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Ellipsometric Measurements of Plastically Deformed Copper

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Chemically pure copper (99.99) prepared in the sample of square cross-section (10×10 mm^2) and length about 50 mm was extremely plastically deformed with the repeated application of equal channel angular pressing. Equal channel angular pressing was applied as an effective technique for producing bulk nanoscaled structures. It is well known that severe plastic deformation of metallic materials often leads to microstructure with ultrafine grains and cross-sections which remain about equal before and after deformation. Optical properties of the sample were studied using spectroscopic ellipsometry in UV-VIS range. The parameters of the sample like copper oxide and surface roughness overlayer were calculated using two-film model together with the Bruggeman effective medium approximation.

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1. Introduction

Hydrometallurgical extraction of metals is a branch of industry for which the research work is ongoing to develop processes which cost less, more environmentally friendly and economically acceptable. Copper is used in vast variety of products in domestic and industrial domains as thermal and electrical conductor and as a constituent of various metal alloys [1]. Among metals, only silver has higher electrical conductivity, but copper is much cheaper and abundant. Due to this property, copper has been widely used as electrode in electrochemical studies [2]. Copper is easy to treat, since it is both: ductile and malleable. The ease with which it can be drawn into wire makes it useful for electrical work in addition to its excellent electrical properties. Copper can be machined, although it is usually necessary to use an alloy for complicated parts, such as threaded components, to get really good mixed characteristics. Good thermal conduction makes it useful for heat sinks and in heat exchangers. Copper has good corrosion resistance, but not as good as gold. It has excellent brazing and soldering properties and can also be welded, although best results are obtained with gas metal arc welding [3].

The color of copper samples is usually red or brown due to existence of thin layers on their surface (including oxide) which are gradually formed when gases (especially oxygen) react with them in the air. Still, the color of the clean surface is much brighter (pink or bright brown). Copper has its characteristic color because of its unique band structure. Copper, cesium and gold are the only three elemental metals with a natural color other than gray or silver [4]. The usual gray color of metals depends on their "electron sea" that is capable of absorbing and re-emitting photons over a wide range of frequencies.

In this paper we will present results of ellipsometric measurements of plastically deformed copper.

2. Experiment

Chemically pure copper sample (99.99) prepared as the specimen of square cross-sections (10×10 mm^2) and of length of about 50 mm was extremely plastically deformed with repeated application of equal channel angular pressing (ECAP). ECAP, which is known as one of discontinuous processes of severe plastic deformation was applied as an effective technique for producing bulk nanoscaled structures. It is well known that severe plastic deformation of metallic materials often leads to microstructure with ultrafine grains and cross-sections which remain almost equal before and after deformation.

The experiments were performed in our experimental hydraulic press (VEB WEMA 250 MP) equipped with tool for ECAP. The tool consists of two intersecting channels of the same cross-section (10×10 mm^2) that meet at angle $2\Phi = 90^{\circ}$. The geometry of tool provides that the material is deformed by simple shear at ideal, frictionless conditions. The cross-section of the specimen remains almost equal before and after each step of the process, thus it is possible to subject one specimen several times to ECAP in order to reach high degrees of plastic deformation. In our case the sample of chemically pure copper was subjected eight times to the ECAP process at room

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temperature (20 °C). This processing performed at low homologous temperatures led to a subdivision of the initially coarse grained microstructure into a hierarchical system of cell blocks and dislocation cells. With increasing strain of the material, the size of both of these constituents decreased in size, which is confirmed by the Raman measurements [5].

For microstructure investigation two samples were prepared: Cu 1.1 P — cross-section surface, Cu 1.2 V — longitudinal section surface.

The ellipsometric measurements were performed using variable angle spectroscopic ellipsometer (VASE) SOPRA GES5-IR in the rotating polarizer configuration. The data were collected over the range 1.5–4.2 eV with the step of 0.05 eV for three different angles of incidence 65°, 70° and 75°. The 70° angle was chosen for its maximum sensitivity of the ellipsometric data.

The fitting of model to experimental data was done using Levenberg–Marquardt algorithm, to minimize the value of the following merit function [6, 7]:

$$\chi^2 = \frac{1}{2N-P-1}\sum_{i=1}^{N}\frac{\left(\langle\tan(\psi)\rangle_{\rm exp}-\langle\tan(\psi)\rangle_{\rm cal}\right)^2}{\sigma_{1,i}^2} + \frac{\left(\langle\cos(\Delta)\rangle_{\rm exp}-\langle\cos(\Delta)\rangle_{\rm cal}\right)^2}{\sigma_{2,i}^2}, \quad (1)$$

where N is the total number of data points, P is the number of fitted parameters, $\langle\tan(\psi)\rangle_{\rm exp}$, $\langle\tan(\psi)\rangle_{\rm cal}$ and $\langle\cos(\Delta)\rangle_{\rm exp}$, $\langle\cos(\Delta)\rangle_{\rm cal}$ represent the experimental and calculated values of ellipsometric quantities $\tan(\psi)$ and $\cos(\Delta)$, and σ_i is the error of each measured quantity. All calculations were made using Winelli_II Version 2.0.0.0.

3. Results and discussion

Spectroscopic ellipsometry (SE) is a surface-sensitive, non-destructive optical technique used to characterize surface changes, optical constants of bulk or layered materials, overlayer thicknesses, multilayer structures, and surface or interface roughness [7]. Ellipsometry measures $\tan(\psi)$ and $\cos(\Delta)$ spectra, which are, respectively, amplitude and projected phase of the complex ratio

$$\rho = r_p/r_s = \tan(\psi)\,{\rm e}^{{\rm i}\,\Delta}, \quad (2)$$

where r_p and r_s are the complex reflectance coefficients of light polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively. Ellipsometric quantities ψ and Δ are sensitive to changes of different parameters like surface conditions, overlayer structure, dielectric function of the material and others.

When it is exposed to oxygen, copper naturally oxidizes to copper(I) oxide (Cu_2O). The influence of the surface roughness has to be also taken into account. In Fig. 1, real and imaginary parts of pseudodielectric function for the bulk copper and samples Cu 1.1 P and Cu 1.2 V are presented. Therefore, the ellipsometric spectra ($\tan(\psi)$, $\cos(\Delta)$) of the two samples Cu 1.1 P and Cu 1.2 V were fitted using two-film model: Cu as a substrate, overlayer of Cu_2O and surface-roughness layer, Fig. 2c. The surface roughness overlayer is composed of the bulk copper oxide and ambient. Using Bruggeman effective medium approximation [7], we calculated volume fraction of the constituents.

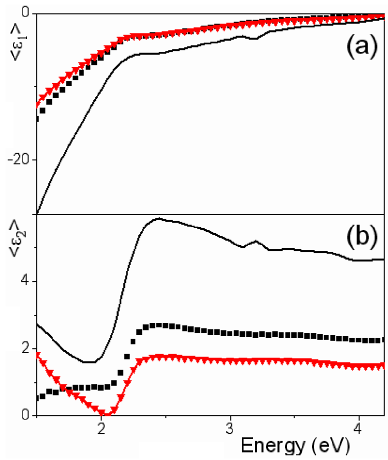

Fig. 1. (a) Real and (b) imaginary part of pseudodielectric function for Cu 1.1 P (squares), Cu 1.2 V (triangles) and bulk copper (solid line).

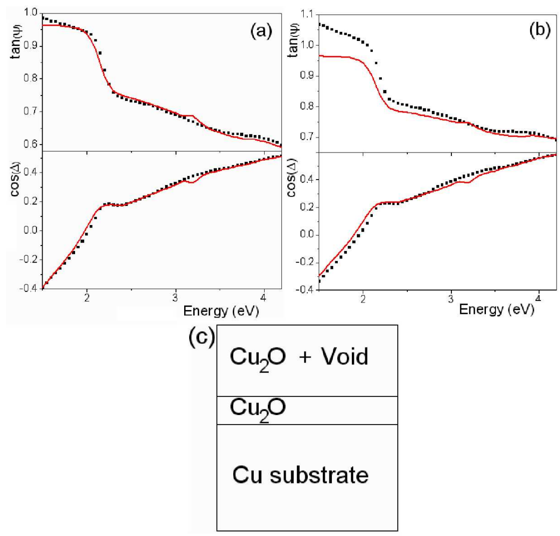

Fig. 2. (a) Experimental data (dots) and fitted data (solid line) of the sample Cu 1.1 P; (b) experimental data (dots) and fitted data (solid line) of the sample Cu 1.2 V; (c) sketched model.

In Fig. 2a experimental and the best fit data of the sample Cu 1.1 P are presented. The thickness of the Cu_2O is ≈ 1.5 nm, and the roughness overlayer with 80% of Cu_2O and 20% of void is ≈ 25.6 nm. For the energies above 2 eV this fit is better than for the energies around and below this value. This may indicate that the dielectric function of the sample substrate is different from the one of the bulk copper taken from Palik [8], and that these changes are due to plastic deformation.

The best fit to the model of the sample Cu 1.2 V is presented in Fig. 2b. The thickness of the copper oxide is ≈ 1.7 nm, and the roughness overlayer with 81% of the oxide and 19% of the void is ≈ 35 nm. Comparing these two fits, one can see that in the case of the sample Cu 1.1 P, the model with Cu_2O and surface roughness suits better than in the case of the sample Cu 1.2 V. This result indicates that the sample Cu 1.2 V is more plastically deformed than the sample Cu 1.1 P, which can be seen in Fig. 1 as well, for the energies less than 2 eV.

4. Conclusion

Results of ellipsometric measurements of plastically deformed copper are presented. The three-layer model was used to calculate thickness of spontaneously formed copper oxide and surface roughness. It is shown that this model suits better for microstructure investigation of the sample Cu 1.1 P — cross-section surface than for Cu 1.2 V — longitudinal section surface. The obtained results indicated that the plastic deformation of the sample did not lead to total amorphization of the specimen.

Acknowledgments

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References

[1] N. Habbache, N. Alane, S. Djerad, L. Tifouti, *Chem. Eng. J.* **152**, 503 (2009).

[2] J.R. Davis, *Copper and Copper Alloys*, ASM International, 2001 p. 3.

[3] W.F. Smith, J. Hashemi, *Foundations Mater. Sci. Eng.*, 223 (2003).

[4] W. Chambers, R. Chambers, *Chambers's Information for the People*, 5th ed., W. & R. Chambers, 1884, p. 312, Digitized Aug 29, 2007 at Harvard University.

[5] J. Trajić, R. Rudolf, I. Anžel, M. Romčević, M. Mirić, B. Hadžić, N. Romčević, *Book of Abstracts, YUCOMAT 2009, Herceg Novi; Acta Phys. Pol. A*, to be published.

[6] M. Losurdo, *Thin Solid Films* **455-456**, 301 (2004).

[7] R.M.A. Azzam, N.M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam 1977.

[8] E.D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, USA 1985.