X-RAY DIFFRACTOMETRY OF THIN LAYERS - POSSIBILITIES AND PROBLEMS

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Summary Efficiency of two deconvolution methods used in X-ray powder diffraction analysis is compared for thin films of Pd and Pt. The first method is the classical Stokes method and the second one is method of indirect deconvolution. But calculated integral breadth of Gauss and Cauchy components of Voigt function which describe the physical broadening are different. The analysis of the all found pheromones show that the method of indirect deconvolution gives more accurate results.

1. INTRODUCTION

Thin polycrystalline films deposited on substrates by different sputtering techniques have in the majority of cases a very strong preferred orientation of crystallites in a certain direction. In the most cases the preferred orientation of crystallites is directed perpendicular to the substrate. When we investigate such films by X-ray powder diffraction techniques, we can sometimes observe only one diffraction line and at most its second order [1]. In spite of that, X-ray diffraction analysis of such films, give a lot of information about the state and structure of investigation films.

Moreover we find that the second order lines have others parameters as first order lines, which are not according to using model.

In our contribution, we concentrated upon a line profile analysis, particularly on an influence of methods of calculation of domain size, microstrains, probability of stacking faults and values of lattice strain.

We used the integral method [2] for the calculation of domain size, microstrains and probability of stacking faults and also for the method of indirect deconvolution [3]. These methods assume and the same model, that the physical broadening of diffraction line shall be described by the Voigt function.

2. THEORY

When the physical broadening of diffraction line is caused only by a small dimension of coherently diffracting domains, stacking faults and microstrains, the physical profile is a convolution of Gaussian and Cauchy functions

$$f(x) = \int_{-\infty}^{\infty} f_G(x-u) f_C(u)\, du, \qquad (1)$$

where

$$f_G = \exp(-\ln 2 \frac{4(x-x_0)^2}{\beta_G^2}) \qquad (2)$$

and

$$f_C = \frac{1}{1+\dfrac{4(x-x_0)^2}{\beta_C^2}} \qquad (3)$$

and x_0 is the position of the top of profiles. Experimentally obtained line profile h (x) will also be a convolution of an instrumental, and a physical profile.

$$h(x) = \int_{-\infty}^{\infty} f(x-y)\, g(y)\, dy. \qquad (4)$$

There are various methods for the finding the function of physical broadening of the diffraction line alternatively for finding its definition by the parameters. We select two methods, which maybe applied for profile analysis of one diffraction line. At first the integral method described by Langford [2] and at second the method of indirect deconvolution [2]. Booth methods use approximation of experimental diffraction line by theoretical curve, which is put in by the parameters. Now it is necessary to look for optimal parameters to reach the minimal a sum of squares of differences noticed W of calculated and experimentally obtained intensities.

$$W = \left[h(x_i) \quad h_T(x_i)\right]^2 \qquad (5)$$

For the calculation the probability of stacking faults we used the method of sine [4] and direct calculation from the shift of the peaks of the components of diffraction lines [5].

3. EXPERIMENTAL PROCEDURE

The investigated samples were prepared by the method of r.f. reactive sputtering. The palladium thin film was deposited on glass (amorphous) substrate. Its thickness was 0,58 μm. The platinum thin film was deposited on Si [100] and its thickness was 1 μm. The preparation of samples is described in [1,6].

X-ray diffraction analysis was carried out on an automatic powder diffractometer URD-6 with a Bragg-Brentano goniometer, using a cooper X-ray tube. Data were collected with a constant step of 0,02 deg in 2θ scale and with the constant counting time of 20 second in each step. The ceramic Al_2O_3 from NIST was used as a instrumental standard.

The experimental data as well as the instrumental data were modificated before the application of approximation by Voigt function. The data modification involved the smoothing of the tails and the subtraction of the background. The position of the top of the line peak was qualified by the cubic splain method.

The PC executable program was used for finding the optimal parameters to minimize the function (5). The program was implemented in C++ programming language. The minimal value for the function (5) was calculating in two steps. In the first step there were specified the parameter borders by a splain method and in the second step the gradient method was using. The parameters obtained by such way were much more precise then those obtained by using a integral method [2].

4. RESULTS AND DISCUSSION

It has been found from the X-ray diffraction line profile analysis there are very strong preferred orientation of crystallites in the [111] direction in palladium and platinum thin films [1]. This is certain information about the structure of thin film. The information may be enlarged in the case of ω-scan performing.

The intensity of diffraction line in second range is very small and smaller as intensity from polycrystalline sample. Consequently the second range of (111) diffraction line was measureless. It is apparent from the Table 1 where ratio of intensities diffraction lines (222) to (111) are presented.

Table1 Ratio of intensities diffraction lines (222) to (111)

Sample	Theoretically	Experimentally
Palladium	0,05	0,022
Platinum	0,03	0,014

We found that the integral breadth of Gauss component of Voigt function for the (222) line of palladium is practically zero. In the case of platinum sample the integral breadth of Gauss component of Voigt function for the (222) line is broader as that calculated from the (111) line. Values of integral breadths Gauss and Cauchy components are given in Table 2.

Table 2 Values of integral breadth.

Sample	Line	Integral method		Method of indirect deconvolution	
		Gauss β (2θ)	Cauchy β (2θ)	Gauss β (2θ)	Cauchy β (2θ)
Pd	111	0,091	0,104	0,021	0,055
	222	0	0,293	0,0001	0,195
Pt	111	0,153	0,123	0,014	0,127
	222	0,375	0,352	0,077	0,377

Method of indirect deconvolution give smaller integral breadth of Gauss component of Voigt function than its calculated from integral method. The integral breadths of Cauchy component of Voigt function detected by indirect deconvolution are smaller with Pd sample than these calculated from integral method. Both methods calculated nearly the same integral breadth of Cauchy component of Voigt function in the case of sample Pt.

Therefore we examine the dimension of irradiated volume and depth of penetration of X-ray. The depth of penetration of X-ray was calculated according to [7]. The calculated values of irradiated volume and depth of X-ray penetration are given in Table 3. The irradiated volume of palladium sample is equal for booth diffraction lines. The X-ray radiation penetrates the whole thin layer. Because the reason of small intensity of (222) line must be another. The ω-scans of Pd and Pd are presented on Fig.1. The ω-scan of the Pd is broader as the ω-scan of platinum. It is possible to observe the reflection from crystallites those are not strongly perpendicular oriented to the substrate. This effect is caused by the heat oscillations and by the disordered crystallites. Probably these crystallites are more disordered than crystallites which are oriented strongly perpendicular to substrate. The crystallites oriented strongly perpendicular to substrate are very perfectly and therefore for these is Gauss component of Voigt function nearly zero, what correspond the reflection for the (222) planes. This is presence of the second enstinction and therefore the intensities of (222) lines are smaller then were expected.

Table 3 Depth of penetration of X-ray and irradiated volume of samples

Sample	Line	Depths of [μm]	Irradiated volume $[\mu m]^3$
Palladium	111	1,43	75,5
	222	2,86	75,4
Platinum	111	0,80	100,4
	222	1,50	131,0

The (222) line is reflected only from the upper layers. In these layers is probability of stacking faults is bigger then in lower layers. Therefore the Cauchy component of Voigt function is more broader.

The similar case is also for the Cauchy component of Voigt function for (222) line of platinum. But in this case the detect profile of (111) line is not reflected from all layers. Therefore the growth of Gauss component of Voigt function for (222) line is made the lower layers, which are more disorder than the upper layers.

The reason of the different results of the using methods can be assumption that the instrumental line has the Voigt profile. The integral methods [2] use this assumption. The approximation functions correspond very good with the experimental lines in booth case [1,3]. But in the case of the integral method there is obtained only approximation experimental curve by α_1 and α_2 components of the theoretical curve and the integral breadth is calculation by Stokes method. In the case of the indirect deconvolution the theoretical curve is convolution of measured instrumental line and theoretical Voigt profile. These follows evidently that the method of indirect deconvolution is more appropriated for profile analysis. Moreover the method of indirect deconvolution enable to find the presence of diffusion lines or presence of very low intensity line of other phases [8]. It is possible by this method to find also the probability of stacking faults only from one line. The results of calculation of the probability of stacking faults by the method of indirect convolution are credible as in the method of sine, especially in case that the lines are broadened, see Fig.2.

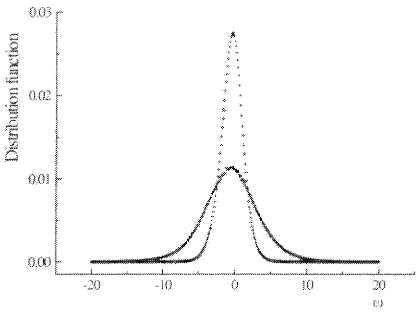

Fig.1 .The ω-scan of samples Pd (x) *and Pt* (+).

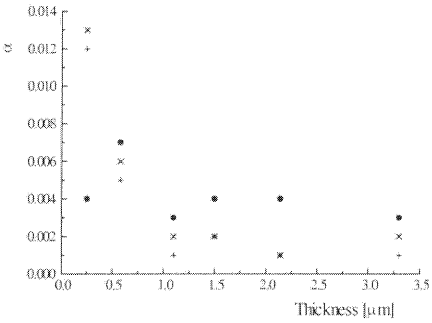

Fig.2. The probability of stacking faults calculated by Sine method (•) *and by the method of indirect deconvolution, from the (111) line* (+) *and from the* (222) *line* (x).

5. CONCLUSIONS

The used method of approximation by Voigt function gives very good agreement between the experimentally measured diffraction lines and the calculated approximation functions.

Therefore the method of indirect deconvolution is more suitable for the profile analysing of thin films.

It is necessary to make the profile analysis and its evaluation of thin film samples for each lines individually in the case a very strong preferred orientation of thin films. Besides measurement the profile of diffraction line it is advisable measure also ω-scan these profiles.

In the case that in the samples are present stacking faults it is necessary made the correction on the stacking faults at calculation of the lattice strain.

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