INTERNAL STRESSES IN PLASTICALLY DEFORMED GOLD FILMS INVESTIGATED BY X-RAY DIFFRACTION

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Abstract

Electrochemical sensors belong to the largest groups of (bio-)chemical sensors with many applications in the environment, medicine and bio-technology. Au thin films are usually used as working/auxiliary electrodes. Well-defined real structure of Au films with preferred orientation of their grains in [111] direction perpendicular to the substrate can influence the other physical properties of the films.

Au films different in thickness deposited by a diode sputtering technique on a single-crystalline silicon substrate were investigated by X-ray powder diffractometer with a Bragg-Brentano goniometer. Biaxial internal stresses and quantitative phase analysis of the „cell wall" and „cell interior" regions in film volume were carried out from the analysis.

Keywords
Au thin films, sputtering, X-ray diffraction, internal stress, quantitative phase analysis

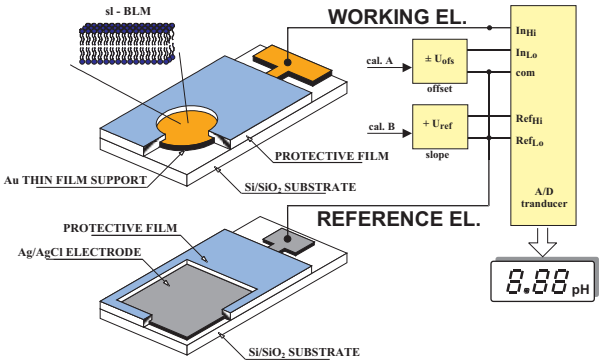

Figure 2. Layout of P-H meter with thin film sl-BLM/Au working and Ag/AgCl reference electrodes

1. Introduction

Gold electrodes together with platinum and carbon electrodes are frequently used in electrochemistry. They are of special interest also in microsystem technology and in different branches of microelectronics as metallic conductive layers [1, 2] (Figures 1-2). Au thin films are prepared by different techniques mostly together with Pd and Ti thin films in Au/Pd/Ti configuration where the Ti layer serves as an adhesion layer and the Pd layer is necessary for the protection of the Ti layer against oxidation.

It has been shown that appropriate X-ray diffraction line profile measurements are a suitable tool for determining the dislocation density. One of the greatest merits of the X-ray diffraction technique is the discovery of characteristically asymmetric line broadening in plastically deformed metals and alloys. The characteristically asymmetric X-ray line broadening has been shown to be direct evidence for the existence of residual long-range internal stresses prevailing in plastically deformed metals and alloys with heterogeneous microstructure [3].

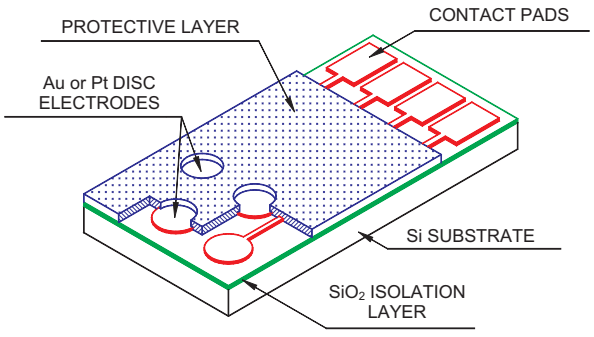

Figure 1. Thin film multielectrode chip with Au or Pt electrodes

Residual internal stresses occur when the tendency of separate portions of a specimen to assume different volumes is counteracted by cohesive forces. By their nature, residual stresses persist in the absence of an external load. X-ray diffraction method has the potential to determine the lattice strain ε by using the lattice spacing d as an internal gauge [4].

$$\varepsilon = \frac{d - d_0}{d_0},$$

where d_0 is the strain free reference lattice spacing and d is the lattice spacing obtained from the experiment. In the majority of cases in thin films only a biaxial stress is formed so that the measurement in the Bragg-Brentano geometry is possible. If the strain is homogeneous and isotropic in the thin film – substrate interface, the lattice stress can be determined from the shift of a diffraction line by using the equation

$$\sigma_1 + \sigma_2 = -\frac{E}{\mu} . \frac{d - d_0}{d_0},$$

where E is Young's modulus and μ is Poisson's ratio of the material investigated. If the simultaneously diffracting volumes of „relaxed" and „constrained" material in the part of the layer probed are unequal, asymmetric line broadening can be expected [5].

The residual long-range internal stresses can be evaluated by a relatively simple and straigthforward procedure in which the investigated asymmetric line profiles are decomposed into two almost symmetric subprofiles. From the shifts of the separated subprofiles relative to centre of gravity of the measured profile or

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relative to strain free reference position, the strains in the hard and soft regions, i.e. in the dislocation cell wall and cell interior material can be obtained.

Furthermore, the quantitative XRD phase analysis of dislocation cell wall and cell interior can be easily performed by using a standardless conception described in [6].

2. Experimental procedure

In this work, Au thin films 100, 200 and 300 nm in thickness were deposited onto silicon substrate by means of diode sputtering. A planar r.f. sputtering system Perkin-Elmer 2400/8L was used. The sputtering chamber was pumped down to $2x10^{-5}$ Pa before admission of working gas (Ar 99.999% in purity). Throughout the sputtering of Au target (203 mm in diameter and 99.95% in purity) a gas pressure 1.3 Pa, room substrate temperature and r.f. power of 500 W were kept constant.

X-ray diffraction analysis was carried out on an automatic X-ray powder diffractometer URD-6 with a Bragg-Brentano goniometer using CuKα radiation (0.154178 nm). The intensities of diffraction lines were collected with a constant step 0.02 deg of 2ϑ and with a constant counting time of 20 seconds at each point. Ceramic Al_2O_3 from NIST (National Institute for Standards and Technology - USA) was used as an instrumental standard. The Ω-scans for the most intensive diffraction lines (111) were also recorded.

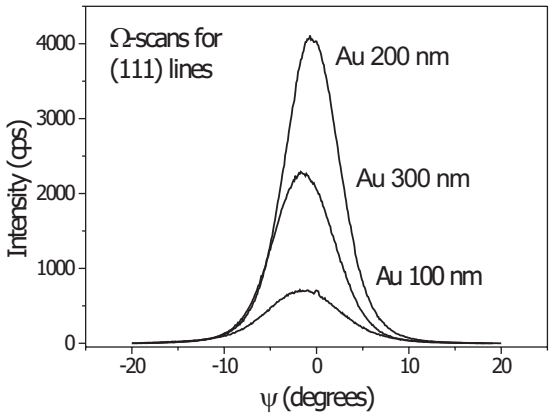

Figure 3. Ω-scans of Au films indicating preferred orientation of crystallities in [111] direction perpendicular to the substrate

3. Results and discussion

X-ray diffraction analysis indicated that the all investigated Au thin films are polycrystalline with a very strong preferred orientation of their grains in the [111] direction perpendicular to the substrate. Only (111) and (222) Au diffraction lines were observed. Widths of the Ω-scans are only 7.0 - 9.3 degrees (Figure 3), which is very low for such thin layers. The shifts of the Ω-scans agains normal do not exceed –0.5 degrees and Pearson VII indexes are 3.4 – 6.7, which indicates that the distribution of crystallities orientation is almost Gaussian.

Figures 4-8 show typical line profiles of the (111) and (222) lines of Au thin film deposited on [100]-oriented single-crystalline silicon. The profiles of the deformed films are broadened and asymmetric. The shape of the (111) and (222) profiles is identical, indicating that the characteristic asymmetry is quantitatively order indepAu thin films, sputtering, X-ray diffraction, internal stress, quantitative phase analysisendent. The asymmetry of the (111) profiles does not appear as split double peaks in the (222) reflection, indicating that the asymmetry is a genuine material property which does not depend on the resolution of the equipment.

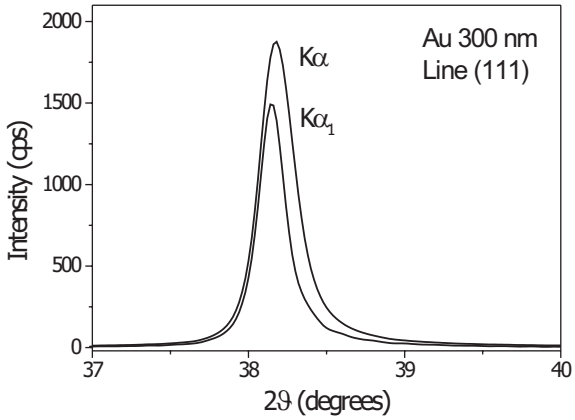

Figure 4. XRD-scan of (111) diffraction line for Au film on Si indicating presence of residual long-range internal stresses in the film

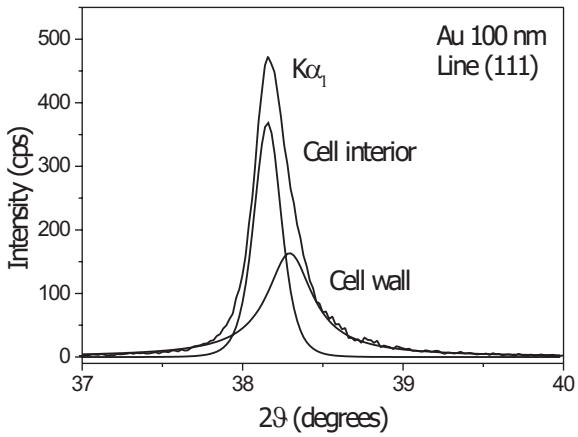

Figure 5. Decomposition of the asymmetrical Au (111) $K\alpha_1$ line for 100 nm film into the two symmetrical Pearson profiles

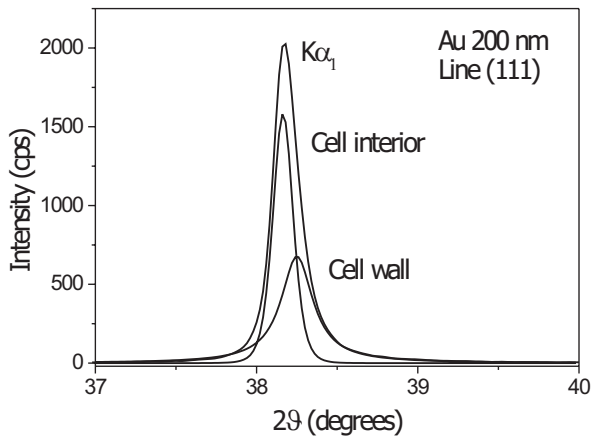

Figure 6. Decomposition of the asymmetrical Au (111) $K\alpha_1$ line for 200 nm film into the two symmetrical Pearson profiles

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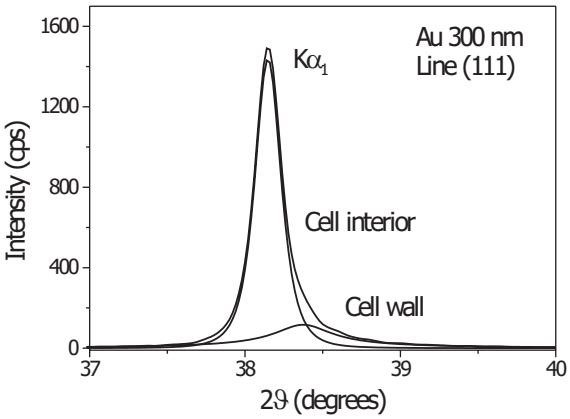

Figure 7. Decomposition of the asymmetrical Au (111) $K\alpha_1$ line for 300 nm film into the two symmetrical Pearson profiles

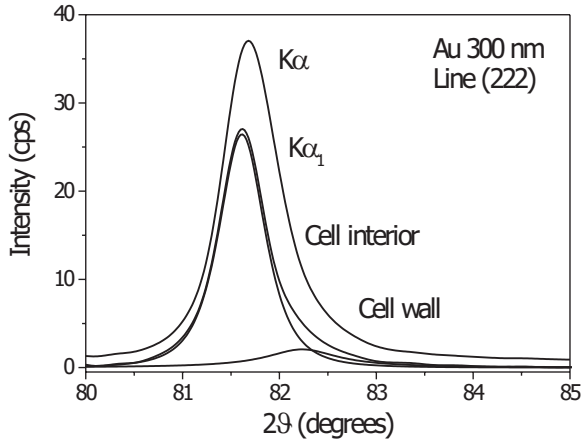

Figure 8. Decomposition of the asymmetrical Au (222) $K\alpha_1$ line for 300 nm film into the two symmetrical Pearson profiles

4. Conclusions

Recently developed method of formation of bilayer lipid membranes on a solid support [7] allows to prepare extremely stable thin molecular layers that makes them attractive candidates for biomolecular electronic devices and biosensor applications.

Well-defined geometric arrangement of sensing interfaces in a nanometer scale can also be controlled by the crystalline structure and orientation of substrates. This can be reached by sputtering of Au, Pt, Pd, and Ag, resulting to a formation of surface with preferential orientation (111) of polycrystalline grains.

Stresses and strains are almost always present in thin films deposited on substrates. In the majority of cases they are residual stresses introduced into the system during deposition or subsequent processing. When a growing film is bombarded by ions with energies of tens or hundreds of electronvolts, compressive stress arises in thin film by a process of „atomic peening".

The lattice stresses and strains in thin films are probably the most important characteristics describing the quality of films. It is very important to know the state of stress in thin films because its critical value can influence the other mechanical properties of the films.

In this work, biaxial internal stress in Au films deposited on single crystalline silicon substrate with [111] orientation perpendicular to the interface was investigated. As demonstrated in Table 1, compressive stress is present in cell interior material, whereas tensile stress is present in cell wall material. This fact demonstrates the presence of plastically deformed regions in Au films deposited on Si-substrate. Furthermore, the quantitative XRD phase analysis indicated (See Table 2) that the mass % of the „cell interior" material increases with increasing of the film thickness. This fact demonstrates that the lattice stress relaxation is coming into consideration only in region close to the thin film – substrate interface.

Table 1. Biaxial internal stress in Au films

Sample	Line	Biaxial stress ($\sigma_1 + \sigma_2$) [MPa]		
		Cell interior	Cell wall	Center of gravity
Au 100 nm	111	-130	480	320
Au 200 nm	111	-126	280	190
Au 300 nm	111	-200	870	-25

Table 2. Quantitative phase analysis of Au films

Sample	Line	Content [mass %]	
		Cell interior	Cell wall
Au 100 nm	111	49	51
Au 200 nm	111	52	48
Au 300 nm	111	79	21

Acknowledgements

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