Electric current distribution in thin Ti-Cu base coatings

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Abstract. The electrical resistivity of thin layer (film, coating) about 5 microns’ thick has been measured by the classical four-point probes method. The layer includes titanium-copper alloy grains up to 5 microns in size. Unexpectedly we encountered a physical phenomenon that spoils the measurements: the fluctuation of measurement results, i.e. the error of measurement may exceed 1000%. Under certain conditions such crystals may exert some long-range influence leading to tenfold fluctuations of results of measuring the electrical resistivity, despite of the fact that these crystals are evenly distributed and do not create large-size clusters. It was found that the relative scatter of measurement results decreases along with the increase of the distance between the electrodes (probes) due to averaging of currents, however, the error decreasing occurs inversely proportional to the logarithm of the distance between the probes. That is why the scatter remains significant at distances between the applied probes thousands times bigger than crystal grains. It decreases much slower than it occurs in case of one dimensional long strip where the error of measurement is simply inversely proportional to the distance between the probes. It creates huge difficulties for measurement of surface resistance. To overcome these difficulties, the method for the statistical proceeding of the non-uniform results of multiple measurements of electrical resistivity in two-dimensional systems has been proposed, which enable to extract information about average surface resistance even from such confusing set of measurements. By help of such statistic the four probe method can be potentially used in industry, for example, for controlling the quality of metal film coatings, used for heating by electrical current for de-icing of aircrafts or wind turbines.

Keywords: Two-dimensional resistivity, four-point probe method, erosion resistant coatings, anti-icing properties, electrical resistivity.

1. Introduction
During the experimental measurement of the electrical resistivity of electro-conductive coatings made of a mixture of titanium and copper deposited on CFRP samples obtained by the method of vacuum sputtering using NNV-6.6-I1 unit within the ERDF project No 1.1.1.1/16/A/073 "High Performance Erosion Resistant Multifunctional coatings for Aircraft Composite Structures (PEROMACS)" in which a separate source for each metal was used. More information about vacuum sputtering used in our lab, can be found here [11], [12].
During this study it became necessary to measure two-dimensional surface resistance of samples for quality control of obtained coatings.

1.1. Definition

The two-dimensional resistivity of a thin film is defined as the resistance $R$ of a square, in which two opposite sides are connected to two perfectly conducting ohmmeter probes along the whole length. $R$ is expressed in ohms. If the film structure is completely homogeneous, the resistance $R$ does not depend on the size of the square.

![Figure 1](image1.png)

**Figure 1** Definition of the surface resistance.

1.2. The Four-Point Probe Method.

The four-point probe method for measuring the resistance of a homogeneous surface involves the application of four probes (electrodes) to the surface. Desired direct current $I$ is supplied to the outer probes, while voltage $U$ is measured between two other (inner) probes. Thus, two-dimensional resistivity can be calculated as voltage divided by current and multiplied by some coefficient that takes into account the geometry of the system.

The four-point probe method allows **fully** exclude the influence of contact resistance between the medium and probes. Meanwhile in more primitive two probe method the contact resistance often exerts upon the result and sometimes may even exceed the resistance of the film itself. This is a classical method: The four-point probe system is sold by various suppliers, for example, [10]. It can be successfully used for uniform homogeneous films, but, as will be shown below for heterogeneous coatings it caused huge random errors of measurement, and that is why multiple measurements and statistical proceeding is a must.

![Figure 2](image2.png)

**Figure 2.** A plane which is practically infinite in all directions (red) and four-point probe.
1.3. The classical formula for an absolutely uniform coating for a plane which is relatively infinite in all directions (i.e. for essentially two-dimensional geometry)
To measure resistance in the centre of a plate, a probe with four spring contacts is used as shown at Figure 2.
Current I is supplied to two external points, while voltage V is measured between midpoints.
As a source of direct current, it is possible to use a battery with a high electromotive force and a high internal resistance, which considerably exceeds the resistance of the sample being measured. In such conditions, the additional resistor completely determines the value of current passing through the sample.
The two-dimensional resistivity of a thin film is calculated by the following formula:
\[
R = \frac{V}{I} + \frac{\pi}{\ln(2)} = \frac{V}{I} * 4.532360142
\]
(1)
The derivation of this formula is available, for example, in [1].
The formula works only if the borders of a sample are far away from all probes. Practically, it is enough if the distance to the border is triple size of the distance between the probes.
Now it is difficult to determine the authorship of the method; for instance, [1] contains a reference to a work by Thomson Kevin, 1882. However, the edition [3] of 1872 of this work does not describe this method, it only sets out the ideas leading to the method, for example, the reflection method.
Work [2] describes the practical application of the given method and proposes to perform several measurements alternating the purpose of contacts (a total of 6 variants). The work states that such measurements can compensate for errors related to the inaccurate position of contacts. There is a reference to an earlier work describing the same method [4], [5]. They all present theoretical ratios that do not include distances between contacts, which as a result excludes the geometric factor (distance between the contacts) and related random error of measurement. Both these and other theoretical studies we are aware of suggest that sheet conductivity is uniform, and it does not have even micron grains being fully amorphous.

2. Problem
During our experiment, an approximately 10-micron thick coating was created as a result of simultaneous vacuum sputtering of copper and titanium from two different evaporator. When studying the cross sections under the electron microscope, it is possible to see grains that differ by the content of titanium and copper atoms which are approximately 5 microns in size. However, on a large scale, this coating is rather uniform because the grains do not create large-scale conglomerates.
Measuring electrical conductivity with the help of the four-point probe method, when the distances between the applied probes are thousands of times larger than grain sizes, it would be logical to expect that inconsiderable non-uniformities will be averaged. However, it was revealed that the value of the results of measuring the sheet resistance can be 10-fold different, and it changes dramatically at the slightest shift of the probe.
Therefore, reasonable presumption is possible: peculiarity of the nature of electrical resistance distribution leads to fact that averaging in case of two-dimensional systems occurs very slowly along with the increase of the scale (logarithmically).
2.1. Measuring the conductivity of coatings with a fine-grained heterogeneous structure
Unlike in the above-mentioned mathematical models, in which conductivity is presumed to be absolutely homogeneous, in reality we had to deal with coatings that have some structural non-uniformities with a typical size of up to 5 microns. Therefore, the following arguments are relevant in this case.
Assume for simplicity that the whole surface consists of areas with two conductivities. Let us denote the higher conductivity in blue and the lower conductivity in red. And let us denote the contact points in white. Intuitively you can wait that if the typical size of inhomogeneities is substantially smaller than the distance between the contacts, the measurement will give an average value between the two conductivities. But it may turn out to be a delusion because the mathematical model of the averaging process may turn out to be non-trivial. It will be discussed below.

Figure 3. Just a scheme for illustration of distribution of locations of areas with different conductivity.

Figure 4. Distribution of areas with different conductivity, which leads to overestimating the surface resistance, because the central voltmeter is practically directly connected to battery. (It is just a scheme for illustration).
Figure 5. Distribution of areas with different conductivity, which leads to underestimating the surface resistance, because the central voltmeter is short circuited, and the battery is also short circuited. (It is just a scheme for illustration).

Figure 6. The lines of current on a plane can be presented approximately like this.

This is only illustrative sketch, but for real picture please look at Figure 9.

On a two-dimensional plane, the current flows unevenly, like rivers flows along curved beds on a slightly uneven land. Therefore, the result of the readings from a voltmeter connected to internal points depends on randomness: whether the probes got into a “river bed” or not.
3. Explanation why in the two-dimensional case the scatter of measurements decreases logarithmically along with the growth of a distance between the probes.

Let us consider geometry, in which one probe is positioned in the centre and is just a small circle and the second probe is a big concentric outer circle.

![Ohmeter](image)

**Figure 7.** Illustration of imaginary experiment. One thin probe is in the centre and the second probe occupies the whole boundary of the circle.

It is possible imaginary to cut the circle into concentric rings, each of which is geometrically similar to the previous one. For instance, in the figure, every next concentric ring is two times bigger than the previous one. They are geometrically similar. It can be easily proved that all flat geometrically similar two-dimensional figures have equal electrical resistance independently on their sizes. So all rings have the equal resistance. Let say the resistance of each ring is R. As they have a serial connection, their total resistance is just a sum of all resistances R+R+R+R+R. So, adding a new ring adds just one more R. It means that the combined resistance is proportional to the number of rings. On the other hand, it should be noted that the geometry grows exponentially to the number of rings. As the logarithm is an inverse function from the exponent, the resistance is proportional to the logarithm of the ratio of small and big probe (electrode) diameters. The scatter of resistance parameters for every next ring will be smaller due to averaging on a larger area. It means that the error of measurement results is caused by non-uniformity in several first stripes, and next stripes almost do not add anything significant to it. Once having appeared, the error, which is expressed in absolute units (ohms), will not disappear along with the introduction of new bigger rings. Meanwhile, the relative error, i.e. the error divided by the total resistance, will decrease. But it will decrease slowly and inversely proportional to total resistance or other words inversely proportional to the logarithm of distance between the probes. Thus, it becomes clear that the error of measured resistance value initiates mostly in the vicinity of the small probe and does not disappear afterwards. That is why the relative error, i.e. the error related to the total resistance, will decrease creating an effect of averaging. But it will decrease inversely proportional to the logarithm of the big probe size, i.e. it is inversely proportional the logarithm of the distance between the probes.
If we measure the resistance between the two small probes located at a distance substantially exceeding their sizes, the main idea will remain the same: a basic contribution to the instability of measurements is made by the areas in the direct vicinity of the both probes. But the decrease due to averaging is very slow – approximately inversely to logarithm of distance between the probes.

Now we can understand why such a huge scatter is observed when applying the four-point probe method onto relatively infinite planes that is in two dimensional case.

But there are no such problems on practically one-dimensional thin stripes. In fact, in a one-dimensional system, the error of measured resistance values also appears in the microscopic zones around the areas where sharp probes touch the surface. However, in one-dimensional case the total resistance of the stripe grows proportional to the distance between the probes, so the relative error decreases inversely proportional to the distance between the probes. That means - not logarithmically but much faster.

4. Measurement on elongated rectangles (i.e. in almost one-dimensional geometry)

During the first series of experiments, elongated rectangular samples were used – 200 mm long and 20 mm wide; and a coating of titanium and copper with various percentage of components was deposited on the samples by using the method of vacuum sputtering.

As the samples have very elongated geometry, it is optimal to position two contacts that create the desired current, i.e. clips 1 and 4, at the ends of the samples. While voltage can be measured with the help of contacts 2 and 3, which can be easily applied at any points.

![Figure 8. Measuring two-dimensional resistivity on a thin stripe.](image)

On the elongated samples, the source of current was connected with clips to the ends of rectangle – 1, 4. The voltage was measured in the central part with two contacts – 2, 3. Thus, the sheet resistance will be as follows:

\[ R = \frac{V}{I} = \frac{A}{S} \quad (2) \]

Where V is the voltage between contacts 2 and 3, I is the current supplied to contact clips 1 and 4, A is the width of the sample, S is the distance between voltmeter contacts 2 and 3. But the length (distance between probes 1 and 4) has no influence and is not included in formulae.

Voltage is measured approximately in the middle of the plate with the help of a voltmeter.

In such utmost one-dimensional geometry, when the probes are positioned rather far from each another, large errors of measured resistance are not observed. Occurs effective uniform distribution of electrical current along the rectangle length, despite the presence of a heterogeneous structure like small grains. The difference of results obtained on a thin stripe and on a plane, which is relatively infinite in all directions, can also be explained in a different way: On a thin stripe, current is clamped on both sides and cannot divert. And by this the random factor is eliminated.

It is possible to cut thin elongated stripes and take measurements on such one-dimensional samples and use simplest formula (2). It is the most precise way how to improve the four probe method. Obtained surface resistance can be used for reference and calibration.

But unfortunately, cutting is a destructive testing method that can be used only in a laboratory but not in the field on real aircraft and wind turbine wings.
5. Statistical description of the scatter of electrical resistance measurement results
The analysis of the samples allowed us to reveal large non-uniformity of results of electrical resistance measurements. Therefore, it is important to formulate a statistical processing method for such data.

5.1. Determining the mean resistance.
As prior to the experiments the nature of distribution is unknown, one of the two algorithms is suitable for determining the mean value in a natural way:

The first one: the results are put in a row in the increasing order and the mean resistance is determined as a result, in comparison to which exactly one half of the measurement results are lower and the other half are higher.

The second one: though the nature of distribution of resistance measurement results will not be Gaussian, it can be hoped that the distribution of the logarithms of measurement results will be similar to the Gaussian distribution; and in this case, as a criterion, it will be possible to use the logarithms of resistance values rather than the values themselves. Then the mean resistance $R_a$ will be determined via the mean logarithm:

$$\ln(R_a) = \frac{(\ln(R_1) + \ln(R_2) + \ldots + \ln(R_n))}{n}$$

(3)

Our practical experiment shows that these two ways of determining of mean value yield the same result, which is an evidence to the assumption that the logarithms of resistance measurement results are distributed according to the normal Gaussian law. (Though it is now too early to make a final conclusion – a more statistic is required).

5.2. Determining the mean deviation from the mean resistance.
After determining the mean value of resistance, it is possible to determine the mean deviation from the mean value and indicate some measure for measuring such deviations $\Delta (R/R_a)$. (The triangle with the cross means average error). It can be defined as a mean deviation of logarithm of resistance from its mean value and calculated as root-mean-square deviation (RMSD):

$$\ln(\Delta (\frac{R}{R_a})) = \sqrt{\frac{(\ln(R_1) - \ln(R_a))^2 + (\ln(R_2) - \ln(R_a))^2 + \ldots + (\ln(R_n) - \ln(R_a))^2}{n}}$$

(4)

In order to understand by how many times the results of measurements may differ on average, it is necessary to take a natural exponent of this number:

$$\Delta (\frac{R}{R_a}) = \exp\left(\sqrt{\frac{(\ln(R_1) - \ln(R_a))^2 + (\ln(R_2) - \ln(R_a))^2 + \ldots + (\ln(R_n) - \ln(R_a))^2}{n}}\right)$$

(5)

6. Analysis of actual experimental data obtained on samples with a deposited mixture of two metals: titanium and copper
This is an example of a data set obtained as a result of measuring resistance on one and the same sample.

6.1. The measurements were performed with the help of a probe system, in which the contacts were installed at a distance of 1.2 mm from each other and positioned along one line with a total length of 3.6 mm respectively. Units of measurement – ohms. Calculated using measured voltage, current and formulae (1).

We present these numbers here specifically so that the reader can independently plot them on the axis and make sure that these results are distributed according to a statistical law that is very far from the normal Gaussian distribution. But if you plot the logarithms of these numbers on the axis, you will easily see that the distribution resembles a Gaussian one.

| 0.95 | 16.89 | 15.4 | 5.82 |
|------|------|------|------|
| 0.40 | 14.11| 16.25| 3.82 |
One can easily make sure that the scatter may be tenfold, and this is surely not the Gaussian distribution; so, in this case it is impossible to apply traditional statistical processing methods (like the calculation of the mean) directly to these numbers. It is better to apply them to the logarithms of these numbers, as proposed in formulae (3), (4), (5).

Thus, applying the above described statistical processing method, we will get the following result:
The mean resistance $R = 6.52$ ohms, the logarithm of root mean square deviation from the mean value calculated by the logarithmic formula = 1.24, which corresponds to the mean error of measurement = 247% (i.e. the scatter is on average 3.47 times upward or downward).

6.2. The following values of resistance in ohms were obtained by increasing the distance between the probes up to 30 mm and repeatedly measuring one and the same sample as before:

| Resistance (ohms) | 2.05  | 1.95  | 0.964 | 0.582 | 3.08  | 1.69  | 1.36  | 0.854 |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                   | 1.04  | 1.02  | 0.932 | 1.29  | 1.62  | 1.72  | 5.27  | 2.07  |

The above-mentioned statistical processing method yields: the mean resistance $R = 1.44$ ohms, the logarithm of root mean square deviation from the mean value calculated by the logarithmic formula = 0.41, which corresponds to the mean error of measurement = 50% (i.e. the scatter is on average 1.50 times upward or downward).

As we see, the application of a larger probe system has decreased the mean deviation of the measured resistances from the mean resistance, however this decrease is still insufficient for objective studies.

7. Control testing of four-point probe method on a glass with a good uniform high-quality amorphous coating without any grains.

| Resistance (ohms) | 67.4  | 68.8  | 73.4  | 88.8  | 73.2  |
|-------------------|-------|-------|-------|-------|-------|
|                   | 77.6  | 73.8  | 70.5  | 75.9  | 77.1  |
The mean resistance $R = 74.5$ ohms, the logarithm of root mean square deviation from the mean value calculated by the logarithmic formula $\log = 0.074$, which corresponds to the mean error of measurement $= 7\%$ (i.e. the scatter is on average 1.07 times upward or downward).

As it is seen, the four-point probe method works well on uniform films. Therefore, it is widely used of uniform films, for example, in [9].

8. Infrared thermal image
To make sure that such non-uniformity does exist, the samples were photographed with an Infrared thermal imaging camera at various moments when the current heats the plate. In the photo the formation of elongated fractal "fingers" corresponding to the places where the flowing current forms the above-mentioned "channels" is clearly seen.

![Infrared thermal image](image.png)

**Figure 9.** Infrared thermal image. Three times moments. The size of the sample is 200x150 mm. It can be clearly seen that heat generation is not uniform, which corresponds to non-uniform current distribution. Which fully supports our original hypothesis.

9. Sample preparation
The vacuum coating method is not a topic of discussion in this article. We discuss here only measurement of electrical conductivity. Still few words should be told about the sample preparation:

![Sample preparation](image.png)

**Figure 10.** Sputtering chamber of NNV-6,6-I1 and the deposition scheme
Two arc sources are used: one for Titanium (L1) and the other for Cuprum (L2). The CFRP substrate is rotated on a rotating table to achieve an even coating.

The arc source has a minimum evaporator current of 40 A. During the evaporation of titanium, rather large number of droplets are formed. They are later visible as micro grains < 5 mcum. More information about coating is available in other publications of our co-authors [11], [12], [13].
10. Analysis of the coating
Under the electron microscope it is possible to see numerous crystal grains up to 5 microns in size with various content of titanium and copper.

![Image](image_url)

**Figure 11.** A photograph taken by the electron microscope. Coating microstructure. Different colours indicate the areas of copper and titanium concentration.

The resistance of titanium is thirty times higher than the resistance of copper. Thus, being included parallel with copper, it will hardly conduct current. Any measurements of resistance with the help of thin probes will lead to a huge scatter of results depending on the area that will come into contact with the sharp probe. This is what could be observed during the experiment. Such non uniformity can be explained by Stranski – Krastanov instability [6]. More information here [8]. This structure looks like solidified liquid drops. Such solidification was discussed here [7]. These references are given for further information but they are not a topic of presented article, because here only electrical resistance is discussed.

Conclusions
1. The surface films created in our laboratory are applicable for heating wind turbine or aircraft wings for preventing icing even if the film consists a mixture of very small crystals of copper and titanium. The de-icing properties of the coatings have been tested in our laboratory and it will be presented in future publications. Here we concentrate only on measurement of surface resistance, which is required to control coating quality.
2. The methods of measuring resistance with classical four-point probe method can be applicable but only after statistical proceeding of hundreds measurement results using statistical method described above. Compare: this is very different from measuring of two-dimensional resistance of homogeneous films, for which the four-point method gives the result immediately after the first measurement.
3. Alternatively producing some larger contacts covering a representative sample of all types of grains can be used. But such idea is not realistic, because it can be done only by soldering. It will not be possible quickly move such tester from one place to the other along big airplane wing.
4. Statistical distribution of electrical currents in two-dimensional system strongly depends on sizes and electrical resistivity of internal small grains. As our experiments have shown, the
currents for such system can be irregular even on large scales because the irregularity decreases approximately inversely to logarithm of scale. But to obtain precise statistical formulae, the further theoretical mathematical study of such dependence is needed. This article is the first to pose such a non-trivial complex mathematical two-dimensional problem (which could probably be solved using computer modelling).

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References
[1] F.M. Smits. Measurement of sheet resistivity with four point probe 1957. http://www.four-point-probes.com/smits.pdf
[2] Burlakov R.B. Kovivchak V.S. To the question of measuring the specific resistance of conducting layers by the four-probe method.
[3] Sir William Tomson Electrostatic and magnetism. London, Macmillian 1872 https://archive.org/details/reprintofpaperso00kelv/page/n5
[4] Van der Pauw L.J. A Method of Measuring Specific Resistivity and Hall Effect of Discs of Arbitrary Shape // Philips Research Reports. 1958. Vol. 13. No. 1. P. 1-9.
[5] Van der Pauw L.J. A Method of Measuring the Resistivity and Hall Coefficient on Lamellae of Arbitrary Shape // Philips Technical Review. 1958/1959. Vol. 20. No. 8. P. 220-224.
[6] Stranski, IN; Krastanov, L. (10 February 1938). "Zur Theorie der orientierten Ausscheidung von Ionenkristallen aufeinander". Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
[7] Volmer, M. ; Weber, A. (1 January 1926). "Keimbildung in übersättigten Gebilden". Zeitschrift für Physikalische Chemie.
[8] Oura K., Lifshits VG, Saranin AA et al. Introduction to surface physics / Ed. V.I.Sergienko. - Moscow: Nauka, 2006. -- 490 p.
[9] Richard S. Waremra, Philipus Betaubun Analysis of Electrical Properties Using the four-point probe method. ICENIS 2018. https://www.e3s-conferences.org/articles/e3sconf/pdf/2018/48/e3sconf_icenis18_13019.pdf
[10] Four-Probe measurement equipment advertising: https://www.ossila.com/products/four-point-probe-system?variant=31916570945
[11] Urbaha, M., Bogdanova, S., Urbahs, A. Evaluation of the physical and mechanical characteristics of ion-plasma decorative-protective coatings (2019) AIP Conference Proceedings, 2077.
[12] Urbaha, M., Bogdanova, S., Urbahs, A. Multi-criteria assessment of physical properties of nanostructured decorative protective coatings (2019) Key Engineering Materials, 799 KEM, pp. 43-51.
[13] Urbahs A. Urbaha M., Savkovs K. and Bogdanova S. Wear resistant nanostructured multi-component coatings. NATO Science for Peace and Security series, Series B: Physics and Biophysics, Nanodevices and Nanomaterials for Ecological Security, Part 1, 2012, pp. 161–170.