Ročník 2019 electroscope Číslo II

Thermoelectric generator in low thermal gradient operation

L.Znbill, J.Boušek
Department of Microelectronics, Faculty of Electrical Engineering and Communication
Brno University of Technology,
Technická 3058/10, Brno 616 00
E-mail : xznbil01@stud.feec.vutbr.cz , bousek@feec.vutbr.cz

Anotace:
Pomocí levných výrobních procesů a dostupných materiálů byl navržen jednoduchý termogenerátor. Výrobní postupy zahrnují sítotisk, vakuové depozice, plazmatickou aktivaci povrchu pomocí výboje s dielektrickou bariérou a modifikované metody depozice PEDOT. Pro zpracování výstupního napětí z termogenerátoru byl navržen jednoduchý a spolehlivý DC/DC měnič pracující se vstupním napětím od několika desítek mV a výstupním napětím na úrovni několika voltů. Pro tento měnič byly připraveny transformátory s velkým převodním poměrem.

Abstract:
A simple thermo-generator was designed using inexpensive manufacturing processes and available materials. Manufacturing processes include screen printing, vacuum deposition, surface plasma activation by dielectric barrier discharge, and modified PEDOT deposition methods. A simple and reliable DC / DC converter working with input voltage from several tens of mV and output voltage on the level of several volts was designed for processing the output voltage from the thermo-generator. Transformers with a large conversion ratio have been prepared for this converter.

INTRODUCTION

Although the thermoelectric effect has been used for a long time to measure temperature, thermoelectric generators are not available in large scale. Therefore, new possibilities of preparation of thermoelectric cells with orientation on available materials and cheap production are of great interest.

For the proper design, the thermal conductivity of thermo-module material between hot and cold side should be as low as possible and the same way the electrical conductivity of the respective thermoelectric materials should be high.

High thermal conductivity is a problem by almost all inorganic semi-conductive materials. Organic semiconductors could have the thermal conductivity almost one order lower but their electrical conductivity is usually very low.

The properties of the resulting thermo-cell depend not only on the material choice but also on preparation methods. The choice of a suitable pair of materials for thermocouples is complicated by the fact that there are only few materials that have a negative Seebeck coefficient. Of these materials, nickel with a Seebeck coefficient (against platinum) of $S = -15\ \mu VK^{-1}$ is the most preferred.

Largely used thermocouple, referred as thermocouple of type K, is based on the combination Ni-NiCr materials and has the temperature sensitivity close to 40μV/K. When made from Ni and NiCr wires it can be used up to 1100°C. The temperature range of thermocouples prepared by mass production methods will be considerably smaller and is determined by deposition techniques of the active layers and substrate properties.

METHODS OF PREPARATION

Screen printing

A major problem here is the tuning of the binder to active component ratio. The binder must provide not only mechanical stability but also electrical properties and the possibility of electron tunneling between conductive grains.

The possibility of tunneling and thus also the conductive properties of the final layer depends considerably on the grain size and the manner of grinding the active ingredient. To facilitate the tunneling process, it is preferred that the micro-particles of the active material have irregular shapes with sharp edges.

Composition and structure of printed layers varies according to the used components. The Seebeck coefficient then could not correspond to pure material.

Vacuum deposition

Deposition of very pure layers is possible. If the choice of technology is appropriate, the composition of the prepared layers corresponds to the composition of the raw material. The mask with apertures in angle of 60 degrees in respect to the axis of the thermocouple tape facilitates a simple mask process. After the deposition of first layer the mask is reversed and the second material of the thermoelectric pair is deposited. The materials are this way mutually bonded on the ends. The straight legs of the structure are also in angle of 60 degrees.

The principle of this mask is shown in figure Fig.1.
A disadvantage of this simple mask is poor utilization of the substrate area. Although the rectangular mask in figure Fig.2 is more complex, the utilization of the substrate area is much better.

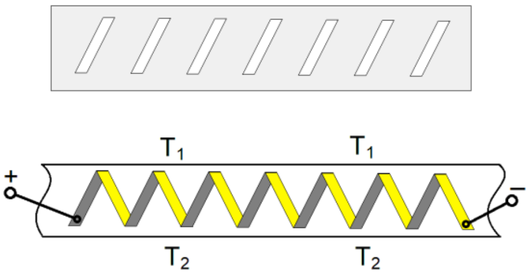

Fig. 1: Simple mask for vacuum coating and resulting structure.

A common disadvantage of both masks is the slow pumping of the gap between the mask and the substrate. This is due to the low vacuum conductivity of the gap. It is necessary to respect this fact when pumping the vacuum system.

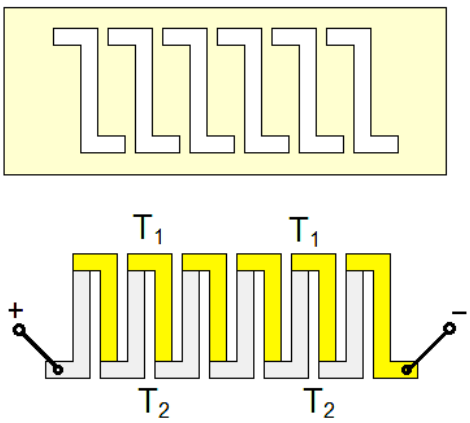

Fig. 2: Rectangular mask for vacuum coating and resulting structure.

Lift off lithography

The structure of thermo-cells is made by means of openings that are etched through the resist layer just in the areas where the final pattern is to be created. The deposited material will reach both the substrate-surface in those regions and the surface of the resist in non-etched areas. When the resist is washed away by means of a solvent, the material deposited on the resist is lifted-off together with the resist.

Vacuum deposition technologies

Vacuum technologies have the common disadvantage of being expensive and time consuming. Because the conductivity of the layers is influenced by their small thickness the dimensions and thicknesses of the structures must be selected with regard to the expected current load. In addition to the above-mentioned disadvantages, the properties of vacuum deposited layers are influenced by the mechanisms of deposition.

Sputtering. NiCr sputtering is a standard technology for the production of resistive layers. However, the optimum ratio of Ni and Cr must be ensured. During sputtering, this ratio is maintained and the layer has a comparable composition to that of the target material. Nickel sputtering complicate its magnetic properties. The use of magnetron sputtering is therefore problematic. In a conventional system, the sputtering rate is of the order of magnitude less.

Evaporation. Nickel vapor deposition is trouble-free. In the case of NiCr, however, due to the very different saturated vapor pressure of Ni and Cr the evaporation rate of both components is uneven and the nickel and chromium content in the deposited layer does not correspond to the original material. This problem is solved with the help of "flash off" technology where the material evaporates by individual grains. However, also in this case, precise distribution of both elements in the deposited layer is not guaranteed.
In addition, there is a problem with the low energy of vaporized particles which condensate on the surface of deposited layer. If the particle has little energy upon impact on the substrate, it cannot migrate across the surface to energy-efficient positions. The particle is then trapped at random positions, the resulting layer having a spongy structure and very poor adhesion.
The solution of bad adhesion and structure problems caused by low energy of evaporated particles is the heating of the substrate. However, for efficient results, the heating temperature usually reaches the temperature of 300°C or higher. This practically eliminates the possibility of using organic substrates.

RESULTS AND DISCUSSION

A counterpart of commonly used Ni-NiCr thermocouple described in previous chapter was designed using PEDOT layers instead of NiCr material.
Depending on the structure and ingredients, PEDOT has a Seebeck coefficient (measured against platinum) from +15 µV/K to +20 µV/K. Therefore, when the two materials, Ni and PEDOT are combined in the thermo-cell, the temperature sensitivity should be between 30µV/K and 35µV/K.
For intended use it is necessary that the total resistance of one thermocouple does not exceed approximately 1Ω. Although PEDOT is used as a highly conductive organic material, its conductivity is very low compared to metals.
Therefore, for use in a thermocouple the cross-section of the thermocouple in the PEDOT section must be substantially larger than the cross-section of the thermocouple in the nickel section. A structure that meets this requirement is shown in figure Fig. 3.

Considering its rheological properties including thixotropic effects, for printing process PEDOT needs to be prepared under continuous stirring at magnetic stirrer.

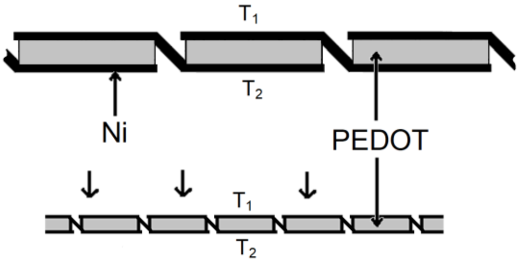

Fig. 3: Structure of PEDOT based organic thermo-generator.

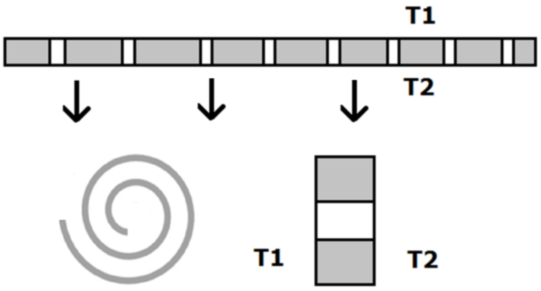

Fig. 4: The spatial arrangement of the thermocouple support strip.

The spatial arrangement of the thermocouple support strip is shown in figure Fig.4. The tape is wound into a coil that also forms the mechanical support. The temperature gradient has the same direction as the coil axis. Great advantage of this arrangement is large heat capture area. However, the number of cells cannot be increased arbitrarily, as the total resistance of the generator increases with the number of cells.
Further, the conductivity of the whole combination is very strongly influenced by the contact resistance, which is added to the series resistance of the cell. If the contact resistance is high, the cell does not work optimally. Therefore, processes of contact formation are most important. This processes include many influences as, for example, surface tension, wettability phenomena, chemistry of contact surfaces and subsequent annealing [5].

Plasma activation. To enhance the adhesion of deposited layers the surface of the films has to being cleaned and plasma activated prior to printing. Plasma activation disrupts the bonds in the molecules that are on the surface of the film. These molecules are then chemically active and tend to bind to the printed material. This process results in a very substantial increase in adhesion. The advantage of using plasma is that the whole process takes place at ambient temperature. The energy required to break the surface bonds is supplied primarily by electrons and excited particles from the plasma. For surface activation device the most advantageous process is the Dielectric Barrier Discharge (DBD). It is a discharge that occurs at atmospheric pressure. The dielectric barrier discharge plasma is non-isothermal. The electrons here have the energy in the order of electronvolts, but the gas atoms and ions that are produced during the gas ionization have a temperature corresponding to the ambient temperature. Electron energy is sufficient to initiate chemical reactions, but the activated surface is not thermally loaded. Depending on the gas composition, there may also be excited particles in the plasma that can transfer the energy upon return to the ground state. This process also takes place at a temperature close to ambient temperature.

DC to DC converter. For utilization of organic thermo-generators it is necessary to consider that the output voltage of one thermoelectric element is very small. Even with the integration of many thermoelectric elements in series is not possible to increase the voltage to a level to power conventional electronic circuits.
For optimal use of thermoelectric energy harvesters is therefore necessary to use a voltage converter with extremely low starting power supply voltage. The circuit that fulfils this requirement and need only microwatts to begin the operation is based on Armstrong oscillator.
Principal scheme of Armstrong oscillator using J-FET transistor is shown in Fig. 5. In order to operate at a supply voltage of tens of millivolts, it is necessary to ensure sufficient transformer conversion. A voltage of the order of volts is required to control the gate. This means that the transformer ratio should be at least in the range 1:30 to 1:100. Such a large transformer ratio is difficult to implement. In any case, the transformer will have a large stray inductance. In the case of an oscillator, however, the stray inductance does not prevent the circuit from functioning. Conversely, a looser bond between the primary and secondary windings is a certain advantage [5].

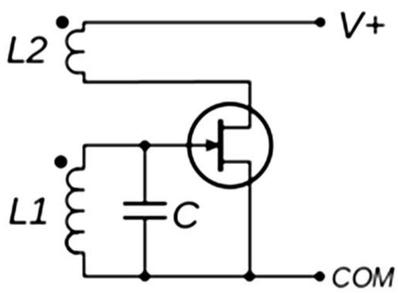

Fig. 5: Principal scheme of Armstrong oscillator.

At resonance the voltage in the resonant circuit on the gate increases significantly. The magnitude of the voltage generated at the resonant circuit is determined by the quality of the resonant circuit. The low serial resistance of the secondary winding is therefore important to achieve high quality resonant circuit.

To ensure this properties two different types of transformers are used.

Flat transformer. Flat transformers use single winding with multiple cores which are packaged in modular block with built-in primary single-turn windings. The entire network of winding elements behaves like a single transformer. Fundamental concept of flat transformer is depicted in Fig.6.

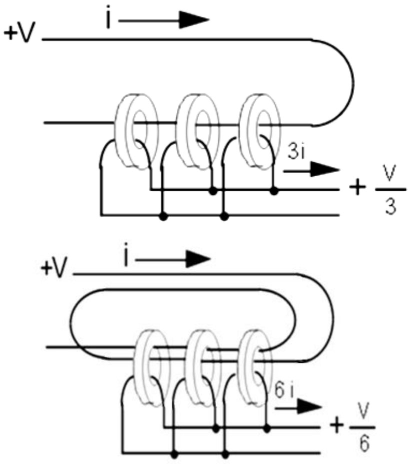

Fig. 6: Flat transformer: Fundamental concept; Transformer ratio 3:1 and 6:1.

In the flat transformers, the tight couplings between the windings and the absence of multiple turns result in very low leakage inductance. This allows faster switching times with increased efficiency. The flat transformer's nominal operating frequency ranges from 25 KHz to 500 kHz.

Because of improved heat dissipation, the flat transformer achieves high magnetic flux densities and allows tighter packaging for higher power density than its conventional counterpart.

Planar transformer can be constructed as stand-alone component, with stacked layer design or small multilayer PCB, or integrated into the multilayer board of the equipment. In the assembled planar transformer, every primary turn is at precise location, governed by the PC board. The primary is always the same distance from the secondary. That means the same value for primary to secondary leakage inductance. Using the same insulating material will always provide the same capacitance between primary and secondary. With this type of planar construction, there is always a tight control over leakage inductance, the resonant frequency, and the common-mode rejection.

CONCLUSION

The original concept of the PEDOT-nickel thermo-generator was proposed. In case that PEDOT layer is deposited on the nickel electrodes on the substrate the possibilities of influencing the contact resistance were limited.

The reverse method, i.e. deposition of the PEDOT layer in the first step and deposition of the nickel layers on the already deposited PEDOT layer, seems more advantageous in terms of optimizing the contacts. However, the PEDOT layer must be stabilized so that it does not decompose during electrode-free nickel deposition.

One more PEDOT layer may be applied to the structure thus prepared. In terms of the series connection of the cells, these two PEDOT layers are connected in parallel and the whole arrangement has greater conductivity. However the number of the cells in series connection is still limited because or great internal resistance of resulting thermo-generator. Extremely low input voltage DC to DC converter is in this case indispensable. Using Armstrong oscillator and properly designed step-up transformer with high conversion ratio the sufficient output voltage of the thermo-generator can be in order of 10 mV.

ACKNOWLEDGEMENT

The work was supported by project no. FEKT-S-17-3934, "Utilization of novel findings in micro and nanotechnologies for complex electronic circuits and sensor applications."

REFERENCES

[1] Sun, S.Zhang, P. Li, Y. Xia, X. Zhang, D. Du, F. H. Isikgor, J. Ouyang: "Review on application of PEDOTs and PEDOT:PSS in energy conversion and storage devices" J. Mater. Sci.: Mater. Electron., 26 (2015), pp. 4438-4462

[2] Wei, M. Mukaida, K. Kirihara, Y. Naitoh, T. Ishida: "Recent Progress on PEDOT-Based Thermoelectric Materials," Materials, 8 (2015), pp. 732-750

[3] K.Kirihara, Q. Wei, M.Mukaida, T.Ishida: "Thermoelectric power generation using nonwoven fabric module impregnated with conducting polymer PEDOT:PSS"; Synthetic Metals, Volume 225, 2017, pp. 41-48

[4] C. Liu, Y. Xu, Y.-Y. Noh: "Contact engineering in organic field-effect transistors " Mater. Today, 18 (2015), pp. 79-96

[5] J.P. Im, S. W. Wang, K. H. Lee, Y. J. Woo, Y. S. Yuk, T. H. Kong, S. W. Hong, S. T. Ryu, and G. H. Cho, "A 40mV transformer-reuse self-startup boost converter with MPPT control for thermoelectric energy harvesting," in 2012 IEEE International Solid-State Circuits Conference, 2012, pp. 104–106