COMPARISON OF METHODS FOR EVALUATION OF MICROSTRUCTURE OF MATERIALS

Q. Jackuliak[1], **P. Šutta**[2]

[1]*Department of Technical Physisc, Faculty of Electrotechnica! Engineering, University of ilina, 010 26 ilina, Slovak Republic*

[2]*Department of Physics, Faculty of Logistics, Military Academy, 03119 Liptovský Mikuláš, Slovak Republic*

1 Introduction

Studying the microstructure of polycrystalline thin films by means of X-ray diffraction on a common X-ray diffractometer with a Bragg-Brentano goniometer we often meet the situation when due to a very strong preferred orientation of crystallites in a certain direction, only one diffraction line can be observed. Its higher orders are often very weak or cannot be observed at all.

In such case, one can obtain information about the microstructure of thin film by means of a method proposed by Langford [1], considering that the physical profile of diffraction line can be described by a Voigt profile. In case when both contributions of broadening of diffraction line i.e. due to microdeformations as well as due to dimensions of areas of coherent scattering can be described by the Voigt profile, there is more convenient to use a method proposed by Balzar and Ledbetter [2]. In their work, Balzar and Ledbetter demonstrated that the results obtained by means of a method proposed by Warren and Averbach [3] express so called "surface weighted domain sizes $<D_s>$", whereas the results of approximative methods express so called "volume weighted domain sizes $<D_t>$". The relation between them can be expressed according to [2] as follows

$$\frac{<D_V>}{<D_S>} = 2\sqrt{\pi}\, k \exp[k^2(1-\mathrm{erf}(k))],$$

where

$$k = \frac{\beta_c}{\sqrt{\pi}\beta_g}$$

Therefore, in our work, we concentrated on a comparison of the three methods proposed by: (i) Warren-Averbach (WA), (ii) Langford (L) and (iii) Balzar-Ledbetter (BL). The conditions for the obtaining of trustworthy results for the (WA)-method were described in detail in [4,5,6,7,8]. Furthermore, the influence of dispersion on accuracy of the results as well as the recommendations how to reach the minimum of the total dispersion and the constant dispersion of Fourier coefficients are demonstrated in [9].

Using the approximative methods we found out that the diffraction line cannot be correctly approximated within the whole profile by one analytical function expressed by a mathematical formula. Therefore, we used a combined method, where the top of diffraction line is approximated by a Pearson VII profile, whereas the tails and the bends are not approximated at all [10].

2 Experimental procedure

In order to verify the individual methods mentioned above, zinc oxide (ZnO) thin films deposited by means of reactive diode sputtering in ZnO-$A1_2O_3$-Al-SiO_2-Si multilayered configuration were used. The zinc oxide layer was about 5 μm thick and the other layers were about 0.1 μm in thickness. More detailed information regarding the thin film preparation can be found in [11]. Ceramic $A1_2O_3$ from NIST was used as an instrumental standard. The $A1_2O_3$ diffraction lines (104) and (030) were used as the standard lines because they are close to (002) and (004) ZnO diffraction lines. The experimental data of (104) and (030) lines are presented in Figures 1, 2.

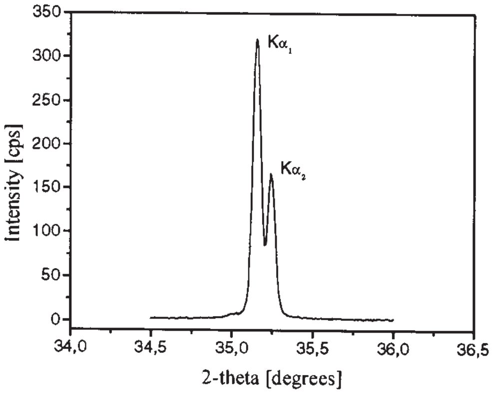


Figure 1. XRD-scan for (104) line of ceramic $A1_2O_3$ used as an instrumental standard

X-ray diffraction analysis was carried out on an automatic X-ray powder diffractometer URD-6 with a Bragg-Brentano goniometer, using a copper X-ray tube (λ = 0.154178 nm). Preliminary diffraction patterns recorded on the film indicated that the zinc oxide film is polycrystalline and that there is also a very strong preferred orientation in the [001]direction perpendicular to the substrate. That is why we concentrated on the analysis of the (002) and (004) diffraction lines. The data collection were done in the range of 33.38-35.38 and 71.5-73 .9 degrees of 2Θ using two dif-

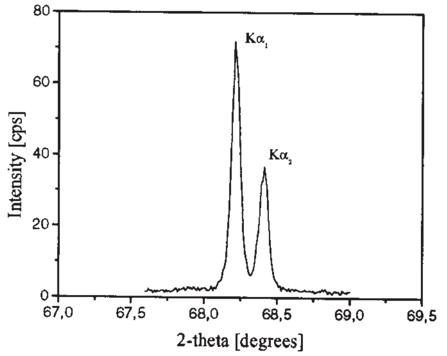


Figure 2. XRD-scan for (030) line of ceramic $A1_2O_3$ used as an instrumental standard

ferent ways: (i) with a constant step of 0.02 deg in 2Θ (total measured points was 101 and 121) and with a constant counting time of 40 seconds at each step, and (ii) with an optimal number of 41 measured points with a different counting time at each step according to [9] in order to obtain constant dispersion at each measured point. The experimental data for (002) and (004) diffraction lines of ZnO thin film recorded by two different ways described above are demonstrated in Figures 3, 4, 5 and 6.

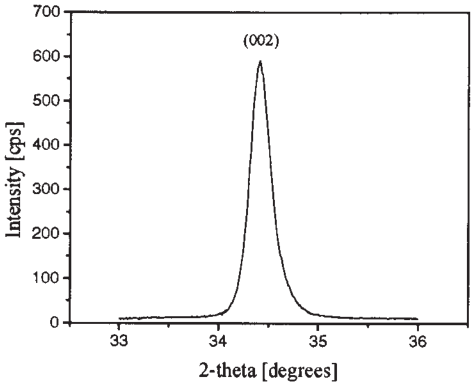


Figure 3. XRD-scan for (002) line of ZnO thin film recorded with a constant counting

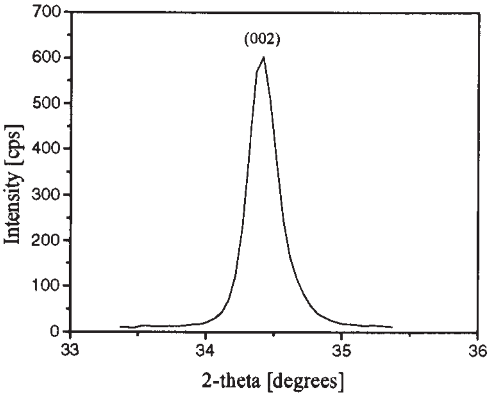
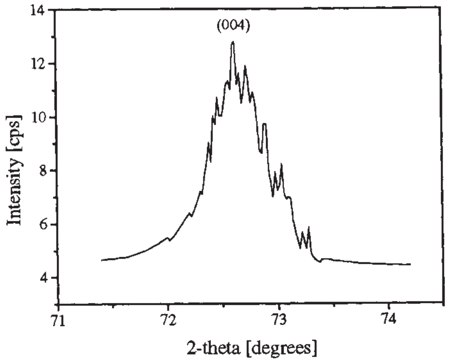


Figure 4 XRD-scan for (002) line of ZnO thin film recorded with a constant statistics



F'igure 5. XRD-scan for (004) line of ZnO thin film recorded with a constant counting

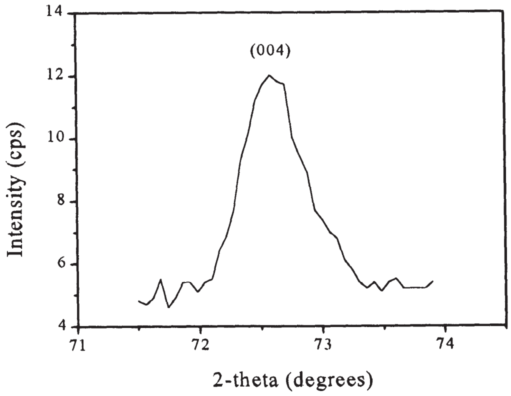


Figure 6. XRD-scan for (004) line of ZnO thin film recorded with a constant statistics

Because all authors [4-9] agree that the all methods mentioned above require precise background determination, a method of background subtraction proposed by Enzo and Parrish [12] was used. After smoothing of tails and bends of diffraction lines by means of programs for preliminary data processing [13] we determined the interval of approximation by Pearson VII profile for each line. When approximating the reference lines we found out that the α_1 and α_2 lines are asymmetric and that they are not identical. Therefore, we decided to use the Pearson VII profile for each line i.e. α_1 and α_2 separately [10).

Considering that the search of the absolute minimum of function of nine variables is a very complicated task, we divided it into the two parts. First, we performed only a rough approximation assuming that the α_2 line has a half of the intensity of α_1 line, it has the same shape and that both lines are shifted by a certain angle of $\Delta 2\Theta$ from each other. When obtained the rough parameters, the method of least square sum was used to evaluate all nine parameters. When applied the method of least square sum, at first we used a spline method and then we used a gradient method in order to determine the absolute minimum of investigated function as it is indicated in [14].

Because the shift of the α_2 line against the aţ line getting worse an accuracy of setting of the Fourier coefficients [4] and at the same time the approximative methods need the integral breadth and FWHM as well, the separation of complete line profile into its individual α_1 and α_2 components was necessary. The top part of the diffraction profile was already separated in the course of approximation by Pearson VII profile so that only tails and outer bends had to be separated. Because a Rachinger method did not satisfy for this purpose (the α_1 and α_2 line profiles are asymmetric), the separation of complete a line profile into its individual α_1 and α_2 components was done by using a Lorentz profile with a variable power which was particularly set up for the each profile. The same widths were used as in case of approximation by Pearson VII profile.

Preliminary processing and the separation of complete a line profiles into their individual α_1 and α_2 components are demonstrated in Figures 7, 8, 9 and 10. Fourier analysis and determination of microdeformations and dimensions of areas of coherent scattering were performed according to Iveronova and Revkevič [15].

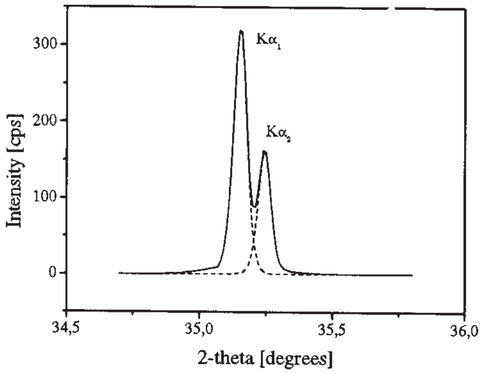


Figure 7. XRD-scan for (104) line of ceramic $A1_2O_3$ after its preliminary processing

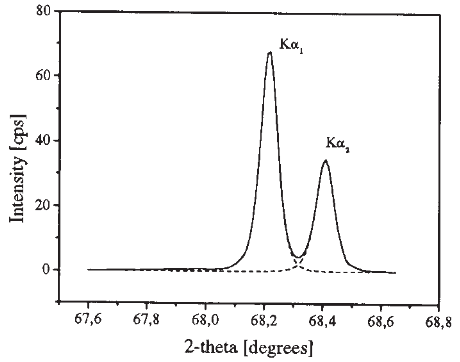


Figure 8. XRD-scan for (030) line of ceramic $A1_2O_3$ after its preliminary processing

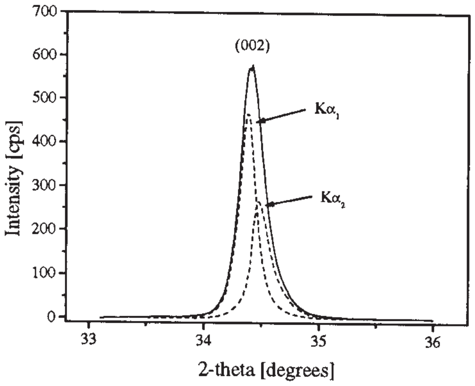


Figure 9. XRD-scan for (002) line of ZnO film recorded with a constant counting

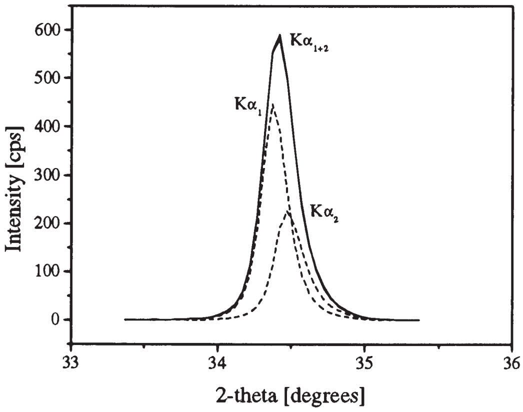


Figure 10. XRD-scan for (002) line of ZnO film recorded with a constant statistics at each step after its preliminary processing and separation into α_1 and α_2 components

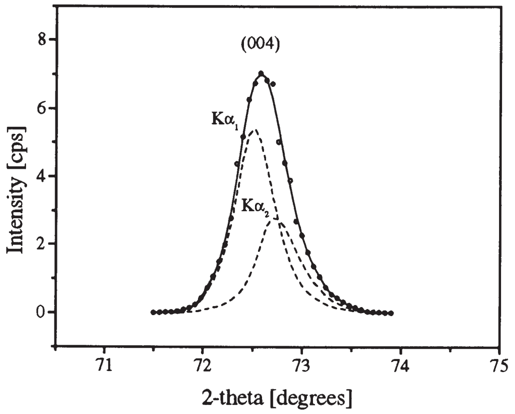


Figure 11. XRD-scan for (004) line of ZnO film recorded with a constant statistics after its preliminary processing and separation into α_1 and α_2 components

3 Results and Discussion

Microdeformations and the dimensions of areas of coherent scattering calculated by different methods are presented in Table 1 and in Figures 12 and 13. When working up the experimental data, we found out that the method of recording with a constant counting time at each step is not quite convenient for diffraction line with a low intensity. Tkačev [16] has demonstrated that for a correct determination of integrated intensity a very high number of counts has to be recorded. In case of recording with a constant counting time at each step, it is not always accepted. In consequence that the (BL)-method could not be used for a sample which was working up by the way mentioned above.

In the approximation of (004) line recorded with a constant time at each step by a Pearson VII profile we always

Table 1. Size-strain parameters obtained by different methods

Langford method		
Sample	$\varepsilon \times 10^3$	D [nm]
$ZnO_{(002)}$ σ^2=const	2.3	90
$ZnO_{(004)}$ σ^2=const	2.4	65
$ZnO_{(002)}$ t=const	1.6	80
$ZnO_{(004)}$ t=const	1.2	30

Balzar & Ledbetter method		
Sample	D_{eff} [nm]	D_V [nm]
$ZnO_{(002)}$ σ^2=const	60	110
$ZnO_{(004)}$ σ^2=const	-	-
$ZnO_{(002)}$ t=const	-	-
$ZnO_{(004)}$ t=const	-	-

Warren & Averbach method		
Sample	$D_{\alpha 1}$ [nm]	D_{α} [nm]
$ZnO_{(002)}$ σ^2=const	85	110
$ZnO_{(004)}$ σ^2=const	-	-
$ZnO_{(002)}$ t=const	92	130
$ZnO_{(004)}$ t=const	-	

obtained powers less than the unity for the α_1 component and for the α_2 component as well. As a consequence of that, when using the method proposed by (BL) we could obtain hugher values for D_{eff} than that for D_V,which is in contradiction to the theory. Therefore, this method could not be used in case of lines recorded with a constant counting time at each step. When compared the (L) and (BL) methods we found out that the domain sizes obtained by the (L)-method are comparable if the results of the second order line is taken into consideration (Table 1). On the other hand, the microstrains obtained by the (L)-method do not depend on the order of reflection at all.

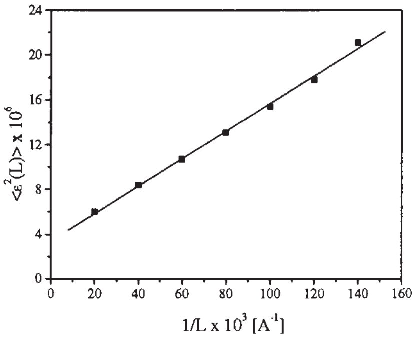


Figure 12. Mean square strains $<\varepsilon^2>$ as a function of the reciprocal of distance L for (002) line of ZnO thin fllm recorded with a constant statistics at each step.

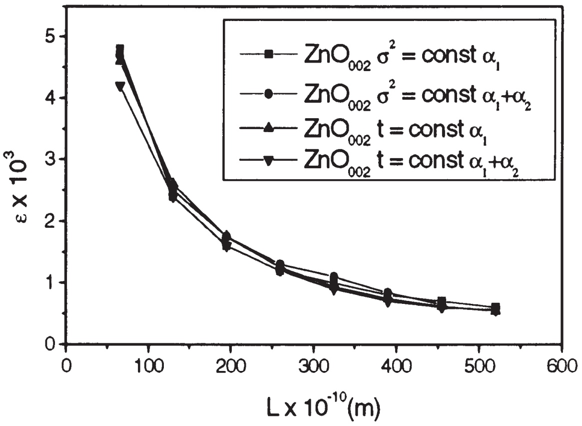


Figure 13. Microstrains in investigated ZnO thin fllms obtained by the Fourier analysis

Microstrains determined by the (L)-method correspond to the microstrains determined by the (BL)-method approximately at 5 nm from the strain source.

Crystallite sizes calculated by means of Fourier analysis and according to the (BL)-method correspond to the theoretical assumption in case of sample investigated with a constant statistics at each point. On the other hand in case of the sample investigated with a constant counting time at each point, the higher values of crystallite sizes and lower microdeformations were observed in comparison with the sample investigated with a constant statistics not depending on the method of evaluation.

Values of microdeformations obtained by the Fourier analysis are in agreement with those obtained from the methods proposed by Langford and by Balzar and Ledbetter, nevertheless, they are a little higher.

4 Conclusions

Our experiments confirmed that the results obtained by means of different methods are comparable and therefore it is possible to use the method proposed by Langford as well as the more precise method proposed by Balzar and Ledbetter depending on the preciseness required.

Weak diffraction lines for the "size-strain" analysis have to be recorded with the constant statistics at each point as it is proposed by Stremel [9]. Lines investigated by a constant counting time at each step seem to be narrower than those investigated by the constant statistics.

The method proposed by Langford gives satisfactory results for determination of microstrains while the domain sizes obtained by this method have to be taken into consideration only as an informative.

Acknowledgements

This work was supported by Copernicus Project CIPA-CT94-0231 and in part under SK Crrant VEGA No.1/4228/97.

References

1. J.I. Langford, *J. Appl. Cryst.***11**,(1978) 10-14
2. D. Balzar, H. Ledbetter *J Appl. Cryst.* **26** (1993) 97-103
3. B.E. Warren, B.L. Averbach, *J. Appl. Phys.***23**,(1952) 497
4. G. Zorn: *Aust. J. Phys.***41** (1988) 237-249
5. Th.H. De Keijser, E.J. Mittemeijer *Z. Naturforsch.***33a**,(1978) 316- 320
6. R. Delhez, Th.H. Keijser, E.J. Mittemeijer Accuracy in Powder Diffraction, NB S Special Publication No. 567, edited by S. BLOCK and C.R. HUBBARD, pp.213-253. Washington DC: National Bureau of Standards.(1980)
7. R. Delhez, Th.H. De Keijser, E.J. Mittemeijer and J.I. Langford, *J. Appl. Cryst.***19** (1986) 459-466
8. R. Delhez, Th.H. De Keijser, E.J. Mittemeijer and J.I. Langford, *Aust. J. Phys*.**4l** (1988) 213-227
9. M.A. Štremel, L.M. Kaputkina, A.I. Sabsaj, *Zavodskaja laboratorija* **8** (1969) 947-954
10. Q. Jackuliak, P. Šutta, *Materials Structure in Chemistry, Biology Physics and Technology*, **3** (1996), No. 3, 267-269
11. P. Šutta, Q. Jackuliak, V. Tvaro ek, I. Novotný: NATO ASI Series E: Applied Sciences - Vol. 284, Edited by O. Auciello and R. Waser, Kluwer Academic Publishers, Dordtecht, (1995) pp. 327-334
12. S. Enzo, W. Parrish,: A Method of Background Subtraction for the Analysis of Broadened Profiles (private announcement)
13. Q. Jackuliak, P..Šutta: *Materials Structure in Chemistry, Biology, Physics and Technology*, **3** (1996) No. 4, 341
14. Q. Jackuliak: Thesis (habilitation) "Röntgenografické štúdium rozpadu martenzitu,1992, ČVUT Praha
15. B.I. Iveronova, G.P. Revkevich.: Teorija rassejanija rentgenovskych lucej. Izdatelstvo Moskovsogo univer siteta,1972 Moskva
16. S.P. Tkačev: *Zavodskaja laborato rija* (1989) 55, 55-57