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DEVELOPMENT OF DEPOSITION TECHNOLOGY AND AC MEASUREMENT OF COPPER ULTRATHIN LAYERS

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Abstract. *In this paper, the transport properties of discontinuous 4 nm copper layers obtained by dual-source non-reactive magnetron sputtering in the presence of argon are presented. The value of resistance and capacitance of the current parallel to the plane of these layers can be adjusted independently by changing the nominal thickness of the metallization. The influence of frequency on the conductivity of the obtained structures in the range from 4 Hz to 8 MHz was studied. Additionally, in order to compare the non-oxidized and oxidized layers, some of them were heated at 500°C. Based on the results obtained, the mechanism of electric charge transfer was determined, the knowledge of which is essential for planning further experiments based on this sputtering method and potential selection of future application of the structures. Statistical measurements at room temperature will serve as a reference for the conductivity and resistivity values obtained by mathematical calculations from measurements of resistance, capacitance, phase shift angle, and dielectric loss tangent as a function of temperature from 20 K to 375 K, which are expected in further studies on the obtained structures. The work is an introduction to the technology of obtaining multi-layer metal-dielectric structures.*

Keywords: magnetron sputtering, ultrathin layers, AC measurement, conductivity measurement, charge transport, Cu films

OPRACOWANIE TECHNOLOGII OSADZANIA I POMIARÓW ZMIENNOPRĄDOWYCH ULTRACIENKICH WARSTW MIEDZI

Streszczenie. *W niniejszej pracy przedstawione zostały właściwości transportowe nieciągłych 4 nm warstw miedzi otrzymanych metodą dwuźródłowego niereaktywnego rozpylania magnetronowego w obecności argonu. Wartość rezystancji i pojemności prądu równoległego do płaszczyzny tych warstw można dostrajać niezależnie poprzez zmianę nominalnej grubości metalizacji. Przebadano wpływ częstotliwości na konduktywność otrzymanych struktur w zakresie od 4 Hz do 8 MHz. Dodatkowo, w celu porównania nieutlenionych i utlenionych warstw niektóre z nich zostały wygrzane w temperaturze 500°C. Na podstawie otrzymanych wyników określono mechanizm przenoszenia ładunków elektrycznych, którego znajomość jest niezbędna do planowania kolejnych eksperymentów bazujących na tej metodzie napylania oraz potencjalnym doborze przyszłego zastosowania struktur. Statystyczne pomiary w temperaturze pokojowej posłużą za punkt odniesienia dla wartości konduktywności i rezystywności otrzymanych na drodze obliczeń matematycznych z pomiarów rezystancji, pojemności, kąta przesunięcia fazowego oraz tangensa strat dielektrycznych w funkcji temperatury od 20 K do 375 K, które przewidywane są w dalszej części badań nad otrzymanymi strukturami. Praca stanowi wstęp do technologii otrzymywania wielowarstwowych struktur typu metal-dielektryk.*

Słowa kluczowe: rozpylanie magnetronowe, ultra cienkie warstwy, pomiary zmiennoprądowe, pomiary konduktywności, transport ładunków, warstwy miedzi

Introduction

In order to meet the continuous demand of the modern semiconductor industry for embedded condensers with smaller dimensions and unchanged or better properties, nanocomposites composed of a matrix of non-conductive materials have become increasingly popular due to their excellent dielectric properties [16]. The essence of conducting research on material properties in an electrical context is to understand the physical phenomena occurring in them. Of particular interest is the possibility of tuning the resistance, capacitance and inductance over a wide range at the stage of obtaining composite structures by various methods [7].

Microprocessor technologies use many conductive materials to build electrical components. One of them is copper, which is used particularly often due to its conductive properties. There are many methods for the deposition of thin copper layers, such as: DC magnetron sputtering (DCMS) [18], high power impulse magnetron sputtering (HiPMS) [3], ion beam deposition [15], quenching [22], chemical vapour deposition (CVD) or more environmentally friendly supercritical fluid chemical deposition (SFCD) [8].

Nowadays, nanotechnology is one of the fastest developing engineering fields in the world due to its possibility of obtaining precisely nanometric structures for many applications [9]. Unfortunately, nanoscale particles don't always have the same properties as micro-scale particles of the same material. X-ray fluorescence (XRF) studies have shown that the measured value of copper nanoparticles in dispersed systems is less than micro-particles [5]. Moreover, grain grinding has a beneficial effect on the electrochemical properties of pure copper. With the reduction of the grain size, the passive and corrosive current density decreases, and the acceptor density decreases. However, the grain size doesn't affect the type of semiconductor in thin films [11]. On the basis of the available structural studies, it can be concluded that the layers ≥ 130 nm are uniform and have an amorphous character, and with the increase in thickness, arched grain clusters appear, which, getting larger and larger, smoothing the surface. In contrast, increasing the metallization thickness reduces the resistivity of the structure to a value of 500 nm. Beyond this level, no effect of film thickness on resistivity is observed. This correlation can be defined as the inverse linear dependence of resistivity on grain size caused by reduced scattering at their boundaries by charge carriers [12].

In the case of ultra-thin copper layers below 10 nm, it has been noticed that they show strong increases in resistivity with decreasing film thickness, which is related to electron scattering by phonons, point defects, impurities, grain boundaries, or substrate / layer boundaries. [12, 17]. It is assumed that copper layers below 5 nm will be discontinuous, therefore they will show quite different electrical properties compared to continuous layers [2, 6, 10].

Using this information, it seems reasonable to use copper as one of the phases of metal-dielectric nanocomposites. Based on the available AC studies, it is assumed that the obtained structures will exhibit a voltage resonance phenomenon at the resonance frequency characteristic of a series RLC system, which was produced by a stepped charge transfer mechanism [7, 13, 21]. An important element in selecting the potential application of nanocomposite structures in which metal grains are embedded in a dielectric matrix is determining the value of the percolation threshold (x_c). In the case of metallic phase content (x) below this threshold ($x < x_c$) or in its vicinity ($x \approx x_c$) it is possible to determine the mechanism of electric charge transfer between the neutrally charged potential wells [9].

The aim of the work was to conduct the process of deposition of ultra-thin discontinuous copper layer, which is an introduction to the development of the technology of multilayer metal-dielectric composites.

1. Materials and technology

Thin-layer structures will be obtained by sputtering the material in the process of magnetron sputtering. This technique is based on the explosion of single particles of a material source under the influence of energy ionized by a strong electric field of a noble gas, in this case argon. The ions with an energy of 100 V to 1 kV formed in the plasma area bombard the target surface and breaking the bonds between individual atoms. High frequency of direct current or its discharges make it possible to obtain sputtering ions. A fluorescent current excitation is created between the anode of the grounded substrate and the cathode of the sputtered material. Magnetron sputtering is an extremely efficient sputtering method because it allows for the extension of the free electron path [1].

The first stage of work on obtaining an ultra-thin layer of copper metallization was mounting laboratory slides with dimensions of approx. 15 mm × 10 mm × 2 mm on a rotating plate. The deposition process was carried out by the technique of non-reactive magnetron sputtering in a sputtering machine Kurt J. Lesker Nano 36^{TM}, which previously had a vacuum of 1×10^{-7} Torr. During spraying, no high temperatures were used that could damage the source material. A 99.999 % purity target purchased from Kurt J. Lesker offer was used to obtain the copper layer. The process was initiated by a DC magnetron in the sputtering parameters: argon flow 75 sccm, plasma power 100 W for about 2 minutes. Thin film structures with dimensions of 10 mm × 5 mm × 4 nm were obtained. Contacts were applied to them using silver paste, as schematically shown in Fig. 1. Then some of them were heated at the temperature of about 500°C in order to oxidize the metallization.

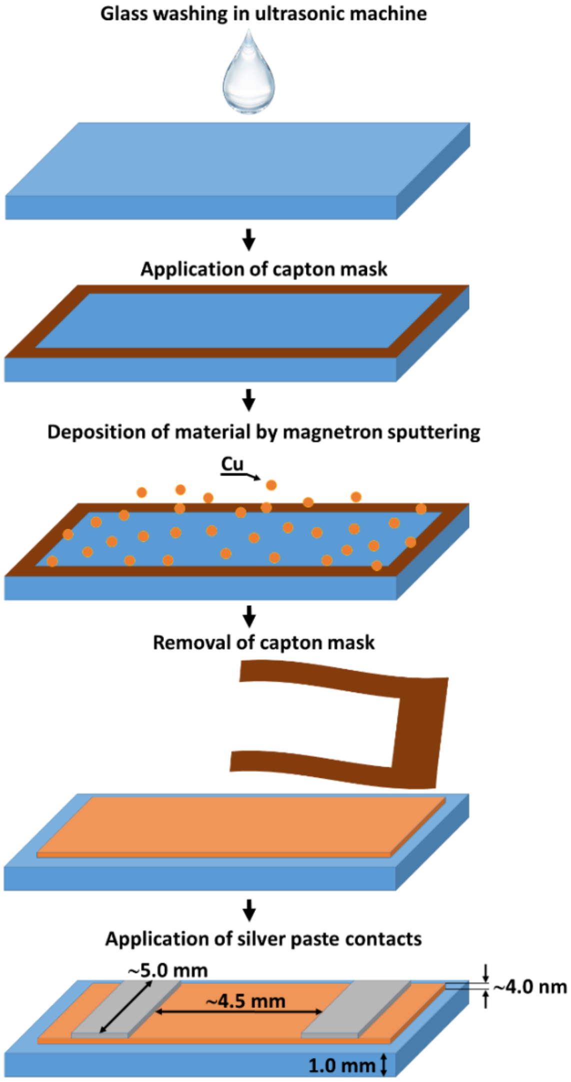

Fig. 1. Scheme and geometrical dimensions of the tested samples

2. Experimental

After applying the silver contacts, measurements were made using the four-point method using a Hioki IM3536 impedance meter. Before starting the measurements, the meter was calibrated using a dedicated test fixture Hioki 9261. The LCR meter program, available on the manufacturer's website for download, was used for the first measurements. The measurement parameters were resistance, conductance, phase angle and capacitance as a function of frequency in the range from 4 Hz to 8 MHz. Measurements were carried out at room temperature 10 times for each frequency and then subjected to statistical calculations. From the obtained measurements by mathematical calculation, the conductivity was determined using the geometric dimensions of the sample between contacts using the electrical conductivity formula of the material:

$$\sigma = \frac{G \cdot l}{S} \tag{1}$$

where: σ – conductivity $\left[\frac{S}{m}\right]$, G – conductance $[S]$, l – side length $[m]$, S – element cross-sectional area $[m^2]$.

In order to visualize the obtained measurement results and parameters from the mathematical calculations, code was written in Matlab.

3. Results and discussion

Fig. 2 and 3 show the dependence of conductivity on the measurement frequency of the deposited copper layer before and after annealing. The graphs show that the conductivity value in the low frequency range up to approx. 10 Hz is practically constant and then increases linearly by approx. 5 orders of magnitude. Based on the AC model of electric charge transfer presented in the works [25, 26, 27], it can be concluded that the layers aren't continuous, and the dominant mechanism is electron hopping or electron tunneling between copper grains. In the case of a continuous copper layer, the conductivity should show a practically constant value with a frequency, as in the case of a thin-film resistor [20].

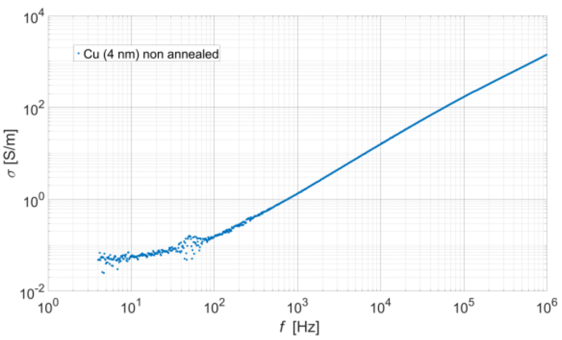

Fig. 2. Dependence of conductivity σ on the measuring frequency f of the copper layer immediately after deposition

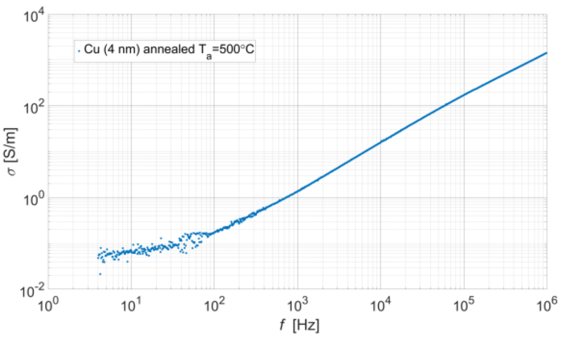

Fig. 3. Dependence of conductivity σ on the measuring frequency f of the copper layer heated at the temperature T_a=500°C

Based on the proposed model, the frequency coefficient m was determined, which is the derivative of lgσ after lg*f* and σ~*f*^{m} [19]. The values of the m(*f*) layer relationship before and after annealing for different frequency ranges are shown in Table 1. As a rule, the value of m(*f*) at the low frequency range should be close to 0, which indicates DC conductivity. For both low-frequency and high-frequency values of m(*f*), it can be seen that they are slightly different from each other. Thus, it can be concluded that the annealing of the structures will not have a significant effect on their electrical properties.

Table 1. Dependence of the frequency coefficient m on the measurement frequency f of the copper layer immediately after deposition and the copper layer heated at temperature T_a=500°C

	Nonannealed copper layer	Annealed Ta=500°C copper layer
m [a.u.] for 4 Hz–80 Hz	0.296865856	0.244488744
m [a.u.] for 1 kHz–100 kHz	1.051019326	1.047038941

Fig. 4–5 show the frequency dependence of the phase shift angle of the samples before and after annealing, respectively. For an ideal resistor, that is, a continuous metallic layer, the angle should be constant at 0° [20]. In the case of the obtained copper layer, in both cases, the angle is negative and decreases with frequency reaching values close to -90°. This is characteristic of a conventional RC parallel system.

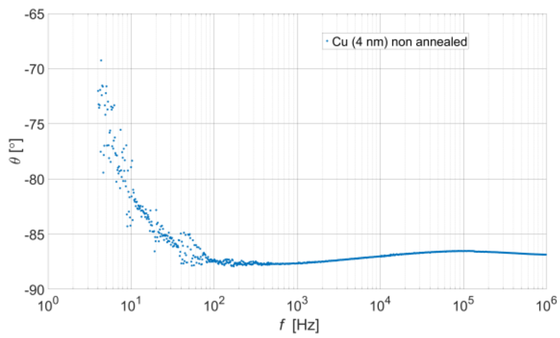

Fig. 4. Dependence of the phase shift angle θ on the measurement frequency f of the copper layer immediately after deposition

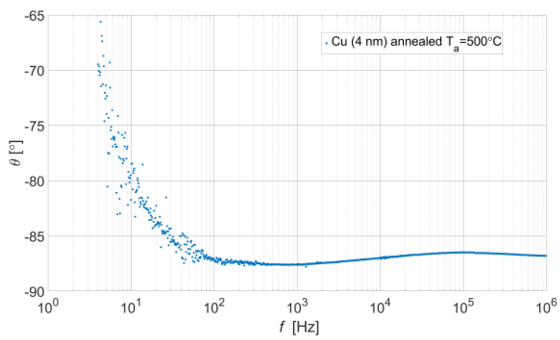

Fig. 5. Dependence of the phase shift angle θ on the measurement frequency f of the copper layer heated at temperature T_a=500°C

Literature data describe that the DC resistance of ultra-thin copper films increases significantly when the films are less than 10 nm thick [3, 14, 23], by up to two orders of magnitude compared to micrometric films [24]. It has also been shown that layers with thicknesses below 5 nm are discontinuous and consist of small islands [10, 17]. Therefore, it is justified to occur abrupt exchange of charges or tunneling between the formed islands and the percolative nature of the obtained structures [2, 6, 10].

4. Conclusions

A technology for deposition of discontinuous thin copper layers using DC magneto-sputtering onto glass substrates was developed. The process was carried out in a vacuum at the level of $1\cdot10^{-7}$ Torr, in an argon atmosphere with a flow of 75 sccm and a plasma power of 100 W for about 2 minutes. In this way, 4 nm of copper was deposited. Then, AC measurements of the obtained structures were carried out before and after annealing at 500°C. On the basis of the obtained results, it can be concluded that the obtained layer shows a percolation character and the dominant mechanism for transferring electric charges is electron hopping or their tunneling between the formed copper islands.

Comparing the obtained results of measurements of non annealed and annealed (oxidized) structures, it can be concluded that the values of the parameters are slightly different from each other, therefore, no influence of the appearance of oxygen particles on nanocomposites exhibiting the previously mentioned charge transfer mechanisms is expected.

Based on these observations, further research will be carried out on the preparation of nanocomposites with the structure of alternately arranged discontinuous metal and dielectric layers by magnetron sputtering. The comparison of results in this paper allows for annealing experiments of the planned structures.

References

[1] Beck R.: Technologia krzemowa. PWN, Warszawa, 1991.
[2] Biegański P., Dobierzewska-Mozrzymas E.: Electrical properties of discontinuous copper films. International Journal of Electronics 70, 1991, 499–504, [http://doi.org/10.1080/00207219108921300].
[3] Cemin F., Lundin D.: Low electrical resistivity in thin and ultrathin copper layers grown by high power impulse magnetron sputtering. Journal of Vacuum Science & Technology A 34(5), 2016, 051506-1–051506-7 [http://doi.org/10.1116/1.4959555].
[4] Chakarvarki S. K.: Track-etch membranes enabled nano-/microtechnology: A review. Radiation Measurements 44(9–10), 2009, 1085–1092, [http://doi.org/10.1016/j.radmeas.2009.10.028].
[5] Chebakova K. A., Dzidziguri E. L. et al.: Open AccessArticle X-ray Fluorescence Spectroscopy Features of Micro- and Nanoscale Copper and Nickel Particle Compositions, Nanomaterials 11(9), 2021, 2388, [http://doi.org/10.3390/nano11092388].
[6] Dingle R. B.: The electrical conducticity of thin wires. Proceeding of the Royal Society A Mathematical, Physical and Engineering Sciences, 1950, [http://doi.org/10.1098/rspa.1950.0077].
[7] Fedotov A., Mazanik A., Svito I., Saad A., Fedotova V., Czarnacka K., Kołtunowicz T. K.: Mechanism of Carrier Transport in Cux(SiO2)1-x Nanocomposites Manufactured by Ion-Beam Sputtering with Ar Ions, Acta Physica Polonica A 128, 2015, [http://doi.org/10.12693/APhysPolA.128.883].
[8] Giroire B., Ali Ahmad M., Aubert G., Teule-Gay L., Michau D., Watkins J. J., Aymonier C., Poulon-Quintin A.: A comparative study of copper thin films deposited using magnetron sputtering and supercritical fluid deposition techniques, Thin Solid Films 643, 2017, 53–59, [http://doi.org/10.1016/j.tsf.2017.09.002].
[9] Grimmet G.: Percolation, 2nd ed. Springer-Verlag, Berlin 1999, [http://doi.org/10.1007/978-3-662-03981-6].
[10] Hill R. M.: Electrical conduction in discontinuous metal films. Contemporary Physics 10, 1969, 221–240, [http://doi.org/10.1080/00107516908224594].
[11] Imantalab O., Fattah-alhosseini A., Keshavarz M. K., Mazaheri Y.: Electrochemical Behavior of Pure Copper in Phosphate Buffer Solutions: A Comparison Between Micro- and Nano-Grained Copper. Journal of Materials Engineering and Performance 25, 2016, 697–703, [http://doi.org/10.1007/s11665-015-1836-z].
[12] Kah-Toong Chan, Teck-Yong Tou, Bee-San Teo: Thickness dependence of the structural and electrical properties of copper films deposited by dc magnetron sputtering technique. Microelectronics Journal 37(7), 2006, 608–612, [http://doi.org/10.1016/j.mejo.2005.09.016].
[13] Kołtunowicz T. N., Żukowski P., Czarnacka K., Bondariev V., Boiko O., Scito I. A., Fedotov A. K.: Dielectric properties of nanocomposite (Cu)x(SiO2)(100−x) produced by ion-beam sputtering. Journal of Alloys and Compounds 652, 2015, 444–449, [http://doi.org/10.1016/j.jallcom.2015.08.240].
[14] Lacy F.: Developing a theoretical relationship between electrical resistivity, temperature, and film thickness for conductors. Nanoscale Research Letters 6, 2011, 1–14, [http://doi.org/10.1186/1556-276X-6-636].
[15] Lim J. W., Isshiki M.: Electrical resistivity of Cu films deposited by ion beam deposition: Effects of grain size, impurities, and morphological defect. Journal of Applied Physics 99, 2006, 094909-1–094909-7, [http://doi.org/10.1063/1.2194247].
[16] Lin Zhang, Xu Lu, Xinyu Zhang, Li Jin, Zhou Xu, Z.-Y. Cheng: All-organic dielectric nanocomposites using conducting polypyrrole nanoclips as filler. Composites Science and Technology 167, 2018, 285–293, [http://doi.org/10.1016/j.compscitech.2018.08.017].
[17] Liu H.-D., Zhao Y.-P., Ramanath G., Murarka S. P., Wang G.-C.: Thickness dependent electrical resistivity of ultrathin (<40 nm) Cu films. Thin Solid Films 384(1), 2011, 151–156, [http://doi.org/10.1016/S0040-6090(00)01818-6].
[18] Mech K., Kowalik R., Żabiński P.: Cu thin films deposited by DC magnetron sputtering for contact surfaces on electronic components. Archives of Metallurgy and Materials 56(4), 2011, 903–908, [http://doi.org/10.2478/v10172-011-0099-4].
[19] Mott N. F., Davies E. A.: Electronic process in non-crystalline materials. Claredon Press, Oxford 1979.
[20] Poklonskii N. A., Gorbachuk N. I.: Fundamentals of impedance Spectroscopy of composites. Belarusian State University, Minsk 2005.
[21] Svito I., Fedotov A. K., Kołtunowicz T. N., Żukowski P., Kalinin Y., Sitnikov A., Czarnacka K., Saad A.: Hopping of electron transport in granular Cux(SiO2)1–x nanocomposite films deposited by ion-beam sputtering. Journal of Alloys and Compounds 615, 2014, S371–S374, [http://doi.org/10.1016/j.jallcom.2014.01.136].
[22] Yang Yu.: Deposited mono-component Cu metallic glass: a molecular dynamics study Materials Today Communications 26, 2021, 102083-1–102083-5, [http://doi.org/10.1016/j.mtcomm.2021.102083].
[23] Yarimbiyik A. E., Schafft H. A., Allen R. A., Vaudin M. D., Zaghloul M. E.: Experimental and simulation studies of resistivity in nanoscale copper films, Microelectronics Reliability 42(2), 2009, 127–134, [http://doi.org/10.1016/j.microrel.2008.11.003].
[24] Zhigal'skii, G. P., Jones B. K.: The physical properties of thin metal films. Vol. 13. CRC Press, London 2003.
[25] Żukowski P., Kołtunowicz T. K., Partyka J., Węgierek P.: Dielectric properties and model of hopping conductivity of GaAs irradiated by H + ions, Vacuum 81(10), 2007, 1137–1140, [http://doi.org/10.1016/j.vacuum.2007.01.070].
[26] Żukowski P., Kołtunowicz T. N., Boiko O., Bondariev V., Czarnacka K., Fedotova J. A., Fedotov A. K., Svito I. A.: Impedance model of metal-dielectric nanocomposites produced by ion-beam sputtering in vacuum conditions and its experimental verification for thin films of (FeCoZr)x(PZT)(100−x), Vacuum 120, 2015, 37–43, [http://doi.org/10.1016/j.vacuum.2015.04.035].
[27] Żukowski P., Kołtunowicz T. N., Partyka J., Fedotova Yu. A., Larkin A. V.: Hopping conductivity of metal-dielectric nanocomposites produced by means of magnetron sputtering with the application of oxygen and argon ions. Vacuum 83(3), 2009, S280–S283, [http://doi.org/10.1016/j.vacuum.2009.01.082].

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