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Temperature and pressure properties of the resistance alloy ZERANIN30 implanted by high dose, middle energy, C^+ ions

Streszczenie. *W pracy przedstawiono wpływ średnio-energetycznej, wysoko dawkowej implantacji węglem Zeraninu30 na charakterystykę rezystancja - temperatura oraz na czułość ciśnieniową. Próbki miały wymiary 20µm x2mm x50mm. Zastosowano energie implantacji 100,150 i 250keV i jednostronną implantację dawkami 1- ,2- i 3x10^{17} jonów C^+ / cm^2, odpowiednio. Do określenia rozkładu jonów węgla użyto kodu SRIM 2000 określającego maksymalny zasięg na 0.5µm. Po implantacji maksymalną energią i dawką zauważono 12% wzrost średniego współczynnika czułości ciśnieniowej. Stosując metodę określania właściwości warstw silnie implantowanych w próbkach planarnych określono jego trzykrotny wzrost w stosunku do czułości ciśnieniowej zeraninu czystego. Zaobserwowano, korzystne dla zastosowań, rozpłaszczanie się charakterystyki R-T w okolicy temperatury pokojowej, oraz niewielki (30%) spadek siły termoelektrycznej zeraninu30 względem miedzi .w temperaturze pokojowe. Metodą SIMS określono rzeczywiste rozkłady podstawowych składników Zeraninu i zaimplantowanych jonów C (z zasięgiem 1µm) stwierdzając anomalne wartości koncentracji składników podstawowych w głębokościach do 200nm. Próbki przed i po implantacji były stabilizowane termicznie w temperaturze 150^{o}C w czasie 100h.* (***Temperaturowe i ciśnieniowe właściwości rezystancyjnych stopów ZERANIN30 implantowanych jonami C^+ o wysokich dawkach i średnich energiach***).

Abstract. *The influence of carbon ions implantation into Zeranin30 alloy on their sensitivities to pressure and temperature has been investigated . Specimens were foil type, 20µm thick and planar dimensions 1x50mm). The C^+ ions, of energy 100, 150 and 250keV, were implanted on the one side of specimens with doses of 1-, 2- and 3x10 ^{17} ions C^+/cm^2 respectively. Depth distribution of carbon ions were calculated using SRIM method. The implantation range was less than 0.5µm. Due to C^+ ions implantation of max energy and dose a12% increase of mean pressure sensitivity of specimens was noted. Using developed earlier method for more accurate interpretation of implanted flat specimens it was possible to determined properties of modified layer we can estimate the pressure sensitivity coefficient (PSC) of the strongly implanted part as three times higher than the value for not implanted one. High-dose implantation with C^+ ions remarkably changes also the temperature - resistance characteristic of Zeranin30 specimens, making it more convenient for the use in the further vicinity of the room temperature. The thermo power of implanted Zeranin30 against copper at room temperature appeared to be about 30% smaller than those for not implanted one. SIMS method of determination of concentration of basic Zeranin30 components and introduced C was used. An anomalous concentration of basic component in depths of 300nm has been observed. The maximal depth of implanted carbon atoms was detected as less than 1µm. Investigated specimens were annealed before and after implantation by 100h at temperature of 150^{o}C.*

Key words: Zeranin30, electrical resistance, thermo power, ion implantation, high pressure, resistivity, carbon ion, pressure sensor.
Słowa kluczowe: Zeranin30, rezystancja, siła termoelektryczna, implantacja jonowa, wysokie ciśnienia, jony węgla, sensory ciśnienia.

Introduction

The main application of Zeranin30 (similar as manganin resistance alloy) is construction of standard resistors [1]. Manganin is the most known classical resistance alloy (developed by K. Feusserand St. Lideck in 1881 and published in 1889). Zeranin30 alloy was developed much latter, namely in 1965 year. The producer - Isabellen Hutte (Dillenburg, Germany) - have made a big effort to improve their working properties such as a smooth temperature dependence of resistance in temperature range (10-30)^{o}C, as small as possible (±1µV/^{o}C) thermo power against copper, long time stability and so on. So, we can speak about two classical alloys: manganin and newer one - Zeranin30. The chemical content of Zeranin30 is 90%Cu, 7%Mn and 2.3%Sn, x%Al, y%Fe, z%Ni. Market available manganin has complex content and the formula 86Cu12Mn2Ni is only a symbol.

Since the 70s in the last century Zeranin30 is also successfully used in high pressure measurement techniques [3, 4]. Its main advantage, in comparison to manganin pressure sensors, is its almost zero-sensitivity to temperature in wide temperature range close to room temperature. Dependence on pressure of relative resistance of the specially constructed and prepared Zeranin30 pressure sensor is almost linear up to 2GPa and changes with the pressure at a rate of about 1,50 x 10^{-5} MPa^{-1} (for manganin is 2,40x10^{-5}MPa^{-1}). This linear resistance dependence on pressure and the use of linear unbalanced DC bridge described in [5] make a base for the construction of a simple system of electronic device for pressure measurement. Miniaturization of pressure sensors in diamond Bridgman anvils techniques (super high pressure) requires thickness of sensor to be of about 1µm. It makes implantation techniques with the energies of the range 200-300 keV/ion sufficient enough for the modification of Zeranin30 properties in it full volume.

Specimens preparing

The investigated specimens were foil type, of 20.0 µm thick, 1.00 mm wide and 75.0 mm long. The Zeranin30 foil was obtained from Isabellen Hute (Germany). The samples of desired planar dimensions, was made using the YaG laser-cutting machine in Tele and Radio Research Institute in Warsaw. After this procedure they had sufficiently well prepared side surfaces. After cutting procedure the samples were heat-treated as typical manganin sensors i.e. at temperature 150ºC by 100 hours in silicon oil. Specimens were carefully cleaned using ethyl alcohol. Its resistance - temperature characteristics, before implantation, in wide temperature range, as published by producer, is shown in Fig.1. For low temperatures up to 20 K, our data - compared with literature data for Zeranin30 and manganin - are shown in Fig.2. After implantations described above annealing procedure was repeated. For resistance measurements four probes method and standard universal multimeter, Fluke corp., was used. An arrangement for measuring thermo power, earlier developed [6] and described in detail, was adopted.

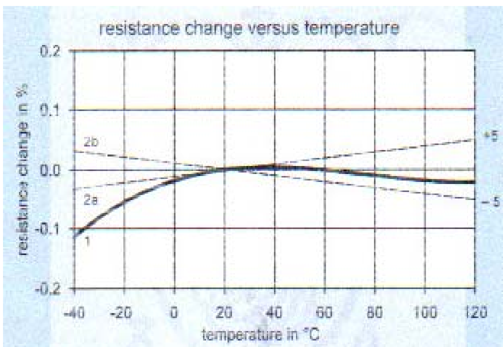

Fig.1. Percentage changes of resistance vs. temperature for Zeranin30 after producer [1]

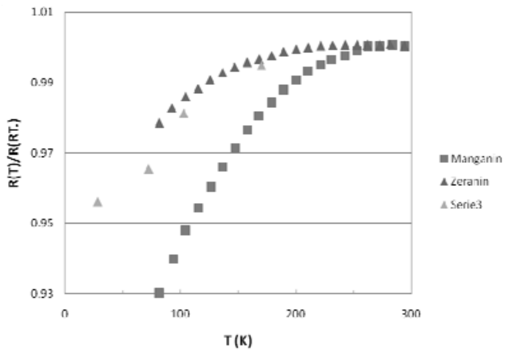

Fig.2. Relative resistance vs. low temperature for manganin (squares) and Zeranin30 (triangles) after literature data and for lower temperature according to authors data

Implantation procedure

For our investigation purposes specimens should have planar, two layers structures, with constant thickness of implanted part. Implantation procedure should guarantee homogenous chemical content of implanted layer. The C^+ ions, of energy 100,150 and 250keV, were implanted into one side of specimen with doses of 1-, 2- and $3x10^{16}$ ions C^+/cm^2, respectively.

The distribution function for implantation with C^+ ions was supposed to be close to that for displaced host atoms. High dose implantation of C^+ ions was performed using the implantation device UNIMAS-79 at the Institute of Physics of University of Marie Curie-Skłodowska in Lublin (Poland). The ion distributions in the samples, calculated using SRIM –2000 code [7] are shown in Figure 3. As we can see, the implanted ions and related structural defects were mainly located in small volumes close to surfaces of specimens with thickness less than 0.5µm. Calculated maximum C^+ ions density equal to $(0.6\text{-}1.2)10^{21}$ /cm^3 was located in all cases approximately in depth of 200 nm.

Other data were obtained by SIMS method using SAJW-05 spectrometer [8].The aim was determination of basic component concentration of Zeranin30: Cu, Mn, Sn and additionally C. Some anomalous concentrations of those metals in depths of 300 nm have been observed. As regards of the manganese atoms in manganin alloy such anomalous was observed earlier [9]. The depth of implantation of carbon ions was detected as less than 1µm. Completed data is presented in Figure 4. The simplest model for implanted Zeranin30 is shown in Figure 5. In fcc copper lattice copper atoms are substituted by Mn and Sn atoms of similar atomic (covalent) radius as that of copper atoms and C atom of two times smaller atomic radius are located in octahedral sites. Copper atomic state in the alloy is Cu^+, manganese atoms is probably Mn^{-4}, tin atoms Sn^{-2} and, probably, carbon atoms C^{+4}.Electon structure of carbon:$1s^2 2s^2 2p^2$ is quite different from electron structure of copper $[Ar]3d^{10}4s1$ where 4s1 electron is fully delocalized.

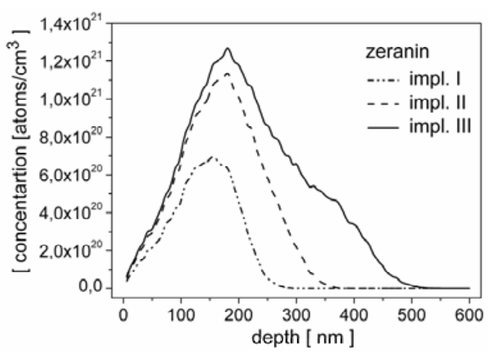

Fig.3. Depth distribution of C ion concentration after [6]

May be some carbon valence electrons $2s^2 2p^2$ in metallic bonds environment will also be delocalized, may be all, since all supposition. Mn and Sn atoms do not significantly change phonon and point scattering source in electrical charges transport mechanism. Carbon atoms and implantation damages should increase residual part of electrical resistance. So the observed decrease of resistance (see following text) can be explained as an increase a number of free electrons.

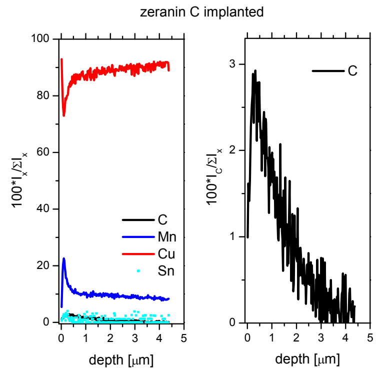

Fig.4. Depth distribution of main Zeranin30 components and C atom after implantation obtained from SIMS method

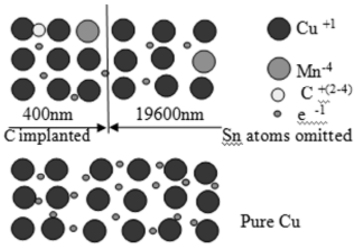

Fig.5. The 2D simplest model for implanted Zeranin30. Red circles – copper atoms, blue – manganese, yellow small circle – carbon atoms, tin atoms (2.3%) are omitted

Results

In Fig. 6 there are shown two *R-T* characteristics for not implanted Zeranin30 and implanted with dose $2x10^{17}$ C^+ ions/cm^2. We can observe in the first case thermal coefficient of resistance (*TCR*) equal to $+1.4x10^{-5}$ /^{o}C and in the second case *TCR*=$-1.2x10^{-5}$/^{o}C in temperature range from 15 to 120ºC. It means that there are possibilities to optimize such characteristics for which *TCR* will be close to zero.

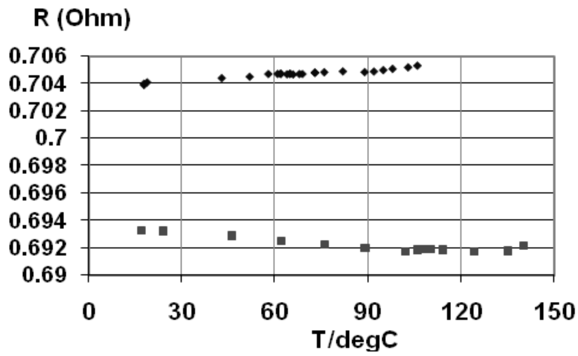

Fig.6. Resistance of Zeranin30 specimens vs. temperature. Upper points for not implanted, lower for implanted specimen, with dose equal to $2x10^{16}$ C atoms/cm^2

Fig. 7 shows pressure dependence of relative resistance of implanted and not implanted Zeranin30 specimens. One can see that pressure sensitivity of implanted Zeranin30 specimen is about 12% higher than that of the not implanted one. In this example a dose of $3x10^{17}$C ions/cm^2 was applied.

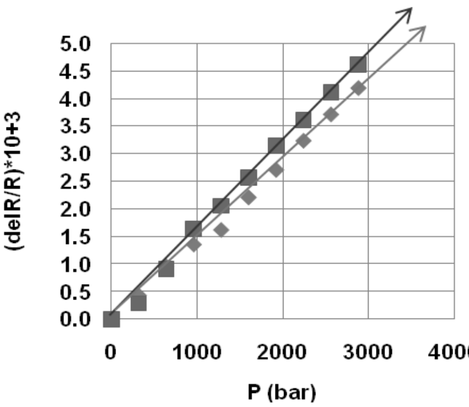

Fig.7. The relative resistance vs. pressure characteristics for Zeranin30 – implanted and Zeranin30 - not implanted lower line

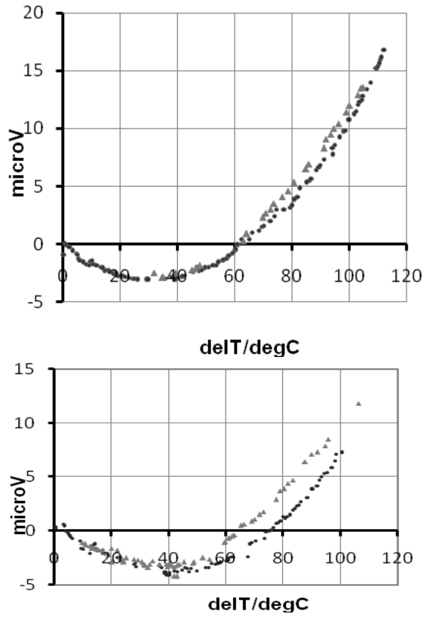

Fig.8. Thermo voltage vs. difference of hot and cold ends temperatures of Zeranin30 – pure copper thermocouples. For not implanted specimen - upper dependencies. Red points for increasing DT values

Data for strong implanted layer

In Fig. 8 we present another phenomenon of interest to us i.e. influence of C ion implantation on thermal voltage of Zeranin30 against copper. We can see rather small changes but going in desirable direction. In vicinity of room temperature the TVC decreases by about 30%.

The volume of specimens being under influence of implantation mechanism is only a small part of specimen volume but creates well defined layer in geometric and chemical sense.

In this situation a simple method for deeper interpretation of electrical resistance properties of Zeranin30 specimen seems to be appropriate [2]. If the pressure sensitivity (PS) of Zeranin30 element (a sensor) is defined as $k=\Delta R/(R_o\ p)$, then, when k=const, the sensor resistance is described by the simple formula – $R=R_o(1+k\ p)$. Pressure measurement is here equivalent to the measurement of R, assuming k and R_o to be known.

Let us introduce the following parameters [2]: $a_1=d/d_1$, $a_2=d/d_2$ where d, d_1, d_2 thicknesses of specimen, implanted and not implanted layers respectively, $K=\rho_{impl}/\rho_0$ – coefficient of resistive changes caused by implantation and $R^r=R_o/\langle R\rangle$ relative after implantation resistance, where $\langle R\rangle$ is a electrical resistance of partially implanted specimen (kind of mean value), R_o – the initial electrical resistance of specimen and k_o, $\langle k\rangle$, k_{impl} - coefficients of pressure sensibility: of pure Zeranin30, its value after implantation and coefficient of fully implanted Zeranin30.

Taking into account the following values, obtained from our experiments, R^r=1.03, a_1=50, a_2=1.04 we have [2] $K=1/(a_1R^r-a_1/a_2)$=0.8. That means a relatively large increase of conductivity. Taking under consideration literature data and data earlier obtained by us for $k_o=1.45x10^{-5}$ MPa^{-1}, data from presented investigation for $\langle k\rangle=1.65x10^{-5}$ MPa^{-1} one can obtain [2] value for $k_{impl}=(R^r\langle k\rangle-k_0/a_2)Ka_1=4.5x10^{-5}$ MPa^{-1} i.e. value being two times higher than that for pure manganin. Using simple high pressure piston-cylinder apparatus with small friction sealing force it was possible to obtain basic pressure changes for not implanted Zeranin30 and carbon implanted Zeranin30 elements. Also we have directly compared Zeranin30 element with manganin element for which characteristics are well known. The obtained results are presented in Figures 7 and 9. Relative uncertainty of those measurements was estimated as about 2%). For more precise determination of metrology properties of implanted Zeranin30 (pressure sensitivity, hysteresis phenomena, repeatability, real accuracy pressure measurements, linearity) the use of the high pressure standard (dead-weight manometer), of accuracy class no lower than 0.05, is predicted.

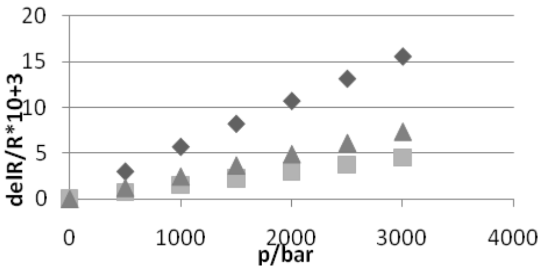

Fig.9. The relative resistance vs. pressure characteristics for (from top): Zeranin30 - fully implanted (♦), Manganin - not implanted (▲), Zeranin30 - not implanted (■)

Comparing properties of two materials as manganin and carbon implanted Zeranin30 properties one can see that, implanted Zeranin30 has two times higher pressure sensitivity then manganin and has also a wider R-T plateau. Thus implanted Zerabin30 is a better material for pressure gauge construction in particular for quick variable pressure and even for dynamic pressure registration, for example during underground (underwater) atomic explosions.

Conclusion

For metallic pressure sensor as Zeranin30 or manganin their PS coefficient can be described by the following equation $k=\Delta\rho/\rho p+\kappa/3$, where ρ - is the resistivity of Zeranin30, and κ is it compressibility. Taking into account the data for PS coefficient $k=1.45x10^{-5}$ MPa^{-1} and compressibility $\kappa=1.1\ 10^{-5}$ MPa^{-1} it is easy to find that dimensional effects is about 25% (for manganin15%) of the piezoresistance effect. It is reasonable to expect that the compressibility of Zeranin30 increases with higher ions dose as a result of the increasing density of different lattice defects. At extremely high-doses one can expect not only Frenkel's and Schottky's defects but also collective defects like multi-vacancies and so on (micro-empty spaces) which should be mainly responsible for the increase in compressibility and consequently the increase of the PS.

Theory of electrical resistance of alloys with anomalous behavior (especially in such porous materials) is very difficult and complicated. Thus it is now impossible to give satisfactory, on high scientific level, interpretation in particular of the plateau-effect described above.

Resistivity of implanted layer significantly decreases despite many different structural damages introduced by implantation process. Most probably the decrease of resistivity is a result of large increase of free electrons density due to change of electronic state of carbon atoms, being in donor state (we are not excluding C^{4+}). In literature it is possible to find information about investigation where different forms of carbon - like diamond structure, graphite, amorphous carbon, different kind of fullerens etc. after high dose implantation to copper and high temperature annealing were obtained [10]. The significant decrease of thermo power has been found. All that give us the reason of our motivation for undertaking presented here investigations.

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