Solar energy conversion through thermally enhanced external photoelectric emission from NaCsSb photocathodes

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Abstract

The combination of thermionic and photoelectric emission for solar energy conversion has been studied for years. There are two concepts for this synergistic process: hot electron conversion (HEC), which supposes that the excited carriers equilibrate among themselves, and photon-enhanced thermionic emission (PETE), which is based on the excited electrons' complete thermalization with the material. Here we present a new concept, thermally enhanced external photoelectric emission (TEPE), which describes the synergistic process under the photoelectric emission model. An experimental setup was applied and a photodiode with a bialkali cathode was tested. A conversion efficiency of $1.97 \times 10^{-2}\%$ under 400 nm illumination at 20°C was achieved, and a double enhancement of the efficiency was observed with the temperature rising to 70°C. Although the conversion efficiencies were small, the experiment demonstrates the energy conversion based on external photoelectric emission and the enhancement effect of heat.

Keywords:

Thermally enhanced external photoelectric emission; solar energy conversion; NaCsSb photocathode

1. Introduction: internal/external photoelectric effect and thermionic effect

As the energy crisis and environmental pollution become more and more serious, there is a growing demand for clean and efficient energy. Among many choices, solar energy has become the most effective solution to this problem, and the conversion of light into electrical energy is a practical way of using solar energy. This conversion usually takes one of two forms: the “thermal” approach and the “quantum” approach. The thermal approach uses solar radiation as the heat source for a classical heat engine, a Stirling engine for example, or converts heat to electricity directly through thermionic emission [1,2]. The quantum approach is realized using photovoltaic (PV) cells, which have been widely used for photoelectric conversion. This takes advantage of the internal photoelectric effect, absorbing solar photons with energies above the semiconductor’s band gap to excite electrons into conduction band, which diffuse into electrodes and generate current [3]. The external photoelectric effect was found a century ago and has been widely used in the photoelectric detection field, rather than for power generation [4-6]. However, the commonality between the external photoelectric effect and thermionic emission is that electrons are emitted into the vacuum and collected by the anode. This makes it worthwhile to use the former for solar energy conversion, and maybe both of the them simultaneously. The benefits of this combination are that both high-energy photons, used in photoemission, and low-energy photons, used in thermionic emission, could be well used together.

Smestad previously presented an experimental setup showing that a combination of photoemission and thermionic emission could be used to increase current from a commercial photocathode [7]. In this experiment, the combined action of light and heat was explained with the concept of hot electron conversion (HEC) [8]. More recently, Schwede and coworkers at Stanford University proposed a new concept for high-temperature electron harvesting. Photon-enhanced thermionic emission (PETE) is based on vacuum thermionic emission, enhanced by photon excitation, causing an increase in the conduction band electron concentration [9]. These two mechanisms can be distinguished for the fate of carriers given excess energy by high-energy photons. In HEC systems, the excited electrons equilibrate among themselves, reaching a thermal equilibrium temperature that is much higher than the environmental temperature. However, when it comes to PETE systems, photoexcited electrons rapidly thermalize within the conduction band to the equilibrium thermal distribution according to the material’s temperature.

In this paper, the conversion of light into electrical energy based on the external photoelectric effect is studied, and the enhancement of heat is also considered. A photodiode comprising a bialkali photocathode is employed at different temperatures, $T < 100^\circ\text{C}$, to demonstrate that the power converted by a heated and illuminated phototube is greater than that obtained either heated in the dark or illuminated at room temperature. Although the conversion efficiency is small in this example ($\sim 10^{-2}\%$), the experiment demonstrates how two forms of solar energy can be used simultaneously.

2. External photoelectric effect with photodiodes

A typical photodiode with the vacuum-gap parallel-plate architecture is shown in Fig. 1(a). Usually the cathode is a semiconductor material and the anode is a kind of metal material, with a bias voltage or load resistance between two electrodes. An external photoelectric effect occurs in a simple three-step process: first, electrons in the cathode are excited by solar radiation into the conduction band. Second, these excited electrons diffuse throughout the cathode. Third, electrons that arrive at the surface with sufficient energies can emit directly into vacuum and are collected by the anode, generating current (Fig. 1(b)). In the solar spectrum, all the photons with energies above the semiconductor's band gap energy, E_g , could be absorbed by a certain probability. $n(E)$ is the energy distribution of the excited electrons in the conduction band and $N(E)$ the collected electrons. These would, for example, be in units of $\text{cm}^{-3}\text{eV}^{-1}$. Among the excited electrons, only those with energies above semiconductor's electron affinity, χ , could be emitted, and only a fraction of the emitted electrons are collected by the anode, so $N(E) \leq n(E)$. The fraction collected depends on the input photon energy, $h\nu$, the work function of the materials, and the bias voltage V ($V > 0$ means that the anode is connected to a positive voltage and the cathode to a negative voltage, and vice versa).

Fig. 1. (a) Typical photodiode architecture. Photons incident on the back surface of the cathode and electrons are emitted from the front surface, collected by the anode (transmission mode). Or photons can be incident on the front

surface, if the anode is transparent or pierced (reflection model). A bias voltage should be applied between two electrodes or a load (working as an energy converter). (b) Energy band diagram for a nondegenerate semiconductor-based photodiode. E_C is the bottom of the conduction band energy and E_V is the top of the valence band energy, the difference between which is equal to the band gap, E_g . E_0 is the vacuum energy level. In a p-doped semiconductor material, the Fermi level, E_{fC} , is close to the top of the valence band. φ_C and φ_A are the cathode and anode work functions, respectively.

It was Einstein who first proposed that the kinetic energy (KE) of the emitted electron is equal to the difference between the energy of the incident photon, $h\nu$, and the work function, φ_C , of the absorber material.

$$KE = h\nu - \varphi_C \quad (1)$$

E_T is the threshold energy barrier that the emitted electrons must overcome to arrive at the anode ($KE > E_T$).

$$E_T - E_0 = \varphi_A - \varphi_C - qV \quad (2)$$

In Fig. 1(b), V is big enough so that E_T is lower than E_0 . This is the saturated condition, which means that all the emitted electrons could be collected by the anode. (Another case, $E_T > E_0$, will be discussed later.) J represents the net output current density (current per unit area), which is the difference between the cathode current, J_C , and the anode current, J_A :

$$J = J_C - J_A \quad (3)$$

In most cases, the anode is a kind of metal material, which has so high a work function that J_A is negligible. However, when the temperature of the anode is quite high or the work function quite low, the anode current cannot be ignored. Now, the power of the photodiode, P , can be calculated by Ampere's law:

$$P = J \times V \quad (4)$$

Most phototube detectors are operated under positive bias conditions. In this case, P is a positive value, which means that the device is consuming energy from an external supply. However, a solar converter must produce energy. That is to say, P should be negative and the phototube should be operated under a negative bias voltage. Under this condition, electrons depend entirely on their own kinetic energy to reach the anode, generating current and power output. In fact, according to the circuit equivalence principle, the applied negative bias is equal to a resistor with the equivalent

voltage drop. This point of view is verified by the following experimental setup, and a positive output power is indeed obtained.

3. Bialkali photodiode experimental setup

Fig 2. (a) Experimental setup. A xenon lamp and a monochromator are used to provide monochromatic light, which is transferred by an optical fiber. The photodiode is anode side up so that the cathode can be heated by the resistor under it. The temperature could be controlled from 20°C to 70°C by adjusting the electric current of the external DC power source. (b) Schematic circuit diagram used to determine the current-voltage (I–V) curve and corresponding power-voltage (P–V) curve of the bialkali photodiode. The direction of a positive current I is counterclockwise. A positive bias voltage V means that the anode is applied with a high potential, and a negative V means that the cathode is applied with a high potential. (c) Spectral sensitivity curve of the NaCsSb photocathode.

An experimental setup was applied and a photodiode with a bialkali cathode was tested (Fig. 2(a)). The structure of the photodiode is a vacuum ceramic cylinder chamber, each side of which is a piece

of glass. The cathode material (NaCsSb) is on the inner surface of the front glass (this side down in the experimental setup). The anode is a metal mesh, and this makes it possible to illuminate the cathode from the back side of the photodiode (Fig. 2(b)). The material of the anode is Ni-Al alloy. The work function of the Ni-Al alloys is not constant within the several miscibility gaps of the Ni-Al phase diagram, and is not lower than the work function of the respective pure metals (4.6 eV for Ni and 4.3 eV for Al) [10]. This value of work function is too high for collecting electrons under a negative bias voltage. However, we know that cesium coating can reduce the work function of metals. For example, cesiated tungsten anodes are used in thermionic converters for their high-temperature stability and low work function (1.7 eV), and cesiated titanium's work function can reach nearly 1 eV[9]. So we speculate that some cesium atoms attached to the surface of the anode during the process of manufacturing the photodiode. The specific value of the work function has not been measured. But we can estimate from Fig. 1(b) and Fig. 3(a) that ϕ_A , the work function of the anode, is about 2.8 eV ($\phi_A = \phi_C + qV_{ss}$; ϕ_C is the work function of the cathode, 1.8 eV; V_{ss} is the saturation bias voltage, about 1 eV). The spectral sensitivity of this photodiode is shown in Fig. 2(c). The distance between the two electrodes is about 5 mm. The vacuum sealing material of this photodiode is indium alloy, whose melting point is about 90°C, so the photodiode could not be heated to a higher temperature (no more than 70°C in this experiment). The monochromatic light was provided by a xenon lamp and a monochromator, and the wavelength varied from 200 to 2000 nm, with an accuracy of 1 nm. Different input optical power of 5~9 $\mu\text{W}/\text{cm}^2$ was measured by a Rm-3700 Universal radiometer, and the output current, on the order of nA, was measured by a Keithley model 6517B electrometer, which also provided a bias voltage. The illuminated area of the cathode was about 1 cm^2 , so the current values, I , are numerically equal to the current density values, J .

4. Experimental results

The full I–V curve measured using the setup of Fig. 2(a), at room temperature (20°C), is shown in Fig. 3(a). The green highlighted area illustrates the power consumption regime, where electrons are pulled to the anode by a positive bias voltage. This means that the photodiode consumes energy from the power supply. The red highlighted area illustrates the power generation regime, where electrons overcome a negative bias voltage to reach then anode. Unlike the former, electrons rely on their own kinetic energy and have the ability to generate power. Three typical operating points are marked in

Fig. 3(a), and the corresponding energy band diagrams are shown separately in Fig. 1(b), Fig. 3(b), and Fig. 3(c). Despite being illustrated by monochromatic light, the excited electrons in the conduction band form a certain energy distribution at temperatures above absolute zero, instead of focusing on one energy position. This makes it possible for some high-energy electrons to emit to the anode. The quantity is affected by the potential barrier height of the anode, which could be controlled by the bias voltage.

Fig. 3. (a) External photoelectric emission current of the photodiode versus the applied voltage (full I-V curve), under 400 nm 6.6 $\mu\text{W}/\text{cm}^2$ illumination. The range of the applied voltage ranges from the negative cutoff voltage to the positive saturation voltage. Points a, b, and c correspond to saturation, zero bias, and a cutoff situation, respectively. The energy band diagram of the saturation situation is shown in Fig. 1(b), where all the emitted electrons were collected by the anode. (b) Energy band diagram of the zero bias situation. (c) Energy band diagram of the cutoff situation.

In order to observe the influence of heat, an external power source was applied to heat the cathode, and the I-V curves are measured at different temperatures (Fig. 4(a)). The power production of each corresponding curve is also shown in Fig. 4(a). At such low temperatures, purely thermionic emission was negligible, and that is therefore removed from Fig. 4(a). Nonetheless, the results are

sufficient to show that external photoelectric emission can be enhanced by heat. Furthermore, the I–V curves under different wavelength illuminations were measured, including low- and high-temperature conditions. With different wavelength illuminations, the energy conversion efficiencies were different. Relatively high-energy conversion efficiency, $1.97 \times 10^{-2}\%$ at 20°C , is achieved when the wavelength is around 400 nm, compared to $1.48 \times 10^{-2}\%$ around 300 nm and $0.16 \times 10^{-2}\%$ around 500 nm (Fig. 4(b)). When the cathode is heated to 70°C , the conversion efficiency almost doubles, reaching $3.82 \times 10^{-2}\%$ ($1.61 \times 10^{-2}\%$ around 300 nm and $0.28 \times 10^{-2}\%$ around 500 nm). Although the conversion efficiency is very small, these experiments demonstrate the possibility of using the external photoelectric effect for solar energy conversion and the enhancement effect of heat.

Fig. 4. (a) I–V curves and P–V curves (power versus voltage) of the photodiode under 400 nm illumination. Solid lines with different colors represent current curves at different temperatures, and dashed lines with the same colors represent corresponding power curves. The temperature was controlled by adjusting current of the resistor, and it was difficult to accurately control the temperature. Therefore, this is just a qualitative result, rather than quantitative one. (b) I–V curves of the photodiode under different illuminations and different temperatures. Solid lines with different colors represent different wavelength illuminations, dotted in black and red representing 20°C and 70°C , respectively.

5. Analysis and discussion

It has been demonstrated in the above experiment that the conversion of light into electrical energy can be realized through the external photoelectric effect and that this process can be enhanced by heat, despite the low conversion efficiency. In this section, some theoretical details will be discussed.

5.1. External photoelectric conversion theory

For a photoelectric converter, or a solar cell, the key point is the characteristics of the output voltage and current, which can be well reflected in its I–V curve. Therefore, it is necessary to calculate the current of the photodiode under different reverse bias voltages. In other words, we need to know how many electrons could be collected by the anode in unit time, $N(E)$, and the current density is as follows:

$$J_c = q \cdot \int N(E) dE \quad (5)$$

where q is the electron charge.

Under a certain illumination, the excited electrons will form an energy distribution, $n(E)$, in the conduction band, but only the normal component of any electrons' kinetic energy contributes to the emission process. Consider the emitting surface of the cathode to be the xy -plane and the outward direction to be the positive z -direction. Let v_x , v_y , and v_z be the x , y , and z components of the velocity of any electron. We define $n_z(E)$ for z -component energy distribution of all excited electrons, whose normal component of energy E is defined as follows:

$$E = \frac{1}{2} m |v_z|^2 \quad (6)$$

where m is the mass of the electron. Here, E could be a negative value when v_z is negative. A negative E is not conducive to the emission. Electrons with a normal component of energies above the vacuum energy level, E_0 , could be emitted, and among them, only those with energies above the threshold energy, E_T , could be collected by the anode. When E_T is negative (Fig. 1(b)), all the emitted electrons can be collected, thus:

$$\int N(E) dE = \int_{E_0}^{\infty} n_z(E) dE \quad (7)$$

when E_T is positive (Fig. 3(b) and Fig. 3(c)).

$$\int N(E) dE = \int_{E_T}^{\infty} n_z(E) dE \quad (8)$$

By substituting Eq. (2), Eq. (7), and Eq. (8) to Eq. (5), the current density of the photoelectric converter can be derived as follows:

$$J_c = \begin{cases} q \cdot \int_{E_0}^{\infty} n_z(E) dE, qV > \varphi_A - \varphi_C \\ q \cdot \int_{E_T}^{\infty} n_z(E) dE, qV < \varphi_A - \varphi_C \end{cases} \quad (9)$$

As stated earlier, if energy is to be generated, the photodiode must be operated under a converse bias voltage. If φ_A is bigger than φ_C (usually, metal anodes have high work functions), E_T is consequentially bigger than E_0 (Fig. 3(c)). The photodiode works against a retarding field, where many electrons with lower energies cannot reach the anode, so the current density is rather small and rapidly decreases as the voltage increases. Under this condition, the power output of the photodiode is quite small and the fill factor (FF) is small too. This is the main reason for the low conversion efficiency of the experiment in this paper. However, if materials with a low work function are used as the anode, φ_A will be smaller than φ_B and the situation will be quite different. Recently, a phosphorus-doped diamond was reported to have a work function of 0.9 eV; this value has been used in many PETE theoretical simulations [11,12]. While $\varphi_A - \varphi_C < qV < 0$, there will be a flat-band condition, where the current density, J_C , remains unchanged. If the reverse bias exceeds the difference of the work functions of the two electrodes, J_C will decrease as E_T increases. The shape of the I-V curve depends on the z -component energy distribution, $n_z(E)$. The problem of photoelectric emission is very complicated, as it is very difficult to evaluate the effect of illumination on the velocity distribution of the electrons. Some classic theoretical models can help, for example, Wentzel's formulation and the theory of Tamm and Schubin [4].

With Eq. (9), it is easy to calculate the power output, P_{out} , by

$$P_{out} = -(J_c - J_A) \cdot V = \begin{cases} J_A \cdot V - qV \cdot \int_{E_0}^{\infty} n_z(E) dE, qV > \varphi_A - \varphi_C \\ J_A \cdot V - qV \cdot \int_{E_T}^{\infty} n_z(E) dE, qV < \varphi_A - \varphi_C \end{cases} \quad (10)$$

where the symbol “—” stands for a positive power generation. J_A is the reverse current from the anode's photoelectric and thermionic emission.

5.2. Enhancement effect of heat

Thermionic and photoelectric emissions are two kinds of electron emission mechanisms; they can be combined in one process. However, the synergistic effect of these two mechanisms is worthy of study. Ross et al. proposed an idea of hot electrons for the full use of the solar spectrum, where the

excited carriers equilibrate among themselves but not with the surroundings [8]. On the other hand, in the PETE system proposed by Schwede, all the excited electrons rapidly thermalize within the conduction band to the equilibrium thermal distribution according to the material's temperature [9]. These are two opposite kinds of extreme situations: in the HEC system, hot carriers must be removed before equilibrating with the surroundings; in the PETE system, electrons are supposed to be fully thermalized to the ambient temperature. However, conditions are usually not this ideal, so thermally enhanced external photoelectric emission (TEPE) is proposed here. In a TEPE system, the excited electrons will not completely equilibrate among themselves or thermalize to the material's temperature. The energy distribution of excited electrons is associated with the incident photon energy.

Unlike the results in Ref. 8, wavelength-related electron energy distribution was observed at low temperatures (Fig. 5). Obviously, with shorter wavelength illumination (greater photon energy), the curve of normalized electron energy distribution moves to the right. This provides evidence for photoelectric emission rather than thermionic emission. Similar results were also obtained in nitrogen-doped diamond films [13].

Fig. 5. Electron energy distributions at 20°C under 300 nm, 400 nm, and 500 nm illumination. The value of the electron energy is relative to the threshold energy barrier, E_T . A negative value means that the electron was emitted with energy below E_T .

As we all know, photoelectric follows Einstein's formula (Eq. 1) at absolute zero temperature. A certain threshold frequency of light, ν_0 , which will just eject electrons with zero velocity, could be easily defined by

$$\nu_0 = \frac{\phi_c}{h} \quad (11)$$

But when the temperature rises above zero, there will not be a distinct threshold frequency. Photons with frequencies below ν_0 also eject electrons. In other words, electrons ejected by the same frequency photons gain higher kinetic energies at higher temperatures. This is because there are electrons with energy greater than the Fermi level, E_f , at temperatures above zero. As a result, electrons' energy distribution under certain illumination changes with increasing temperatures and eventually enhances the photoelectric emission current.

Actually, PETE and TEPE are the same in essence, as in both electrons gain sufficient energy from photons and heat. The difference is the way of describing the synergistic process: PETE is based on thermionic emission, while photo-excitation plays an enhancement role; TEPE is a photoelectric emission process, which is enhanced by heat. It is hard to define which description is more accurate. From the experimental results, the energy distribution of emitted electrons has the characteristics of thermionic emission under high temperatures, but it is relative to the wavelength of incident photons under low temperatures. The advantage of TEPE is that it does not require too high a temperature, which is demanded in a PETE system. After all, the thermal stability of cathode materials is limited, especially for cesiated coatings, which have been widely used for work-function lowering [14].

5.3. Several issues for future research

Although this experiment demonstrated TEPE solar energy conversion, there are still many improvements needed for TEPE devices for higher conversion efficiency. As we can see in the energy band diagram in Fig. 3(b), electron emission is restricted by the surface barrier. The application of negative electron affinity (NEA) semiconductor materials is a very good solution to this problem. In an NEA cathode, an electron excited to the conduction band will be emitted from the surface because it can gain energy by dropping to the vacuum level [6,15]. Therefore, an NEA surface is very important for increasing the cathode's emission efficiency.

In addition, it is necessary to take the anode work function into consideration. It determines how many emitted electrons can be collected by the anode and how high the operating voltage could be. Whether in PETE systems or in TEPE systems, anodes with low work functions are essential [9,16]. However, low work function anodes bring another problem: large reverse current. Fortunately, this can be restrained by some techniques, for example by cooling or shading the anode.

A varied-doping structure, gradient or exponential, has been applied on III–V semiconductors to

improve photoelectric emission performance [17,18]. In a varied-doping photocathode, a built-in electric field is formed by the downward band bending region from the bulk to the surface, which contributes to electron diffusion and emission. Compared to a uniform-doping structure, higher quantum efficiencies are obtained in varied-doping photocathodes. More importantly, the built-in electric field is conducive to elevate the z-component energy distribution of all excited electrons; this is of great significance for photoelectric energy conversion.

Additionally, the space charge effect is another issue that should be taken into consideration. At high current densities, a large quantity of space charge will develop near the surface of the cathode. A negative potential, generated by the space charge, can force the emitted electrons to return to the cathode. Ito and Cappelli suggested using optically pumped cesium plasma to neutralize the space charge in PETE converters [19]. This method is useful for TEPE systems.

6. Conclusions

Thermionic and photoelectric emission are two traditional ways for the conversion of light into electrical energy. The combination of these two processes has been studied for its high-energy conversion efficiency. Unlike two previous mechanisms, HEC and PETE, a new concept, TEPE, has been proposed for solar energy conversion. The TEPE process has been observed with an experimental setup with a NaCsSb photodiode. The correlation of the electron kinetic energy distribution and the incident light wavelength indicates that it is a photoemission process rather than a thermionic one. The enhancement effect of heat is obvious, as shown in the experimental results. Because the quantum efficiency of the alkali cathode is not high and the photodiode cannot be heated to high temperatures, the conversion efficiencies in the experiment are very low. There are many things that can be done to improve the conversion efficiency, including light trapping [20], varied doping, NEA, space charge neutralization, and using low work function anodes. Compared to PETE, low demand for temperature makes TEPE devices easier to use. The combination of thermionic and photoelectric emission through TEPE is a very promising mechanism for solar energy conversion.

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