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Thin film thickness determination using X-ray reflectivity and Savitzky–Golay algorithm

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X-ray reflectivity (XRR) is one of the primary measurement techniques for thickness calculation of thin films and multilayer period determination. This technique can also be used for the analysis of organic thin film multilayer structures. In this method, the accuracy of thickness calculation depends on precision of the determination of the local maxima of XRR curve. The analysis of the XRR curves is cumbersome because of the noise which is recorded while measurement. It can be improved using computer data analysis algorithms for noise reduction and determination of the local maxima on the XRR curve. One of such algorithms, widely used in the data spectroscopy analysis, is Savitzky–Golay (S–G) algorithm. In this paper, the application of S–G algorithm for thickness determination of self-assembled ion liquid nanolayer of dimethyldiallylammonium chloride (PDDA) is shown.

Keywords: X-ray reflectivity, thickness determination, Savitzky–Golay algorithm.

1. Introduction

One of the most frequently used methods of the thin film thickness determination is the X-ray reflectivity (XRR) [1]. This is the non-destructive procedure, which enables to determine the film thickness with the angstrom resolution [1]. In the XRR method, the recorded diffraction peaks are correlated with the thickness of the investigated layer (Fig. 1).

The resolution of this method depends on the accuracy of the position determination of the diffraction peaks. The identification of the peaks is disturbed by the noise recorded while spectra measurement. Therefore, the development for the improvement of the signal-to-noise ratio (SNR) is required. The influence of the noise can be reduced

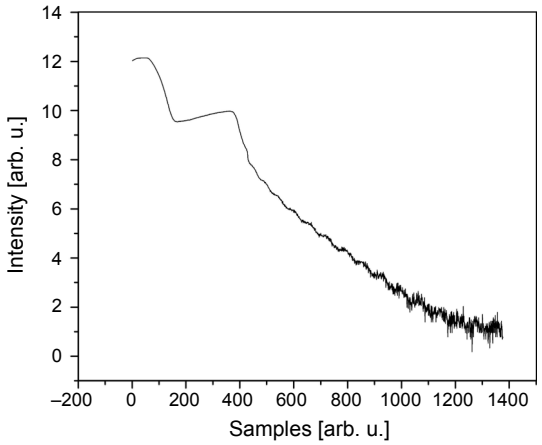

Fig. 1. XRR curve of self-assembled ion liquid nanolayer of PDDA.

by averaging in long time measurements or using noise reducing data analysis procedures. In this paper, we show the application of S–G algorithm for the noise reduction and thickness determination of self-assembled ion liquid nanolayer of dimethyldiallylammonium chloride (PDDA).

2. Savitzky–Golay algorithm theory

The Savitzky–Golay filtration depends on the approximation of a moving window using a higher order polynomial [2, 3]. It can be done by the least square method, in which the centre point of this polynomial is calculated as follows:

$$y(i) = \sum_{j=1}^{n} c_j \, y(i-j) \tag{1}$$

In this way, the problem to be solved can be reduced to the determination of n parameters of the S–G filter. In this case, the polynomial $a_0 + a_1 p + \ldots + a_M p^M$ of degree M is expressed by the filter of n degree with the following parameters $f_n, \ldots, f_0$. Since the mathematical model of the object is the linear function, the Hahn–Banach theorem [4] can be applied. The matrix, which describes the solution, is given as follows:

$$A_{ij} = p^q \tag{2}$$

where p and q are natural numbers, *i.e.*, $p = 0, ..., n$, and $q = 0, ..., M$. Using vector equations, we have:

$$\left(A^T A\right) a = A^T f \tag{3}$$

where [5]:

$$A = \begin{bmatrix} 1 & p_1 & p_1^M \\ 1 & p_2 & p_2^M \\ 1 & p_n & p_n^M \end{bmatrix} \tag{4}$$

$$a = \begin{bmatrix} a_0 \\ a_1 \\ a_M \end{bmatrix} \tag{5}$$

$$f = \begin{bmatrix} f_0 \\ f_1 \\ f_n \end{bmatrix} \tag{6}$$

$$\{A^T A\}_{pq} = \sum_{k=0}^{n} k^{p+q} \tag{7}$$

$$\{A^T f\}_p = \sum_{k=0}^{n} k^q f_k \tag{8}$$

If we replace the value f with the unit vector e_n, then the matrix of factors is equal to [2, 4]:

$$c_n = \left\{ (A^T A)^{-1} (A^T e_n) \right\}_0 = \sum_{m=0}^{M} \left\{ \left(A^T A \right)^{-1} \right\}_{0m} n^m \tag{9}$$

According to (5), the only one row of the inverted matrix A is used, which can be obtained by the decomposition of a Lower Upper triangular matrix [5]. Such factors are used to the reduction of the noise on the XRR curves.

3. Noise reduction using S–G algorithm in XRR curve

To determine the thickness of the thin layers, the precise peak position determination on the XRR curve is necessary. The noise reduction and peak determination are done in few steps. At first, the noise on the raw data of the XRR curve (Fig. 1) is reduced using the algorithm described in Section 2. The result of this procedure is shown in Fig. 2. It should be noted that in the developed procedure each point of the measured XRR curve is treated as one sample of data.

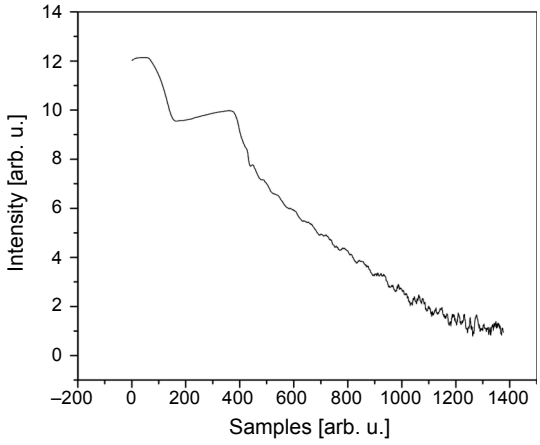

Fig. 2. XRR curve after noise reduction using S–G algorithm.

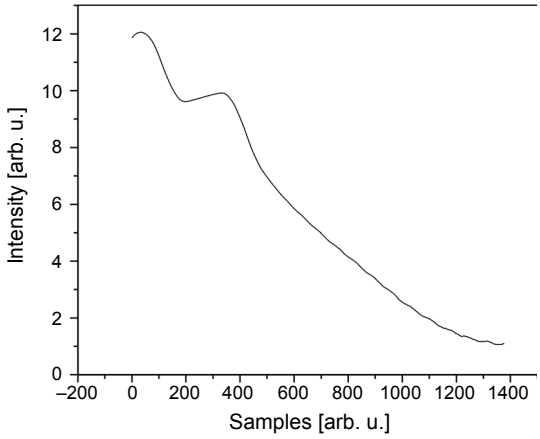

Fig. 3. Linearized XRR curve.

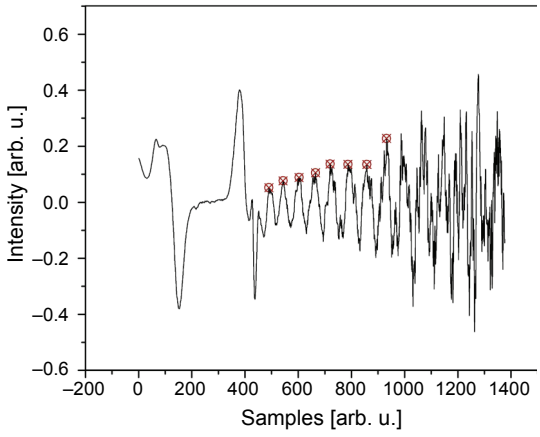

Fig. 4. Periodical changes in the XRR intensity after subtraction S–G and average curves.

Furthermore, the same curve was linearized using simply the step average method [2, 5] (Fig. 3).

The innate nature of this method causes that the information about local maxima with the small amplitudes is lost. However, by the subtracting both curves (see Figs. 2 and 3), characteristic periodical changes in the XRR intensity are revealed (Fig. 4).

It can be seen that the local maxima on the XRR curve (Fig. 4) can be determined with higher resolution [6] than for the measurement of the rough curve or for the curve, that are only processed using the S–G algorithm.

4. Results and discussion

The described methodology is a component of the designed and implemented in the X-ray diffraction measurement data analysis program of the nitride compounds (Nitride Semiconductor Crystal Analysis – NSCA) [7] (Fig. 5).

The NSCA software was used to determine the thickness of self-assembled ion liquid nanolayers of PDDA [8]. This electrostatic self-assembly monolayer (Fig. 6) was discovered and described by DECHER and HONG [9].

Structures consisting of n = 5, 10, 20, 30, 40 and 50 PDDA layers were investigated by means of the high resolution X-ray diffractometer supported with the Ge(220) four-crystal Bartels monochromator in the incidence beam, and an open detector with a 0.45 mm slit in the diffracted beam and $\lambda_{\mathrm{CuK}\alpha 1}$ = 1.540597 Å radiation. In Figure 7, a set of the recorded XRR curves is presented.

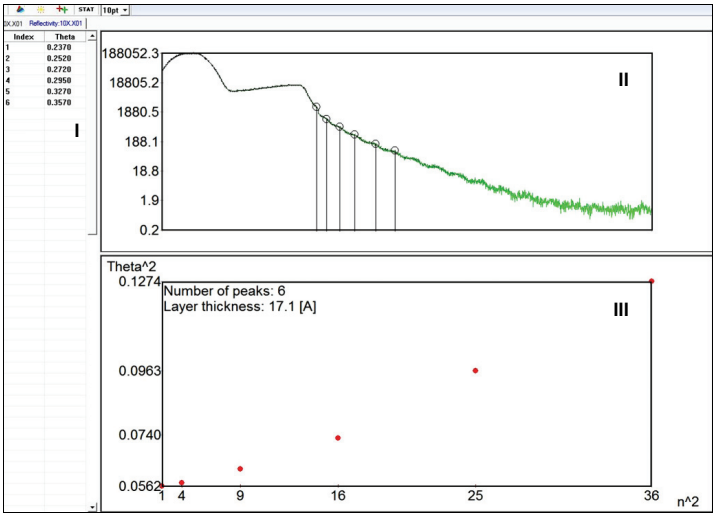

Fig. 5. XRR data analysis window in the NSCA software; detected maxima and their position on the XRR curve (part I); XRR curve with the detected maxima (part II); points used to create straight line function $\theta_1^2 = f(n^2)$ used for thickness calculation (part III).

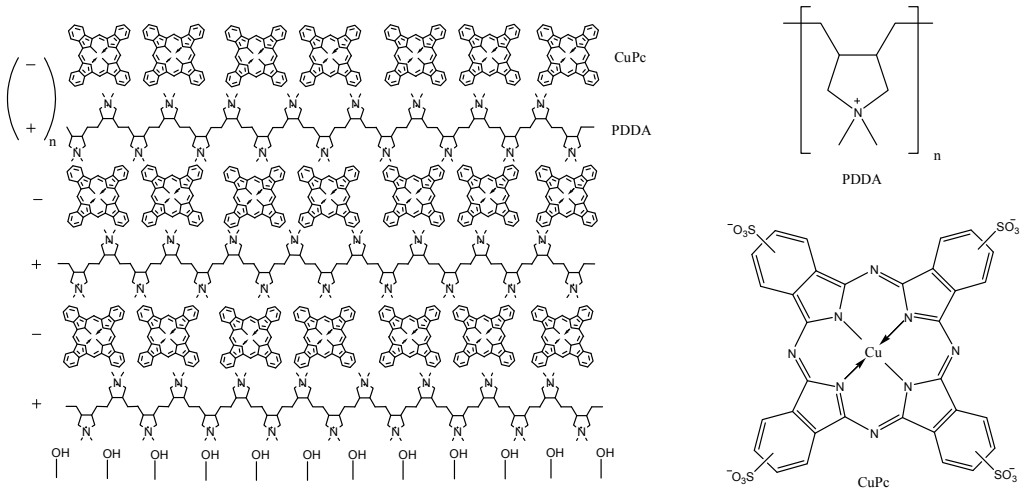

Fig. 6. Structure of self-assembled ion liquid nanolayers of PDDA.

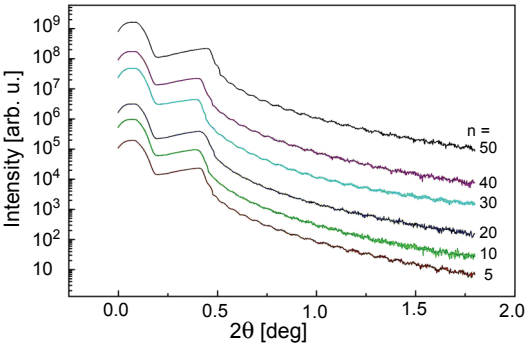

Fig. 7. XRR curves of PDDA multilayer samples formed by n = 5, 10, 20, 30, 40 and 50 PDDA layers.

The thickness of investigated PDDA layers was calculated using the developed algorithm integrated with the NSCA application (Fig. 5) and the following equation:

$$\theta_1^2 = \frac{\lambda^2}{4t^2} n^2 + 2\delta_2 \tag{10}$$

where λ is the X-ray wavelength, t is the thickness of a single layer, δ is the X-ray beam dispersion factor, θ is the Bragg angle of incidence and n is the number of XRR maxima.

The thickness of a layer is calculated based on Eq. (10) and a straight line of function $\theta_1^2 = f(n^2)$.

The relative error of the thickness determination is given by:

$$\frac{\Delta t}{t} = \frac{\delta \Theta_1}{\Theta_c} \approx \frac{1}{n_{\max}} \tag{11}$$

T a b l e. Calculated parameters of analyzed PDDA multilayers.

n	t [Å]	δ	$\Delta t/t$ [%]
5	17.81	0.034	0.14
10	17.10	0.036	0.13
20	18.31	0.020	0.18
30	17.49	0.027	0.15
40	16.73	0.036	0.13
50	17.67	0.034	0.14
Average value	17.52	0.031	0.14

where $\delta\Theta_1$ is the step width of the goniometer, Θ_c is the critical angle of incidence and $n_{\max}$ is the largest fringe order that is detected in the XRR curve with an accuracy of one-half of a fringe period.

The average thickness of the single molecular PDDA layers is 17.5 Å (see the Table). This agrees with the results of the molecular modelling and confirms that the proposed calculation methodology improves significantly the resolution of the analysis. The average relative error of the PDDA multilayer thickness is 0.14%. The biggest difference between the determined and expected value of the height of the single molecular layer was obtained for the sample with 20 periods. It is connected with almost smooth shape of XRR curve and the most difficult determination of the positions of the curve maxima, which results additionally in the largest error of the calculation. The curves with the highest maxima contrast were obtained for samples with the largest number of the periods n = 40 and 50.

5. Summary

In this paper, we describe the novel methodology which is used to determine the thickness of the molecular multilayer. The widely used in data analysis S–G algorithm was applied in the XRR investigations. The determined thickness of the PDDA molecular multilayers was in agreement with the results of the molecular modelling. This methodology was integrated with the NSCA – X-ray diffraction data analysis computer program designed and developed by the article authors.

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