Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 43
ISSUE 1
November
2010

Crystallographic texture and anisotropy of electrolytic deposited copper coating analysis

S.J. Skrzypek*, W. Ratuszek, A. Bunsch, M. Witkowska, J. Kowalska, M. Goły, K. Chruściel
AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland
* Corresponding author: E-mail address: skrzypek@agh.edu.pl

Received 01.09.2010; published in revised form 01.11.2010

Properties

ABSTRACT

Purpose: To investigate of texture and microstructure of electrodeposited copper thin films.

Design/methodology/approach: nfluence of the electrodepositing parameters e.g. applied electric current as variable on texture formation of copper films was studied at presented work. Experiment was done for copper deposition from sulphate bath under galvanostatic and pulse current with different additives in the bath. X-ray examination included texture measurements phase analysis by means of Bragg-Brentano, grazing incidence diffraction and crystallite size using broadening of X-ray diffraction line.

Findings: Electrodeposited copper coatings exhibit different texture and microstructure depending on applied conditions in which they were obtained. Pulse and direct current conditions leads to different texture of electrodeposited copper coatings. For each type of current texture depends on deposition time and current intensity. Only in some cases {111} component was obtained.

Research limitations/implications: extures of the investigated samples are very sensitive for applied current conditions of electrodepositing. At the copper coatings obtained with reverse current texture components {110} is dominating one. Relations between texture and properties (hardness, Young module and grain size) of copper layer were found.

Originality/value: The texture of electrodeposited copper should be influential structural characteristic when anisotropy is considered. It is already known that electromigration depends on texture of copper films.

Keywords: Copper films; Texture; Electrodepositing

Reference to this paper should be given in the following way:
S.J. Skrzypek, W. Ratuszek, A. Bunsch, M. Witkowska, J. Kowalska, M. Goły, K. Chruściel, Crystallographic texture and anisotropy of electrolytic deposited copper coating analysis, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 264-268.

1. Introduction

Electrodepositing is one of the employed methods to obtain metallic films of adequate physical, mechanical properties and good adhesion. Electrodeposited copper is most extensively used in circuit boards production and often as a base for further formation of metallic films. Electrodeposited copper thin coatings are widely used in electronic and automotive industry so electrical and mechanical properties of copper layers are very important [1,2].

The texture of electrodeposited copper should be influential structural characteristic when anisotropy is considered. It is already known that electromigration depends on texture of copper films [4]. Texture component {111} is recognized as one, which increases electric conductivity at the copper electrodeposited layers [3]. We could also expect that mechanical and visual properties of copper coatings depend on their texture as well e.g. in calculation of anisotropic elastic modulus and residual stresses [5-8,10,11,14,16]. For that reason texture of copper coatings and relation between texture and anisotropy of mechanical properties were investigated in presented work.

2. Material and experimental description

2.1. Sample preparation

The substrate of all samples was brass with previously deposited nickel coating, i.e. before copper deposition. The unipolar and bipolar (with anodic current) pulse current sequences were used to obtain copper coatings (Tab. 1). Layers sequences are presented in Figure 1. Samples were in a form of flat plate with size of 40x40x2.5 mm.

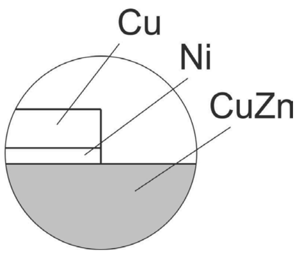

Fig. 1. Layers sequences on the experimental samples

Table 1.
Electrodepositing parameters for experimental samples

Sample description	Parameters of pulse sequence				
	Forward - cathode current time and density		Reverse - anodic current time and density		Deposition time
	t_c [ms]	i_c [A/dm^2]	t_a [ms]	i_a [A/dm^2]	t_{dep} [sec]
pulse					
S-01	25	1.5	1	2	1400
S-02	25	2.5	1	3	1000
S-03	25	3.5	1	4	700
S-04	25	1.5	0	0	1400
S-05	25	2.5	0	0	1000
S-06	25	3.5	0	0	700
S-07	45	1.5	2	2	1400
S-08	45	2.5	2	3	1000
S-09	45	3.5	2	4	700
direct					
SD-01	-	-	-	-	1400
SD-02	-	-	-	-	1000
SD-03	-	-	-	-	700

2.2. Experimental procedure

X-ray investigations were conducted by means of Siemens diffractometer D500, using Cu K_α radiation ($\lambda_{K\alpha}$=0.154nm) and Bruker diffractometer D8 Advance, using Co K_α.radiation ($\lambda_{K\alpha}$=0.179nm). X-ray examination included the texture measurements and the phase analysis from the centre of the samples [9]. The incomplete pole figures were recorded for three crystallographic planes {111}, {200}and {220}. Texture analysis was performed on the basis of the calculation of the orientation distribution function (ODF) [10], pole figures (PF). Also ODF_{max} and ODF texture index as quantitative value describing the sharpness of the texture were calculated. Value of the ODF index is 1.0 for randomly oriented grains and for monocrystals its value is infinity. The stronger is texture of the sample the higher is value of this index.

In addition some simplifications of texture analyse were done based on measurements of intensity of the selected diffraction lines. Such approach can be important in technology like non-destructive quality control.

The following texture indexes were applied to these analyses:

- **Intensity ratio - I_{h1k1l1}/I_{h2k2l2}** – relation between intensities of particular diffraction lines measured by standard Bragg-Brentano (B-B) or grazing incidence diffraction [11,14] e.g. I_{111}/I_{200}, I_{111}/I_{220} etc. For not textured materials value of these indexes can be found at ICCD standards or can be measured for randomly oriented powder. The more intensity ratios differ from standards the strongest is texture of the sample.
- **Orientation index - M_{hkl}** – calculated on the base of Bragg-Bertano or grazing incidence diffraction measurements using formula:
  $M_{hkl} = \{I_{(hkl)} / (I_{(110)} + I_{(200)} + \ldots)\} / \{IF_{(hkl)} / (IF_{(110)} + IF_{(200)} + \ldots)\}$

  where: $I_{(hkl)}$ - measured intensity of diffraction line, $IF_{(hkl)}$ - intensity of diffraction line received from standard pattern in ICDD card

Crystallite size was calculated on the base of Scherrer methods by the measurement of the diffraction peak physical broadening (β_K) [12,13].

3. Results and discussion

The recorded diffraction patterns (Fig. 2) present different intensities and shape of peaks. Both were used for calculations selected parameters (Tab. 2, Fig. 6).

Textures of the investigated samples are very sensitive for applied current conditions of electrodepositing. They are presented in the form of calculated pole figures and ODF (Fig. 3-5) [2-4,10]. The copper coatings obtained with reverse current (samples S01-S03) had texture components {110} which was dominating one. This component was strongest for longest deposition time (t_{dep}). If the reverse current is not applied (samples S04-S06) three texture components are created namely: (110), (111) and (100). These components with the increase of deposition time become stronger. Sample preparation in reverse mode with different relation between deposition time for forward and reverse current (samples S07-S09) leads to texture with three components in the copper coatings. They are strengthened with total deposition time. For the direct current technique (samples SD01-SD03) very weak textures are created at electrodeposited copper layers and they do not depend on deposition time. The axial symmetry of texture was found in majority samples (Fig. 3-5).

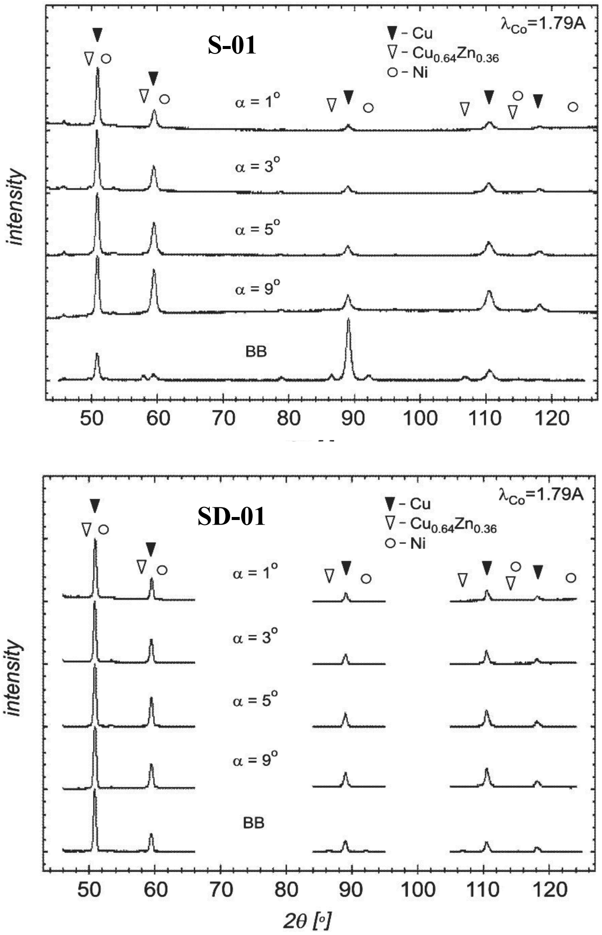

Fig. 2. Diffraction patterns of S-01 and SD-01 sample obtained with D8-Advance diffractometer using $\lambda_{CoK\alpha}$ wavelength, GID geometry with incidence angle α = 1,3, 5 and 9 deg and BB geometry

Textures of the samples in term of its strength are presented by M_{hkl} texture index and ODF index. Texture indexes, crystallite size and mechanical properties of experimental samples are given in Tables 2, 3 and on Figure 6.

In the Figure 7 anisotropy of Young modulus and Poisson ratio (ν) versus orientation factor 3Γ calculated from single crystal data s_{ij} for Cu according to iso-stress Reuss model is shown.

Table 2.
Texture indexes and crystallite size for thin electrodeposited copper coatings

Sample	Texture index M_{220}	Texture index (ODF)	ODF max	Crystallite size [nm]
not textured standard	1.0	1.0	-	-
S-01	4.1	2.07	4.9	36
S-02	2.7	1.38	3.0	58
S-03	1.0	1.07	1.4	127
S-04	0.6	1.36	3.1	133
S-05	0.9	1.58	3.0	134
S-06	0.7	1.04	1.3	129
S-07	0.7	1.05	1.4	122
S-08	0.8	1.39	2.9	124
S-09	0.9	1.36	2.3	143
SD-01	0.8	1.04	1.5	99
SD-02	0.7	1.06	1.4	111
SD-03	0.7	1.06	1.4	135

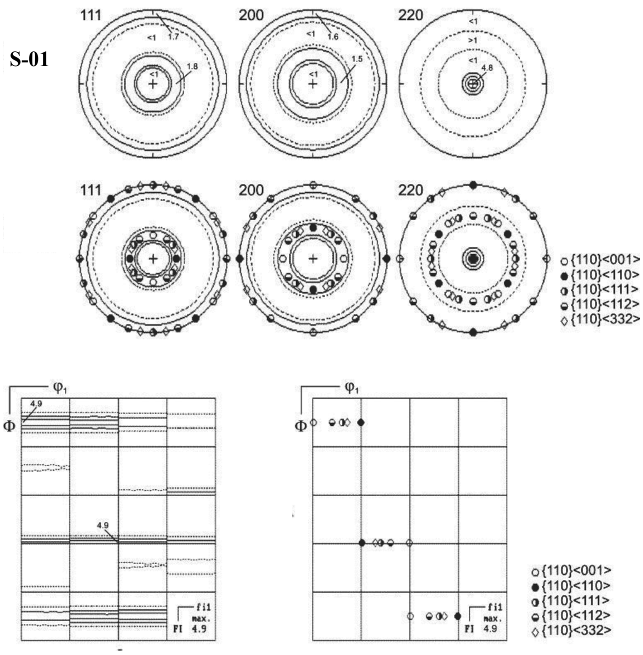

Fig. 3. Measured and calculated pole figures and ODF for S-01 sample. Ideal orientations fitted to pole figures and ODF

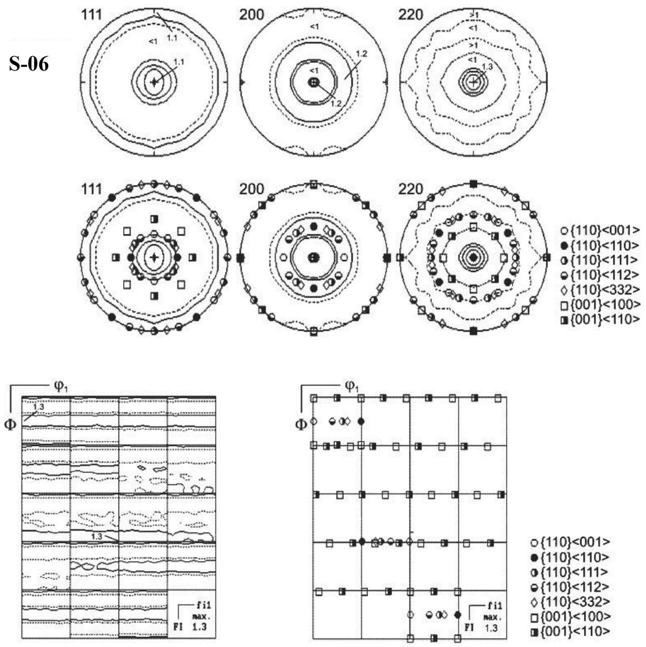

Fig. 4. Measured and calculated pole figures and ODF for S-06 sample. Ideal orientations fitted to pole figures and ODF

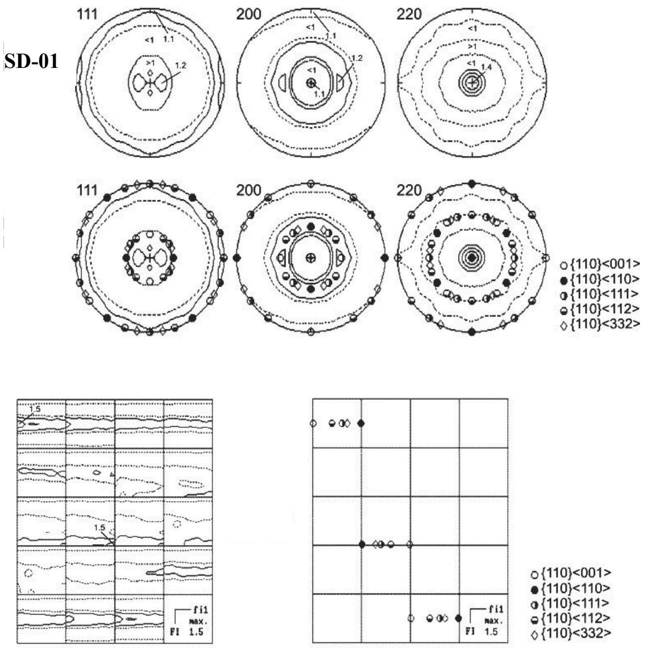

Fig. 5. Measured and calculated pole figures and ODF for SD-01 sample. Ideal orientations fitted to pole figures and ODF

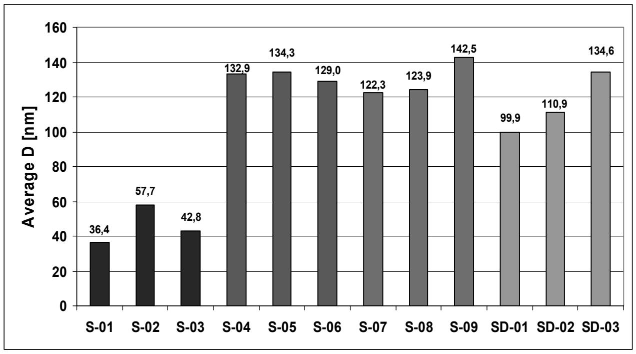

Fig. 6. Calculated average crystallite size (D) by Scherrer method for particular samples series

Table. 3.
Hardness and Young modulus

Sample	HV	HIT [GPa]	E [GPa]	E_{TEX} [GPa]
S-01	262	2,77	109,4	98
S-02	268	2,83	116,5	78
S-03	269	2,84	110,4	44
S-04	151	1,60	81,5	38
S-05	140	1,49	80,2	43
S-06	156	1,65	90,0	41
S-07	263	2,79	96,4	40
S-08	148	1,56	84,9	50
S-09	139	1,47	78,5	41
SD-01	168	1,77	93,0	54
SD-02	176	1,86	96,4	51
SD-03	163	1,73	91,7	55

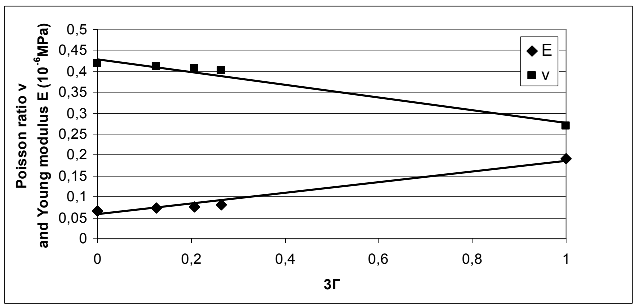

Fig. 7. Anisotropy of Young modulus and Poisson ratio (ν) versus orientation factor 3Γ calculated from single crystal data s_{ij} for Cu according to iso-stress Reuss model

4. Conclusions

- Electrodeposited copper coatings exhibits different texture and microstructure depending on applied conditions in which they were obtained. Pulse and direct current conditions leads to different texture of electrodeposited copper coatings. For each type of current texture depends on deposition time (t_{dep}) and current intensity (i_{av}). Only in some cases (111) component was obtained. This component is recognized in literature as this one, which gives the best conductivity of the copper layers.

- Mechanical properties of the copper layers are sensitive to the texture changes. Relations between properties (hardness, Young module and grain size) and texture of copper layer were found. These indicate that mechanical properties depend on structure and texture of the layers.
- Using quantitative texture analysis and elastic compliance for single crystal the anisotropy behaviour of elastic constancies can be calculated.
- Simplified texture indexes (intensity ratios and M_{hkl} index) obtained on the base of B-B measurements are not complex but suitable indication of the texture of electrodeposited copper coatings. Since these parameters could be used for the on line coatings structure and properties non-destructive control directly in production (e.g. industrial application for copper layers quality control).

Acknowledgements

The Polish Committee supported this work for Scientific Research (KBN) and Faculty of Metals Eng. and Industrial Computer Science AGH under contract No. 11.11.110.712.

References

[1] A. Ibanez, E. Fatas, Mechanical and structural properties of electrodeposited copper and their relation with the electrodeposition parameters, Surface & Coatings Technology 191/1 (2005) 7-16.

[2] A.L. Fan, Sh.K. Li, W.H. Tian, Grain growth and texture evolution in electroformed copper liners of shaped charges, Materials Science and Engineering A 474 (2008) 208-213.

[3] A.U. Mane, S.A. Shivashankar, Growth of (111)-textured copper thin films by atomic layer deposition, Journal of Crystal Growth 275/1-2 (2005) 1253-57.

[4] B. Hong, C. Jiang, X. Wang, Influence of complexing agents on texture formation of electrodeposited copper, Surface & Coatings Technology 201/16-17 (2007) 7449-7452.

[5] S.J. Skrzypek, A. Baczmański, W. Ratuszek, E. Kusior, New approach to stress analysis based on grazing-incidence X-ray diffraction, Journal of Applied Crystallography 34/4 (2001) 427-435.

[6] C.H. Seah, S. Mridha, L.H. Chan, Fabrication of D.C.-plated nanocrystalline copper electrodeposits, Journal of Materials Processing Technology 89-90 (1999) 432-436.

[7] S. Lagrange, S.H. Brongersma, M. Judelewicz, A. Saerens, I. Vervoort, E. Richard, R. Palmans, K. Maex, Self-annealing characterization of electroplated copper films, Microelectronic Engineering 50/1-4 (2000) 449-457.

[8] Y. Zhou, C. Yang, J. Chen, G. Ding, W. Ding, L. Wang, M. Wang, Y. Zhang, T. Zhang, Measurement of Young's modulus and residual stress of copper film electroplated on silicon wafer, Thin Solid Films 460/1-2 (2004) 175-180.

[9] L.G. Schultz, A Direct method of determining preferred orientation of a flat reflection sample using Geiger counter X-ray spectrometer, Journal Applied Physics 20/11 (1949) 1030 - 1033.

[10] H.J. Bunge, Matematischen Methoden der Texturanalyese, Berlin Akademie-Verlag, 1969.

[11] A. Baczmański, Stress field in polycrystalline materials studied using diffraction and self-consistent modeling, Department of Physics and Applied Computer Science AGH, Cracow, 2005.

[12] B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, Prenttice Hall (2003).

[13] T. Hara, T. Yamasaki, K. Kinoshita, Grain sizes in electroplated thin copper interconnection layers, Journal of the Electrochemical Society 153/12 (2006) 1059-1063.

[14] S.J. Skrzypek, New approach to residual macro-stresses measurement due to grazing angle X-ray diffraction geometry, Dissertations and Monographs 108, Institutional Learning and Scientific Publishing AGH, Cracow, 2002.

[15] L.A. Dobrzański, S.J. Skrzypek, D. Pakuła, J. Mikuła, Residual macro-stresses of PVD and CVD coatings deposited on tool ceramics substrates measured with application of the grazing angle X-ray diffraction geometyry, Contemporary Achievements In Mechanics, Manufacturing And Materials Science (2005) 271-276.

[16] S. J.Skrzypek, T. Borowski, J. Jeleńkowski, T. Wierzchoń, Gradient like structural properties of nitrogen–saturated austenite layers produced on N27T2JMnM steel, Contemporary Achievements In Mechanics, Manufacturing And Materials Science (2005) 1102-1105.