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TEXTURAL ASPECTS OF ELECTRODEPOSITION PROCESSES

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Electrodeposition is the most widely used electrochemical surface treatment process for fabrication of functional and decorative coatings. Electrochemical and hydrodynamic parameters of the electrodeposition process and substrate texture affect the formation of layers of texture and consequently, the physical and mechanical properties of coating associated with their anisotropy. The uniformity and structure of electroplated metals also strongly depend on the deposition kinetics (charge transfer reaction or mass transport control), which determines the conditions of cathode deposit formation and consequently the crystallites orientation. The present work aims to investigate the influence of Cu substrate texture on developing of it in the copper coating electrodeposited under activation control as the simple model system for the first stage of this study. The texture analysis was performed on the basis of the back- reflection pole figures and of ones with a constant information depth , measured by means of X-ray technique. The non-destructive method allowed to analyse the texture for different chosen areas of the deposited layer. The results show the existing texture inhomogenity. The texture of the substrate reveals a strong influence on the texture of the formed Cu layer in its near- interface area. As far as depositing from withdraws from the substrate surface, the texture proceeds to a one component of axis type of (111) <uvw>.

Keywords: Electrodeposition, texture, surface treatment

INTRODUCTION

Electrodeposition is the most widely used electrochemical surface treatment process for fabrication of functional and decorative coatings of various thickness [1]. Compared to vacuum deposition, electrodeposition has some advantages such as it requires only relatively simple equipments, low processing temperature, high deposition rates, low cost and the possibility of tailoring the crystallographic texture and composition of the deposit.

The nature of an electrodeposit is determined by many factors including the electrolyte composition, *p*H, the potential applied between the electrodes, hydrodynamic conditions as well as the cathodic process kinetics [2,3,4]. The resulting films can be crystalline or amorphous, metallic or non-metallic. The uniformity and structure of electroplated metals and alloys strongly depend on the deposition kinetics, which determines the conditions of cathode deposit formation and consequently the crystallites orientation. Charge transfer reactions are responsible for formation of metallic deposit at the metal- electrolyte interface.

In electrodeposition under activation control, the potential generally has pronounced effect upon the deposit structure and properties. Nevertheless the rate of an electrode reaction depends not only on charge transfer kinetics but also on mass transport to the cathode. Only for limited number of electrochemical systems such as the rotating disc electrode (RDE) under laminar flow conditions, convective mass transport problems can be solved exactly starting from fundamental hydrodynamic equations [5]. Hence, in our studies, the electrolysis was carried out in a system with the rotating disc cathode.

The texture of ten changes with film thickness as the film structure evolves. Hence, the texture analysis and its inhomogenity in the normal direction to electrodeposited layers as well as the influence of the substrate texture are very important. In analysed case such a texture inhomogenity caused by applied deposition technique is expected. Because the classically measured pole figures are intrinsically contradictory in some degree, leading to the serious errors in texture analysis [6]. The errors can be avoided using so called monolayer pole figures giving measured data referred to chosen depth only. This can be achieved by varying simultaneously the sample tilting angles which is easily possible with modern texture goniometers [7].

The variations in texture and also in grain size with deposition conditions allows multilayers to be made with a fixed composition but a structural modulation, as has been seen in Cu/Cu multilayers with a variation in grain size [8]. Copper layers are the most widely used component for fabrication of the various type of multilayers, so at first the preferential orientation of electrodeposited Cu films on electrolytic copper textured substrates as a simple model system was examined.

The present work aims to investigate the preferential orientation in the copper coatings electrodeposited under activation control, as well as the analysis of the texture and its inhomogeneity in the normal direction to the Cu deposit.

EXPERIMENTAL

The copper film was deposited from an acid sulfate bath containing 230 g/l $CuSO_4 . 5H_2O$ and 60 g/l H_2SO_4 with no other additives. The cathode in this system was a copper disc 19 mm in diameter (0.028 dm^2) with an appropriately pretreated surface (chemically and electrochemical polishing), while the anode was a platinum sheet (0.05 dm^2). The electrolysis was carried out in 0.75 L cell at 298 K. To ensure constant and controlled hydrodynamic conditions, a system with rotating disc cathode supplied potentiostatically by potentiostat EG & G PAR Model 273 A with Current Interrupt methods of IR compensation was used.

The potentials have been measured against saturated calomel electrode via Luggin capillary, located 1 mm from the disc. The disc electrode rotation speed was varied from 11 to 86 rad/sec. The dependence of current density of Cu discharge as a function of the square root of the rotating disc electrode speed clearly shows that in investigated conditions the process of copper deposition is controlled by charge transfer reaction. At higher over potentials than 0.15 V a mixed activation diffusion control is observed. The Cu specimen for texture investigation was prepared under potentiostatic conditions at the cathode over voltage equal to 0.014 V and at the disc speed 34 rad/sec. The thickness of Cu layers were determined from coulometric measurements and the deposit weight. The thickness of the investigated Cu layer was ca.10 μm.

The pole figures were measured before deposition by Schulz back-reflection technique. The same experimental method was applied to measurement of the pole figures for the sample after deposition process in order to calculate the averaged texture function for substrate-layer composition. Changes of the information depth depends on geometrical conditions. Texture of the deposited layer was investigated in the chosen near surface layers to a depth of 5 μm and 10 μm from the uppermost surface of the sample. In that case the measurement technique of the pole figures with a constant penetration depth of 5 μm and 10 μm, respectively, was applied [9]. During such measurement, besides the scanning of tilting angle (ψ) and rotation angle $\{\varphi\}$, sample position was also scanned by an additional offset angle $\{\omega\}$ in the appropriate range for keeping the constant penetration depth.

For each position, the full profile of reflection was measured with the pseudo-position sensitive detection technique. It consists of registering the intensity of diffracted beam in the chosen angular range, in a ω–2θ scanning mode. Diffraction profiles obtained in this manner were then fitted by the optimal curves of the theoretical distributions. The fitting parameters were the estimators of the respective values of the measured quantities, i.e the angular position of the peak, its width and integrated intensity. The integrated intensity represent the values of the pole figures, which after transformation to symmetrical Bragg-Brentano conditions were used in Orientation Distribution Function (ODF) calculation procedure [10].

RESULTS AND DISCUSSION

To study the texture developing in copper electrodeposited layer, the nondestructive investigation method was applied. Texture was analysed on basis of experimental data measured after finishing process. Fig. 1 shows the three-dimensional texture functions presented in the space of orientation in the section of φ_2 = 45°. The initial texture in the Cu-substrate contains the typical main components for cold rolled copper sheet [11]. It can be described by (112) [111]("C"), (110)[111] ("B") and a small contribution of (110)[001]("Cubic") components. In the 5 μm-near surface layer the axis type (111) <uvw> component of the texture strongly dominates. For the thicker 10 μm-near surface layer, another additional component of axis type (110) <uvw> appears.

The picture of averaged texture contains both, substrate and layer texture components. It is an expected effect, regarding the dimension of deposited layer and measured pole figures with non- constant information depth for the case. Percentage contribution of the 5 μm-texture and the 10 μm-texture in the averaged one equals of 81% and of 96%, respectively. Much lower ODF intensity of the averaged texture compared with the other ones confirms the influence of different type of texture components typical for the both (substrate and deposited layer) sample areas. With regard to chosen layer way of texture analysis, we assumed the both 5 μm and 10 μm texture are homogeneous, however, they vary continuously as long as the electrodepositing process is stable. Analysis of the texture functions revealed its non-homogeneous character. It seems that the strongest texture inhomogeneity exists in a transition area (near-interface) of the deposited layer. In this area of the subjected sample, an inherit phenomena of texture has controlled the crystallographic orientation of sequentially electrodeposited copper particles. The deposition front withdraws from substrate surface, the texture inheritance is weaker. The texture of electrodeposited copper layer in tested sample tends to the own, mono-component one, axis type of (111) <uvw>. It is distinctly observed in Fig. 1 of the 5 μm texture. Such type of texture was formed with applied electrochemical condition of depositing process of rotational symmetry.

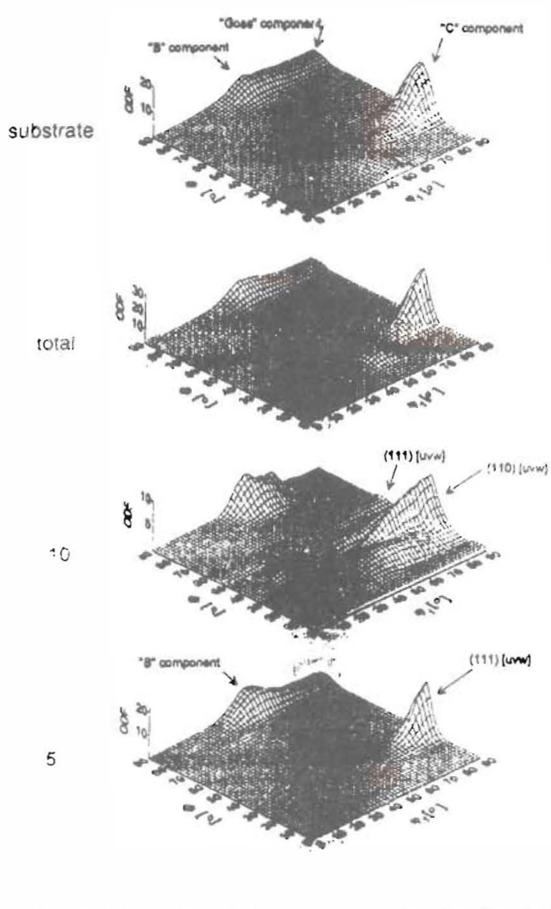

Fig. 1: Texture functions (grain orientatioin distribution densities) presented in the space of orientation (i.e. rotations described by Euler angles φ_1, φ, φ_2 in the sectioin of φ_2 = 45°

Above observations indicate the strong texture inhomogeneity of electrodepositions from the texture point of view and that applying classically measured pole figures gives not clarified information about texture organisation in deposited layer. In such cases, texture analysis should be based on the mono-layer pole figures.

CONCLUSION

Texture of the copper electrodeposited layer shows a strong inhomogeneity. The substrate texture affects the formation of the layer texture in near-interface area of deposition . The influence disappears after a few microns distance from the substrate deposition. The deposition front withdraws from substrate surface, the texture ends to its own, mono-component one, axis type of (111) <uvw> which is the final texture of copper layer electrodeposited on Cu sheet in the described conditions. The applied method of texture analysis based on mono-layer pole figures is useful in the study of texture organisation in such kind of deposited layers.

REFERENCES

1. D Landolt, *Electrochim Acta,* **39** (1994) 1075
2. I Tomov, Chr Ovetkova and V Velinov, *J Appl Electrochem,* **19** (1989) 377
3. E Beltowska-Lehman, E Chassaing and K Vu Quang, *J Appl Electrochem,* **21** (1991) 606
4. V Velinov, E Beltowska-Lehman and A RiesenKampf, *Surf Coat Technol,* **29** (1986) 77
5. V G Levich (Ed) Physicochemical Hydrodynamics, Prentice Hall, New York (1962)
6. H J Bunge, *Z Metallkunde,* **73** (1982) 483
7. J T Bonarski, L weislak and H J Bunge, Proc ICOTOM-10, 10th Int conf on texture of Materials, Materials Science forum 111-117, Switzerland (1994)
8. C A Ross, *Annu Rev Mater Sci,* **24** (1994) 159
9. K Pawlik, *Phys Stat Sol,* (b) **134** (1986) 477
10. L G Schulz, *J Apply Phys,* **20** (1949) 1030
11. Z Jasienski, J Pospiech and A Piatkowski, in Proc ICOTOM-11, 11th Int conf on texture of Materials, 281-86, Xi-an, China (1996)