two-, three-, and four-terminal types, as shown in Fig. 1.

In a two-terminal PETE-PV solar cell, the PETE electrons are collected by the anode and then injected in to the valence band of the PV sub-device (a PV cell). The collected PETE electrons recombine with photo-generated holes in the valence band of the PV sub-device. The photo-generated electrons of the PV sub-device are extracted from the conduction-band to an external load. Finally, electrons are reinjected into the cathode. Two-terminal PETE-PV solar cells increase the output voltage of PETE sub-device through the PV effect. However, the PETE current must equal to the PV current. Keeping the two sub-devices operate at their respective MPPs requires specific conditions. In addition, two-terminal PETE-PV solar cell also requires the anode' surface to be a hole-selective contact (e.g., p-type semiconductor), in which the anode work function is raised due to Fermi level pinning. A threeterminal configuration can solve the two issues, in which the n-type, instead of p-type, contact of the PV sub-device faces the cathode. PETE electrons are injected into the conduction band of the semiconductor and the PV electrons are also collected into the n-type contact. The PETE and PV currents are separated independently into to two respective circuits, but share a negative terminal. Whereas, the PETE anode or layer between the anode and PV cell should be a n-type semiconductor with a relatively lager bandgap, to prevent recombination of the collected PETE electrons and the valence-band holes. In a four-terminal PETE-PV solar cell, the PETE anode is light-transparent and separated by an electrical insulating and light-transmitting layer. Therefore, the PETE and the PV sub-devices operate independently in two respective circuits according to the respective principles, and the PV sub-device utilizes only the transmitted photons. Compared to the other two configurations, the type of PV sub-device in a four-terminal PETE-PV solar cell is not limited, including semiconductor PN junction cells, heterojunction cells, perovskite cells, etc.



Fig. 1. Band diagram of PETE-PV solar cells with (a) two-, (b) three-, and (c) four-terminals, respectively. Here, $\Phi_{\rm C}$ and $\Phi_{\rm A}$ are work functions of the cathode and the anode, respectively. $E_{\rm Fn,C}$ and $E_{\rm Fn,A}$ are the Fermi level of the cathode and the anode, respectively. $E_{\rm g,C}$ and $E_{\rm g,PV}$ are the band gap of the cathode and the PV cell, respectively. $V_{\rm TI}$ and $J_{\rm TI}$ are voltage and current density of the PETE sub-device, respectively. $V_{\rm PV}$ and $J_{\rm PV}$ are voltage and current density of the PV sub-device, respectively. $\psi_{\rm m}$ denotes the maximum electron barrier in the vacuum gap. $\Phi_{\rm MC}$ and $\Phi_{\rm MA}$ are the difference between the $\psi_{\rm m}$ and the vacuum levels of the cathode and the anode, respectively. The cathode Fermi level is viewed as zero reference.

2.2. Mathematical model

2.2.1. Modelling of PETE sub-device

Considering space-charge limitation, the net current density J_{TI} of a PETE sub-device is calculated by Eq. (1).

$$J_{\rm TI} = \frac{\Delta n + n_{\rm eq}}{n_{\rm eq}} A_{\rm C} T_{\rm C}^2 \exp\left(-\frac{\psi_{\rm m}}{kT_{\rm C}}\right) - A_{\rm A} T_{\rm A}^2 \exp\left(-\frac{\psi_{\rm m}}{kT_{\rm A}}\right) \tag{1}$$

Here $A_{\rm C}$ and $A_{\rm A}$ are the Richardson's constant of the cathode and the anode, respectively, which can be calculated by $4\pi q m_{\rm h}^* k^2 / h^3$ (being *q* the electron charge, $m_{\rm h}^*$ the effective mass of electrons in the conductionband, *k* the Boltzmann's constant, *h* the Planck constant). Δn and $n_{\rm eq}$ are the non-equilibrium and equilibrium electron concentration in conduction-band on the electron emitting surface, respectively. V_{TI} is the output voltage of PETE sub-device. The maximum output power density of the PETE sub-device can be calculated by Eq. (2).

$$P_{\rm TI} = \max(J_{\rm TI} \cdot V_{\rm TI}) \tag{2}$$

Thus, power conversion efficiency of the PETE sub-device can be calculated by Eq. (3).

$$\eta_{\rm TI} = \frac{P_{\rm TI}}{Q_{\rm sun}} \tag{3}$$

where Q_{sun} is the incident solar energy density.

In Eq. (1), ψ_m is the maximum electron barrier in the interelectrode gap and can be evaluated by Langmuir theory. The electron motive distribution can be obtained by solving Poisson equation, expressed by Eq. (4).

$$\frac{d^2\psi(x)}{dx^2} = -\frac{e^2n(x)}{\varepsilon_0} \tag{4}$$

Here ψ is the electron motive, *n* the electron concentration, ε_0 the vacuum permittivity, and *x* the one-dimensional position. Solving details of the electron motive distribution can be referred in previous works [3,4, 12,13].

Carrier distribution of the semiconductor cathode under solar illumination is also required to obtain J_{TI} according to Eq. (1). Thus, a semiconductor model considering carrier excitation, diffusion and emission is developed. Electron and hole distributions can be obtained by solving Eqs. (5) and (6), respectively.

$$-D_n \frac{d^2 \Delta n}{dx^2} = G - R \tag{5}$$

$$-D_p \frac{d^2 \Delta p}{dx^2} = G - R \tag{6}$$

Here Δn and Δp are the non-equilibrium concentrations of conductionband electron and valence-band hole, respectively. D_n (D_p) is the diffusion coefficient of electron (hole). *G* and *R* are the generation and recombination rates of photon-excited electrons, respectively. *G* is calculated by considering AM1.5 direct + circumsolar spectrum and temperature-dependent absorption coefficient spectrum [3]. *R* includes Radiative, Shockley-Read-Hall and Auger recombinations [14]. The boundary conditions are expressed by Eqs. 7–10.

$$-D_n \frac{d\Delta n}{dx}\Big|_{x=0} = -S_{n,0}\Delta n(0)$$
⁽⁷⁾

$$-D_n \frac{d\Delta n}{dx} \bigg|_{x=t} = S_{n,t} \Delta n(t) + J_{\text{TI}} / q$$
(8)

$$-D_{\rho} \frac{d\Delta p}{dx}\Big|_{x=0} = -S_{\rho,0}\Delta p(0)$$
⁽⁹⁾

$$-D_{p}\frac{d\Delta p}{dx}\Big|_{x=t} = S_{p,t}\Delta p(t)$$
(10)

here S is surface recombination rate and t is the cathode thickness.

In addition, the cathode temperature is determined by the energy balance equation of the cathode, as expressed by Eq. (11).

$$Q_{\rm sun} - Q_{\rm ele} - Q_{\rm rad,C_amb} - Q_{\rm rad,C_A} - Q_{\rm rad,recom} - Q_{\rm unabsorbed} = 0$$
(11)

Here Q_{sun} is the concentrated solar energy, Q_{ele} the heat transferred between the two electrodes by emitted electrons [4], Q_{rad, C_amb} the radiative heat loss from the cathode to the ambient (calculated by the Stefan-Boltzmann law), Q_{rad,C_A} the radiative heat loss between the two electrodes [15,16], $Q_{rad, recom}$ the radiative energy of emitted blackbody photons above the bandgap [2], and $Q_{\text{unabsorbed}}$ the solar energy not absorbed by the cathode.

In our previous work, we have described the model modelling of PETE sub-device in detail [17]. Thus, only the basic principle is introduced in this work and more details are not repeated. A p-type doped GaAs cathode and a ITO anode were applied for the PETE sub-device in the simulation, and material parameters are listed in Table 1.

2.2.2. Modelling of the PV sub-device

A classical PV model is applied to evaluate the performance of the PV cell. The short-circuit current density of PV cell J_{SC} can be obtained by Eq. (13).

$$J_{\rm SC} = q \int_{\omega_0}^{\infty} \frac{Q(\omega)}{\hbar\omega} \cdot EQE(\omega) d\omega$$
(13)

Here ω is photon frequency, \hbar is Planck's constant over 2π , Q is photon energy density irradiated on the PV cell and EQE is the external quantum efficiency of the PV cell.

For a single-junction PV cell, the current density of PV cell is expressed by Eq. (14).

$$J_{\rm PV} = J_{\rm SC} - J_0 \left[\exp\left(\frac{qV_{\rm PV}}{NkT_{\rm PV}}\right) - 1 \right]$$
(14)

Here J_0 is the dark saturation current density, V_{PV} the output voltage of PV cell, T_{PV} the temperature of PV cell, and *N* the ideal factor. The limit of J_0 is a function of the band gap, expressed by Eq. (15).

$$J_0 = J_{00} \exp\left(-\frac{qE_{\rm g,PV}}{NkT_{\rm PV}}\right)$$
(15)

Here $E_{g,PV}$ is the band gap of PV cell. J_{00} can be calculated by Eq. (16).

$$J_{00} = \frac{2\pi k T_{\rm PV} q^3 E_{\rm g,PV}^2}{h^3 c^2} \tag{16}$$

where c is the speed of light. The maximum output power density of the PV sub-device can be calculated by Eq. (17).

 $P_{\rm PV} = \max(J_{\rm PV} \cdot V_{\rm PV}) \tag{17}$

Therefore, power conversion efficiency of the PV sub-device can be calculated by Eq. (18).

Table 1

|--|

Parameter	Value or model		
Bandgap	^a [18]		
Photon absorption spectrum	^a [18,19]		
Carrier mobilities	^a [20]		
Impurity acceptor concentration, N_A	$1 imes 10^{19}~{ m cm}^{-3}$		
Impurity energy level, <i>E</i> _A	0.02 eV [3]		
Effective mass of electrons at the conduction band minimum, m_n^*	0.067 <i>m</i> _e [5,14]		
Effective mass of holes at valence band maximum, m_p^*	0.47 m _e [14]		
Electron Auger recombination coefficient	$1.6 \times 10^{-29} \text{ cm}^6/\text{s}$		
	[19]		
Hole Auger recombination coefficient	$4.6\times10^{-31}~\text{cm}^6\text{/s}$		
	[19]		
SRH lifetime of electrons and holes	both $1\times 10^{-6}s[21]$		
Carrier surface recombination rate on light incident surface,	both 100 cm/s [3,		
$S_{n,0}$ and $S_{p,0}$	22]		
Carrier surface recombination rate on emitting surface, $S_{n_{a}}$ d and $S_{p,d}$	both 0 cm/s [3,14]		
Dielectric function of the cathode	^b [23]		
Dielectric function of the anode	^b [24–26]		
Electron affinity of the cathode	0.6–1.5 eV		
Work function of the anode	0.9 eV		

^a Temperature-dependent models from the cited references.

^b Data or model acquired from the cited references.

$$\eta_{\rm PV} = \frac{P_{\rm PV}}{Q_{\rm sun}} \tag{18}$$

Therefore, the maximum output power density P and power conversion efficiency PCE of the PETE-PV solar cell can be obitain by summing that of the sub-devices. In the simulation, a GaSb PV cell is used for the PV sub-device. The external quantum efficiency (EQE) spectrum can be obtained from experimental report [27]. The band gap of the GaSb PV cell is 0.7 eV (1771 nm).

2.3. Experimental system

We developed the first prototype of PETE converter with light incident through a transparent anode to a cathode surface. The experiment of this prototype can verify both the feasibility of light-transparent anode and concept of anode light-incident PETE device. Fig. 2 illustrates the experimental system, in which the cathode is a p-type silicon wafer and the anode is an ITO on borosilicate glass substrate. Crystalline phase of the Si is $<100>\pm0.5^\circ,$ the resistivity is 0.001–0.01 $\Omega cm,$ and the emission surface roughness is Ra < 0.5 nm. The current-voltage (*I–U*) relation was measured by a Keithley B2901A system source meter. The Si cathode was mounted on a 5-axis manipulator with a 2.93 µm translational precision. The gap size between emitter and collector was kept at \sim 50 µm. The light was provided by a xenon lamp (GLORIA-X500A, Beijing Zolix Instruments Co., Ltd.) with spectral range of about 250-1100 nm. The two electrodes were encapsulated in a vacuum chamber. Vacuum conditions ($<10^{-5}$ Pa) were maintained by a dry scroll vacuum pump (Agilent IDP 7) and a turbo molecular pump (Agilent TwisTorr 304 FS).

Work function of the cathode and the anode samples were determined by using an ultraviolet photoelectron spectrometer (UPS, Thermo ESCALAB XI+). In detail, He I light source (21.2eV) was used to obtain the valence band spectra. The kinetic energy can be calculated by the difference between the photon energy (21.2 eV) and the binding energy. The characteristic cut-off energy in the spectra at low kinetic energy is equal to the work function. Before measurement, Ar + sputtering was applied to remove surface adsorption contamination.

3. Results and discussion

3.1. Simulation results of a PETE-PV solar cell

Fig. 3 shows working characteristics of a four-terminal PETE-PV solar cell for solar concentration ratio of 500. In Fig. 3(a), the PETE subdevice operates at the maximum power output point (MPP) with the output voltage of 0.73 V. The cathode temperature at MPP is 1318 K and the cathode bandgap is 0.9 eV (1378 nm). Fig. 3(a) clearly demonstrates that solar photons are split into three parts of utilization, i.e., quantum and thermal forms for PETE sub-device, and the rest for PV sub-device. Almost all photons with wavelengths greater than 1378 nm pass through the cathode, in which the photons with wavelengths <1771 nm are absorbed by the PV sub-devices to generate electricity by the PV effect. Photons with wavelengths >1771 nm are absorbed in the form of thermal energy, which will increase the temperature of the PV subdevice, and destroy its performance. For simplicity, thermal balance calculations were not considered in the PV sub-device's model. In the simulation, we assumed that the PV sub-device can maintain 373 K with reasonable cooling. Fig. 3(b) demonstrates that the current densities of the two sub-devices at their respective MPPs are not equal. The PETE and the PV sub-devices yield power densities of 9.95 and 6.95 W/cm², respectively. The total power density obtains 16.90 W/cm². If the configuration is two-terminal, the PETE current density should be biased from 13.68 A/cm² at U = 0.727 V to 12.72 A/cm² at U = 0.755 V, reaching the current-match condition. The solar cell yields a power density of 16.55 W/cm² with the voltage of U = 1.301 V. The simulation in this work are based on a four-terminal configuration.



Fig. 2. The experimental system, where panel (a) is schematic diagram, panels (b) and (c) are the practical photos of pure thermionic and PETE modes, respectively. Panel (d) is the front view of the emitting surface.



Fig. 3. (a) The proportion of the AM1.5 \times 500 spectrum utilized by the PV sub-device and by the PETE sub-device in the form of photons and thermal energy, respectively. (b) The current density-voltage (*J*-*U*) and the power-voltage (*P*-*U*) relations of the PETE and the PV sub-devices at solar concentration ratio of 500, respectively.

Solar photon allocation of the two sub-devices can be tuned by the cathode thickness. Fig. 4 gives the power densities varying as a function of the cathode thickness. The power output density of PETE sub-device first increases and then decreases, reaching a maximum value around 1 μ m. Photons absorbed by the PV sub-device decreases monotonously as the cathode thickness increases, leading to a decreasing PV power output density. As shown in Fig. 5, for a low solar energy concentration ratio (e.g., 100), n/n_{eq} drops by about three orders of magnitude as the cathode increases from 0.1 to 100 μ m. As the cathode thickness increases, electron recombination during diffusion process increases, and the cathode temperature and a gradual decrease of the photon enhancement factor n/n_{eq} .

For an electron affinity of 1 eV at 100 solar concentration ratio (Fig. 4 (a)), the PETE-PV solar cell is dominated by PV sub-device and the output power density of the PETE-PV solar cell decreases monotonically with the increase of the cathode thickness. When the electron affinity decreases to 0.6 eV, more electrons can overcome the electron affinity and this lead to a higher PETE performance. The PETE sub-device dominates the whole performance when the cathode thickness excess 0.2 μ m. Fig. 4 (a) and (b) demonstrate a dramatic increase of the

maximum power density of the PETE sub-device from 0.38 W/cm^2 at electron affinity of 1 eV–1.86 W/cm² at electron affinity of 0.6 eV. For electron affinity of 0.6 eV, the total output power density varies as the trend of the PETE one, while reaching a maximum value of 2.48 W/cm² around 550 nm, which increases 33% compared with that of the PETE sub-device (1.86 W/cm²).

For high solar concentration ratio, n/n_{eq} is relatively small and the PETE sub-device mainly relies on thermionic emission due to high cathode temperature. Fig. 4 (c) and (d) shows the power density variations for solar concentration ratios of 500 and 1000, respectively. The output power densities of the PETE sub-device first increase and then remain basically unchanged as the cathode thickness increases. The output power of the total solar cell first slowly increases and then decreases slowly, reaching maximum values at 500 and 350 nm for solar concentration ratios of 500 and 1000, respectively. In all cases, the total output power densities are significantly enhanced by applying the PV sub-device.

Solar concentration ratio is a key factor affecting the performance of PETE-PV solar cells. Fig. 6 shows the output power density and the power conversion efficiency PCE as a function of the solar concentration ratio. For all solar concentration ratio, the optimum cathode thickness



Fig. 4. The output power densities of the PETE sub-device, the PV sub-device, and the whole PETE-PV solar cell as a function of the cathode thickness for different solar concentration ratios, respectively. (a) Solar concentration ratios of 100 and electron affinity of 1 eV. (b) Solar concentration ratio of 100 and electron affinity of 0.6 eV. (c) Solar concentration ratio of 200 and electron affinity of 1 eV. (d) Solar concentration ratio of 100 and electron affinity of 1 eV.



Fig. 5. (a) The photon enhancement factor n/n_{eq} and (b) the cathode temperature of the PETE sub-device as a function of the cathode thickness for different solar concentration ratios, respectively.

changes in the range of 200–600 nm. The three power densities increase linearly with solar concentration ratio and the solar cell can yield a power output density of 25.3 W/cm² at 1000 suns. PCEs of both the PETE sub-device and the total PETE-PV solar cell increases with solar

concentration ratio for the solar concentration ratio of <500. The two PCEs keeps stable for solar concentration ratio of >500 at about 25.5% and 21.5%, respectively. In total, the PETE-PV solar cell gains a 4–8% point PCE boost thanks to PV utilization of remaining photons.

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Fig. 6. (a) The power densities as a function of solar concentration ratio and cathode thickness. (b) The power densities as a function of solar concentration ratio for optimum cathode thickness. (c) The energy conversion efficiency as a function of solar concentration ratio and cathode thickness. (d) The energy conversion efficiency as a function of solar concentration ratio for optimum cathode thickness. For each solar concentration ratio, the cathode thickness is optimized for the maximum output power of the PETE-PV solar cell and the electron affinity is 1 eV.

Electron affinity is an important factor determining electron emission current of the PETE sub-device. Fig. 7 gives the power densities as a function of electron affinity for solar concentration ratios of 100 and 500, respectively. A low electron affinity means a low cathode work function, thus leading to an enhancement in PETE current while a reduction in PETE voltage. Therefore, the PETE sub-device has an optimal electron affinity range. As shown in Fig. 7, the electron affinity ranges of 0.4–0.6 eV and 0.7–0.9 eV are recommended for 100 and 500 solar concentration ratios, respectively. In practical applications, the electron affinity should be optimized according to specific working conditions.

3.2. Experimental demonstration of a PETE sub-device

In order to demonstrate a PETE sub-device with a light-transparent anode, we developed a PETE converter with light impinging through a ITO anode to a Si cathode. Fig. 8(a) gives the measured I–U relations of pure thermionic and PETE modes, respectively, at the cathode temperature of 1223 K. It demonstrates that the cathode saturation current increases by nearly 300 times from 14.6 nA to 4.32 μ A thanks to the photon enhancement. The corresponding cathode work function can be obtained according to Richardson-Dushman equation [28], expressed by Eq. (19).

$$J_{\rm S} = A_{\rm C} T^2 \exp\left(-\frac{\phi_{\rm C}}{kT_{\rm C}}\right) \tag{19}$$

The photo-enhancement effect is embedded into effective work function of the cathode, i.e., the work function under illumination refers to equivalent work function corresponding to pure thermionic emission at the same temperature. The cathode work function of pure thermionic mode is measured 3.91 eV, which is very close to that measured by UPS (4.03 eV, Fig. A2(a)). With illumination, the cathode work function is decreased by 0.6 eV and the open-circuit voltage is enhanced by 0.96 V. In addition, the ITO anode work function is measured 3.15 eV by using an UPS (Fig. A2(b)). Fig. 8(b) illustrates that the cathode saturation current of PETE mode increases gradually from 0.17 μ A to 4.32 μ A as the cathode temperature increases from 973 K to 1223 K. The corresponding cathode work function increases from 2.86 eV to 3.31 eV. The experimental results prove that the PETE converter has extremely high



Fig. 7. The power densities of the PETE sub-device, PV sub-device, and the whole converter as a function of the electron affinity for solar concentration ratio of (a) 100 and (b) 500, respectively. The cathode thickness is 1 μm.



Fig. 8. Experimental results of the thermionic converter with Si cathode. (a) *I*–*U* relations of pure thermionic and PETE modes, respectively, at the cathode temperature of 1223 K. (b) The cathode saturation current and the effective work function as a function of the cathode temperature.

advantages over pure thermionic emission converter.

The *y* axis in Fig. 8(a) represents the absolute value of the current. It should be noted that the net current of the experimental device is negative for positive output voltage, implying that the device consumes energy instead of generating electricity. This phenomenon can be explained as follows. The anode fixture absorbs radiation from the high-temperature cathode, and thus the anode temperature increases. The ITO/borosilicate glass substrate, with a spectral transmittance of 80–90%, absorbs the cathode radiation and incident light energy, also raising the anode temperature. Since the anode work function is lower

than that of the cathode, the anode emission current exceeds the cathode one. Electricity output can be achieved by optimizing the fixture structure, selecting a better anode material (e.g., graphene layer under a quartz substrate, and hydrogen-terminated diamond), or adding cooling measures. In addition, as shown in Fig. 8(a), the open-circuit voltage shifts to the right when the illumination is applied. On the one hand, this is contributed by the large increase in the current emitted by the cathode due to illumination. On the other hand, ITO is an n-type degenerate semiconductor with an optical band gap of 3.5–4.3 eV [29]. Light illumination or high temperatures might reduce the ITO's effective work



Fig. 9. Experimental results of the thermionic converter with molybdenum cathode. (a) *I*–*U* relations of thermionic emission converter at the cathode temperature of 1373 K, with and without illumination, respectively. (b) *P*–*U* relations of thermionic converter with illumination at different cathode temperatures. (c) The output power, (d) the saturation current, the cathode effective work function, (e) the MPP current, MPP voltage, (f) the short-circuit current and the open-circuit voltage as a function of the cathode temperature with illumination.

function, which increases the capability of voltage generation.

Although PETE solar cells have a dramatic potential, it can be found by previous simulation that photo-enhancement effect is not obvious for a Si cathode, n/n_{eq} on emitting surface is usually <10 under AM1.5 concentrating conditions [3]. This is inconsistent with the 300-fold enhancement effect of the experimental results. We speculate that the tested PETE prototype contains not only the PETE effect but also direct photoelectric emission (DPE) process simultaneously. The dramatic coupling enhancement of the PETE and DPE gives an innate advantage. Although this is not the primary interest of this work, an anode incident thermionic converter with a molybdenum cathode was developed and measured to further verify this windfall. Fig. 9 gives the experimental results of the thermionic converter with molybdenum cathode. The y axis in Fig. 9(a) represents the absolute value of the current. At the cathode temperature of 1373 K, the thermionic converter transfers from power consuming mode to electricity generating mode by applying illumination, with the open-circuit voltage changing from -1.2 V to 1.56 V. The cathode saturation current is enhanced by 210 times and the cathode effective work function is reduced from 4.34 eV to 3.69 eV. It should be pointed out that the device consumes energy in the cathode temperature range of 1173–1373 K without illumination. Applying light illumination can enhance electron emission and the device yields output power. The saturation current is increased by two orders of magnitude and the work function is reduced by an average value of 0.55 eV in the whole temperature range by applying illumination. As the cathode temperature increases to 1373 K, the maximum output power and the MPP current increase to 3.02 µW and 3.5 µA, respectively, under illumination. The trends of short-circuit current and open-circuit voltage are similar to the corresponding values at MPP condition. This experimental results verify that introducing light to directly illuminate the cathode electron-emitting surface contributes a great output enhancement. This is due to direct photoelectric emission.

4. Conclusions

In summary, we proposed an original concept of PETE-PV solar cells and compared the working principles of two-terminal, three-terminal and four-terminal configurations. In a PETE-PV solar, solar photons penetrating through PETE sub-device are utilized by PV sub-device to yield additional output power. A photo-thermo-electric model of the PETE-PV solar cell was developed by considering the practical properties of the cathode and the anode materials. The operating

Appendix

characteristics and superiority of a four-terminal PETE-PV solar cell was demonstrated by using the model. Results demonstrated that the PETE-PV solar cell gains a 4–8% point PCE boost due to PV utilization of remaining photons. The optimum cathode thickness range of 200–600 nm were recommended. The PETE-PV solar cell can yield a power output density of 25.3 W/cm² with a PCE of 25.5% for solar concentration ratio of 1000. In addition, we developed a PETE converter prototype with light impinging through a ITO anode to a Si cathode. Our work demonstrates the saturated current of the cathode under illumination is ~300-fold larger than that of pure thermionic mode, and the cathode work function can be reduced by 0.6 eV.

For future work, an experimental research of a complete PETE-PV solar cell should be conducted to have a complete proof-of-concept and study the practical operating characteristics.

CRediT authorship contribution statement

Hao Qiu: Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Visualization, Writing - original draft, Writing - review & editing. Haoran Xu: Writing - review & editing. Gang Xiao: Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gang Xiao reports financial support was provided by Zhejiang Provincial Natural Science Foundation. Gang Xiao reports financial support was provided by Fundamental Research Funds for the Central Universities.

Data availability

Data will be made available on request.

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Fig. A1 gives the EQE spectrum of the GaSb solar cell, which is obtained from Ref. [27]. Fig. A2 (a) and (b) show the valence band spectra of the silicon cathode and the ITO anode as a function of the kinetic energy, respectively. The corresponding work functions of the silicon cathode and the ITO anode were measured 4.03 eV and 3.15 eV, respectively. Fig. A3 shows the experiment photographs of the thermionic converter with a molybdenum cathode and a ITO anode.



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Fig. A2. UPS spectrums for (a) the silicon cathode and (b) the ITO anode as a function of the kinetic energy. The red lines were introduced to visualize the cut off level.



Fig. A3. Photographs of the thermionic converter. (a) Molybdenum cathode and its electric heater. The converter was encapsulated in a vacuum chamber. Panel (b) is the side view of the emitting surface. Panel (c) and (d) are the front views of the emitting surface without and with illumination, respectively.

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