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Frank laboratory of Neutron Physics

FINAL REPORT ON THE SUMMER STUDENT PROGRAM

Structural investigations of thin films by neutron and X-ray reflectometry

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Abstract

The present report reflects key points on the student's practice which was carried out in Frank Laboratory of Neutron Physics (FLNP) of Joint Institute for Nuclear Research. The subject of the student's work was to get acquainted with experimental methods of neutron and X-ray scattering to study the morphology (internal structure) of thin films deposited on crystal surface. To achieve the goal, the training task was formulated to determine the structural characteristics of standard samples, which were previously studied in the framework of other scientific work and were stored at the REFLEX group in FLNP. So, the structure of nanocsale coatings of TiO_x (x=1..2), VN and ZrN on a glass substrate have been studied by the methods of neutron and X-ray reflectometry. The experimental dependencies of the reflection coefficient on the scattering vector (reflectivities) were analyzed. The average thicknesses of the layers and their roughness were obtained.

Introduction

Development of new materials with attractive operational properties is of great interest for the modern industry. An evolution of some industrial branches is extremely important for improvement the quality of the human life and high technologies. For that reason the application of nanostructured materials substrates are of great interest form the modern science. There are several types of nanostructured materials, or nanomaterials, can be met in an industry science from the physics point of view – 1-D (*'dimensional'*), 2-D and 3-D. The common feature to all mentioned types is a size of objects that has to belong to nano-metric scale, at least in one direction (for example, a strand polymer molecule may be considered as 1-D nanoscaled object). To implement some new functionalized materials with extraordinary surface properties nano-scaled coatings based on transition metals nitride (TMN) can be used in industry and material science. The deposition of such coatings is capable to improve the mechanical properties, wear and corrosion resistance, can be used as a decorative items etc. [1-3]. It is known that coatings of AlN, TiN, etc. deposited by direct current (DC) magnetron sputtering improves significantly the mechanical properties, corrosion resistance at high temperature, as it is known that tools covered by TiN films can operate between 2.5 – 10 times longer in comparison with uncoated one. Coatings of TiO_2 are widely used for biocompatibility purposes as well as optical filters etc. The investigations [4] on DC magnetron co-sputtered TiN films with different silver concentration have shown that with increasing of the concentration of the silver, antibacterial activities also increases, while the microhardness decreases.

Methods

Neutron reflectometry is a kind of neutron diffraction technique for measuring the structure of thin films, similar to the often complementary techniques of X-ray reflectivity and ellipsometry [5]. The technique provides valuable information over a wide variety of scientific and technological applications including chemical aggregation, polymer and surfactant adsorption, structure of thin film magnetic systems, biological membranes, etc.

The technique involves shining a highly collimated beam of neutrons onto an extremely flat surface and measuring the intensity of reflected radiation as a function of angle or neutron wavelength. The exact shape of the reflectivity profile provides detailed

information about the structure of the surface, including the thickness, density, and roughness of any thin films layered on the substrate. Neutron reflectometry is a specular reflection technique, where the angle of the incident beam is equal to the angle of the reflected beam. The reflection is usually described in terms of a momentum transfer vector, denoted q_z, which describes the change in momentum of a neutron after reflecting from the material. Conventionally the '*z'* direction is defined to be the direction normal to the surface, and for specular reflection, the scattering vector has only a *z*-component. A typical neutron reflectometry plot displays the reflected intensity (relative to the incident beam) as a function of the scattering vector:

$$q_z = (4\pi / \lambda)\sin(\theta) \ , \tag{1}$$

where λ is the neutron wavelength, and θ theta is the angle of incidence.

The wavelength of the neutrons used for reflectivity are typically on the order of 0.2 to 1 nm (2 to 10 Å). This technique requires a neutron source, which may be either a research reactor or a spallation source (based on a particle accelerator). Like all neutron scattering techniques, neutron reflectometry is sensitive to contrast arising from different nuclei (as compared to electron density, which is measured in x-ray scattering). This allows the technique to differentiate between various isotopes of elements. Neutron reflectometry measures the neutron scattering length density (SLD) and can be used to accurately calculate material density if the atomic composition is known.

Although other reflectivity techniques (in particular optical reflectivity, X-ray reflectometry) operate using the same general principles, neutron measurements are advantageous in a few significant ways. Most notably, since the technique probes nuclear contrast, rather than electron density, it is more sensitive for measuring some elements, especially lighter elements (hydrogen, carbon, nitrogen, oxygen, etc.). Sensitivity to isotopes also allows contrast to be greatly (and selectively) enhanced for some systems of interest using isotopic substitution, and multiple experiments that differ only by isotopic substitution can be used to resolve the phase problem that is general to scattering techniques. Finally, neutrons are highly penetrating and typically non-perturbing: which allows for great flexibility in sample environments, and the use of delicate sample materials (e.g., biological specimens). By contrast X-ray exposure may damage some materials, and laser light can modify some materials (e.g. photoresists). Also, optical techniques may include ambiguity due to optical anisotropy (birefringence), which complementary neutron measurements can resolve. Dual polarisation interferometry is one optical method which provides analogous results to neutron reflectometry at comparable resolution although the underpinning mathematical model is somewhat simpler, i.e. it can only derive a thickness (or birefringence) for a uniform layer density.

Disadvantages of neutron reflectometry include the higher cost of the required infrastructure, the fact that some materials may become radioactive upon exposure to the beam, and insensitivity to the chemical state of constituent atoms. Moreover, the relatively lower flux and higher background of the technique (when compared to X-ray reflectivity) limit the maximum value of q_z that can be probed (and hence the measurement resolution).

The specular reflectivity is calculated using the Abeles [6] formulation (giving identical results to Parratts [7] recursion formula for stratified thin films), as a function of the perpendicular momentum transfer q_z (1). Specular reflectivity R is defined as the ratio of reflected intensity over incident intensity, where the angle of reflection θ is equal to the angle of incidence (Fig.1).

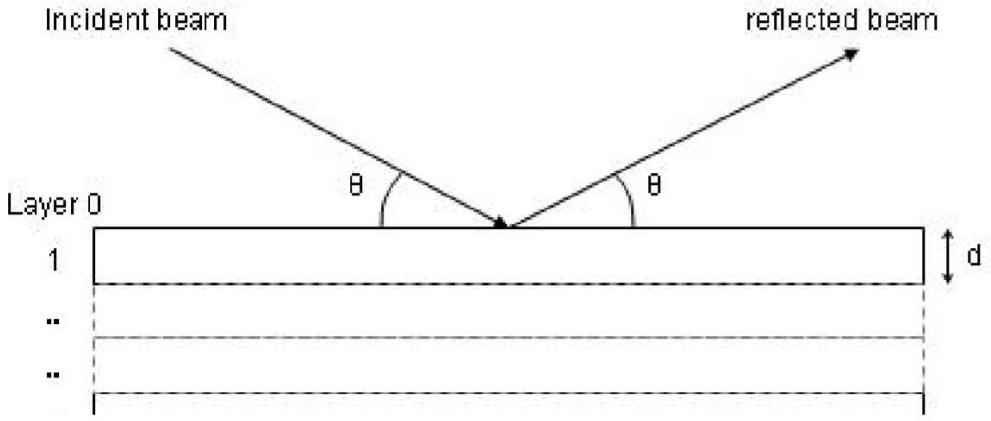

Fig.1. Reflection from a stratified medium

The measured reflectivity depends on the variation in the scattering length density (SLD) profile, $\rho(z)$ perpendicular to the interface. Although the scattering length density profile is normally a continuously varying function, the interfacial structure can often be well approximated by a slab model in which layers of thickness (d_n) , scattering length density (ρ_n) and roughness $\left(\sigma_{n,n+1}\right)$ are sandwiched between the super- and sub-phases. One then uses a refinement procedure to minimise the differences between the theoretical and measured reflectivity curves, by changing the parameters that describe each layer. In this description the interface is split into n layers. Since the incident neutron beam is refracted by each of the layers the wavevector, k , in layer n , is given by:

$$k_n = \sqrt{k_0^2 - 4\pi(\rho_n - \rho_0)} \ , \tag{2}$$

where $k_0 = q/2$. Note that the wavevector can be complex if $4\pi(\rho_n - \rho_0)$ is greater than k_0^2 . The Fresnel reflection coefficient between layer *n* and *n*+1 is then given by:

$$r_{n,n+1} = \frac{k_n - k_{n+1}}{k_n + k_{n+1}} \ , \tag{3}$$

Since the interface between each layer is unlikely to be perfectly smooth the roughness/diffuseness of each interface modifies the Fresnel coefficient 4 and is accounted for by an error function, as described by Nevot and Croce [8].

$$r_{n,n+1} = \frac{k_n - k_{n+1}}{k_n + k_{n+1}} \exp(-2k_n k_{n+1}\sigma_{n,n+1}^2) \ . \tag{4}$$

A phase factor, β is introduced, which accounts for the thickness of each layer.

$$\beta_n = k_n d_n \ . \tag{5}$$

A characteristic matrix, c_n is then calculated for each layer.

$$c_n = \begin{bmatrix} \exp(\beta_n) & r_n \exp(\beta_n) \\ r_n \exp(-\beta_n) & \exp(-\beta_n) \end{bmatrix} . \tag{6}$$

The resultant matrix is defined as the product of these characteristic matrices, from which the reflectivity is calculated.

$$M = \prod_0^n c_n \tag{7}$$

$$R = \left| \frac{M_{00}}{M_{10}} \right|^2 \ . \tag{8}$$

Results and discussion

Neutron reflectometry on Glass/VN coating.

The interface air – 'VN' deposited on a glass substrate (SiO_2) was probed by the Neutron Reflectometry (NR) method in a non-polarized mode using spectrometer REFLEX located at the pulsed reactor IBR-2. Experimental data on NR is presented in Fig.1, the measured dependence of reflection coefficient, *Reflectivity*, is plotted versus the momentum transfer normal to the sample plane, q_z. A monolayer structure is resolved quite well from analysis of the data. The recovered Scattering Length Density (SLD) profile is shown in the inset; resolved regions (air, coating film and glass substrate) are highlighted by colours. The obtained structural parameters are gathered into a table 1.

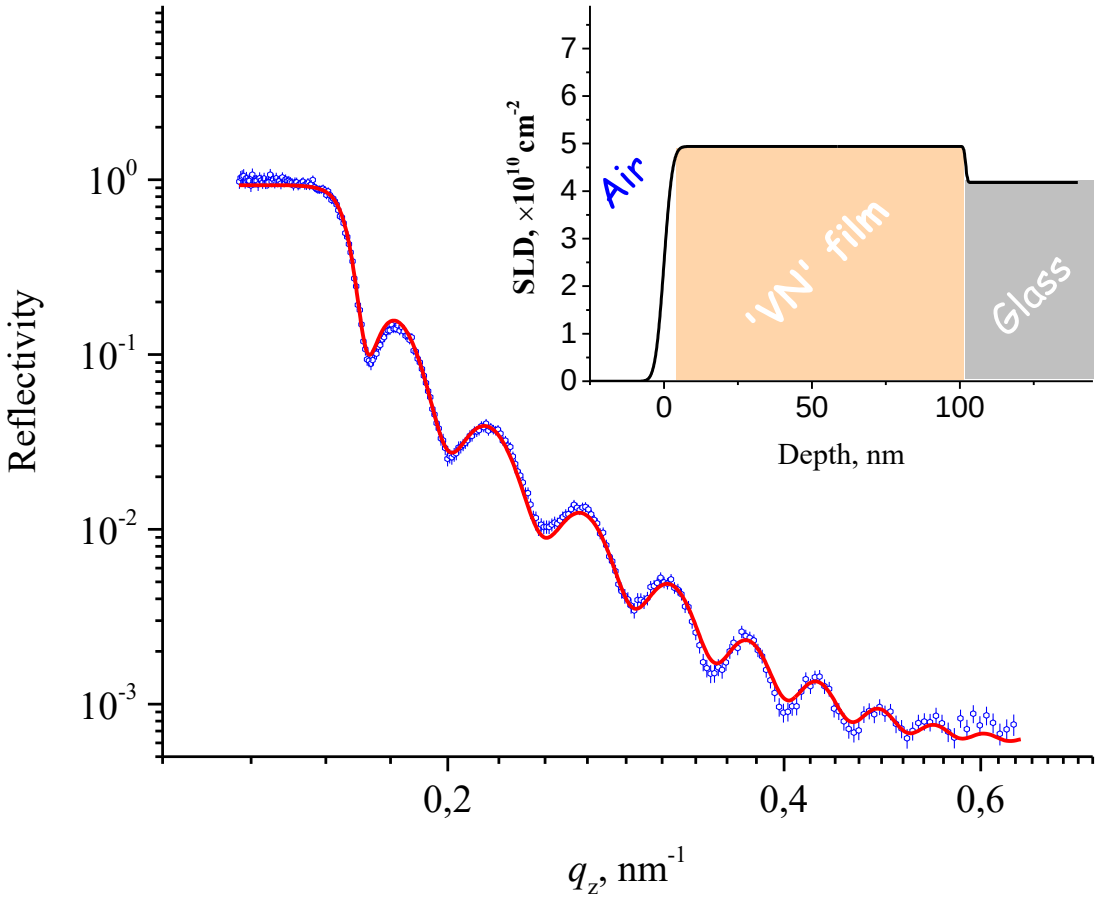

Fig.1. Reflectivity curve for the SiO_2 //VN (102 nm) film measured by means of neutron reflectometry. The points designate the experimental values, and continuous lines correspond to fitting. The dependence between the SLD and the film depth along the normal to the surface from the film–vacuum (air) interface are shown in the inset.

Table 1. Structural parameters of 'VN' coating

Thickness of the 'VN' layer	102 ±1 nm	
SLD of the 'VN' layer	$(4.94\pm0.01)\times10^{10}$ cm^{-2}	
Roughness "coating film / air"	23.1 (±0.1) Å	
Roughness "glass / coating film"	4 Å	Fixed parameter
SLD of glass substrate	4.18 10^{10} см$^{-2}$	Fixed parameter

Neutron reflectometry on Glass/ZrN coating.

The sample of 'ZrN' coating deposited on a glass substrate was measured by means of the NR method. Experimental NR data is presented in Fig.2, the measured dependence of reflection coefficient, *Reflectivity*, is plotted versus the momentum transfer normal to the sample plane, q_z. The structure of interface can be appropriate resolved accounting at least two-layered model of the coating. The recovered Scattering Length Density (SLD) profile is shown in the inset; resolved characteristic regions (air, coating layers and glass substrate) are highlighted by colours. The obtained structural parameters are placed into the table 2.

A possible explanation of obtained structural model (density distribution in depth from the sample's surface) may lie in the assumption that 'ZrN' coating has a complex morphology: a dense layer on a glass surface and a loose layer above it. This situation can be caused by sputtering conditions during a coating growth. For example, the first layer is densely laid on the substrate surface following its contour until some threshold thickness is grown. However, the next strata is deposited forming a less quality layer, with porous or loose morphological structure.

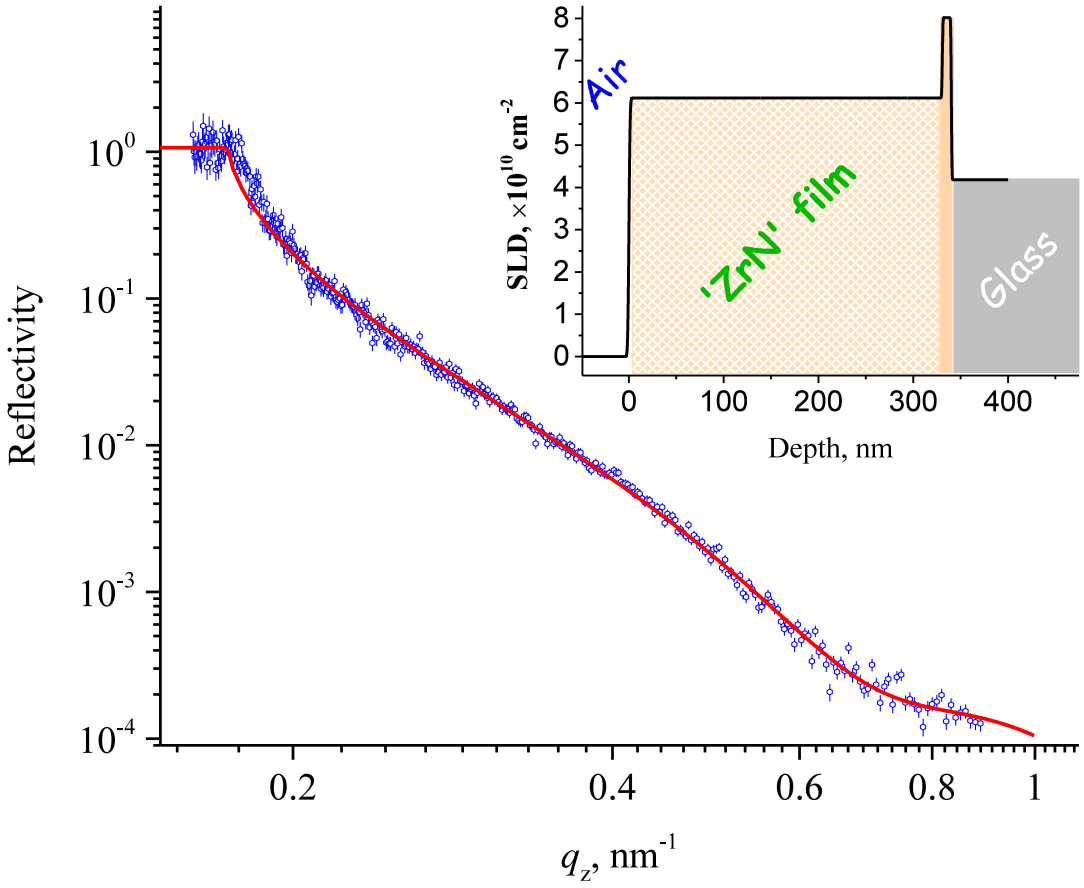

Fig.2. Reflectivity curve for the SiO_2 / ZrN film measured by means of neutron reflectometry. The points designate the experimental values, and continuous lines correspond to fitting. The dependence between the SLD and the film depth along the normal to the surface from the film–vacuum (air) interface are shown in the inset.

Table 2. Structural parameters of 'ZrN' coating

SLD of the air (vacuum)	0	
Thickness of the 2nd layer	331 ±2 nm	
SLD of the 2nd layer	(6.13±0.04) ×10^{10} cm^{-2}	
Thickness of the 1st layer	9.5 ±0.6 nm	
SLD of the 1st layer	(8.06±0.06) ×10^{10} cm^{-2}	
Roughness "coating film / air"	10 Å	Fixed parameter
Roughness "1st layer / 2nd layer"	5 Å	Fixed parameter
Roughness "glass / coating film"	4 Å	Fixed parameter
SLD of glass substrate	4.18 10^{10} см$^{-2}$	Fixed parameter

X-ray reflectometry on Glass/TiO_2 coating.

The interface air – 'TiO_2' deposited on a glass substrate (SiO_2) was probed by the X-ray Reflectometry (XR) method using X-ray reflectometer. Experimental data is presented in Fig.3, the measured dependence of reflection coefficient, *Reflectivity*, is plotted versus the momentum transfer normal to the sample plane, q_z. A monolayer structure is resolved quite well. The reconstructed Scattering Length Density (SLD_{Xray}) profile is shown in the inset. The obtained structural parameters are gathered into a table 3.

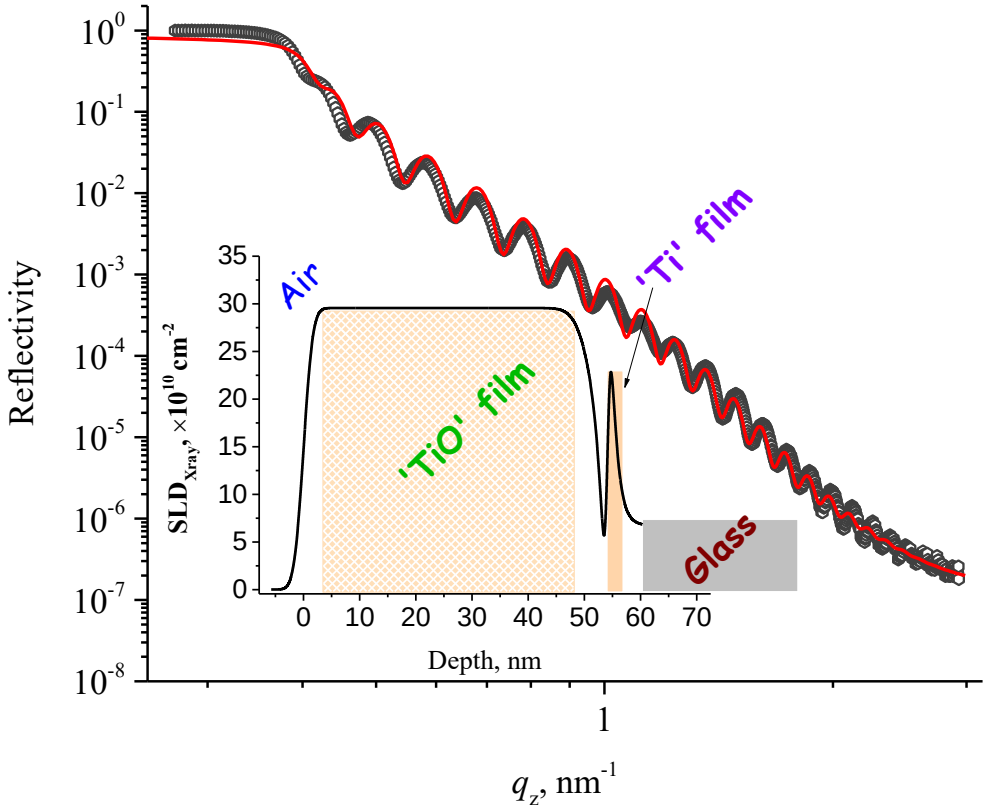

Fig.3. Reflectivity curve for the SiO_2 // Ti/TiO/TiO_2 film measured by means of X-ray reflectometry. The points designate the experimental values, and continuous lines correspond to fitting. The dependence between the SLD_{Xray} and the film depth along the normal to the surface from the film–vacuum (air) interface are shown in the inset.

Table 3. Structural parameters of 'TiO2' coating

SLD of the air (vacuum)	0	
Thickness of the 2nd layer	1.5 ±0,1 nm	
SLD of the 2nd layer	(24.7±0.4) $\times 10^{10}$ cm^{-2}	
Thickness of the 1st layer	50.1 ±1 nm	
SLD of the 1st layer	(32±0.3) $\times 10^{10}$ cm^{-2}	

Roughness "coating film / air"	12 Å	
Roughness "1st layer / 2nd layer"	5.8 Å	
Roughness "glass / coating film"	14.6 Å	
SLD of glass substrate	6.73×10^{10} см$^{-2}$	

Conclusions

The methods of neutron and X-ray reflectometry were applied to observe morphological structure of metallic coatings at nanoscale. The presence of nanoscale layers deposited on a glass substrate by DC magnetron sputtering has been experimentally confirmed; it was revealed that ultra-thin buffer films of metals (Zr and Ti) formed right on the surface of glass during sputtering process, thus coursing to complex structure at interface. The anticipated films of 'ZrN' and 'TiO_2' were deposited on the top of those buffering layers.

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