VOIGT SIZE-STRAIN BROADENING OF Pd THIN FILMS

Vladimír Žucha, Quido Jackuliak
Department of Physics, University of Žilina, Veľký diel, 010 26, Žilina, Slovak Republic

Summary Pd thin films were deposited onto Si (100) and glass/Pd/etching substrates by means of r.f. reactive sputtering under the same sputtering condition in order to appreciate the influence of substrate structure. The aim of this study was to appreciate the main X-ray diffraction line profile characteristic by the approximation method. As an approximation function was used the Voigt profile which was calculated by convolution of Gaussian and Cauchy profiles. As an instrumental standard was used ceramic Al_2O_3 from Nist. Results of size-strain analysis was obtained according to Langford method for one diffraction line and method suggested by Balzar and Ledbetter for two orders of the same diffraction line.

1. INTRODUCTION

The aim of this study was to verify the suitableness of the approximation method by the Voigt function for study size-strain broadening of thin films. Because of the presence of texture often only one line may be measured, we compared the results of size-strain analysis obtained to Langford method [1] with the results obtained to method suggested by Balzar and Ledbeter [2].

As material for study of applicability of the approximation method by the Voigt profile were used thin films of palladium because palladium is appropriate material for study of dimensionality of thin films, because of its high density, good chemical stability and for its very good X-ray reflectivity under common conditions.

Lattice strain and the probability of the stacking faults were calculated from experimental data also.

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

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

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 profiles

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

The main point of the indirect deconvolution method is a least square method. The instrumental as well as the investigated line are recorded by a certain step and that is why the integrals have to be substituted by the sums from a certain interval where the functions have non-zero values. Functions f_G and f_C are expressed in a parametric form. Because it is not possible to establish the position of the top of the measured profile in advance, one of the parameters will characterise the shift of the coordinate belonging to the top of the physical profile against the experimentally obtained coordinate of the top of the line. Then, the function (2) and (3) are expressed as follows

$$f_G = \exp(-\ln 2 \frac{4(x-x_0-p_3)^2}{p_1^2}), \qquad (5)$$

$$f_C = \frac{1}{1+\frac{4(x-x_0)^2}{p_2^2}}. \qquad (6)$$

Let us their convolution as a theoretical curve of the physical broadening f_T and their convolution with the instrumental curve as a theoretical profile of the investigated line h_T. Now, it is necessary to look for such optimal parameters p_1, p_2 and p_3 in order to be minimal a sum of squares of differences of experimentally obtained intensities.

$$W = [h(x_i) - h_T(x_i)]^2 = W_{\min} \qquad (7)$$

Then the average size of coherently diffracting domains and microstrains can be directly obtained from the calculated parameters of the physical broadening $2w_C$, $2w_G$, β_C, β_G, because the integrals of (2) and (3) functions are tabular.

According to [3], for the parameter of unit cell a_{hkl} calculated from (hkl) line is valid this equation

$$a_{hkl} = a_0 + (S_1)_{hkl}\sigma a_0 + G_{hkl}\alpha a_0, \qquad (8)$$

where

a_0 is the parameter of unit cell without lattice strain, stacking faults and without strain and size broadening:

S_1(hkl) is elastic constant for (hkl) plane;

σ is present lattice strain;

$$G = (\frac{\sqrt{3}}{4\pi})[\sum_b \pm (h+k+l)] \Big/ (h^2+k^2+l^2)(u+b);$$

u is the number of planes which are not broadened;

b is the number of planes which are broadened.

3. EXPERIMENTAL PROCEDURE

Palladium thin films were deposited onto Si (100) single crystalline (sample 1), glass (amorphous) substrates (sample 2) booth 0,5 μm thickness by means of r.f. reactive sputtering under the same sputtering conditions in order to appreciate the influence of substrate structure on the X-ray diffraction line profile characteristics, i.e. peak position, intensity, FWHM (full with at the half maximum and integral breadth.

The third sample was prepared in the following way. At first thin film of the palladium was deposited on glass substrate. Its thickness was 0,5 μm. Afterward thin film of palladium was etching with the molecules of Ar. Then its thickness was decrease to 0,4 μm. At last the thin film of palladium with thickness 0,5 μm was deposited. The summary thickness of thin film of palladium in sample was 0,9 μm.

X-ray diffraction patterns 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 X-ray diffraction analysis of the third sample was carried in for direction, always after when the sample was turned about 90^0. 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.

For the finding of optimal parameters minimizing function (7)was made program for the calculation on PC. The programming language was C^{++}. Minimizing function (7) has been solved by using two steps. In the first step the parameter borders were specified 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 [4].

The method proposed by Langford [1] and Balzar and Ledbetter [2] was used to determine the microstructural properties of palladium thin films.

4. RESULTS AND DISCUSSION

It has been found from the X-ray diffraction line profile analysis that very strong preferred orientation of crystallites in the [111] direction in palladium thin films occurs in all investigated cases. The intensity of the diffraction line depends very strong on the substrate. The intensity of diffraction line in second range is very small. Consequently the second range of (111) diffraction line was measureless. It is to apparent from the Table 1. The angles of the top of the diffraction lines have very small difference. The ω-scan another samples of palladium [5] have the deviation of the ω-scan curve from c-axis very small too.

The result of the approximation the experimental profile by Voigt profile is presented on Fig. 1.This is in a good agreement with the experimental data and the Voigt function. The computed parameters of the Voigt function are presented in Table 1.

Tab. 1. Parameters of the Voigt function and the top of peak of (111) line.

Sample	Parameter (2θ)		Top of the peak
	p_1 (Gauss)	p_2 Cauchy)	
3a	0,0076	0,0207	40,1923
3b	0,0090	0,0204	40,1928
3c	0.0101	0,0202	40,1904
3d	0,0091	0,0202	40,1924

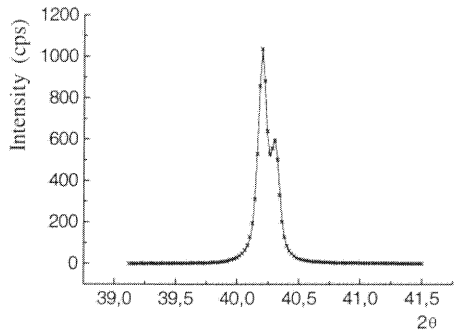

Fig. 1. XRD-scan of (111) line for sample 3c (cross) and its approximation by Foigt function (line).

The result of the size-strain analysis by the method proposed by Langford [1] are presented in the Table 2. It is apparent from the Table 2 that the substrate etching (the bottom layer of palladium) create the increasing of microstrain and crystallite size too.

Tab. 2. Results of size-stain analysis according to Langford method for one line.

Sample	Line	$<\varepsilon^2>\times 10^8$	$<D>$ [nm]
1	(111)	<< 1	80
	(222)	<< 1	40
2	(111)	<< 1	80
	(222)	<< 1	40
3a	(111)	3,7	145
3b	(111)	5,1	145
3c	(111)	6,4	150
3d	(111)	5,1	150

The microstrans in palladium thin film on substrates Si (100) and glass are very small, lesser than $1\cdot10^{-4}$, that the Voigt approximation function is very near the Cauchy function.

Results of size-strain analysis proposed by Balzar and Ledbetter [2] are presented in Table 3. The values of the microstrains were much the same. But the surface-weighted domain size D_{ef} has values approximately the middle values of the values of do-

main size calculated by method proposed by Langford for the (111) and (222) lines. It is seen from the comparison the values of domain size that the method proposed by Langford may be using only to comparison of the investigated samples.

Tab. 3. Probability of stacking faults and the values of surface-weighted domain size.

Sample	α	D_{ef} [nm]	D_0 [nm]
1	0,005	190	275
2	0,007	225	480

In the Table 3 is presented the probability of stacking faults in samples 1 and 2. Influence the stacking faults on the values of surface-weighted domain size is apparent from Table 3. The correction on stacking faults for the values of surface-weighted domain size was calculated according to formula

$$\frac{1}{D_{eff}} = \frac{1}{D_0} + \frac{1{,}5\alpha}{a\sqrt{h^2+k^2+l^2}} \frac{\sum_b |h+k+l|}{u+b},$$

posed by [6]. The values of surface-weighted domain size after correction are presented in Table 3 too.

The lattice strain was calculated without and with the correction on the stacking faults. Wern at all [7] proposed for the thin films the elastic constant S_1 calculate by constraint Voigt model

$$S_1 = \frac{\Gamma S^* - 2s_{12}s_{44}}{3\Gamma(2s_{44}+s_{12}-s_{11})-2s_{44}},$$

where

$$S^* = 4s_{12}s_{44} + 2s_{11}s_{44} + 2(s_{12})^2 - s_{11}s_{12} - s_{11}^2$$

and $\Gamma = \dfrac{h^2k^2+h^2l^2+k^2l^2}{h^2+k^2+l^2}$.

The data for calculation the S_1 was used from [8]. The correction on stacking faults was calculated in accordance with the formula (8). The calculated values of lattice strain are given in Table 4.

Tab. 4. The values of lattice strain.

Sample	Line	$(\sigma_1+\sigma_2)$ without correction [MPa]	$(\sigma_1+\sigma_2)$ after correction on stacking faults [MPa]
1	(111)	260	235
	(222)	220	235
2	(111)	250	215
	(222)	190	215
3	(111)	290	-

It is apparent from the Table 4 that the values of lattice strain after correction on the stacking faults are the same for the (111) and (222) lines.

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.

The results of approximation are the parameters of the Voigt function which describe the physical profile of the broadening so it is nothing any another deconvolution.

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

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