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Foundations of Polymer Thermoelectronics.

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Abstract

Building the foundations of polymer thermoelectronics became possible only after the correction of thermodynamic errors in traditional, semiconductor electronics. It was these errors that determined the saturation of its operating parameters of semiconductor electronic devices, in particular, the saturation of the maximum clock frequency of processors. But even if in semiconductors, although these thermodynamic errors manifested themselves not only in the instrumental, but also in the technological aspect, they did not prohibit semiconductor electronics themselves.

Whereas, without eliminating thermodynamic errors, the technology of polymers itself made it possible to create only a limited range of materials with low electrical conductivity - materials with low leakage currents, and not polymers with different types of conductivity required for electronics and with given potential barriers for current carriers. In this work, it is shown that there are no fundamental prohibitions either on the creation of polymers with high conductivity, or on the creation of thermionic devices based on them. It's just that ALL polymer physics is "stuck" on the use of flat electron orbitals, which Pauling introduced for "two-dimensional" graphite and for which he received the Nobel Prize. But, Pauling himself, as an honest scientist, having discovered his mistake, tried to correct it by introducing "curved" orbitals for graphite itself. Now, after the restoration of the Planck-Einstein Quantization, it is shown how to get the correct orbitals instead of the mystical Schrödinger wave functions [1, 2, 3].

1. *Stanislav Ordin, «Gaps and Errors of the Schrödinger Equation»», Journal of Materials and Polymer Science (J mate poly sci), 2022; 2(3): p. 1-6.*
2. *Stanislav Vladimirovich Ordin, Book: "FOUNDATIONS OF Planck-Einstein Quantization (Thematic collection of recent studies reviewed in scientific journals)." LAP LAMBERT Academic Publishing, 2021, ISBN 978-620-4-21066-7, 110 pp.*
3. *Stanislav Ordin, "Foundations of Quantization Principles". Jenny Stanford Publishing Pte Ltd, 2023, 235 pp.*

Historical errors of semiconductor electronics and their correction

In Science, unfortunately, it often happens that the Ideas of its Creators are not fully understood, but picked up by interpreters, are actively promoted, but with distortions and errors. So, now that the fundamental sections of Physics have reached the modern level, it became clear that an entire industry has been formed - electronics, the instrumental and technological problems of which are related to the fact that the theory of p-n junction is built in violation of the laws of non-equilibrium thermodynamics and that this is largely determined by distortion Ideas that the Founders of electronics came up with purely intuitively.

So it is in the p-n junction, first discovered in silicon carbide and described in the 30s of the last century by Oleg Losev, who himself immediately intuitively realized that this was a current device. And he was able to use it almost immediately: he created on it an LED, a photodiode, and a resistance transformer, which the Nobel laureates called in short (in English) a transistor. But the physics of the p-n junction and the description of the operation of the listed devices based on the p-n junction were built by analogy with a radio tube, which, in principle, is a field device. Thus, when solving various problems for semiconductor devices in the p-n junction, the cause-current and the effect-voltage were rearranged. And the prominent physicist Abram Fedorovich Ioffe did not fully understand Losev then, who was half a century ahead of modern electronics. But Academician Ioffe, not like the current "luminaries of science," succeeded in conferring on him a candidate of physics and mathematics. Sciences without defending a dissertation. And only after almost 100 years, the return to Losev's current circuit made it possible to significantly improve the characteristics of semiconductor devices.

The thermodynamic discovery by Ilya Prigogine of the production of local entropy helped to restore the correct description of the physics of the p-n junction, which made it possible to understand that in the p-n junction, described for the reasons noted above, within the framework of a truncated concentration-electric phenomenology, it is necessary to use an

extended phenomenology supplemented by a heat flow (Ordin, 1991; Ordin, 1993; Ordin, 1995; Ordin, 1997; Ordin, 1997; Okamoto et al., 1999; Ordin & Wang, 2008; Ordin et al., 2009; Ordin et al., 2010; Ordin & Wang, 2011; Ordin et al., 2017; Ordin, 2017; Ordin, 2017; Ordin, 2017; Ordin, 2018; Ordin, 2018; Ordin, 2018; Ordin, 2018; Ordin, 2018; Ordin, 2020; Ordin, 2020; Ordin, 2021; Ordin, 2021). The standard band structure of the transition itself (Fig. 1) is modified when the temperature force is taken into account (Fig. 2).

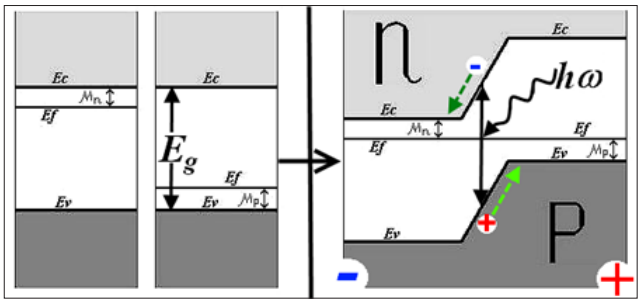

Figure 1: The traditional scheme for the transformation of the energy bands of semiconductors with different types of conductivity upon their contact and the opening of the p-n junction formed in this case when the i-region is irradiated with light.

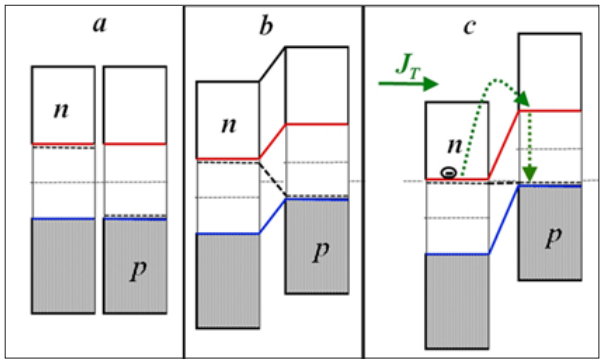

Figure 2: Energy diagrams of two semiconductors of different types of conductivity: a - before bringing them into contact, b - equilibrium state after their contact at equal temperatures, c - equilibrium state with heat flow through the p-n junction.

At the same time, the energy diagram of the equilibrium p-n junction is somewhat modified, which, without taking into account the temperature force, given as shown in Fig. 1, the potential barrier value approximately equal to the band gap of the semiconductor. Taking into account the temperature force, in the absence of a heat flux, the value of the potential barrier turns out to be equal to half the band gap (Fig. 2b). And when it turns on the heat flow, the value of the potential barrier will increase until a tunnel breakdown occurs (Fig. 2c).

As shown in Fig. 2b, between semiconductors brought into contact in an equilibrium state due to the balance of electric and concentration forces, the difference in electric potentials at the contact (red line is the bottom of the conduction band, blue line is the top of the valence band) is equal in magnitude and opposite in sign to the difference at the boundary of the concentration potential (dashed black line). Thus, given in Fig. 2b, in accordance with the complete system of equations for thermodynamic forces and flows, it already allows eliminating the theoretical equal to 2 in the description of the transition without a temperature gradient, which was associated with an empirical coefficient due to the imperfection of materials. The potential difference across the transition plates is equal in this case to half the band gap. And the equality of concentration potentials corresponds to the Local Thermo-EMF and occurs, of course, only with a heat flow through the transition (Fig. 2c). In this case, the current-voltage characteristic (CVC) of the p-n junction, of course, depends on the temperature difference on its plates (Fig. 3). And on the I–V characteristic of the upper left quadrant, an area of positive currents arises at negative voltages at the p-n junction, which, in full accordance with the concepts of generators (the simplest - an electric battery), is an area for generating electrical energy due to the flow of heat flowing through the junction.

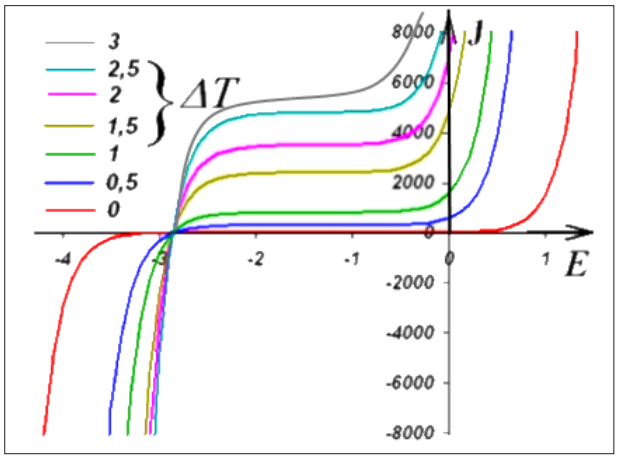

Figure 3: Generator characteristic of a p-n junction, showing its tunneling self-breakdown.

The oscillator characteristic of the transition is constructed without taking full account of the specifics of the equilibrium state, taking into account the local production of Prigogine's entropy. In this case, zero current through the junction corresponds to a zero temperature drop. But in fact, the p-n junction is Maxwell's demon - a "gear" wheel separating hot and cold current carriers, in principle, allowed at the micro level by the production of Prigogine's Local Entropy. And the mechanism of its operation is obvious from Fig. 2: when semiconductors come into contact, its asymmetry (polarity) occurs.

At the same time, to start the electron transfer process, an energy equal to half the band gap is sufficient, while after their transfer and annihilation with holes, their reverse transfer requires an energy equal to the full band gap. So, a local temperature drop occurs on the plates of the p-n junction, which determines the local thermodynamic equilibrium. In this case, the experiment shows that the CVC has a shape fundamentally similar to that shown in Fig. 3.

The use of extended concentration-electrical-thermal phenomenology made it possible to correctly take into account

Losev's current p-n junction, and to transfer the "anomalous" thermoelectric power discovered by Tauc in the p-n junction to the category of normal-local, and to describe new experimental results of studies of contact thermoelectric power. In addition, the extended phenomenology made it possible to understand that macroscopic thermoelectricity is artificially limited only by diffuse thermoelectric materials and showed that for diffuse thermoelectrics, the efficiency of thermoelectric conversion achieved in practice is already close to the theoretical limit.

In addition, extended phenomenology has shown that the efficiency of thermoelectric conversion based on local thermoelectric power has no diffuse limit and can be radically increased by several times compared to that achieved with traditional diffuse thermoelectrics. This was experimentally confirmed on the developed detectors based on Local Thermo-EMF in silicon junctions, the volt-watt sensitivity of which was obtained three orders of magnitude higher than that of detectors based on the traditional macroscopic Seebeck effect.

At the same time, the extended phenomenology shows that there can be complex, three-phase effects in the p-n junction, which makes it possible to optimize, in particular, the combination of local thermoelectric effects with photoelectric effects in it.

Polymer Thermoelectronics

The historical consideration of electronics without taking into account heat flows has imposed a number of restrictions on the design of devices and devices based on it. In addition, they led to a number of "theoretical" bans on the existence and the possibility of registration, which was revealed in the study of the Local thermo-EMF described above. At the same time, before turning specifically to polymers, it is necessary to make a significant clarification. Lack of understanding of the physics of Local thermodynamic effects not only imposed a ban on the Local Effects themselves, but also led to a false attribution (even .WIKIPEDIA) of the device to a photo thermoelectric converter, while it contains a simple photo-conversion of the thermal radiation flux.

But, at the same time, if the very existence of the base of electronics - semiconductor crystals was not "forbidden" theoretically: the theory of semiconductor devices, although with errors, was built on crystal physics, then there were "prohibitions" regarding polymers - not taking into account heat flows leads to erroneous ideas about the polymers themselves (Ordin, 2022) and, thus, about the very basis of polymer electronics.

As shown earlier, polymers have two fundamental differences from crystals. First, the polymerization process itself is based on endothermic chemical reactions. And, as a consequence, the minimum of potential energy during the formation of a polymer does not exist without taking into account the decrease in the kinetic energy of not only the polymer itself, but also the environment. Secondly, polymerization, as a kind of rough similarity to LIFE, is necessarily not a static, but a dynamic process, which leads to a certain metastable state when the flow of kinetic energy in the form of heat from the environment stops.

The neglect of these fundamental points led to a purely formal use of the correlation of the chemical structure and electrical conductivity of polymers, which was initially (without doping) considered negligible for electronics - it was taken into account only as small leakage currents in polymer insulators. Although Professor Rosenstein and Dr. Vlasova R.M. at the Leningrad Physico-Technical Institute. A.F. Ioffe Academy of Sciences of the USSR hatched half a century ago the idea that in polymer films not only high electrical conductivity, but also superconductivity can be obtained. Apparently, the misunderstanding of the two fundamental points noted above did not allow them then to realize their idea (Vlasova et al., 1971; Vlasova et al., 1975; Vlasova et al., 1977).

The noted correlation was attempted to be described using the flat orbitals introduced by Pauling and the van der Waals forces (György Inzelt, 2008; Naarmann, 2000; McGinness, 1972; Sirringhaus, 2005).

This in itself, as was previously shown for graphite and boron nitride, is a rough consideration even for layered crystals (Ordin & Sharrupin, 1998; Ordin et al., 2003; Ordin, 2018).

But the endothermic nature of the formation of not only a single molecule, but the entire polymer radically changes the idea of the position of the molecular energy level of an electron on a chemical bond. If in crystal physics the molecular level of an electron is located below the atomic level, then for a polymer it is higher than the atomic level, and the (thermo) stabilization of the polymer is fundamentally related to its nonlocality and the total decrease in the potential energy of the polymer and the environment. In this regard, polymers are similar to the same graphite, which has an enormous electrical conductivity in layers (Ordin, 2018). So, in fact, the "gate" is the end of the polymer chain, where there is a violation of electron delocalization at the polymer level. Misunderstanding by Rosenstein and Vlasova R.M. the role of delocalization at the polymer boundaries, as it has now become clear, and then gave a negative result on the monoatomic polymer films grown by them on the surface of solutions. Whereas the implementation of the Idea of Professor V.N. Bogomolov on the creation of monoatomic metal chains in dehydrated 6-angstrom mordenite channels made it possible for the author of this article (then a young employee of the Ioffe Institute of the Academy of Sciences) to detect anomalously high conductivity in these chains back in 1975. As it has now become clear that the formation of these "metal polymers" occurred precisely due to the technologically used pressure of 35 kbar, which is necessary to overcome the surface tension of the molten metal so that it enters the mordenite crystal in the form of monatomic jets. The method of Foucault currents used for registration gave a sharp jump in the conductivity of the crystal, when the metal compressed by high pressure was destructured into atomic filaments. The usual metallic three-dimensional delocalization of the so-called "free" electrons is a really common phenomenon

and leads to a high, but significantly limited in magnitude, electrical conductivity of metals. Artificially created at the expense, as V.N. Bogomolov, non-wetting forces at the metal-insulator interface, and ensured complete (one-dimensional) delocalization of metallic materials and a cardinal (by orders of magnitude) increase in the average electrical conductivity of the sample. These pioneering results with nano-objects were obtained even before the advent of nano-technologies, which now, in principle, make it possible to create artificial metal polymers without ultrahigh pressures. This will make it possible to drastically reduce, in comparison with electronics, energy consumption in thermoelectronics and make high-temperature superconductors more meaningful.

Conclusion

As already noted, if energy diagrams of semiconductor transitions have already been constructed for semiconductor electronics, albeit with errors, then for polymers one must start from "ZERO", i.e. from the construction of zone diagrams of the polymers themselves in the bulk and at the boundary, taking into account the Endothermic nature of their formation. But this is better than stupidly sorting out options from erroneous cubes to explain purely empirical patterns, which, of course, are not of a General Character. But there are NO theoretical prohibitions on the creation of a new class of polymers and thermionic devices based on them.

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