Features of the Implementation of Methods for a Comprehensive Study of Properties of Thermoelectric Materials

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Abstract

Methods for the implementation of software and hardware tools for comprehensive nondestructive research of thermoelectric parameters of semiconductors have been analyzed and adapted. An information-measuring system has been developed, in which, due to a combination of different research methods, it is possible to perform the whole complex of thermoelectric measurements in one technological cycle and on one sample of typical configuration, in particular, thermo-EMF, electrical conductivity, Hall coefficient, magnetoresistance, Nernst-Ettingshausen coefficient, thermal conductivity, and thermoelectric figure of merit. The use of digital algorithms for filtering and processing the received data made it possible to obtain important parameters that are difficult to measure directly, in particular, the mobility and concentration of charge carriers, parameters of near-surface layers, to reconstruct the profiles of the distribution of thermoelectric parameters over the thickness. An important advantage of these methods is the absence of the need for accurate measurements of heat fluxes, which greatly simplifies and reduces the time for conducting experimental studies.

Keywords

Thermoelectric properties, information-measuring systems, measurement methods, computer tools, signal processing, defects identification

1. Introduction

Thermoelectric materials are becoming more widespread as simple and reliable energy converters, but their efficiency is still quite low. Therefore, a large number of studies are carried out aimed at increasing the efficiency of thermoelectric materials. Such studies require measurements of electrical conductivity, Seebeck coefficient, thermal conductivity, which, when using classical techniques, is a rather laborious task, since samples of various configurations and accurate measurement of heat fluxes are required. A large number of universal tools for laboratory research have been developed, but their effective use is not always possible due to the narrow specialization of thermoelectric research. Therefore, an urgent task is the adaptation of methods and the development of tools both for the study of the main thermoelectric parameters of semiconductor materials and for express methods for determining the operating characteristics of thermoelectric energy conversion modules.

2. Selection and adaptation of measurement methods

When studying thermoelectric and photoelectric properties, it becomes necessary to measure a sufficiently large number of quantities of different nature (electrical conductivity,

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Seebeck coefficient, thermal conductivity, efficiency, etc.) depending on various factors (temperature, film thickness, production parameters, type of substrate), which makes such experiments quite laborious.

Since the preparation of a sample makes up most of the labor costs in thermoelectric research, it is urgent to develop an automated computer system that will allow combining direct and indirect research methods on one sample. In particular, the implementation of the Hall methods will make it possible to study the galvanomagnetic, temperature, thickness and time dependences of the properties, in particular, to determine the electrical conductivity, the concentration of charge carriers, the Seebeck coefficient, and magnetoresistance.

Despite the rather slow processes in the implementation of Hall methods, a number of difficulties arise associated with low signal levels and the large influence of parasitic effects.

Spectral methods of analysis are especially sensitive to signal noise, in particular, methods of analysis of the "mobility spectrum" [1]. This method consists in the fact that the components of the conductivity tensor are represented in the form of integral equations depending on the concentration and mobility of charge carriers. Such methods require a decrease in the measurement error of the Hall voltage and magnetoresistance, since in the presence of noise in the experimental data it is difficult to correctly determine the search area for the parameters.

For a more visual analysis, we have constructed a model of the measuring channel, in particular, Fig. 1 shows a model of the measuring channel in the study of the galvanomagnetic properties of the material, taking into account the influence of parasitic effects, such as EMF of nonequipotentiality, EMF of magnetoresistive effect, thermo-EMF $\Sigma U_i(B,I,T)$, distortions caused by electronic nodes and inaccuracies of actuators G(B,I,T), as well as the influence of external noise and interference $\eta(B,I,T)$.

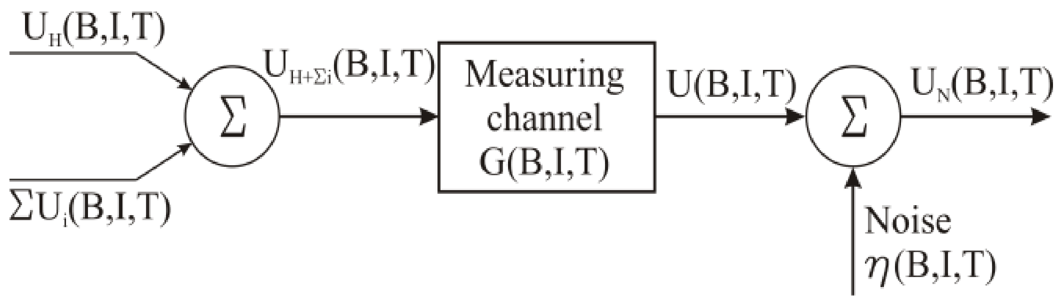

Figure 1: Model of the measuring channel in the study of the galvanomagnetic properties of the material.

As a result, the measured Hall voltage will consist of a useful signal and noise, according to the expression

$$UH(B,I,T) = UH + \qquad (1)$$
$$+Si(B,I,T)G(B,I,T) + \eta(B,I,T),$$

where $U_H(B,I,T)$ is the Hall voltage signal with both linear and nonlinear distortion. A similar situation will be in the study of other thermoelectric and photoelectric properties associated with voltage measurement.

In thermoelectric materials, parasitic effects that make the main contribution to the error include the EMF of nonequipotentiality, thermoelectric and thermomagnetic effects, which, even with a small change in the temperature gradient, significantly distort the result due to the large coefficient of thermo-EMF. A special cryostat design, where the sample is clamped between massive copper plates [2], and the measurements are carried out at a minimum sufficient current, at which there is no noticeable heating of the sample, the power released must not exceed a few mW, has been developed to deal with the occurrence of uncontrolled temperature gradients. Low currents lead to a decrease in the useful signal, but they can effectively deal with the uncontrolled heating of the sample.

The automatic compensation circuitry has been designed to eliminate the error associated with the nonequipotentiality voltage. In the absence of a magnetic field and a given current flowing through the sample, the nonequipotentiality voltage is measured by the analog-to-digital converter ADC and compensated using the compensation circuit on the operational amplifier, which is guided by the voltage from the DAC.

In the developed hardware-software complex, several stages of data filtering are performed, in particular, at the first stage, the signal is amplified, brought to the ADC range and passed through the hardware low-pass filter. After digitizing the signal, a median filter is applied to the data obtained from the ADC. This filter gets rid of the random spikes associated with the operation of the ADC. The third step is to apply a digital low-pass filter to the entire measured relationship. To reduce the noise component in the measured data, including the quantization noise level, a digital low-pass filter with a finite impulse response based on the Blackman weight function is used [3]. The use of a low-pass filter is due to the fact that the measured signals change at a rather low frequency, tenths and hundredths of hertz. Considering that the Hall voltage and magnetoresistance do not change with time, but with a change in the magnitude of the magnetic induction, the speed of the experiment, and therefore the maximum frequency of the measured signal, can be controlled. This system can significantly reduce the noise component in the signal (Fig. 2).

Both modeling of the effect of noise on the results and experimental studies on real test samples have been carried out to study the effectiveness of noise control and the effect of digital filtering on the parameter determination error. As a result of using the developed system, it was possible to significantly reduce the error in determining the concentration and mobility of charge carriers, in particular in the presence of several types of charge carriers, the error in determining the concentration and mobility of heavy holes decreased by 4 times, light holes and electrons – by 1.5-2 times.

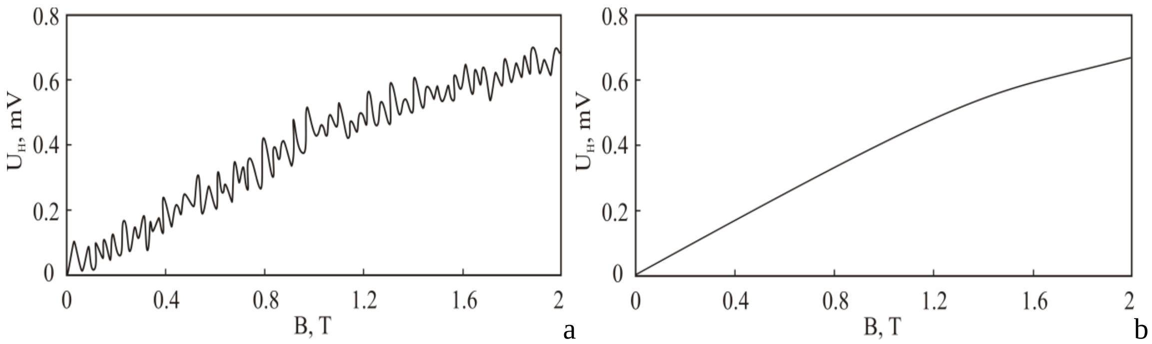

Figure 2: Dependence of the Hall voltage on the magnetic field: noisy (a) and after digital filtering (b).

The design of the cryostat provides for the presence of a gradient heater and a differential thermocouple to determine the thermo-EMF coefficient and the Nernst-Ettingshausen coefficient by direct methods. Along with direct methods, indirect methods based on the modified Harman method [4] and impedance spectroscopy [5,6] are implemented in the measuring complex for the complete characterization of thermoelectric material and automated express diagnostics of thermoelectric elements. These methods are indirect measurement methods and are favorably distinguished by a short experiment time and do not require complex and laborious measurements of heat fluxes through the sample. This combination of methods made it possible to solve two main problems of classical methods, namely, the need for accurate measurement of heat fluxes through the sample and the need to prepare samples of various configurations to measure thermal conductivity, heat capacity, thermoelectric figure of merit, and other quantities. The combination of direct and indirect methods makes it possible to determine electrical conductivity, carrier concentration, Seebeck coefficient, Nernst-Ettingshausen coefficient, magnetoresistance, thermal conductivity, as well as thermoelectric figure of merit, and to carry out express diagnostics of finished thermoelectric energy conversion modules on one sample in one technological cycle.

3. Hardware and software tools for research implementation

The set of methods for complex nondestructive research of thermoelectric parameters of semiconductors determines the characteristics of the system that it implements, namely, the amount of input information, the speed of information receipt and the processing time of the input information.

The process of measuring the parameters of the sample determines the maximum amount of input information and the maximum rate of its entry into the system. The largest amount of input information will be in the implementation of galvanomagnetic methods, and the maximum data input speed will be in the implementation of the impedance spectroscopy and will be no more than 20×10^6 counts/s.

The minimum processing time of the input information is determined by the process of controlling the operating conditions of the test sample, that is, the formation of control signals to the actuators, and the shortest time between two control signals will be when the Harman pulse method is implemented and will be 0.1 μs.

That is, the system that ensures the implementation of the set of these methods will not only be information-measuring, but also control at the same time. On the other hand, the implementation of the system should optimally combine the known approaches to the construction of computer systems – purely hardware implementation and software and hardware implementation. The hardware implementation provides maximum performance, but it requires redesigning each time in case of changes in the system's algorithm. The hardware and software implementation as a whole has a lower performance, but its operation can only be reprogrammed when the operation algorithm is changed. In turn, software and hardware tools are divided into universal and specialized – microprocessor tools that work without operating systems, and microcomputer tools that run under operating systems. When constructing a system for complex nondestructive research of thermoelectric parameters of semiconductors, it is necessary to determine the solution of which problems will be implemented in hardware, and which ones – by specialized and universal tools. The criterion for this can be the comparison of the given time for solving the problem and the time for solving it by hardware or software and hardware tools, which is given in [7].

Taking this into account, the system that ensures the implementation of the set of these methods is implemented as a three-level specialized computer system (Fig. 3), optimized to obtain the maximum number of parameters that fully characterize the sample without destroying it and without the need to change the configuration of the sample for various research methods. This concept, combined with modular structuring techniques, makes it possible to design an information-measuring and control system that can be easily upgraded or expanded. At the lower level, the actuators are controlled to create the necessary conditions for the experiment; sensor polling, analog processing and filtering of signals are carried out. At the middle level, digital signal processing, control signal generation, and self-diagnostics are performed. Depending on the required performance, this level can be implemented both on a single microcontroller and on an FPGA or their combination. The upper level is implemented in software on a standard personal computer, which made it possible to develop a convenient graphical interface for control and visualization of results. In addition, the transfer of all calculations and simulations to the PC makes it easy to expand the capabilities of software data processing without interfering with the hardware.

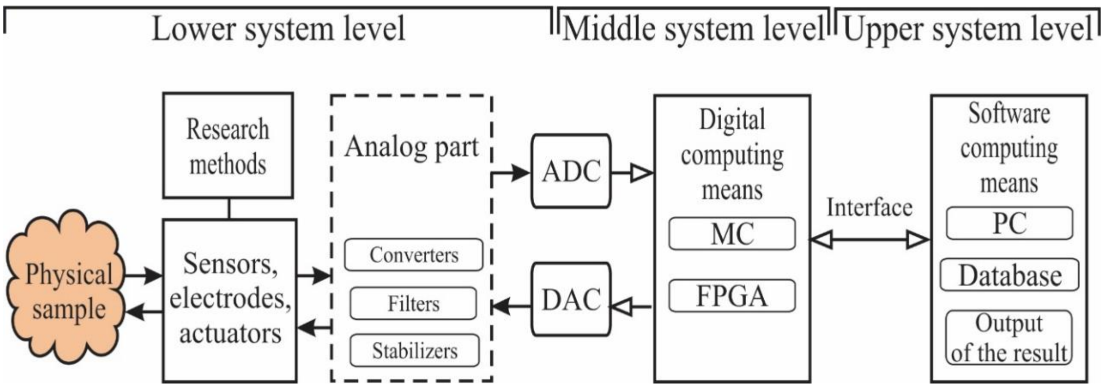

Figure 3: General concept of a specialized computer system for comprehensive thermoelectric and photoelectric research.

Guided by the principles of modular structuring, all the implemented methods for studying the properties of semiconductors are combined into groups and implemented as separate subsystems.

In particular, the subsystem for studying the galvanomagnetic properties of semiconductors implements the classical methods of Hall measurements in constant magnetic fields, measurements of thermo-EMF, electrical conductivity, Hall coefficient, magnetoresistance, and Nernst-Ettingshausen coefficient.

The subsystem for express studies of thermoelectric elements implements pulse methods and, for sufficiently thin film samples, requires high frequencies and, accordingly, high speed of the system for generating and processing signals. In addition, a highly stable source of both DC and AC of 10 μA to 500 mA, with a frequency of up to 2 MHz [7], and voltage measurement from 1 μV up to 1 V with a resolution of 12 bits, up to 100 Mps with noise filtering and taking into account errors from parasitic physical processes has been implemented. Also, based on the obtained data and the adaptive algorithm, which compares not only the absolute values, but also their deviations from those typical for a given series, defects identification of the studied element with the determination of the probable type of defect is provided [7].

The generation and synchronous detection of signals with a frequency of up to 2 MHz and their mathematical processing based on fast Fourier transforms to determine the amplitude and phase shift between them have been implemented for the subsystem for studying thermoelectric properties based on impedance spectroscopy [8]. The main task of fast digitalization of an analog signal is solved using a high-speed analog-to-digital converter, for example, AD9643 (Analog Devices, USA), which has two independent high-quality sample-hold devices and a built-in reference voltage source. Generation of a signal of the required frequency, filtering and mathematical processing of data have been implemented on the FPGA, and a 32-bit microcontroller has been chosen for signal generation, control of switching and operation of operational amplifiers, and communication with a computer [7,8].

For analyzing the quality of contacts and self-diagnostics, algorithms and a subsystem for automated analysis of the ohmicity of contacts have been developed, in particular, for analysing the I–V curve for linearity by software methods, for detecting breakage and instability of contact parameters by analyzing the scatter of the received data, which reduces the probability of receiving incorrect data and outliers.

For automated processing and visualization of the results, a software analytical module has been developed for the application of physical and mathematical models to determine the main thermoelectric parameters, including those that cannot be measured directly, such as the concentration and mobility of charge carriers, and the reconstruction of the profiles of these parameters over the sample thickness [9,10]. Approximation and fitting were carried out by the least squares method using the algorithm for minimizing functions of many variables by the Nelder-Mead deformed polyhedron method. The analytical module also provides automatic decoding of spectrograms and determination of thermoelectric parameters that are difficult to measure directly, for example, thermal conductivity and thermoelectric figure of merit, as well as automatic diagnostics and defects identification of thermoelectric elements.

4. Conclusions

The analysis has been carried out, methods for studying the thermoelectric properties of semiconductors have been selected and adapted, and a computer system has been implemented, which makes it possible to obtain all the necessary parameters of the test sample in one technological cycle on a sample of one configuration by nondestructive methods, which several times reduces the time for preparing and conducting an experiment.

A special design of a cryostat and a sample holder, an algorithm and a circuit for compensation of nonequipotential voltage have been developed, which makes it possible to minimize parasitic effects during Hall measurements. It is shown that the use of digital signal filtering algorithms to effectively reduce the noise component in the measured data has made it possible to reduce the error in determining the concentration and mobility of charge carriers by 2-4 times.

The use of indirect methods for studying thermoelectric properties made it possible to avoid the need to measure heat fluxes, to implement algorithms for fast diagnostics of thermoelements and to reduce the error in measuring thermoelectric figure of merit by 1.5-2 times.

A decrease in the laboriousness of processing the obtained data has been achieved by developing software tools for automated data preprocessing in accordance with physical and mathematical models that describe thermoelectric properties and make it possible to determine parameters that cannot be measured directly.

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