Advanced Energy Conversion Materials
http://ojs.wiserpub.com/index.php/AECM/

Perspective

Local Thermo-EMF and Nano-Limits of Efficiency

Stanislav Ordin

Russian Academy of Sciences, Moscow, Russia
E-mail: stas_ordin@mail.ru

Received: 18 September 2024; **Revised:** 24 October 2024; **Accepted:** 29 October 2024

Abstract: Thermoelectronics includes invariant elements of thermoelectricity, thermoemission and theory of p-n junction. And the local Nano-Thermo-Electromotive Forces (EMFs) discovered and used to build this unified theory of nano-scale, which are orders of magnitude superior to the seebeck EMF, are not only a diagnostic tool for any microelements, but can also be used to increase the Energy conversion efficiency of all traditional electronic devices. But most importantly, they prompted understanding that between the micro and marco-worlds, Physics missed a scale where their linear approximations do not work, but the Thermoelectronic Laws of the nano-scale work. Whereas the macroscopic response from nano-effects, in contrast to its acceptance as due from quantum effects, with reference to Thermodynamics, due to not taking into account prigogine's production of Local Entropy, was generally considered forbidden. Thus, Thermoelectricity, which was initially included in the fundamentals of Nonequilibrium Thermodynamics, returned again to the Fundamental Science of the nano-scale missed by Physics and actually expanded Electronics to thermoelectronics. Taking into account the thermoelectronic effects allowed us to identify previously unaccounted aspects of increasing the efficiency of energy conversion of the scale missed in theories. In addition, the refinement and expansion of the theory of thermoelectricity became the background (basis) of all evidence-based fundamental physics.

Keywords: thermoelectricity, potential barriers, thermal emission, nano-effects, thermoelectronics

1. Introduction

The well-known thermoelectric Seebeck effect and its inverse Peltier effect [1-4] allowed to establish the principle of symmetry of the Casimir-Onsager kinetic coefficients and, thus, formed the basis of nonequilibrium Thermodynamics of diffuse flows [5, 6]. But ballistic local effects were actually dropped from consideration under the erroneous pretext that Thermodynamics supposedly forbids the macroscopic manifestation of local effects. Whereas the question of whether it is allowed to use macroscopic manifestations of quantum effects was not even raised. And as was shown in the cycle of my works, previously it was diffuse thermoelectricity that was considered [7], which does not take into account the concentration thermodynamic force, like the theory of p-n junction [8-10], and does not fully take into account the temperature force, like in the theory of thermoemission [11, 12]. That is why thermoelectricity has a low efficiency limit for converting thermal energy into electrical energy, which cannot be exceeded by any technical tricks.

But the technology of modern thermoelectricity is still based on the purely diffuse Ioffe model. Whereas the discovered local Thermo-EMFs allow the efficiency limit to be raised several times due to ballistic effects. Refinement

DOI: https://doi.org/10.37256/aecm.6120255740

and expansion of the theory of thermoelectricity allowed not only to raise the efficiency of traditional macroscopic thermoelectric devices several times, but also to increase the sensitivity of thermal detectors by an order of magnitude.

Previously, the upper limit of the prevalence of Local Thermo-EMFs over conventional diffuse seebeck coefficients, which are observed on macro scales, was analyzed and investigated in detail. And it was shown that already on scales of the order of several microns, local Thermo-EMFs, due to their gigantic value of the order of a volt, like the photoelectric effect, prevail over diffuse thermo-EMFs, usually less than a millivolt. It follows from this that it is impossible to neglect the temperature force when calculating p-n junctions in micron-scale Electronics-their real energy characteristics can differ from the calculated ones by several times, and current-by orders of magnitude.

But modern Electronics, unlike Thermoelectricity, has long ago, purely empirically mastered the nano-scale of the element. But it is the local Thermo-EMF that allows diagnostics of extremely thin energy barriers that can be used to control currents in nano-elements.

The schottky effect leads to a fairly extended bend in the energy bands near the boundary of semiconductors with different types of conductivity, which, in fact, leads to a decline (negative resistance) on the Volt-Ampere Characteristic (VAC) in tunnel diodes. So for reliable operation in the initial section of the VAC, it is necessary to use semiconductors with a large bandgap and low permittivity. The ultimate analysis of the lower boundary of the “normal” initial section of the current-voltage characteristic and local Thermo-EMF can be carried out on the basis of a vacuum contact of metals with different work functions. In this area, in principle, there is a large reserve from the area of the above-mentioned thermoemission. But it should be taken into account that earlier thermionic models were built on the basis of experiments with large currents and also use diffuse models for their analysis.

When current flows over barriers at the boundary of a metal with a semiconductor, a counter-EMF also arises, which is actually equivalent to a decrease in the applied voltage. This is probably related to the fact that the measured change in the work function from the metal to the semiconductor is usually an order of magnitude less than the change in the work function from the metal to the vacuum.

The nano-scale of electronic devices and the impetus for the need to take into account local Thermo-EMF on potential barriers in solids. On the other hand, it allowed to conduct their precision measurements.

And taking into account these local effects in p-n junctions, on the one hand, showed that on scales of the order of the electron mean free path, their efficiency is several times greater than the theoretical maximum achievable using traditional diffuse seebeck and peltier thermoelectric effects used in thermoelectric generators and thermoelectric refrigerators. This theoretical conclusion was preceded by a large cycle of experimental and theoretical studies on increasing the efficiency of homogeneous, superstructured and textured thermoelectrics [13-28], which showed that the saturation of the efficiency of thermoelectrics observed for several decades is due to the fact that the theoretical limit has actually been reached for the diffuse seebeck and peltier effects. On this basis, the guidelines were chosen for both precision experiments on contacts and artificial structures, and for refinement and expansion of the theory of Thermoelectricity [29-39], due to the construction of a unified phenomenology of thermo-electronics. And methodically, these studies became the basis (background) for the development of evidence-based physics [40], which resulted in a revision of the basic concepts of physics concerning quantization and the principle of relativity. And as was shown in my noted works, the technology was fixed at the level of the last century. And even modern nano-calculations of p-n junctions are built on the basis of models developed for experiments with large elements and for average statistical temperatures throughout the element, i.e. they do not take into account the main thermodynamic force of thermo-electronics-temperature.

2. Local Thermo-EMF of contact areas

Initial studies of anomalous contact effects occurring in massive thermoelectrics resulted in normal studies of the dependence of the Thermo-EMF and output resistances on the size of the sample along the direction of heat flow propagation. And, as a consequence, both the occurrence of anomalously large EMFs on contacts and their small output resistance were explained as local ballistic effects (Figure 1).

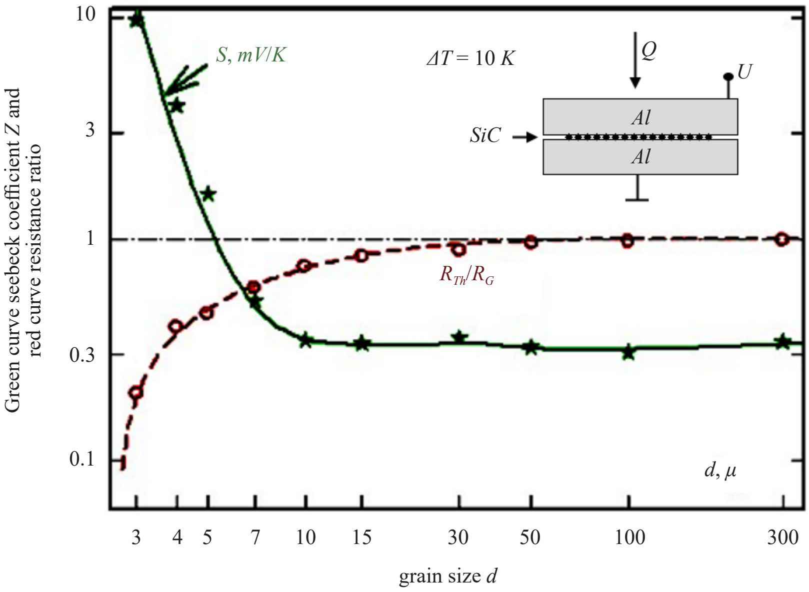


Figure 1. Dependence of Thermo-EMF *S* and the ratio of their output resistances to input (galvanic) R_{Th}/R_G on the size of silicon carbide crystals *d*

As shown in Figure 1, at sample thicknesses *d* of less than 10 microns, an anomalous (for the diffusion theory of thermoelectricity) increase of the thermoelectric power *S* by an order of magnitude is observed. At the same time, the drop in their output resistance R_{Th}/R_G indicates the prevalence of local ballistic effects over diffuse ones not only in voltage, but also several times in power. But, since no fundamental changes in the volume properties were revealed when the crystal sizes were reduced, a more detailed study of their influence on the contact areas was required.

It followed from this that an experimental object of study on a micron scale with well-studied technical and physical characteristics was needed. And it was understood that the proven technology of microelectronics just gives a well-isolated from extraneous influences and well-studied contact-this is the p-n junction.

That is why the main analysis of local Thermo-EMF was aimed at the p-n junction, which, it would seem, had already been studied up and down since the time of Losev. And that is why it was so reluctantly accepted by electronics specialists that the known empirical discrepancies in their characteristics are related to the limitations of the theory of this p-n junction itself. Although the most advanced of them were happy, because an explanation was found for the discrepancy between the theory of the transistor and its real characteristics. If the diffusion theory of thermoelectricity missed the main thermodynamic force of the theory of the p-n junction-the concentration one, then the theory of the p-n junction missed the main thermodynamic force of thermoelectricity-the temperature one. That is, in the theory of the p-n junction, only its average temperature was taken into account, while Prigogine's local entropy Production and, as a consequence, temperature differences in the p-n junction itself were not taken into account.

And the correction of the physics of the p-n junction itself, following from the cycle of thermoelectric studies, taking into account the local EMF, was carried out on the basis of the photoelectric effect, which was also well studied in it, since the photo-EMF and Local thermo-EMF in it, as was shown in previous works, are determined by the value of the potential barrier and are of the same order. This also prompted, as was noted earlier, to use the method of their displacement by current (Figure 2) for qualitative assessments of the shift of the Volt-Ampere Characteristic (VAC) of the p-n junction by the temperature force, tested in photo-detectors.

As was shown in previous works, the corrected physics of the p-n junction allowed us to understand that the high efficiency of local Thermo-EMF with their antiphase connection with photo-EMF reduces the efficiency of photodetectors. But the role of near-contact nano-regions in devices using was not well enough understood. Therefore, the creation of contacts to the p-n junctions themselves remains rather an art-the lot of empirical technology. So the use of artificial shift of the work function of metal contacts on silicon crystals gave the Thermo-EMF values, the magnitude of which (according to Seebeck) poorly correlated with the change in the work function of the metals used for the contacts: copper (approximately 4.7 eV), magnesium (3.66 eV), platinum (approximately 5.5 eV) (Table 1).

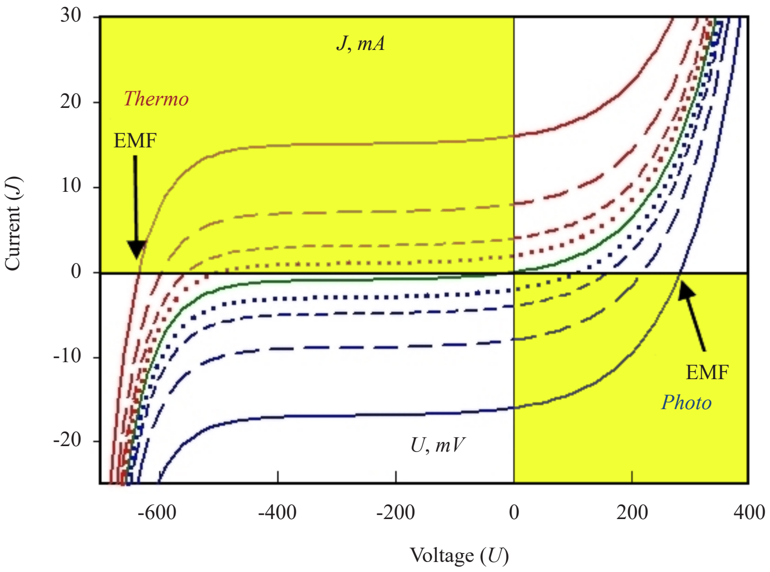


Figure 2. Calculated current shifts of the I-V characteristics of an ideal p-n junction by equivalent (in power) flows: thermal (red curves) and light (blue curves), with a 2-fold increase in flows. Generation quadrants are shown in yellow

Table 1. Dependence of Thermo-EMF of silicon samples on the direction

Sample	Longitudinal *α*, *mV*/*K* seebeck coefficient	Anode	Cathode	Transverse *α*, *mV*/*K* total Thermo-EMF
i-Si	-1.5	Cu	Cu	-1.01
		Pt	Cu	-0.37
		Pt	Mg	-0.72
n-Si	-0.8	Cu	Cu	-0.80
		Pt	Mg	-0.73
p-Si	+1.2	Cu	Cu	+0.56
		Pt	Mg	+1.01

As can be seen from Table 1, if the measurements of the Thermo-EMF of 300-micron-thick silicon plates at a temperature difference of 50 K along the plate yield a volumetric (independent of the contact material) Seebeck coefficient, then at a temperature difference across the plates the role of the near-contact regions significantly affects the total Thermo-EMF of the sample. The scale at which local Thermo-EMF prevails in silicon carbide is, as shown in Figure 1, and confirmed by studies of silicon p-n junctions, several microns. On the other hand, as shown, at thicknesses of the order of tens of angstroms, tunneling of local Thermo-EMF sharply decreases, similar to how the negative branch of the current-voltage characteristic arises in tunnel diodes. However, from these control experiments it is clear that at the nano scale it is necessary to additionally take into account the distortion of the energy diagram of the semiconductor in the near-contact region. But for a more qualitative consideration of local Thermo-EMF, a comparison of their characteristics with thermionic ones, which were initially used in setting up the experiments, was also used. In thermoemission, within the framework of its primitive models and using the work of metals exiting into vacuum, a displacement technique similar to Figure 2 (Figure 3) was used in principle.

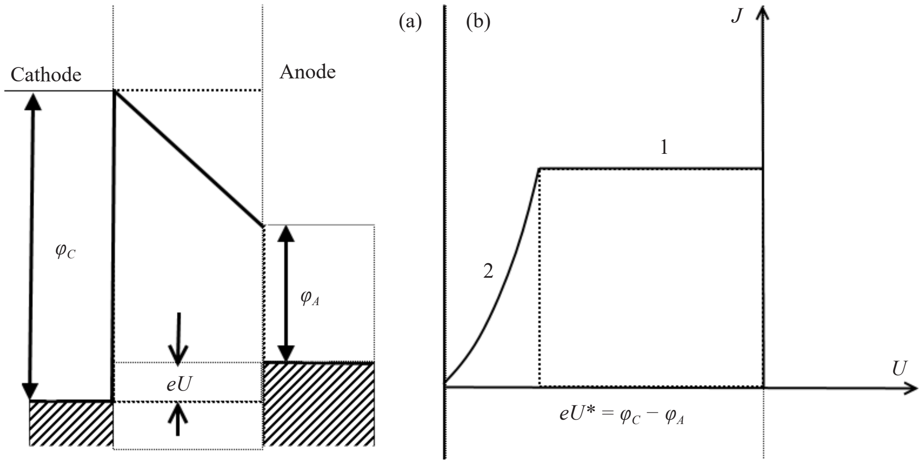


Figure 3. Energy diagram (a) and ideal current-voltage characteristic (b) of thermionic converter (from work [10])

But in the theory of thermionic emission itself, in the phenomenology of which only temperature and concentration thermodynamic forces were used, and the electric force was used only as a small correction when adjusting the experimental data to the theory, remained. So the experimental current-voltage characteristics of both electron tubes with a vacuum gap and converters with low-temperature plasma are far from the "ideal" current-voltage characteristic shown in Figure 3, but are qualitatively similar to the current-voltage characteristic in Figure 2 (shifted by local Thermo-EMF). In the theory of thermionic emission itself, the work function is not strictly used for the exit of electrons into a vacuum. In fact, it is identified with the value of the potential barrier, which is small for the metal-vacuum contact (Figure 4).

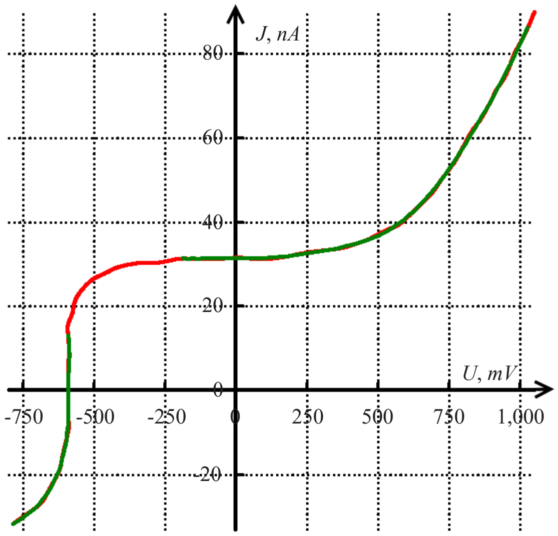


Figure 4. Initial section of the V-A characteristic of the vacuum gap with slight heating of the cathode with the work function of the cathode being less than the work function of the anode by approximately 0.6 eV

Both the ideal model emission current-voltage characteristic (Figure 3) and the experimental current-voltage characteristic of the vacuum gap confirm the correctness of the choice of the current-voltage characteristic bias by the temperature force precisely by the current. But for the exit of electrons from the metal into the semiconductor, the barriers that arise near the boundary (measured) also correlate with the work function only qualitatively, but often differ from it even by the order of magnitude. To determine such strong changes in the measured potential barriers in semiconductors, the current-voltage characteristic of an analog of a thermionic converter was measured, in which a single crystal of silicon carbide 100 microns thick was used instead of a vacuum gap (Figure 5).

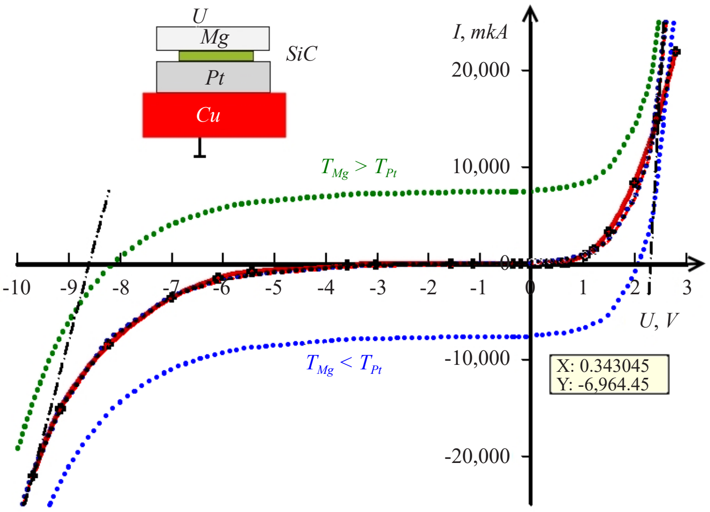


Figure 5. Experimental current-voltage characteristic of a converter on a silicon crystal and its model temperature bias by current (the work function of magnesium is approximately 3.66 eV, the work function of platinum is approximately 2 eV higher)

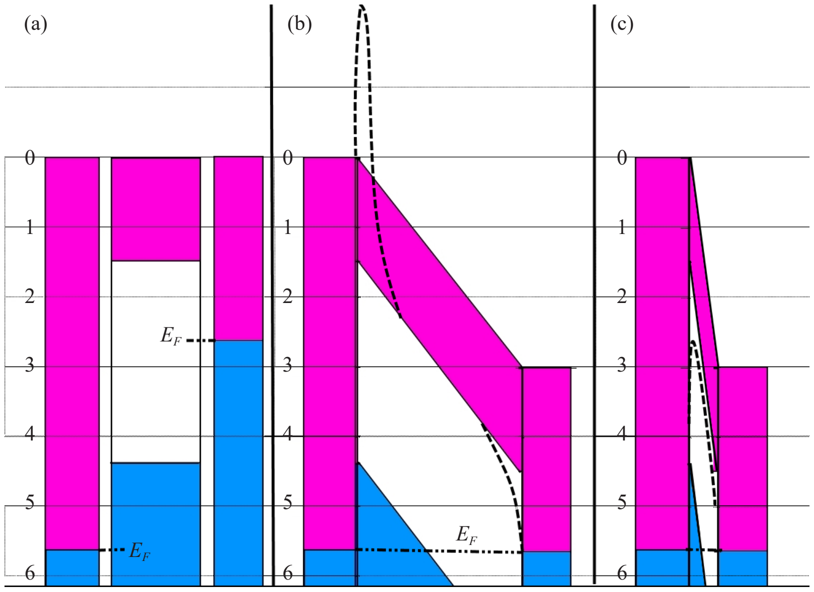
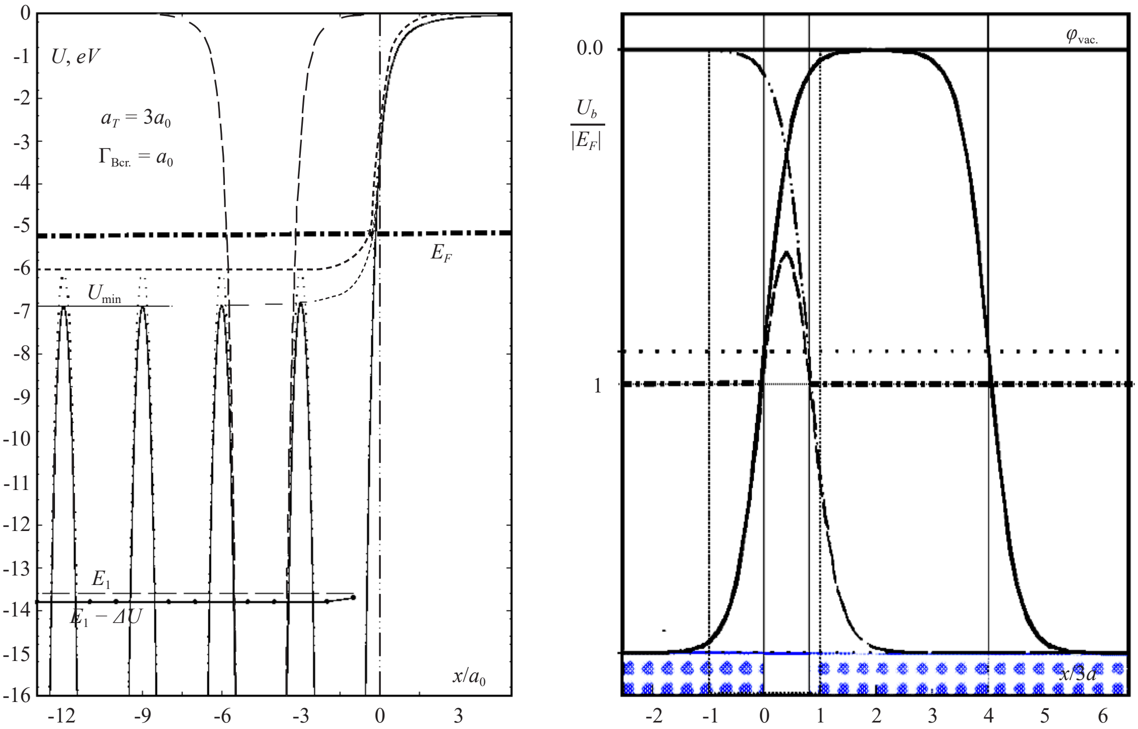


Figure 6. Transformation of the bottom of the conduction band of silicon carbide (dashed line) due to contact effects for a thick (b) and thin (c) single crystal in the gap between magnesium and platinum

The potential barrier of approximately 2.3 electron volts observed on the positive branch in Figure 5, which is somewhat lower than the work function of magnesium in vacuum, can be easily explained by the fact that the conduction band of carbide lies 1.4 electron volts below the vacuum level. So the additional potential barrier near the contact of silicon carbide with magnesium is anti-blocking. The potential barrier of approximately 8.8 electron volts observed on the negative branch of the current-voltage characteristic in Figure 5, which is somewhat higher than the work function of platinum in vacuum and approximately 2 times higher-in the conduction band of silicon carbide. So, a blocking barrier appears at this boundary of silicon carbide (Figure 6).

The decrease in the vacuum level in the gap between metal contacts, similar to the description in [41-43], is a consequence of the formation of a Schottky barrier near the metal boundary (Figure 7a) and the imposition of Schottky potentials of adjacent boundaries (Figure 7b).



(a) (b)

Figure 7. Formation of a surface barrier from atomic potentials (a) and lowering of the barrier in the gap between metals due to the superposition of surface potentials when metal surfaces approach each other (b)

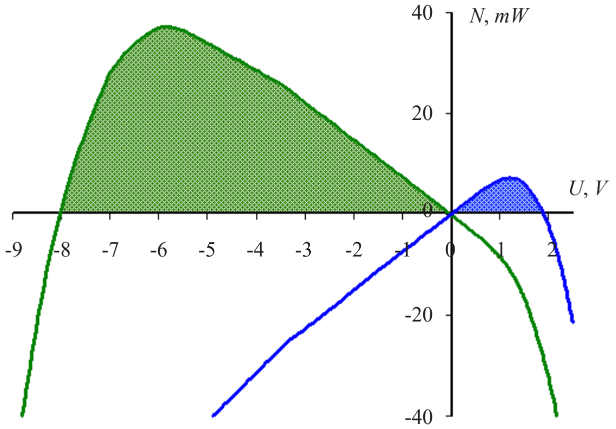


Figure 8. Power output (shaded areas under the curves) of a converter based on silicon carbide, corresponding to its model-shifted I-V characteristics in Figure 5

The energy diagram in Figure 6 allows you to see/understand the fundamental difference between local Thermo-EMF in this thermionic converter and p-n junction. Unlike the p-n junction, where the sign of Local Thermo-EMF is determined exclusively by the polarity of the p-n junction itself, for the crystal, heating from the magnesium side will simply give high conversion efficiency, and heating from the platinum side will give the same sign of local Thermo-EMF as the photo-EMF, but low conversion efficiency (Figure 8).

3. Conclusion

It was previously shown that the thermionic model, due to the temperature force, gives a significant correction to the p-n junction energy diagram itself. The analysis presented in this paper showed that local Thermo-EMF themselves, due to the Schottky effect, can change significantly on nano scales-from tunneling (about 10 Angstroms) to microns. So the choice of the optimal thickness and a separate crystal between the plates of metals with different work functions affects the efficiency of converting electrical and thermal energy (both in one direction and vice versa). At the same time, in the p-n junction, it is necessary to take into account the additional distortion of the energy diagram, even when creating ohmic contacts, which were previously believed not to affect the p-n junction itself.

Conflict of interest

The author declares no competing financial interest.

References

[1] Rowe DM. *CRC Handbook of Thermoelectrics*. Boca Raton, FL: CRC Press; 1995.

[2] Ordin SV. Refinement and supplement of phenomenology of thermoelectricity. *American Journal of Modern Physics*. 2017; 6(5): 96-107.

[3] Stilbans LS. The thermoelectric phenomena. In: *Semiconductors in a Science and Engineering*. Moscow: Publishing House an Academy of Sciences USSR; 1957. p.113-132.

[4] Jan T. *Photo-and Thermo-Electric Phenomena in Semiconductors*. Moscow: Publishing House of the Foreign Literature; 1962. p.254.

[5] Prigogine I. *Modern Thermodynamics: From Heat Engines to Dissipative Structures*. John Wiley; 1998.

[6] Gyarmati I. *Non-Equilibrium Thermodynamics, Field Theory And Variational Principles.* Berlin, Heidelberg: Springer-Verland; 1970.

[7] Ordin SV. Refinement and supplement of phenomenology of thermoelectricity. *American Journal of Modern Physics*. 2017; 6(5): 96-107.

[8] Sze SM, Li Y, Ng KK. *Physics of Semiconductor Devices*. John Wiley & Sons; 2021.

[9] Epifanov GI. *Physical Foundations of Microelectronics*. Moscow: Mir Publisher; 1971.

[10] Roderick EH. *Metal-Semiconductor Contacts*. Moscow: Publishing House "Radio and Communications"; 1982.

[11] Ordin S. Ballistic thermoelectricity. *Advanced Energy Conversion Materials*. 2023; 4(2): 139-146.

[12] Moizhes BY, Pikus GE. *Thermoemission Converters and Low-Temperature Plasma*. 1973.

[13] Ordin S. Nano and frontier aspects of biomedicine. *Biomedical Journal of Scientific & Technical Research*. 2022; 46(2): 007335.

[14] Ordin SV. *Detector of Radiation on base HSM*. Accepted Application for Russian Patent No 93036965/25 (037129). 1994.

[15] Ordin SV. Thermoelectric waves in anisotropic cristal of higher manganese silicide. In: *Proceedings of the XV International Conference on Thermoelectrics*. Pasadena, CA; 1995. p.212-214.

[16] Ordin SV. Optimization of the operating conditions of thermocouples allowing for nonlinearity of the temperature distribution. *Semiconductors*. 1997; 31: 1091-1093.

[17] Ordin SV. Peltier heat as a volume property and optimization of working regimes of thermo elements in real conditions. In: *XVI International Conference on Thermoelectrics*. Dresden; 1997.

[18] Ordin SV, Fedorov MI. Phenomenological analysis of thermoelectric processes in heavy and doped semiconductors.

In: *XVII International Conference on Thermoelectrics*. Japan; 1998.
[19] Ordin SV, Wang WN. *An Extension of Linear Phenomenology and New Thermoelectric Effects*. MRS; 1999.
[20] Okamoto Y, Ordin SV, Kawahara T, Fedorov MI, Miida Y, Miyakawa T. Infrared-reflection characterization of sintered SiC thermoelectric semiconductors with the use of a four-component effective medium model. *Journal of Applied Physics*. 1999; 85(9): 6728-6737.
[21] Ordin SV, Wang WN. Thermoelectric effects on micro and nano level. *Advances in Energy Research*. 2011; 9: 311-342.
[22] Sokolov IA, Ordin SV. Dimension effect in lattice absorption of silicon carbide. In: *CLEO/Europe. 2005 Conference on Lasers and Electro-Optics Europe.* Munich, Germany: IEEE; 2005. p.317.
[23] Ordin SV, Sokolov IA, Zjuzin AJ. *Thermoelectric Processes in p-n Junctions, Works of X Interstate Seminar: Thermoelectrics and Their Application*. Petersburg, Russia: Russian Academy of Sciences; 2006. p.41-47.
[24] Ordin SV, Zjuzin AY, Ivanov Y, Yamaguchi S. Nano-structured materials for thermoelectric devices. In: *NATO Workshop "Advanced Materials and Technologies for Micro/Nano-Devices, Sensors and Actuators"*. Petersburg, Russia; 2009.
[25] Ordin SV, Zjuzin AY, Ivanov Y, Yamaguchi S. Nano-structured materials for thermoelectric devices. In: *The 29th International Conference on Thermoelectrics*. Shanghai, China; 2010.
[26] Ordin SV. Optimization of the operating conditions of thermocouples allowing for nonlinearity of the temperature distribution. *Semiconductors*. 1997; 31: 1091-1093.
[27] Ordin SV. Ballistic model of the movement of electrons over potential hill. In: *Interstate Conference: Thermoelectrics and Their Application*. Petersburg, Russia; 2015. p.199-203.
[28] Ordin S. *Achievements and Challenges of Thermoelectricity*. Rusnor. Available from: http://rusnor.org/pubs/articles/12707.htm [Accessed 2 August 2015].
[29] Ordin SV, Zhilyaev YV, Zelenin VV, Panteleev VN. Local thermoelectric effects in wide-gap semiconductors. *Semiconductors*. 2017; 51: 883-886.
[30] Ordin SV. Cardinal increase in the efficiency of energy conversion based on local thermoelectric effects. *International Journal of Advanced Research in Physical Science*. 2017; 4(12): 5-9.
[31] Ordin S. *Refinement of Basic Physical Models*. LAP Lambert Academic Publishing; 2017.
[32] Ordin SV. Experimental and theoretical expansion of the phenomenology of thermoelectricity. *Global Journal of Science Frontier Research-Physics & Space Science (GJSFR-A)*. 2018; 18(1): 1-8.
[33] Ordin SV. Anomalies in thermoelectricity and reality are local thermo-EMFs. *Global Journal of Science Frontier Research-Physics & Space Science (GJSFR-A)*. 2018; 18(2): 59-64.
[34] Ordin SV. Local (NANO) thermoelectric effects. *Journal of Modern Technology & Engineering*. 2020; 5(1): 107-109.
[35] Ordin S. *Modern Physics*. LAP Lambert Academic Publishing; 2021.
[36] Ordin SV. Mistakes in the theory of p-n junction and fundamentals of thermophotoelectronics. *World Journal of Condensed Matter Physics (WJCMP)*. 2023.
[37] Ordin S. Foundations of thermoelectronics. *Journal of Materials and Polymer Science*. 2022; 2(3): 1-6.
[38] Ordin SV. Introduction to thermo-photo-electronics. *Journal of Electronic & Information Systems*. 2023; 5(1): 51-66.
[39] Ordin S, Snytkina S. Resonant thermo electronic effects. *Academic Journal of Engineering Studies*. 2023; 3(4): 1-7.
[40] Ordin S. Exclusion of exclusivity. Bridge between Quantization and Relativity above the stormy stream of pseudo-scientific speculation. In: *Foundations of Quantization Principles*. Jenny Stanford Publishing Pte Ltd; 2024.
[41] Ordin S. Foundations of quantization principles (thematic collection of recent studies reviewed in Scientific Journals). *Journal of Advances in Social Science and Humanities*. 2022; 8(4): 69-72.
[42] Abdelhady S. Proper understanding of the natures of electrons, protons, and modifying redundancies in electromagnetism. *Journal of Electromagnetic Analysis and Applications*. 2023; 15(5): 59-72.
[43] Ordin S. Foundations of magnetic field definition. *Applied Sciences Research Periodicals*. 2024; 2(5): 1-10.