A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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Cu THIN FILMS DEPOSITED BY DC MAGNETRON SPUTTERING FOR CONTACT SURFACES ON ELECTRONIC COMPONENTS

OTRZYMYWANIE CIENKICH POWŁOK Cu DLA EKTRONIKI METODĄ STAŁOPRĄDOWEGO ROZPYLANIA MAGNETRONOWEGO

The results of the DC magnetron sputtering of copper thin films with different parameters of deposition are presented. The main aim of studies was to determine the influence of current value, time of deposition and target-substrate distance on morphology and grain size of obtained copper thin films. The effects of film's thickness on the resistivity of copper thin films were investigated. The influence of parameters on the rate of deposition was also determined. The possibility of application of resulting films for contact surface in electronic components was discussed. The morphology was characterized by AFM method, the size of Cu deposited grains was calculated using Scherrer's method. The WDXRF method was used for estimate of thickness of sputtered films. The resistivity of obtained films was measured using four probe method.
Keywords: DC magnetron sputtering, Cu films, electronic contact

W pracy przedstawiono wyniki badań nad wpływem parametrów napylania magnetronowego cienkich warstw Cu na ich własności. Głównym celem przeprowadzonych badań było określenie wpływu natężenia prądu, czasu osadzania, odległości pomiędzy targetem a napylaną powierzchnią na wielkość ziarna oraz morfologię cienkich warstw. Przeprowadzono również badania nad wpływem grubości warstwy na jej opór właściwy. Omówiona została możliwość stosowania warstw nanoszonych tą metodą w przemyśle elektronicznym. Morfologię otrzymanych warstw charakteryzowano przy użyciu mikroskopu AFM. Wielkość ziarna oszacowana została na podstawie wzoru Scherrera. Grubość warstw wyznaczono techniką WDXRF. Do pomiarów oporu właściwego wykorzystano metodę pomiaru czteropunktowego.

1. Introduction

The studies on physical properties of Cu thin films have been the object of investigations for many years. Copper, because of its high thermal and electrical conductivity, has various applications in electronic industries. The electrical conductivity of commercially pure copper is second only to silver, but lower costs and accessibility causes that Cu is the metal used most often in electronic applications. The disadvantage of copper for electronic contacts is its tendency to form oxides of high resistance. This effect is particularly harmful for lower voltages and currents. Formation of oxides also results in an decrease of the active contact surface [1]. Many methods such as electrodeposition [2, 3], CVD (Chemical Vapour Deposition) [4], pulsed laser deposition (PLD) [5] and magnetron sputtering have been developed for the fabrication of copper thin films. The magnetron sputtering is a simple and low-cost method of obtaining thin films of metals, alloys, nitrides, carbides or oxides [6, 7]. Sputtering is a suitable method for manufacturing of integrated circuits and microsystems or semiconductors interconnects [8] and multilayers [21]. Integrated circuits are used in almost all electronics equipment. This method has a lot of advantages like: high deposition rate, high purity and homogeneity of obtained films, high adhesion and high precision of the control of thickness or grain size of obtained films [9]. The control of grain size is special importance in deposition of semiconductors, because of the grain size-band gap dependence [10]. The grain size effect on physical properties is also a particularly important in contact surfaces for electronic applications [11]. Magnetron sputtering can be also effective method for metallization of surfaces in fabrication of integrated circuits. The main aim of this study is to determine the influence of various parameters of Cu metallization process on the

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parameters having decisive consequences on electronic application.

2. Experimental details

Copper was deposited onto quartz glasses in order to limit the influence of the texture of the substrate on morphology of films. The pressure in the chamber for deposition for each of the samples was p=5×10^{-3} mbar. The purity of copper targets was 99.9999% and their diameter was 57 mm. The substrate used for deposition was not heated. As a working gas Ar (99.999%) was used. Influence of the current value, time of deposition and target – substrate distance on the rate of deposition, thickness, grain size, roughness of obtained films was studied. DC magnetron sputter Emitech K575XD was used for deposition of films. The thickness of obtained films was determined by Wavelength Dispersive X-Ray Fluorescence (WDXRF) method on the spectrofluorimeter Rigaku Primini using scintillation counters (LiF1 crystall). Topography and roughness of films were measured with the use of AFM microscope NT-MDT Ntegra Prima with probe NSG01. Four probe method was used to measure the resistivity of obtained films at 77K [12]. The films were analysed by X-ray method on the diffractometer Rigaku Mini Flex II. The grain size was determined using Scherrer's equation [13]. The results of resistivity measurement was discussed based on Fuchs-Sondheimer (F-S) model for electron surface scattering [14,15] and Mayadas-Shatzkes (M-S) grain boundary scattering model [16].

3. Experimental results

The thickness-fluorescent intensity dependence. The first stage of conducted investigations was determination of the dependence between the intensity of Cu Kα radiation and thickness of films calculated using weight measurement method. In this aim about 50 measuring point were determined. The attenuated Kα radiation coming back to detector can be expressed by the following equation [17]:

$$I_i = \frac{I_0 \cdot C_i \cdot \mu_i \cdot Q \cdot \dfrac{\Omega}{4 \cdot \pi}}{\mu_s + \mu_{s,E_i}} \cdot \left(1 - e^{-\rho \cdot h \cdot \left(\mu_s + \mu_{s,E_i}\right)}\right) \quad (1)$$

where: I_0 – initial intensity, C_i – element's concentration, h – thickness of layer, μ_s – mass absorption coefficient of alloys, ρ – sample density, μ_i – mass absorption coefficient of i element, Q – excitation factor, $\dfrac{\Omega}{4 \cdot \pi}$ – fraction of radiation that enters the detector, μ_{s,E_i} – fluorescence radiation absorption coefficient.

For the pure Cu metal: $\mu_i = \mu_s$ and $C_i = 1$, so one can write:

$$I_{Cu} = \frac{I_0 \cdot \mu_{Cu} \cdot Q \cdot \dfrac{\Omega}{4 \cdot \pi}}{\mu_{Cu} + \mu_{s,E_i}} \cdot \left(1 - e^{-\rho \cdot h \cdot \left(\mu_{Cu} + \mu_{s,E_i}\right)}\right) \quad (2)$$

It is clear form eq. (2) that Cu Kα intensity isn't directly proportional to the thickness of the film. WDXRF method is the most exact in the range in which the changes of the signal per unit of film's thickness are the biggest. The resulted experimental points were fitted with the function:

$$y = A \cdot \left(1 - e^{-b \cdot h}\right) \quad (3)$$

where: $A = \dfrac{I_0 \cdot \mu_{Cu} \cdot Q \cdot \dfrac{\Omega}{4 \cdot \pi}}{\mu_{Cu} + \mu_{s,E_i}}$ and $b = \rho \cdot (\mu_{Cu} + \mu_{s,E_i})$. Using experimental points showed in Fig. 1, the coefficients A and b were determined. The eq. (3) was used later in this work to estimate the thickness of deposited films based on registered intensity of Cu Kα radiation.

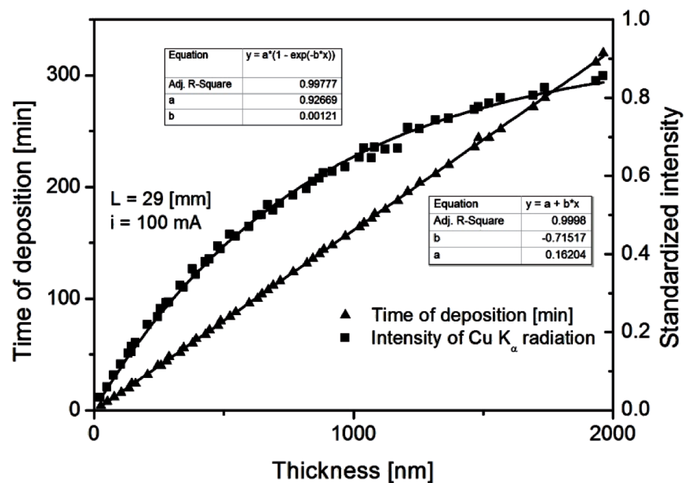

Fig. 1. Thickness-intensity of Cu Kα radiation and Thickness-time of deposition dependences for films deposited using i = 100 mA

Influence of the current on the rate of deposition. To estimate the rate of deposition, the thickness of films after deposition time 4 min for different current values was measured. With increasing current value for the same Ar pressure the probability of collision of Ar atoms with electrons coming from copper target increases. It results in the increase of the rate of deposition. Conducted studies show that relation between the rate and the current is linear. The dependence shown in Figs 2 and 3 is based on the results of WDXRF analysis. Fig. 2b shows the dependence between the current of deposition and the intensity of Cu - Kα radiation. Diffraction patterns for obtained films are shown in Fig. 4. There one can see three peaks corresponding to Cu FCC structure of (111), (200) and (220) planes (Fig. 4). The presence of peaks

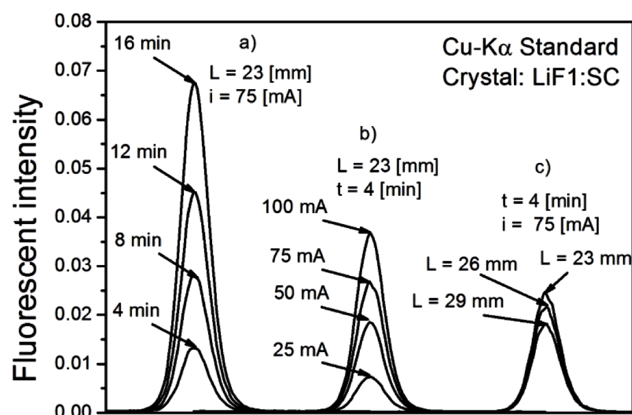

Fig. 2. Kα spectra measured at 45° of 2 theta for a) films deposited in different time, b) films deposited in the same time and with the different deposition current value, c) films deposited for different target – substrate distance

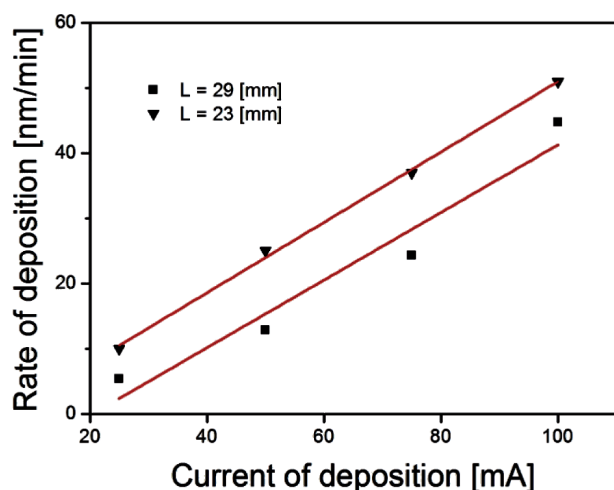

Fig. 3. Dependence between the current and the rate of deposition for different L values (L = target – substrate distance)

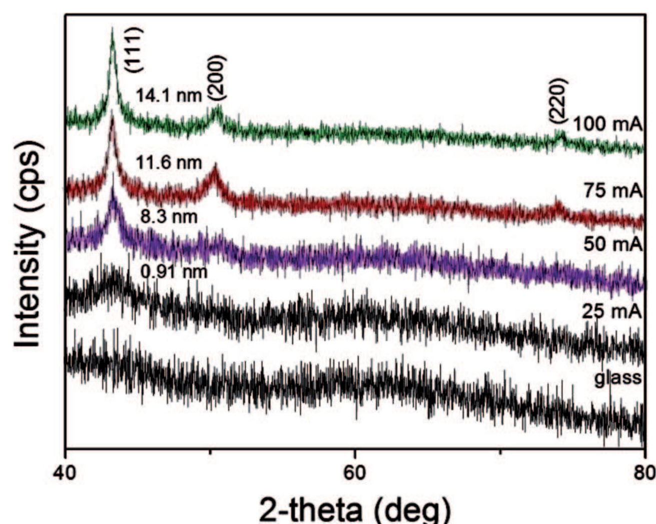

Fig. 4. XRD diffraction pattern for samples received with the different current of deposition for t = 4 min

coming from (200) and (220) plans are not visible for deposition at 25 mA. In diffraction pattern for film deposited at 50 mA the peak coming from (200) plane was appeared. The increase of current results in increase of peaks intensity. This is connected with the increase of the rate of deposition with the increase of current value. We suppose also that the peaks obtained for the films deposited at 50 mA and 75 mA show on presence of more crystalline phase than the films deposited at lower than 50 mA current value. Consequently for applied current FCC structure of Cu deposit was obtained.

Influence of deposition current on morphology of obtained films. The grain size was calculated by Scherrer's method for Cu [111] reflex (Fig. 9). The grains size-current and the grains size-sputter time dependences are linear as shown in Fig. 9. It means that using magnetron sputtering technique the choice of suitable parameters of deposition can produce films with the grains of required size. Despite the different scale is visible that the surface of deposited Cu is more unequal than the surface of glass substrate (Fig. 6). The results of roughness measured by the AFM are presented in Fig. 5. As one can see, the increase of the current of deposition caused the increase of roughness parameters (Ra – average roughness, Rz – ten point height method) values. The increase of roughness has an effect on the decrease of the surface of point contact between electronic components, and on the decrease of the effective cross section of films. As one can see in Fig. 5, to obtain the surface with high surface of point contact, the low current value should be applied. The grain size has also significant effect on the resistivity of the electronic contacts. As shows in Fig. 9 the increase of the current value results in larger grain formation. With the increase of grain size the mean free path of the electron for non dislocated grains is increasing. This both features decide about the possibility of applying sputtered copper thin films as a material for electronic contacts surface.

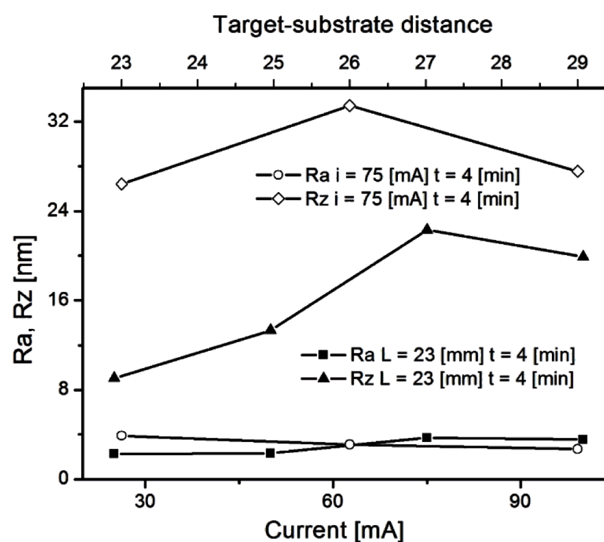

Fig. 5. Roughness of sputtered Cu layer using AFM for films deposited for a different current (area 5 μm×5 μm) and for different target-substrate distance (area 10 μm×10 μm)

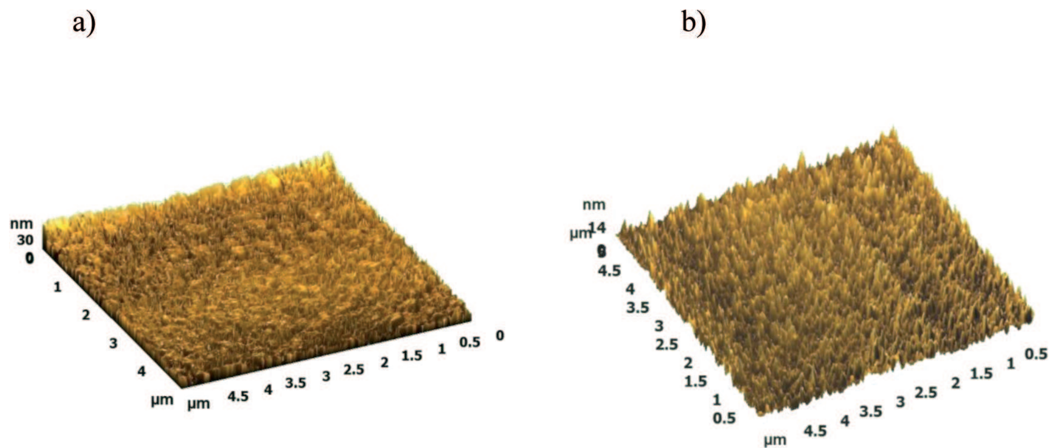

Fig. 6. Topography of substrate (a) and sputtered copper (i = 75 mA, t = 4 min, L = 23 mm) for area 5 μm×5 μm

Influence of time of deposition on the morphology of the films. To determine the influence of time on thickness and grain size of copper films, target-substrate distance L = 23 mm and i = 75 mA were used. Conducted studies let us affirm that the thickness changes linear with the time of deposition. Fig. 9 shows that the grain size-time of deposition dependence is also linear. These dependences creates possibility for obtaining the films with given thickness or grain size. To obtain the smaller grain size, the lower current value and longer time of deposition should be applied. This create the possibility of maintaining roughness on the low level and to obtain larger grain size. As the result the contact surface and the mean free path of the electron will be increased. The XRD diffraction patterns for films deposited in different time using i = 75 mA and L = 23 mm are shown in Fig. 7. There are visible three peaks corresponding to (111), (200) and (220) FCC Cu phase.

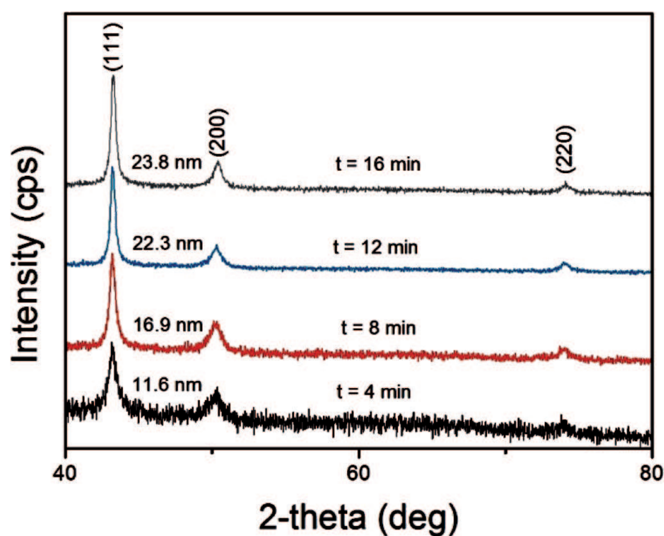

Fig. 7. XRD diffraction pattern for the samples obtained for different time of deposition. Current value and target-substrate distance were kept constant (L = 23 mm and i =.75 mA)

Influence of target – substrate distance on morphology of obtained films. The dependence between target-substrate distance and grain size in the range 23 – 29 mm is linear (Fig. 9). It means that one can simply change the distance between target and substrate to control thickness and grain size of films. The summary effect of the increase of current value, time of deposition and decrease of target-substrate distance on the grain size is shown in Fig. 9. For different distance values the roughness was measured (Fig. 5) and it increases when the target-substrate distance is decreased. As one can see in Fig. 5, the increase of target-substrate distance value caused the decrease of roughness parameters (Ra, Rz) values. Conducted studies shows possibility of influence on parameters of films by the target-substrate distance. The XRD diffraction patterns in Fig. 8 shows that the highest rate of deposition was reached for L = 23 mm. In this case the three peaks coming from Cu FCC structure are visible. The changes in the intensity are most perceptible for peaks coming form (200) and (111) planes.

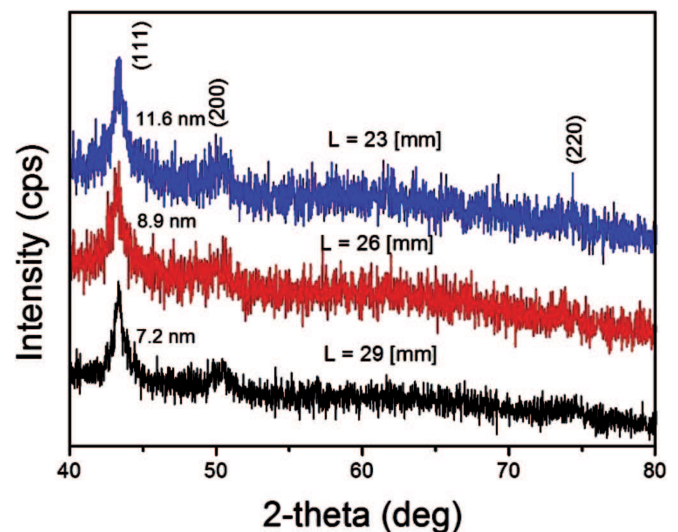

Fig. 8. XRD diffraction pattern for the samples obtained for the different target – substrate distance

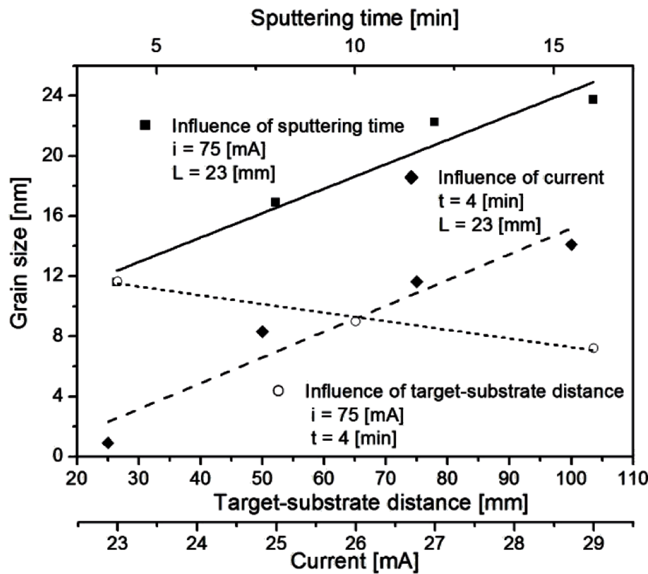

Fig. 9. Influence of sputtering time, current and target-substrate distance on grain size of deposited films

Resistivity of obtained films. In this section the thickness effect on resistivity of resulting films was reported. It is well known that increase of thickness results in decrease of resistivity of films. The influence of surface, interface electron scattering and grain boundary scattering on resistivity of thin films can be described by the FS-MS combined theory. According to literature [18] the film resistivity considered the electron scattering on the surface, interface and grain boundary ρ_{s-g} can be expressed by the following equation:

$$\rho_{s-g} = \rho_0 \cdot \left[1 + \frac{3}{8 \cdot k} \cdot (1-p) + \frac{3}{2} \cdot \alpha \right] \quad (4)$$
$$\text{if} k >> 1, \quad \text{and } \alpha << 1$$

where: ρ_0 – is the bulk resistivity, $k = \frac{d}{\lambda}$ – is the ratio of film thickness (d) to the bulk mean free path (λ), $\alpha = \frac{\lambda}{d} \cdot \frac{R}{1-R}$, where R – is the grain boundary reflection coefficient, p – reflection coefficient. After replacement of α and p it's can be writed:

$$\rho_{s-g} \approx \rho_0 + \left(\frac{3 \cdot \lambda \cdot \rho_0}{8} \cdot (1-p) + \frac{3 \cdot \lambda \cdot \rho_0}{2} \cdot \frac{R}{1-R} \right) \cdot \frac{1}{d} \quad (5)$$

As shown by equation (6) the factor ρ_{s-g} is linear function of inversely of film's thickness. Based on eq. (5) the bulk resistivity of sputtered films were estimated. For prepared films the bulk resistivity ρ_0=1.87 [$\mu\Omega \cdot cm$] were obtained. According to literature the bulk resistivity for Cu is ρ_0=1.67 [$\mu\Omega \cdot cm$][20]. The higher bulk resistivity of sputtered films can be a result of either internal stress or large quantity of dislocations in deposited films. The electrical resistivity measurements let affirm that for the Cu layer of thickness higher than 250 nm the resistivity are constant. That is why the application of Cu layer of thickness higher than 250 nm seems to unjustified by the economic point of view.

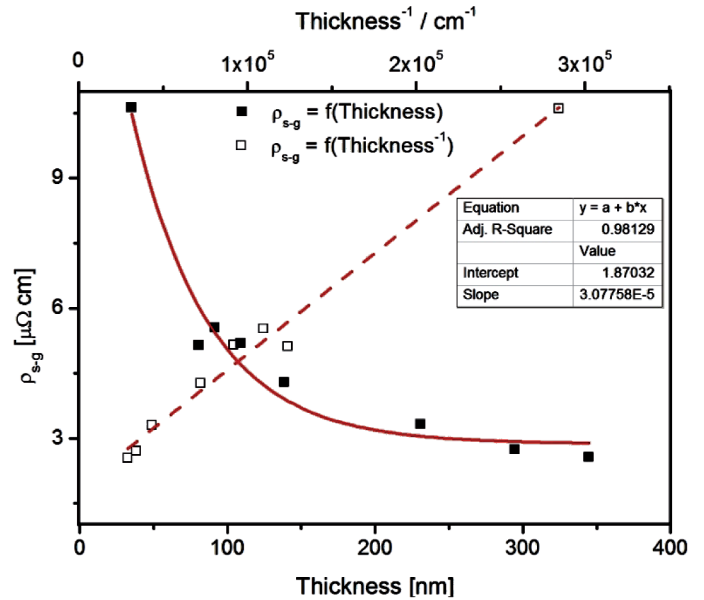

Fig. 10. Thickness and thickness inversely dependences of resistivity for obtained films

Conclusions. This work enabled us determine the dependence between parameters of deposition process and properties of resulting Cu thin films for contact surface in electronic application. It's very important that the better adhesion of deposited films to substrate was observed when lower current value and longer time of deposition were applied. XRD analysis shows FCC structure of deposited films. The increase of current value or time of deposition and decrease of target-substrate distance result in increase the grain size and R_a, R_z parameters. Conducted studies shows that the resistivity for films thicker than 250 nm is constant. The measured bulk resistivity of sputtered films was ρ_0=1.87 [$\mu\Omega \cdot cm$].

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