Influence of microstructure and surface topography on the electrical conductivity of Cu and Ag thin films obtained by magnetron sputtering

D A Polonyankin, A I Blesman and D V Postnikov

Omsk State Technical University (OmSTU), 11 Mira Avenue, Omsk, 644050, Russia

E-mail: nano@omgtu.ru

Abstract. Conductive thin films formation by copper and silver magnetron sputtering is one of high technological areas for industrial production of solar energy converters, energy-saving coatings, flat panel displays and touch control panels because of their high electrical and optical properties. Surface roughness and porosity, average grain size, internal stresses, orientation and crystal lattice type, the crystallinity degree are the main physical properties of metal films affecting their electrical resistivity and conductivity. Depending on the film thickness, the dominant conduction mechanism can affect bulk conductivity due to the flow of electron gas, and grain boundary conductivity. The present investigation assesses the effect of microstructure and surface topography on the electrical conductivity of magnetron sputtered Cu and Ag thin films using X-ray diffraction analysis, scanning electron and laser interference microscopy. The highest specific conductivity (78.3 MS m⁻¹ and 84.2 MS m⁻¹, respectively, for copper and silver films at the thickness of 350 nm) were obtained with the minimum values of roughness and grain size as well as a high degree of lattice structuredness.

1. Introduction

Designing insulating, conducting and semiconducting films from metals and their oxides onto substrates is one of the high technological areas in microelectronics and optical industries due to their distinctive electrical and optical properties [1].

In the field of electronic and optical devices, silver is an exceptional material because of its reflectivity which reaches 97.7% at a wavelength of 500 nm and the smallest resistivity among all the metals [2]. High reflecting ability in the visible range of wavelengths as well as large electrical conductivity cause the widespread pure silver application for optical reflectors and for producing electrical conductors in microprocessor technology. However, the impact of environmental factors (temperature, humidity) and the aggressive exposure of chlorine and sulfur reduce the performance of silver coatings [3].

Copper metal coatings are widely used in microelectronics because of its low electrical resistivity (1.67 μΩ cm at room temperature), small degree of atom surface migration and high melting point [4]. Nanostructured thin copper films formed on silicon substrates by magnetron sputtering are used for protective electromagnetic screens production [5]. Application of copper magnetron sputtering for integrated microcircuits manufacture is caused by its high thermal and electrical conductivity (only silver has a better electrical conductivity at a higher material cost) [6]. Thin copper films sputtered on porous silicon substrate with high optical and electrical properties are widely used in production of LEDs, optical fibers and filter, photovoltaic diodes and different type of sensors [7].
The review of published data on the problem of thin copper and silver films formation by magnetron sputtering allows us to formulate the following statements. Conductive copper and silver coatings can be divided into two groups: the first one contains ultrathin films with the thickness less than 40 nm, which exhibit size effect property [8], and the second one contains films related to submicron scale with the thickness ranging from 50 to 800 nm [9] having grain-boundary mechanism of conductivity, which also obeys the classic laws of conductivity theory (Ohm's law, resistivity dependence on temperature and conductor geometry, etc.). According to film with the thickness related to submicron region, the dominant conduction mechanism can impact bulk conductivity due to the electron gas flow and grain boundary conductivity [10]. The most significant physical, chemical and structural properties of films affecting their electrical conductivity include surface roughness [11], its porosity [12], adhesion force and energy [13], average grain size [8, 14], internal stresses [15], crystal lattice type and coating crystallinity degree [16, 17]. The physical and electrical properties of films considerably depend on such process parameters of their production as temperature [2], substrate material [11], chamber pressure [18], sputtering type (high–frequency [9, 19] or DC [17] sputtering) and power [20], deposition rate [11], electromagnetic field configuration and target area [21].

Thus, magnetron sputtering is extensively used for surface modification of products demanded in various industries, while thin–film coating design is the basic part or a constituent of the production technology for protective, wear–resistant, low–friction, anti–corrosion and decorative copper and silver coating with special optical and electrical properties [22]. Thus, obtaining Cu and Ag conductive coatings by magnetron sputtering is a topical problem of modern materials science and nanotechnology due to significant application value of these method and materials in technologies of thin–film coatings production with high physical, chemical and performance characteristics.

The object of this study is to conduct a comparative research of microstructure and surface topography influence on electrical conductivity of Cu and Ag thin films produced under identical conditions by RF magnetron sputtering having the thickness ranging from 100 nm to 500 nm with 50-nm step.

2. Experimental details

For Cu and Ag films preparation, ADVAVAC VSM–200 magnetron setup was used. Thin Cu and Ag films with the thickness ranging from 100 nm to 500 nm and 50 nm step were sputtered on soda–lime silicate glass substrate at high vacuum RF mode with the source power of 100 W under (3.2–3.4)·10⁻³ mbar argon pressure and pre-ionic chamber cleaning for 10 minutes. The selection of the thickness range is conditioned by the reason that such thickness is far from the size effect region [9] and bulk properties are expected. Thin films were sputtered with pure argon (Ar) by using Cu and Ag targets (99.95% purity, with 50-mm diameter).

Cu and Ag qualitative and quantitative analysis was performed by scanning electron microscopy (JEOL JCM–5700) and energy dispersive spectroscopy (EDS). XRD investigation of silver and copper films with the thickness in the range from 100 nm to 500 nm and 50 nm step was carried out by a sliding X–ray beam method (fixed tube angle \(\theta = 5^\circ\)) in Bragg–Brentano configuration with 2\(\theta\) from 40° to 80° for Cu films and from 30° to 80° for Ag films and Cu–Ka radiation (\(\lambda = 0.154 \text{ nm}\)). Shimadzu XRD–7000 diffractometer allowed obtaining values of 2\(\theta\) angle and corresponding full–width at half–maximum (FWHM) for all identified peaks.

Surface roughness analysis was provided by laser interference microscopy (LIM) performed in dependence on the film thickness. Laser interference microscope MIM–340 (Shvabe) is designed for non–contact and non–destructive submicron measurements in nanometer region and is equipped with 405 nm wavelength violet laser.

3. Results and discussion

SEM images and EDS results of Ag and Cu films with 350 nm thicknesses are shown in Figures 1 and 2, respectively. Results of quantitative EDS analysis demonstrate that Ag and Cu films do not contain impurity atoms, which is also confirmed by XRD results.
As seen from mixed XRD pattern presented in Figure 3 and 4, it contains the peaks reflected by Ag and Cu crystal lattice and peaks related to planes with [(111), (200), (220) and (311)] Miller indices was detected. The intensity of (111) peaks surpasses manifold the intensities of other peaks. The shape of (111) peak indicates a high crystallinity degree of sputtered Ag and Cu films. Thus, we can conclude that Ag and Cu films with the thickness ranging from 100 nm to 500 nm possess polycrystalline face-centered cubic structure of bulk materials and their crystallographic plane orientation preferentially has (111) texture. Applying sliding X–ray beam allowed us to detect scattering radiation only from Ag and Cu, because the film thickness is greater than X–ray penetration depth, and the signal coming from the substrate is not observed.

![Figure 1. SEM image and EDS results of Ag film with 350 nm thickness.](image1)

![Figure 2. SEM image and EDS results of Cu film with 350 nm thickness.](image2)

![Figure 3. Mixed XRD pattern of Ag films with the thickness in the range from 100 nm to 500 nm and 50 nm step.](image3)

3D LIM images and surface roughness profiles of Ag and Cu films with 350 nm thicknesses are shown in Figures 5 and 6, correspondingly. RMS values of surface roughness were calculated by MIM–Soft program for the base length of 80 nm after bonding together four surface profiles by MIM–Series software for each film thickness value. The average roughness of Ag films ranges from 3.59 nm (for 350-nm film) to 4.86 nm (for 100-nm film), while the average roughness of Cu films ranges from 5.44 nm (for 350-nm film) to 7.69 nm (for 500-nm film) depending on the film thickness (Figure 7).
Figure 4. Mixed XRD pattern of Cu films with thickness in the range from 100 nm to 500 nm and 50 nm step.

Figure 5. 3D LIM image and surface roughness profile of 350-nm Ag film.

On the basis of XRD data, according to Debye–Scherrer formula, the average grain size was calculated in dependence on the film thickness (see Figure 7). The average grain size of Ag films ranges from the minimum 10.02 nm (for 350-nm film) to maximum of 11.12 nm (for 500-nm film). The average grain size of Cu films ranges from the minimum of 11.43 nm (for 350-nm film) to maximum of 13.24 nm (for 500-nm film). The roughness and the average grain size dependences on the film thickness can be explained by island mechanism, when the force and energy of adhesion to the substrate is less than the mutual binding energy of the deposited atoms, and film properties with the thickness growth become close to that of bulk material.
Figure 6. 3D LIM image and surface roughness profile of 350-nm Cu film.

Copper and silver resistivity was measured by ohmmeter for all values of films thickness from 100 to 500 nm with 50 nm step, formed on the substrate of the cover glass (with the length and the width of 7.5 and 2.5 mm, respectively), as well as their specific conductivity was calculated. The dependencies of specific conductivity on film thickness are shown in Figure 8.

Figure 7. The average grain size and roughness vs. Cu and Ag film thickness.

Specific conductivity of Ag ranges from the minimum of 76.2 MS m$^{-1}$ (for 100-nm film) to the maximum of 84.2 MS m$^{-1}$ (for 350-nm film), while the specific conductivity of Cu films ranges from 70.2 MS m$^{-1}$ (for 200-nm film) to 78.3 MS m$^{-1}$ (for 350-nm film).

4. Conclusion
Cu and Ag films produced by RF magnetron sputtering having the thickness ranging from 100 nm to 500 nm and with 50 nm step according to XRD results possess polycrystalline face–centered cubic
structure of bulk materials and their crystallographic plane orientation preferentially have (111) texture.

The average roughness of Ag films ranges from 3.59 nm (for 350-nm film) to 4.86 nm (for 100-nm film), while the average roughness of Cu films ranges from 5.44 nm (for 350-nm film) to 7.69 nm (for 500-nm film) in dependence on the film thickness. The average grain size of Ag films ranges from the minimum of 10.02 nm (for 350-nm film) to the maximum of 11.12 nm (for 500-nm film). The average grain size of Cu films ranges from the minimum of 11.43 nm (for 350-nm film) to the maximum of 13.24 nm (for 500-nm film). The roughness and the average grain size dependencies from the film thickness can be explained by island mechanism, when the force and energy of adhesion to the substrate is less than the mutual binding energy of the deposited atoms, and film properties with the thickness growth become close to the bulk material.

The highest specific conductivity (78.3 MS m⁻¹ and 84.2 MS m⁻¹, respectively for copper and silver films at the thickness of 350 nm) were obtained with the minimum values of roughness and grain size as well as a high degree of lattice structuredness.

References
[1] Gordon R 1997 J. Non–Cryst. Solids 218 81
[2] Suzuki T, Abe Y, Kawamura M, Sasaki K, Shouzu T and Kawamata K 2002 Vacuum 66 501
[3] Nakanishi Y, Kato K, Omoto H and Yonekura M 2013 Thin Solid Films 532 141
[4] Cao B, Yang T R, Li G P, Cho S J and Kim H 2012 Advanced Materials Research 430 419
[5] Desideri D, Natali M, Cavallin T and Maschio A 2014 IET Science, Measurement & Technology 8 1
[6] Mech K, Kowalik R and Żabiński P 2011 Archives of Metallurgy and Materials 56 903
[7] Ansari Z A and Hong C L 2002 Mater. Sci. Eng., B 90 103
[8] Ke Y, Zahid F, Timoshkovskii V, Xia K, Gall D and Guo H 2009 Phys. Rev. B 79 155406
[9] Marechal N, Quesnel E and Pauleau Y 1994 Thin Solid Films 241 34
[10] Rossnagel S M and Kuan T S 2004 J. Vac. Sci. Technol. B 22 240
[11] Yang J, Huang Y and Xu K 2007 Surf. Coat. Technol. 201 5574
[12] Carton O, Ghaymouni J, Lejeune M and Zeinert A 2013 Journal of Spectroscopy 2013 1
[13] Tkachenko E A, Postnikov D V, Blesman A I and Polonyankin D A 2016 IOP Conf. Ser.: Mater. Sci. Eng. 110 012009
[14] Sursaeva V G, Gottstein G and Shvindlerman L S 2016 Scripta Mater. 116 91
[15] Sun X, Hong R, Hou H, Fan Z and Shao J 2007 Thin Solid Films 515 6962
[16] Jiang H 1998 J. Vac. Sci. Technol. A 16 3376
[17] Chan K–Y, Luo P–Q, Zhou Z–B, Tou T–Y and Teo B–S 2009 Appl. Surf. Sci. 255 5186
[18] Del Re M, Gouttebaron R, Dauchot J P, Leclère P, Lazzaroni R, Wautelet M and Hecq M 2002 Surf. Coat. Technol. 151 86
[19] Jiang H, Klemmer T, Barnard J, Doyle W and Payzant E 1998 Thin Solid Films 315 13
[20] Chan K–Y and Teo B–S 2007 Microelectron. J. 38 60
[21] Promros N, Sittimart P, Pananoo N, Kongnithichalerm S, Horpratham M, Bhamumnavin W and Paosawatayanyong B 2016 Key Eng. Mater. 675 193
[22] Kelly P J and Arnell R D 2000 Vacuum 141 159