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Conductive and resistive layers based on Ni-P alloy made by selective metallization

Streszczenie. *W artykule przedstawiono wyniki prac autorów nad zastosowaniem warstw na bazie stopu Ni-P w elektronice. Autorzy udowodnili, że warstwy te można wykorzystać do wykonywania ścieżek przewodzących i rezystancyjnych na podłożach ceramicznych i krzemowych. Innowacyjność prowadzonych prac wyraża się w połączeniu technologii metalizacji bezprądowej oraz technologii fotochemicznej do selektywnego osadzania warstw o dowolnym kształcie. (**Warstwy przewodzące i rezystancyjne na bazie stopu Ni-P wykonane metodą selektywnej metalizacji**)*

Abstract*. The article presents the results of the authors work on the application of layers based on Ni-P alloy in electronics. The authors proved that these layers can be used to make conductive and resistive paths on ceramic and silicon substrates. The innovativeness of the work carried out is expressed in the combination of electroless metallization technology and photochemical technology for selective deposition of layers of any shape.*

Słowa kluczowe: selektywna metalizacja, warstwy Ni-P, warstwy przewodzące, warstwy rezystywne.
Keywords: selective metallization, Ni-P alloy, conductive layers, resistive layers.

Selective metallization - short characteristics and stages

The technology of electroless metallization with nickel alloys has been used in electronics since the 1970s [1]. Initially, the method was used to produce resistive layers in precision film resistors [2, 3, 4, 5, 6]. Currently, the method of selective metallization can be used for:

- production of resistive and conductive paths made on ceramic and silicon substrates, [7, 8, 9],
- forming contacts in photovoltaic structures [10, 11],
- production of electrodes and heaters in sensor structures [12].

The selective metallization technology makes it possible to deposit a Ni-P alloy of any shape on any substrate used in electronics. The only limitation of this technology is the quality of the mask used [7, 13].

The selective metallization process is carried out in the following steps:

- surface degreasing - carried out in a solution of acetone or ethyl alcohol; in the case of visible dirt, it is recommended to use an ultrasonic cleaner,
- production of a mask on a substrate in a photochemical process (the process is carried out in accordance with the recommendations of the POSITIV20 emulsion manufacturer),
- sensitization and activation of the substrate - processes related to the formation of centers on the substrate, around which the process of forming a metallic layer will be initiated; the sensitization process is carried out in a $SnCl_2$ solution with a concentration of 0.5 g/ml, activation in a $PdCl_2$ solution with a concentration of 0.05 g/ml
- chemical metallization with Ni-P based alloys at 343K,
- removal of the mask after the metallization process.

Due to the final sheet resistances, various metallization solutions were used:

- Ni-P - $NiCl_2$ solution with a concentration of 30g/100ml and H_2PO_2 with a concentration of 10g/100ml,
- Ni-Cu-P - $NiCl_2$ solution with a concentration of 30g/100 ml, $CuCl_2$ with a concentration of 1g/100ml and H_2PO_2 with a concentration of 10g/100 ml [14],
- Ni-W-P - $NiCl_2$ solution with a concentration of 30g/100ml, $(NH_4)_{10}W_{12}O_{41}$ with a concentration of 1,5g/100 ml and H_2PO_2 with a concentration of 10g/100ml [15, 16].

Conductive and resistive layers

The technology of chemical metallization with Ni-P alloys in the production of resistors has so far been used to cover the entire surface of ceramic substrates. The product with the final resistance was obtained by appropriate cutting of the resistive layer. The authors of this publication were pioneers in the use of selective metallization to produce layers based on Ni-P alloy of any shape [7].

The technology of producing resistive layers presented by the authors allows obtaining surface resistances in the range of (0.2÷40) Ω/sq. In the case of low resistances, copper should be added, for higher resistances, tungsten.

Before the metallization process, masks were made through which the chemical metallization process was carried out. The designed paths had shapes enabling easy determination of the resistance based on the sheet resistance. Examples of masks applied to a ceramic surface are shown in the pictures below (Fig.1)

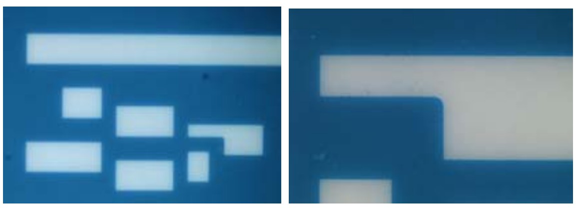


Fig.1. Examples of masks used in electroless metallization

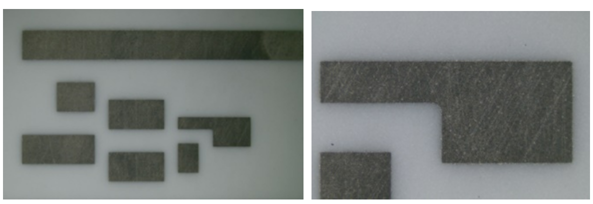


Fig.2. Examples of metallization on a ceramic substrate

In the next stage, metallizations were made with Ni-P, Ni-Cu-P and Ni-W-P alloys in the concentrations specified in the previous chapter. Pictures of exemplary metallizations, consistent with the above masks, are shown in the pictures below (Fig. 2).

The photos show a perfect representation of the areas defined on the mask. This effect can be clearly seen in the following high-magnification microscopic photo (fig.3).

Fig.3. Examples of metallization on a ceramic substrate

In the next stage, measurements of the surface resistance of the obtained layers as a function of metallization time were performed (Fig. 4).

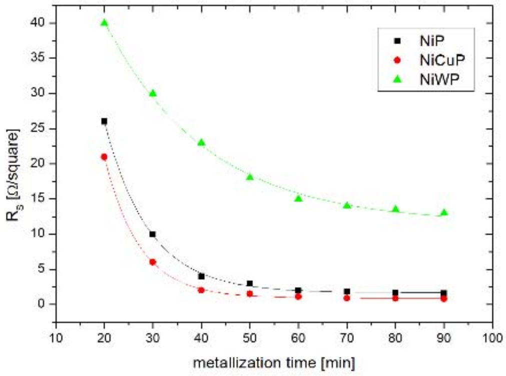


Fig.4. Dependence of sheet resistance as a function of metallization time

The results show that it is possible to control the final resistance by appropriate selection of metallization time and alloy composition. The time of 20 minutes enables the production of layers with a continuous structure and full coverage of the surface. It is therefore possible to obtain sheet resistances in the range (0.2÷40) Ω/sq. The possibility of using different compositions of the metallizing bath allows the use of different metallization times, and thus reduce the production costs (metallization time).

Photovoltaic structures

Research on the Ni-P alloy inspired the authors to use the electroless metallization technology for an innovative method of forming contacts in the photovoltaic structure [12]. So far, thick-film technology has been mainly used to produce the top and bottom electrodes of the cell. The screen printing method used silver and aluminum based pastes. The use of the Ni-P layer allows the electrodes of any shape to be guided while reducing the costs resulting from the use of screen printing technology.
The production of electrodes using electroless metallization required the development of a technology for selective deposition of metallic layers on a silicon substrate, unlike the previous production of these layers on ceramic substrates [13].

Test photovoltaic structures with electrodes deposited by selective metallization with Ni-P alloy with the addition of copper were made. Earlier work showed that the Ni-Cu-P layer is characterized by higher conductivity [10]. After metallization, the layers were thermally treated to create ohmic contacts. Dependence of sheet resistance on temperature for metallic layers are shown in Figure 5.

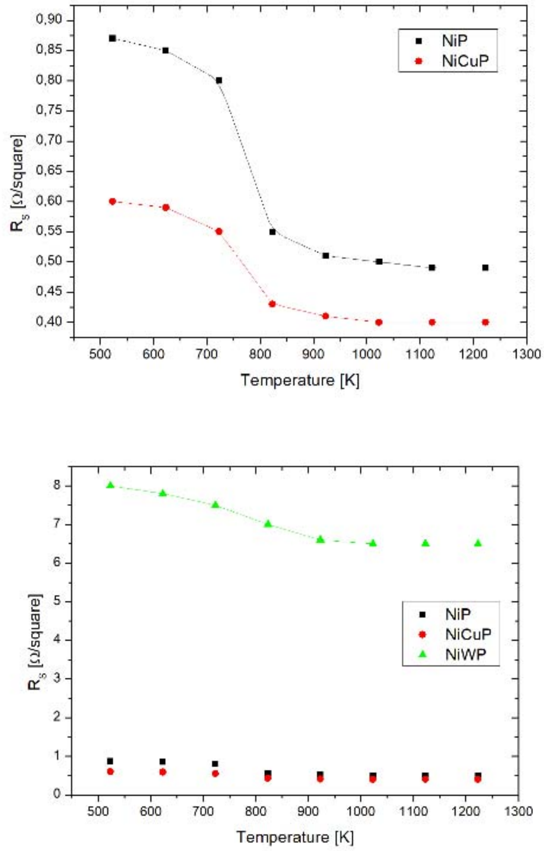


Fig.5. Dependence of sheet resistance on temperature for metallic layers of different composition (at the top Ni-P and Ni-Cu-P, at the bottom Ni-P, Ni-Cu-P with Ni-W-P)

The obtained results of the sheet resistance (shown in Fig. 5) at the level of (0.4÷0.9) Ω/sq for metallization with Ni-P alloy and (0.36÷0.57) Ω/sq for metallization with Ni-Cu-P alloy were comparable to available literature data [10, 17]. The rapid decrease in the sheet resistance at a temperature of about 600 K is the result of the crystallization of the amorphous structure.

The obtained results confirm the ohmic contact of the layers. The electrodes used in the cells should have a linear I-U characteristic, which is confirmed by the results [10].
The surface morphology of the obtained layers was also determined using scanning electron microscopy (SEM) and composition analysis (EDS). The results are shown in the SEM images in Figure 6

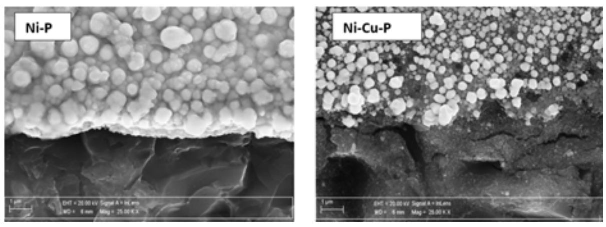
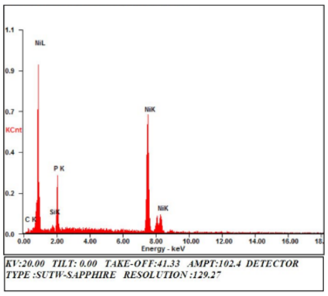


Fig.6. SEM photos of Ni-P and Ni-Cu-P metallization on multi-crystalline silicon

The obtained images show grain reduction and increased packing of the Ni-Cu-P layer compared to the Ni-P layer. This is the main factor in reducing its sheet resistance.

Figures 7 and 8 show the composition analysis (EDS) of contacts made on the basis of Ni-P and Ni-Cu-P alloys.

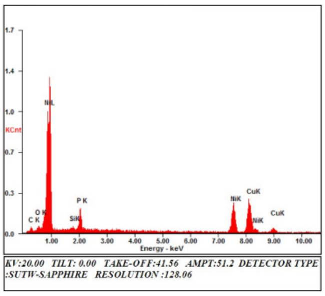


Element	Wt %	At %
C K	04.41	17.10
SiK	01.18	01.95
P K	08.46	12.72
NiK	85.96	68.22

EDAX ZAF QUANTIFICATION STANDARDLESS SEC TABLE : DEFAULT

Fig.7. Analysis of Ni-P layer composition

The high content of nickel in the layer is responsible for a correspondingly low sheet resistance.



Element	Wt %	At %
C K	06.68	24.71
O K	01.37	03.81
SiK	00.83	01.31
P K	06.08	08.72
NiK	34.50	26.11
CuK	50.54	35.34

EDAX ZAF QUANTIFICATION STANDARDLESS SEC TABLE : DEFAULT

Fig.8. Analysis of Ni-Cu-P layer composition

Note that copper takes the place of nickel in the alloy, resulting in a reduction in sheet resistance.

Humidity sensors

Another application of Ni-P and Ni-Cu-P alloys can be electrodes and contact fields in sensor structures. The authors of the paper extended previous research on humidity sensors [12].

On an alumina ceramic substrate (Al_2O_3) with dimensions of 20 mm x 30 mm x 0.55 mm, the conductive layer shown in Figure 9 was made by electroless metallization.

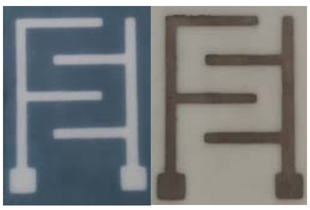


Fig.9. Optical image of the mask and metallization of the electrodes and contact fields of the humiditv sensor

In the next stage, several layers of doped-silicon glass, which is a sensory layer, were applied. The spray-on method of phosphorus-silicon solutions was used, which after thermal treatment transform into a stable layer of glass. Previous studies have shown that a thicker layer of glass (five individual layers applied one after the other) is more sensitive than a single layer. The authors have created an even thicker sensory layer (7-fold), which covers the substrate more tightly and is characterized by better parameters, such as:

- resistance change when humidity changes,
- faster response of the sensor to a jump in humidity.

Optical images of the sensor layers are shown in Figure 10.

5-fold layer 7-fold layer

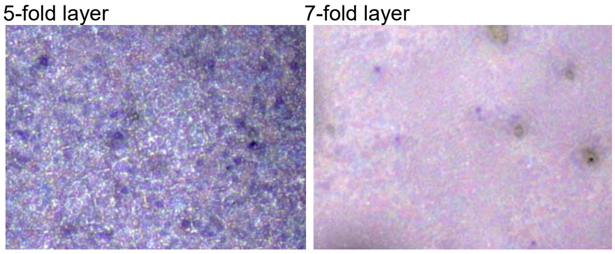


Fig.10. Optical image of the sensor layers

Figure 11 shows the response of the sensors (with a 5-fold and 7-fold sensory layer) to stimulation with 50% humidity.

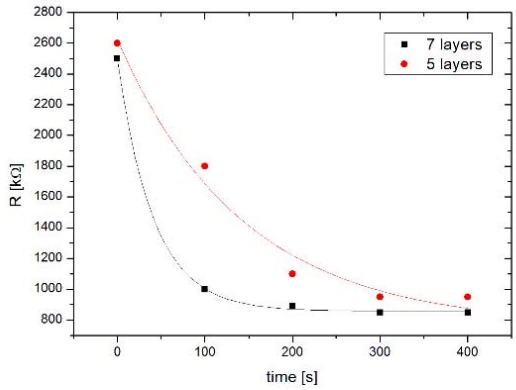


Fig.11. Sensor response to 50% humidity stimulation

Figure 12 shows the dependence of the resistance of both sensors on humidity.

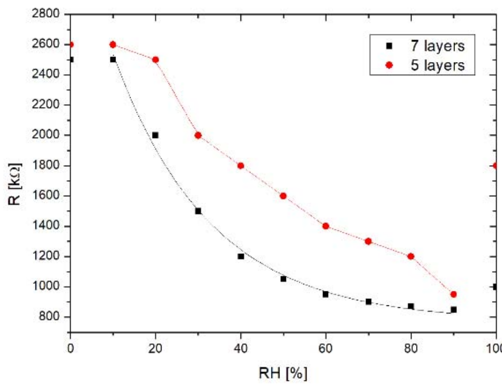


Fig.12. Dependence of resistance as a function of humidity

The use of the selective electroless metallization process does not affect the parameters of the sensor. An additional advantage is the possibility of making electrodes of any shape. The Ni-Cu-P layer, characterized by a lower sheet resistance, should be used for the production of electrodes, and the Ni-P layer, due to its higher sheet resistance, can be used for forming heaters.

Conclusions

The performed experiments show that the layers based on the Ni-P alloy can be widely used in modern electronics. The innovative method of selective metallization enables:

- production of resistive and conductive layers of any shape on ceramic substrates in the range of sheet resistance 0.2-40 Ω/sq,
- production of conductive layers on silicon substrates (except for polished silicon).

Thanks to the use of the POSITIV20 photosensitive emulsion, selective metallization is an easy-to-use process that does not require complicated technological equipment. The quality of the layers produced is at a very high level. The use of selective metallization technology in many cases simplifies the processes leading to the production of the finished structure (humidity sensor, photovoltaic cell).

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