Thermal EMF in film resistors under focused semiconductor laser irradiation

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Abstract. The work studies thermal EMF generation in thick-film and thin-film resistors under focused semiconductor laser irradiation. The thermal EMF in film resistors is maximum in the case of laser irradiation of the boundaries of the resistant film contact with electrodes. The signal sign depends on the polarity of resistors brought into the measurement circuit, location of the laser spot on the boundaries of the resistive film contacts with electrodes and on the edges of nonuniformities. Thermal EMF includes direct and pulsed components during local irradiation of the surface of resistors by periodic laser pulses. The frequency and duration of the edge of unipolar EMF pulses on the electrodes of the resistors are equal to the frequency and duration of the laser pulses, respectively. In silver-palladium thick-film resistors, the maximum of the thermal EMF signal can be used to determine the boundaries of the surface section with palladium reduced by hydrogen.

1. Introduction

Films resistors are resistive and protective films applied to a dielectric substrate with contact pads (electrodes). The resistors are made from nanostructured material as per thin-film or thick-film technology. The thick-film resistors include metal oxides as functional materials, for instance tin oxide SnO₂, ruthenium oxide RuO₂, palladium oxide PdO and other. These oxides possess semiconductive properties; hence, the resistive elements with no protective layer allow transforming the physical and chemical energy into electric signal occurring on the electrodes.

The studies of the photogalvanic effects induced by laser pulses in silver-palladium (Ag-Pd) thick-film resistors [1–4] formed by consequent application and burning in of conductive and resistant pastes on a ceramic substrate VK-94 shed light on the properties of palladium oxide PdO. In Ag-Pd resistors, PdO and microparticles of the alloy of palladium with silver PdAg are formed after high-temperature physicochemical reactions in the material of the resistive paste containing silver oxide Ag₂O, palladium Pd and glass S-660a in specific proportions. PdO is a p-type semiconductor, while PdAg alloy is known to be a catalyst of many chemical reactions. The quickness of electric signal appearance on the electrodes of Ag-Pd resistor under pulsed laser irradiation of the resistive film can be explained by the fact that the resistive film material is a distributed multitude of nanosized contacts between metal and p-type semiconductor having the properties of the Schottky barrier. PdO can be reduced by hydrogen to metallic Pd. In this connection, the interaction of Ag-Pd resistors with hydrogen was studied. It was established that Ag-Pd thick-film resistors are sensitive to gaseous
hydrogen at temperatures higher than 50 °C and atomic hydrogen at the room temperature [5]. Due to the reduction of fine palladium by hydrogen from palladium oxide on the resistive film surface. This gives rise to metallic conductivity of the surface, while the total resistance of the resistors reduces [5, 6]. The interaction of the resistive film with hydrogen causes the alteration of surface thermal EMF defined in Ag-Pd resistors by thermal probe method [5, 7].

The present work is aimed at the investigation of thermal EMF in Ag-Pd resistors under local heating of their surface by a metal thermal probe and focused laser irradiation.

2. Materials and methods

A fraction of Pg-Pd thick-film resistors produced from paste PR-100 had the resistance of about 60 Ω. The dimensions of the resistive film was 6×6×0.02 mm, while the electrode formed from the silver-palladium paste PP-3 at the distance of 5.5 mm were 0.5 mm wide. Another part of the specimens with resistive film having the dimensions of 2.5×2×0.02 mm featured 0.3 mm wide electrodes with the distance between them of 2.3 mm. The specimens were manufactured from different resistive pastes (PR-500 ÷ PR-50K) and possessed resistance from 300 Ω to 36 kΩ.

The conical thermal probe was made from a 5 mm round copper rod. The diameter of the base at the end contacting with the surface of studied specimens was 0.3 mm. The thermal probe was heated by a tubular heater powered by the voltage of 12 V. Its temperature was controlled by a C-A thermocouple and supported by an electronic temperature stabilizer. The thermal EMF occurring between the thermal probe and any of the resistor electrodes after approaching the thermal probe tip to the resistive film surface was measured by a multimeter. To record the dependence of thermal EMF on the thermal probe temperature and time, the thermal EMF signal was sent to the Y-input of N307/1 recorder. X-input was receiving the signal from the thermocouple that was used to measure the thermal probe temperature or establish the time block.

To perform experiments with local heating of the surface sections by the laser beam, a semiconductor source of pulsed laser radiation was fabricated on the basis of FA-016 laser pointer with the radiation power of 100 mW with the wavelength of 532 nm in continuous mode. The pointer was fitted with a lens and mounter on a tripod using a cylindrical guide. At the lens focus length of 55 mm, the laser beam spot diameter was 0.5 mm. The continuous focused laser beam irradiation of the Cr/Al thermocouple junction surface with the diameter of 0.48 mm, manufactured from chromel and alumel wire with the diameter of 0.2 mm, heated up the junction up to 210 °C over 30 sec. To work in pulsed regime, the laser pointer’s accumulator was connected through a power field transistor IRFZ44N controlled by a generator of square pulses built on the basis of NE555 chip. The measurements by FD-263 photodiode have demonstrated that the device can produce laser pulses with a frequency from 1 Hz up to 15 kHz.

The pulsed irradiation of the Cr/Al thermocouple junction surface by the FA-016 laser pointer have demonstrated that at the ends of the thermocouple, thermal EMF has direct and pulsed components. The thermocouple was used to record laser pulses with a frequency of up to 1 kHz. At the frequency of 100 Hz and laser pulse duration of 5 ms, the direct component was 2.4 mV at which the joint was heating up to 80 °C. The amplitude of unipolar thermal EMF pulses reached 80 μV, which corresponds to the joint temperature fluctuation of 2 °C over the laser pulse duration period.

The thermal EMF in the thermocouple and film resistors under periodic laser pulses was recorded using an amplifier with amplification coefficient of 1000 based on AD620 chip and two-channel oscilloscope S1-55. The second channel of the oscilloscope was receiving the signals from the square pulse generator controlling the laser the frequency of which was controlled by Ch3-34 frequency indicator.

To protect the samples from noise, they were placed in a copper cell on a movable table. The laser beam was fed vertically and normally to the resistor surface; the distance from the output laser lens to the irradiated resistor surface was 55 mm. The laser spot was displaced on the surface of the resistors by moving the table relative to the laser beam using a screw. The movement was controlled by a micrometer with dial indicator with the scale factor of 10 μm.
3. Results and discussion

The studies of thermal EMF in silver-palladium resistors by the thermal probing have shown that the thermal EMF signal is sensitive to palladium reduction by hydrogen immediately in the contact zone of the thermal probe tip with the resistor surface. Indeed, in Figure 1 one can see the dependencies of the thermal EMF between the thermal probe and one of the thick-film electrodes of Ag-Pd resistor on the thermal probe temperature located near the surface of the resistive film.

![Figure 1. Surface thermal EMF in Ag-Pd resistor depending on thermal probe temperature in air atmosphere and hydrogen flow of 5 cm³/min](image)

The curves were plotted by the automatic recorder during heating the thermal probe contacting with the resistor surface in air and in gaseous hydrogen fed to the resistor surface from an electrolytic hydrogen generator with the rate of 5 cm³/min. In hydrogen, the plot of thermal EMF begins to deviate from the linear law at the temperature above 50 °C, which denotes the beginning of palladium reduction by hydrogen at the section of the resistive film surface contact with the thermal probe. At preset thermal probe temperature, the thermal EMF begins to drop starting from the moment of hydrogen feeding into the cell with the resistor (Figure 2).

![Figure 2. Alteration of surface thermal EMF in Ag-Pd resistor after hydrogen feeding](image)

With increased temperature of the thermal probe, the thermal EMF reduction accelerates. The dimensions of the resistor surface section with reduced palladium did not exceed 0.15–0.20 mm. After moving the thermal probe with the preset temperature to another surface section of the resistive film, the thermal EMF value gradually returns to the initial value.

The heating by focused continuous laser irradiation of the resistor surface gave rise to thermal EMF on thick-film electrodes. The maximum EMF was detected during irradiation of the resistive film surface sections at the boundaries of contact with electrodes (Figure 3).
The sign of the thermal EMF depended on the location of the laser spot at the boundaries of the resistive film contacts with the electrodes and polarity of these electrodes connected to the amplifier input. After moving the laser spot immediately along the resistive film surface between the electrodes, the thermal EMF again can change the sign, which denotes the boundaries of metallic microparticles in the composition of the resistive film. The change of the EMF sign is possible for the laser spot displacement of as less as 10 μm.

During the irradiation of the surface of thick-film Ag-Pd resistors by laser pulses focused into a 0.5-mm beam, the thermal EMF has direct and pulsed component, similarly to the thermocouple. The edge duration of the thermal EMF unipolar pulses under irradiation of the resistors by laser pulses with the frequencies of 100 Hz and higher is equal to the laser pulse duration. The maximum signal amplitude was detected after irradiation of the boundary of resistive film contacts with the electrodes (Figure 4).
Partial metalization of the resistor surface by palladium reduction by atomic and gaseous hydrogen causes the formation of sections which boundaries under laser beam irradiation also lead to increased thermal EMF signal. The EMF signals, in this case, were larger as compared to the signals received after irradiation of the boundaries of resistive film contacts with silver-palladium electrodes. In the resistors where palladium was reduced on the resistive film section overlapping the silver-palladium electrode, the thermal EMF under irradiation of the boundary of resistive film contact with the thick-film electrode was of opposite sign as compared to the thermal EMF occurring after irradiation of the boundary of resistive film contact with an electrode in the initial resistors (Fig. 5).

Figure 5. Thermal EMF in Ag-Pd resistor \((R = 560 \, \Omega)\) with Pd reduced on the surface section of the resistive film by atomic hydrogen under irradiation by laser pulses with the frequency of 100 Hz.

In addition, the experiments were conducted on the resistors with the surface where palladium was reduced by a semiconductor laser. To do so, gaseous hydrogen was fed into the cell with the resistor. The cell was closed by a 0.2-mm thick quartz glass. The laser pointer irradiation was beamed through this glass to the resistor surface. The laser was moved with the speed of 1 mm/s along the line parallel to the thick-film electrodes of the resistor. The palladium reduction process was accompanied by the occurrence of EMF on the resistor electrodes. The signal was recorded continuously by both oscilloscope and automatic recorder. In the resistor with the resistive film dimensions of 2.5×2×0.02 mm and initial resistance of 340, the EMF signal reached 0.2 mV. The resistor resistance reduced only by 4 \(\Omega\).

Consequent measurements of the thermal EMF at local heating of the surface of these resistors by the semiconductor laser have demonstrated that in the resistors with the surface with palladium reduced by local laser beam heating in hydrogen, the thermal EMF value appreciably increased after irradiation of the boundaries of the resistive film section contact with palladium (Figure 6). The width of the stripe with palladium reduced by laser beam heating in hydrogen on the sample surface with resistive film dimensions of 6×6×0.02 mm and resistance of 60 \(\Omega\) amounted to 80 \(\mu\)m. In Ag-Pd resistors, depending on their resistance, the thermal EMF was recorded during the irradiation of the boundaries of contacts with thick-film electrodes by the laser pulses with a frequency up to 1.5–2.0 kHz and boundaries of reduced palladium with that of up to 3.0–4.0 kHz.

The occurrence of thermal EMF on the electrodes of Ag-Pd thick-film resistors under local heating of their surface by laser indicates the Seebeck effect conditioned by the heating of the contacting region of electrodes with resistive film formed from dissimilar materials. This necessitated the experiments on detection of thermal EMF during irradiation by semiconductor laser in film resistors.
produced from different materials. We used thick-film chip resistors on the basis of ruthenium oxide RuO\(_2\) and thin-film structures with the resistive film of chrome.

**Figure 6.** Thermal EMF in Ag-Pd resistor \((R=58\ \Omega)\) with Pd reduced on the surface of the resistive film stripe by laser beam in hydrogen medium during irradiation by laser pulses with the frequency of 100 Hz (the insert shows the shapes of the pulsed thermal EMF signals at irradiation of the boundaries of the electrode \(1\) and section with palladium \(2\)).

Figure 7 depicts the dependencies of thermal EMF in the electrodes of the thick-film chip resistor with the resistance of 100 \(\Omega\) on the coordinates of the laser spot on its surface. The dimensions of the chip resistor were 6.4×3.2×0.6 mm. Before the experiment, the protective layer was removed. The maximum EMF signal in the chip resistor was observed after heating by the laser beam of the surface sections of the resistive film contact with electrodes. However, the thermal EMF signal, as compared to that in Ag-Pd resistors, was appreciably lower because RuO\(_2\) is a n-type semiconductor. In the experiment, the chip resistors were recording the laser pulses with the frequency of up to 1 kHz.

**Figure 7.** Thermal EMF in chip resistor \((R=100\ \Omega)\) under local hearing by focused semiconductor laser beam: 1) EMF during continuous irradiation, 2) EMF during irradiation by 100-Hz laser pulses, 3) pulsed component of thermal EMF at the frequency of laser pulses of 100 Hz.
Figure 8. Thermal EMF in thin-film resistor (R=80 Ω) with three resistive sections under local heating by focused semiconductor laser beam: 1) during continuous irradiation, 2) during irradiation by 100-Hz laser pulses, 3) pulsed component of thermal EMF at the frequency of laser pulses of 100 Hz.

The thin-film resistors were fabricated from Cr-Cu-Ni film produced by magnetron sputtering on a sitall substrate with the dimensions of 60×48×0.6 mm. Chrome in the Cr-Cu-Ni film was deposited as the adhesion layer with the thickness of less than 5 nm. The thickness of the copper layer was 500–800 nm, that of nickel layer was not more than 20 nm. The thin-film resistors were represented by a 2-mm wide film stripe on which the sections with resistive layer from Cr were created by selective leaching of Ni and Cu by nitric acid.

The studies have demonstrated that the irradiation of thin-film resistors by focused semiconductor laser beam also induces EMF. The maximum signal was detected in the cases when the laser spot stays within the resistor surface sections with the boundaries of contacts of the copper-nickel electrodes with the chrome resistive film. Fig. 8 represent the dependencies of thermal EMF on the coordinates of the laser irradiation spot on the thin-film resistor surface with three resistive sections. The resistor with a single resistive film section, the thermal EMF curve has two extremums. The pulsed irradiation of these thin-film structures has demonstrated that they allow recording laser pulses with the frequency of up to 2 kHz.

4. Conclusions

The thermal EMF of silver-palladium thick-film resistors after heating of the surface by thermal probe and irradiation by focused laser is sensitive to the reduction of palladium by hydrogen at a separate section of the resistive film. In these resistors, the thermal EMF signal under the action of focused semiconductor laser beam is maximum under the irradiation of the section boundaries of resistive film contact with palladium and those with thick-film electrodes. The thermal EMF in film resistors is conditioned by the Seebeck effect, since the contacts of the electrodes with resistive film during laser beam heating behave as a distributed film thermocouple.

The study results can be used for the development of thermoelectric nanostructured sensors of pulse laser radiation. The sensitivity of the thermal EMF signal in film resistors under local heating by laser beam to relative movement of the laser spot enables application of such resistors in combination with semiconductor laser as a vibration and movement sensors.

The reduction of palladium on the sections of thick-film silver-palladium resistors by laser beam heating in hydrogen medium indicates the possibility of creation of thermoelectric sensors and hydrogen sensors having larger sensitivity as compared to resistive sensors that are used to monitor explosive production, control and regulate the processes of hydrogen power industry and can serve as the basis of laser-hydrogen technology for controlling the properties of semiconductor nanostructures.
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