X-ray Reflectometry of Planar Nanoheterostructures: a New Model-less Approach

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ABSTRACT

This work is devoted to a new model-less method of obtaining the density profile of elements in planar nanostructures from X-ray reflectivity data. The method has been tested using numerical simulations and experimental data for the simple multilayer systems composed of Cr and Fe nanolayers. It is shown that layers thicknesses can be determined using an approach developped, based on the kinematical theory. The calculating error does not exceed 1 Å.

Keywords: nanoheterostructures, multilayers, x-ray reflectometry, regularization, density profile

1 INTRODUCTION

Metallic multilayer nanoheterostructures are the films, consisting of interlaced layers of various metals with a thickness from several angstroms to several nanometers. The particular interest to these materials has arisen after finding of their unique electric and magnetic properties, e.g. the effect of giant magnetoresistance [1, 2] having the practical importance. Multilayer nanoheterostructures are of interest for the pure science too – they are the objects for studying the spin-dependent electron transport and the magnetic interactions in low-dimensional systems.

X-ray reflectometry is a highly sensitive non-destructive method of the electron density profile determination along a normal to the surface of multilayer nanostructures. To evaluate the electron density variation with depth from the reflectivity data one uses traditionally the least squares method based on Parratt theory [3], when calculating the intensity of a scattered wave to obtain the agreement of the calculated signal with the experimental data by varying the parameters of the postulated model. However, it is known that in this case the solution has no stability and no uniqueness.

In this paper we describe the numerical simulations which were used for checking the model-less method of reflectometry data processing. It is shown that one can define the thicknesses of individual layers as well as full thickness of a multilayer film with error less than 1 Å. Also the experimental data for various multilayer types have been processed.

2 THEORY

Let us define the depth-profile of element. Consider a multilayer sample consisting of layers of elements A and B. The atomic density of element A at a certain depth z

$$n(z,A)=\frac{N(z,A)}{V}, \tag{1}$$

where V is a volume (for example, unit cell volume), $N(z,A)$ - the number of atoms of type A at the depth z in this volume.

We denote the atomic density $n_0(A)$ for a «pure» layer of the element A. Then we can introduce the function

$$p(z,A)=\frac{n(z,A)}{n_0(A)}, \tag{2}$$

which is a probability of finding an atom of type A at a depth z.

Properties of this function are:

- $p(z,A)=1$ in the layer A without mixing of atoms of different kinds;
- $p(z,A)=0$ in the layer B;
- at the interfaces $p(z,A)$ increases (decreases).

Function $p(z,A)$ is called the depth profile of the element A in the sample.

The electron density at the depth z according [4], may be written as

$$\rho(z)=\frac{n_e d_m(z) N_A}{M(z)}, \tag{3}$$

where n_e - the number of electrons in the atom (molecule, unit cell), $d_m(z)$- the mass density at depth z, N_A - Avogadro's number, $M(z)$ - molar mass at depth z.

Using (3) one can obtain a relationship between electron density $\rho(z)$ and the density profiles $p(z)$:

$$\rho(z)=\sum_{i=1}^{K} p_i(z)\cdot n_e^i\cdot n_0^i. \tag{4}$$

The sum here is over all sorts K of atoms in the sample under investigation.

Using the relationship (4) we have shown, that integral equation, derived in the framework of the first Born approximation [5], which describes the relationship of the reflection coefficient $R(s,E)$ and the reflected intensity $I(s,E)=R(s,E)R^{*}(s,E)$ with the electron density distribution, can be transformed into an equation relating the reflection coefficient $R(s,E)$ with density profiles of elements $p_i(z)$

$$R(s) = \frac{4\pi r_e}{s^2}\sum_{j=1}^{K} n_0^j f_j(E,s)\int_0^D \frac{dp_j(z)}{dz}e^{isz}dz, \quad (5)$$

where r_e is classical radius of electron, s is z-component of the scattering vector, $f_j(E,s)$ is the atomic amplitude of scattering, E – photon energy, D – sample thickness.

In real reflectivity experiment, the recorded intensity of the reflected rays is proportional to the square of the reflection coefficient modulus, i.e. phase information is lost. To find a phase we use the logarithmic dispersion relation proposed by Klibanov [6]. Then we have found a solution of the inverse problem for a Fredholm integral equation (5) using approach, that does not demands initial approximation.

Equation (5) can be represented in a symbolic form:

$$y = Ax, \quad (6)$$

where A is an itegral operator, x is an unknown function, y is an input (experimental) data. A conventional method of obtaining the solution for a Fredholm integral equation of the first kind (6) consists in the approximation of:

- operator A by matrix A_{qp} using a collocation method,
- y and x functions by y_q and x_p vectors, where q and p are vector lengths,

and in solving a system of linear algebraic equations (SLAE):

$$y_q = A_{qp}x_p. \quad (7)$$

There is a well-known mathematical term – condition number – which is used to describe how sensitive the solution is to changes in the input data. If we change y to $y + \Delta y$, the new solution is $x + \Delta x$ with

$$y + \Delta y = A(x + \Delta x). \quad (8)$$

The change in x is

$$\Delta x = A^{-1}\Delta y. \quad (9)$$

To estimate singularity of the matrix A a condition number is defined as follows:

$$\mathrm{cond}\,(A) = \|A\|\,\|A\|^{-1}, \quad (10)$$

where $\|\ \|$ denotes the matrix norm.

Matrix A is well-conditioned one if cond(A) is small (close to 1): the relative error in x is not much larger than the relative error in y. Matrix A is ill-conditioned one if cond(A) is large: the relative error in x can be much larger than the relative error in y.

The problem (6) is ill-conditioned and has an infinite number of solutions. In order to restrict the class of possible solutions, we take into account a priori physical information about the solution:

A. The solution x must be such that when it is acted upon the matrix of the integral operator A, the residual norm $\|\mathrm{Ax - y}\|$ should not exceed the error in the experimental data δ:

$$\|Ax - y\|_{L_2} = \sqrt{\int (Ax-y)^2 dY} \le \delta \quad (11)$$

B. The solution x and the first derivative of x should be smooth.

C. The solution x should be non-negative for any value of argument.

To solve ill-posed problem (6) numerically, a well-known and highly regarded method of regularization by Tikhonov [7] is applied in our work. In its general form, the regularized solution x_α is defined as the solution which minimizes in space L_2 the Tikhonov functional M:

$$\min M = \min\{\|Ax - y\|_{L_2}^2 + \|Bx\|_{L_2}^2\}. \quad (12)$$

Usually, B is the matrix of dimension $p \times p$ given by

$$B = \begin{bmatrix} \alpha+2\beta & -\beta & 0 & \dots & 0 \\ -\beta & \alpha+2\beta & -\beta & \dots & 0 \\ 0 & -\beta & \alpha+2\beta & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \alpha+2\beta \end{bmatrix} \quad (13)$$

α and β are the regularization parameters.

The first term of Eq. (12) is the first physical requirement **A**, defined above. The presence of the term with small positive parameters α and β in the functional M renders the problem stable and assures that the function x and its derivative are smooth (the requirement **B**). Using the fulfillment of the extremum condition (*min* $M = 0$), we obtain a system of linear algebraic equations:

$$\left(A^T A + B\right)x = A^T y \quad (14)$$

where A^T is a transposed matrix of dimension $p \times q$.

The $p \times p$ matrix $A^T A$ is square, symmetric and positively semi-definite. Then the eigenvalues of the regularized matrix $(A^T A + B)$ are positive. In this case it is possible to use for inversion of the matrix $(A^T A + B)$ the well-known linear algebra methods such as Gauss method, square-root method, etc.. As a result, we have an approximate regularized *Tikhonov* solution:

$$x^0 = \left(A^T A + B\right)^{-1} A^T y \,. \qquad (15)$$

Then we can refine this solution, using the iteration formula

$$x^n = \left(A^T A + B\right)^{-1} \left(A^T y + B x^{(n-1)}\right) \quad (16)$$

where n is an iteration number.

3 EXPERIMENTS

Three samples have been chosen for performing the x-ray reflectivity experiments:

- A thin film of pure Cr on sapphire substrate Cr(150 Å)/Al_2O_3;
- A two-layer film Cr(20 Å)/Fe(130 Å)/Al_2O_3.

Samples have been synthesized by a molecular-beam epitaxy method in the Institute of Metal Physics UB RAS.

Fe and Cr belong to a group of 3d transition metals and there atoms have the similar electronic structure. It results in a small difference of the atomic scattering factors, and this is very difficult to distinguish these metals in the x-ray reflectivity experiment. This is the problem of low contrast. It will be shown, that method of the experimental data processing, which is under consideration in this paper, can solve this problem and give us opportunity to determine the layer thicknesses with sufficient accuracy.

The experiments on x-ray reflectivity have been performed at the station of precise x-ray optics of the synchrotron “Siberia-2” at the Kurchatov centre of synchrotron radiation and nanotechnology (Moscow, Russia).

The photons of required energy (5991 eV, $\lambda = 2{,}06951$ Å) were picked out from primary beam with vacuum double-crystal monochromator. The beam vertical size is 18 μm, horizontal size is 6,2 mm. There is no additional monochromatization for the reflected beam, its intensity was registered with the semiconductor germanium detector and was normalized on the primary beam intensity, which was measured by monitoring camera. All experiments have been performed on the air, at room temperature and atmospheric pressure, without any magnetic fields.

4 RESULTS AND DISCUSSION

The first step is to test the method using the numerical simulations. The models of concentration profiles for our samples have been constructed. Using equation (5), the model reflectivity curves have been calculated. Then we used them as an input data for the inverse problem solving and the determination of the concentration profile and layer thicknesses.

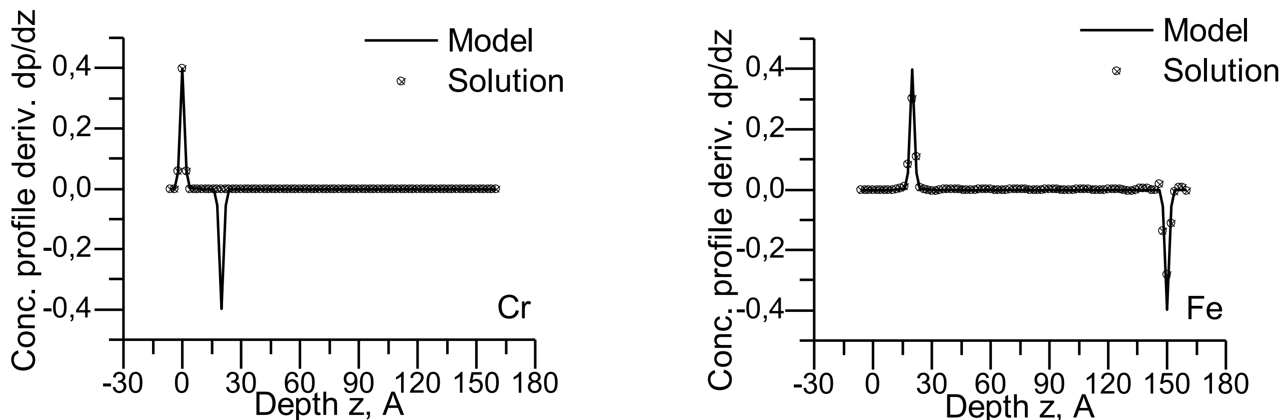

Figure 1: The numerical simulations for structure Cr/Fe/Al_2O_3. Determination of the concentration profile derivatives for Cr (left) and Fe (right).

Layer or interface	Cr oxide	Cr	Cr/Fe	Fe	Fe/Al2O3
Model	4,0	20,0	4,0	130,0	4,0
Solution	4,0	20,1	4,2	130,3	4,5

Table 1: Results of the numerical simulations (layers and interfaces thicknesses) for two-layer structure Cr/Fe/Al_2O_3. All values are given in angstroms.

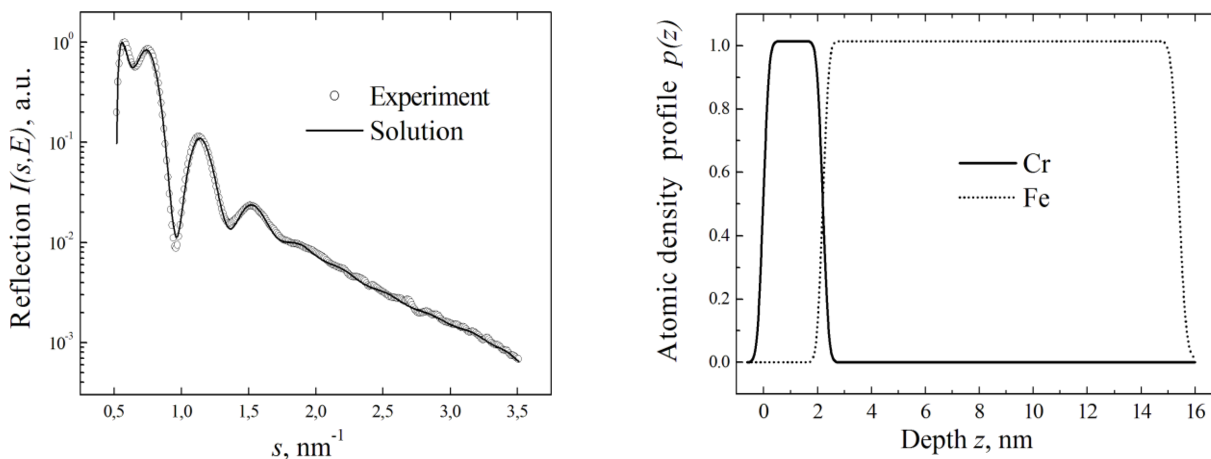

Figure 2: Experimental results for the nanoheterostructure $Cr/Fe/Al_2O_3$: experimental and calculated reflectivity curves (left) and concentration profiles (right).

Layer or interface	Cr oxide	Cr	Cr/Fe	Fe	Fe/Al_2O_3
Thickness	4,0±0,0	22,1±0,1	5,1±0,2	132,4±0,3	3,2±0,5

Table 2: Experimental results: layer and interfaces thicknesses in two-layer system $Cr/Fe/Al_2O_3$. All values are given in angstroms.

Let us consider the model data for the single layer sample Cr/Al_2O_3. According to the solution the film thickness is 144,0 Å, the model value is 143,5 Å. Thus the absolute error of a thickness determination via this method is ±0,5 Å. The R-factor of the model and obtained curves $I(s)$ is 5,3%.

The experimental results have given the thickness value 143,4±0,5 Å, which coincides with the data processing via Parratt method. The R-factor for the reflection intensity curves is 2,4%.

The results for two-layer model are depicted at Fig. 1; numerical data are presented in table 1. One can see that solution reproduces all model features quite good; discrepancy between model and solution values of layers thicknesses and interfaces width does not exceed 0,5 Å. This quantity has been accepted as absolute error of the method.

The experimental results of determining of the layers thicknesses and interfaces width in two-layer sample are depicted at fig. 2; numerical values are presented in table 2.

The experimental values of layers thicknesses does not coincide with the synthesis parameters in the permissible range of absolute error. There are some reasons for this fact:

1. The systematic and random errors which occur in the determination of speed and time of a sample growth. It results in that real layers thicknesses really differ from expected ones.
2. A substrate roughness, which dimensions appreciably exceed the interatomic distances. The statistic model of concentration profile, which is used in the described techniques, does not take such roughness into account. This fact leads to additional errors in the determination of thickness of a layer, which lies directly on the substrate.
3. A necessity to take diffuse scattering and instrument function into account. The effect of diffuse scattering is significant if the roughness inherits through the film.

All of these reasons can be taken into account and consequently the techniques accuracy can be improved. Nevertheless, one already can obtain the results, similar to that come out of Parratt algorithm, but without any specific assumptions about concentration profile of the sample.

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