VOIGT SIZE-STRAIN BROADENING OF PD THIN FILMS

Vladimír Zácha, Quido Jackulik
Department of Physics, University of Žilina, Veľký dieť, 010 26, Žilina, Slovak Republic

Summary. PD thin films were deposited onto Si (100) and glass/Pd/chinichy 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 characteristics. 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 Al2O3 from Nox. Results of size-strain analysis was obtained according to Langford method for one diffraction line and method suggested by Balzar and Leebetter for two orders of the same diffraction line.

1. INTRODUCTION
The aim of this study was to verify the suitability 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 Leebetter [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 domain, stacking faults and microcrystals, the physical profile is a convolution of Gaussian and Cauchy functions

\[ f_x = \frac{1}{\beta_2} \exp \left( -\frac{1}{2} \frac{(x-x_0)^2}{\beta_2^2} \right) \]

and

\[ f_c = \frac{1}{\pi \beta_2^2} \left( \frac{1}{x-x_0} \right)^2 \]

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

\[ h(x) = \int f_x (x-x_0) f_c (y) dy \]

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 small gaussians have to be substituted by the same from a certain interval where the functions have non-zero values. Functions \( f_x \) 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 profile against the experimentally obtained coordinate of the top of the profile. Then, the function (2) and (3) are expressed as follows

\[ f_x = \exp \left( -\ln \frac{2}{4(x-x_0)^2} \right) \]

\[ f_c = \frac{1}{1 + \frac{1}{4(x-x_0)^2}} \]

Let us convolute their as a theoretical model of the physical broadening \( f_x \) and their convolution with the instrumental curve as a theoretical profile of the investigated line \( b_n \). Now, it is necessary to look for such optimal parameters \( p_0, p_1, p_2 \) and \( p_3 \) in order to be minimal a sum of squares of differences of experimentally obtained intensities

\[ W = \sum (h(x) - h_n(x))^2 = W_{\text{min}} \]

Then the average size of coherently diffracting domains and microcrystals can be directly obtained from the calculated parameters of the physical broadening \( 2\omega_c \), \( 2\eta_c \), \( b_n \), \( b_n \), because the integrals of (2) and (3) functions are tabular. According to (3), for the parameter of unit cell \( a_{0n} \) calculated from (hkl) line is valid this equation

\[ a_{0n} = a_0 + S_\gamma (h+k+l) \]

where \( a_0 \) is the parameter of unit cell without lattice strain, stacking faults and without strain and size broadening; \( S_\gamma (hkl) \) is elastic constant for (hkl) plane; \( \eta \) is present lattice strain; \( G = (h+k+l) \) is number of planes which are broadened. The results 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 sample parameters of the Voigt function are presented in Table 1.

3. EXPERIMENTAL PROCEDURE
Palladium thin films were deposited onto Si (100) single crystalline (sample 1), glass (amorphous) substrates (sample 21) both 0.5 \( \mu \)m thickness by means of r.f. reactive sputtering under the same sputtering condition 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 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 \( \mu \)m. Afterward thin film of palladium was etching with the molecules of Ar. Then its thickness was decrease to 0.4 \( \mu \)m. At last the thin film of palladium with thickness 0.5 \( \mu \)m was deposited. The summary thickness of thin film of palladium in sample was 0.9 \( \mu \)m. X-ray diffraction patterns were collected with a constant step of 0.02 deg in 20 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°. The ceramic Al2O3 from NIST was used as an instrumental standard.

The experimental data as well as the instrumental data were modified 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 spline method.

For the finding of optimal parameters minimizing function \( \eta \) was made program for the calculation on PC. The programming language was C++. Minimizing function \( \eta \) has been solved by using two steps. In the first step the parameter borders were specified by a spline 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 Leebetter [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 [111] direction in palladium thin films occurs in all investigated cases. The intensity of the diffraction line depends strongly 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 e-scan angular samples of palladium [5] have the deviation of the r-scan curve from c-axis very small too.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter (20)</th>
<th>Top of the peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.0076</td>
<td>0.0207</td>
</tr>
<tr>
<td>3b</td>
<td>0.0089</td>
<td>0.0224</td>
</tr>
<tr>
<td>3c</td>
<td>0.0101</td>
<td>0.0202</td>
</tr>
<tr>
<td>3d</td>
<td>0.0091</td>
<td>0.0202</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line</th>
<th>( \phi \times \phi )</th>
<th>( D ) [( \mu )m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(111)</td>
<td>&lt;= 1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>(111)</td>
<td>&lt;= 1</td>
<td>80</td>
</tr>
<tr>
<td>3a</td>
<td>(111)</td>
<td>3.7</td>
<td>145</td>
</tr>
<tr>
<td>3b</td>
<td>(111)</td>
<td>5.1</td>
<td>145</td>
</tr>
<tr>
<td>3c</td>
<td>(111)</td>
<td>6.4</td>
<td>150</td>
</tr>
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<td>150</td>
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The microstrain in palladium thin film on substrates Si (100) and glass are very small, lesser than 10°, that the Voigt approximation function is very near the Cauchy function. The results of size-strain analysis proposed by Balzar and Leebetter [2] are presented in Table 3. The values of the microstrain are the same. But the surface-weighted domain size \( D_\gamma \) has values approximately the middle values of the values of do.
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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

\[ f(x) = \int f_G(x) + f_C(x) \, dx, \]

where

\[ f_G(x) = \exp(-\ln 2 \cdot \frac{4\pi(x-x_0)^2}{\beta_G^2}) \]

and

\[ f_C(x) = \frac{1}{1 + \frac{4\pi(x-x_0)^2}{\beta_C^2}} \]

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

\[ h(x) = \int f(h - y) \cdot g(y) \, dy. \]

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 same 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

\[ f_G(x) = \exp(-\ln 2 \cdot \frac{4\pi(x-x_0)^2}{\beta_G^2} + \frac{1}{2} \cdot \frac{\pi^2 \cdot \beta_G^4}{\beta_C^2}) \]

\[ f_C(x) = \frac{1}{1 + \frac{4\pi(x-x_0)^2}{\beta_C^2}} \]

Let us assume they convolution as a theoretical profile of the broadening. \( f_C \) and their convolution with the instrumental curve as a theoretical profile of the investigated line \( h \). Now, it is necessary to look for such optimisation parameters \( p_1, p_2 \) and \( p_3 \), in order to be minimal a sum of squares of differences of experimentally obtained intensities.

\[ W = \left| h(x) - h(x) \right|^2 \]

Then the average size of coherently diffracting domains and microstrains can be directly obtained from the calculated parameters of the physical broadening 2\( \omega \), 2\( w \), \( \beta \), \( \theta \), 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

\[ a_{hkl} = a_0 + S h \delta a_{hkl} a_0 + G a_{hkl} a_0 \]

where

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The results 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 calculated parameters of the Voigt function are presented in Table 1.

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<td>0.0076</td>
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<tr>
<td>3b</td>
<td>0.0207</td>
<td>0.0384</td>
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<tr>
<td>3c</td>
<td>0.0101</td>
<td>0.0202</td>
</tr>
<tr>
<td>3d</td>
<td>0.0091</td>
<td>0.0202</td>
</tr>
</tbody>
</table>

Fig. 1: XRD scan of (111) line for sample 3c (cross) and its approximation by Voigt 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 crystalsize too.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line</th>
<th>( c&lt;\alpha&gt;c ) \times 10²</th>
<th>( D ) [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(111)</td>
<td>&lt;&lt;1</td>
<td>80</td>
</tr>
<tr>
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</table>

The microstrains in palladium thin film on substrates Si (100) and glass are very small, lesser than 1·10⁴, 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 are the same. But the surface-weighted domain size \( D_a \) has values approximately the middle values of the values of...
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 used only to comparison of the investigated samples.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\alpha)</th>
<th>(D_{\alpha}) [mm]</th>
<th>(D_{\alpha}) [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>190</td>
<td>275</td>
</tr>
<tr>
<td>2</td>
<td>0.007</td>
<td>225</td>
<td>480</td>
</tr>
</tbody>
</table>

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

\[
\frac{D_{\alpha}}{D_{\alpha}'} = \frac{1 - \frac{1.5\alpha}{\sqrt[3]{3}}}{1 + \frac{1.5\alpha}{\sqrt[3]{3}}} \sum_{h+k+l = \overline{1}} \frac{h}{1 + \frac{1.5\alpha}{\sqrt[3]{3}}} + \frac{h}{1 + \frac{1.5\alpha}{\sqrt[3]{3}}},
\]

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

\[
S_1 = \frac{3(\alpha + \beta)}{2(\alpha + \beta + \gamma)} + \frac{3(\alpha + \beta)}{2(\alpha + \beta + \gamma)} \sum_{h+k+l = \overline{1}} \frac{h}{1 + \frac{1.5\alpha}{\sqrt[3]{3}}} + \frac{h}{1 + \frac{1.5\alpha}{\sqrt[3]{3}}},
\]

where \(\alpha = h^2 + k^2 + \gamma^2\), \(\beta = h^2 + \gamma^2 + l^2\), and \(\gamma^2 = \gamma^2 + l^2\).

The data for the 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line</th>
<th>((\sigma_1, \sigma_2)) without correction [MPa]</th>
<th>((\sigma_1, \sigma_2)) after correction on stacking faults [MPa]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>(111)</td>
<td>260</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>(222)</td>
<td>220</td>
<td>235</td>
</tr>
<tr>
<td>2</td>
<td>(111)</td>
<td>250</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>(222)</td>
<td>190</td>
<td>215</td>
</tr>
<tr>
<td>3</td>
<td>(111)</td>
<td>290</td>
<td>-</td>
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</tbody>
</table>

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 is it 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 at as calculation the values of domain size as at calculation of the lattice strain.

Acknowledgements

The authors would like to thank to Dr. P. Šušta, Ing. V. Tvářek and Ing. L. Novotný for the providing of the diffraction data.

REFERENCES


1. INTRODUCTION

It is well known that Si surface pre-oxidation treatment and high quality thermal oxide preparation plays crucial role in unipolar technology. From that point of view, great attention has to be paid on the thermal SiO2 growing with bulk and Si–SiO2 interface densities of defects as low as possible. Due to downsizing of device dimensions the thickness of oxides also decreased thereby bulk defects are suppressed, however, one should keep in mind electrically active defects located at the Si–SiO2 interface that can exacerbate stability and reliability of unipolar devices. Moreover, electrical parameters of power devices are partially influenced by defects in the subsurface region of Si. Shrinkage of those defects is permanent task in high-quality substrate preparation and creation of defect-free region, so called doped zone (DZ). Capacitance methods are the most suitable diagnostics tool for investigation of such effects and process optimisation as well.

In this work we characterised MOS capacitors (MOS-C) using both C-V curves from which we evaluated free carriers concentration n(x), flat-band voltages VFB, effective defect charge QD, and energy distribution of Si–SiO2 interface trap density DIT, respectively [1].

Electrically active defects in the subsurface region were explored by measuring of generation lifetime \(\tau\) and surface generation velocity \(S\) using pulsed MOS-C-T technique, furthermore, depth profile of \(\tau(x)\) was obtained using the time domain constant-capacitance technique (CC-t) which is an modification of conventional C-t method [2]. Standard Deep Level Transient Spectroscopy (DLTS) have also been employed to our investigation. Breakdown voltage measurement and time-dependent breakdown were used for determination of SiO2 layer electric strength [3], [4].

2. EXPERIMENT

An n-type, phosphorus doped, <100>-oriented homogeneous silicon wafer with resistivity 2-5 kΩ and thickness 300 µm was used as a substrate of the MOS-Cs. The gate SiO2 layer was prepared by thermal oxidation in an atmosphere of dry oxygen at 1000°C. The thickness of the SiO2 layer was about 40 and 28 nm. All gates were vapour deposited and patterned photolithographically. After manufacturing the MOS structures, the sample was annealed in \(N_2 + H_2\) at 460°C for 20 minutes.

The measurements were performed on the MOS-Cs prepared by standard pre-oxidation treatment (BUS) and samples with intrinsic gettering by poly- Si deposition (DEP).

The MOS-Cs were characterized by capacitance and current methods. High frequency capacitance C-V and non-equilibrium capacitance-time C-t measurements were performed using the 4280 1 MHz C Meter/UV Plotter Hewlett-Packard [5].

Quasi-static C-V measurements were performed using the Keithley 595 Quasi static C-V Meter. DLTS measurements were performed using the Polarion DLTS Spectrometer 4900. This spectrometer uses a boxcar detection system for acquiring the DLTS output signal. Breakdown measurements were performed using the Keithley 238 High Current Source Measure Unit.

3. RESULTS AND DISCUSSION

The flat-band voltage of MOS-C BUS was calculated from C-V curve (Fig. 1) as \(V_{FB} = -0.5\) V, that indicates relatively high effective defect charge of \(Q_{D} = 2.6\times10^{12}\) cm\(^{-2}\). C-V curve (Fig. 2) of