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Y. KOSIACHKIN,[1] L.A. BULAVIN,[1] P. KOPCANSKY[2]

[1] Physics Department, Taras Shevchenko National University of Kyiv
*(4, Hlushkova Ave., Kyiv 03127, Ukraine; e-mail: kosiachkin@gmail.com)*
[2] Institute of Experimental Physics Slovak Academy of Science
*(Kosice, Slovakia)*

# DEVELOPMENT OF NEUTRON REFLECTOMETRY OF SURFACE LAYERS OF LIQUID SYSTEMS

*In order to develop the methods of neutron and X-ray reflectometries for the study of surface layers of liquid systems, a method of increasing the sensitivity of the reflectometric experiment to the appearance and evolution of near-surface layers is proposed. Therefore, Ni/Ti multilayered heterostructures are tested regarding for the practical applicability of the quasi-homogeneous approach with varying effective scattering length density of thin (thickness <100 nm) metal films in X-ray reflectometry experiments on the example of electrochemical interfaces. The structures with extremely low thickness of the Ni/Ti bilayer with different thickness ratios of Ni- and Ti-sublayers are synthesized by magnetron sputtering. Specular reflectivities of X-rays from the heterostructures are analyzed to conclude about the limits of the quasi-homogeneous approximation.*

*Keywords*: thin films, multilayered structures, neutron reflectometry, X-ray reflectometry, electrochemical interfaces, signal optimization.

## 1. Introduction

The modern development of nuclear methods for the study of liquids and liquid systems in the bulk phase (small-angle scattering of neutrons and X-Ray radiation [1–5]) prompted the further development of nuclear methods for studying the structure of near-surface layers – neutron and X-Ray reflectometries. Nowadays, there is a great interest in experiments on neutron reflectometry at planar solid – liquid interfaces, when the evolution of the nanoscaled structure of a near-boundary vicinity under varied conditions is followed [6–11]. In such kind of experiments, a flat neutron beam (in most cases in a horizontal geometry of the sample plane) passes through a relatively massive (thickness of ∼1 cm, length ∼5–8 cm) substrate of single-crystal silicon or quartz which, due to a comparatively low absorption, provides the sufficient transmission of the incident and reflected beams (in total ∼80%). The surface of the substrate is modified prior to the experiment depending on the research objective. For example, when studying the structural organization of liquid colloidal solutions at the interface, the substrate surface should be lyophilic regarding the solvent [7]. For aqueous solutions and a silicon substrate, this can be achieved by the silicon oxidation in the near-surface region [7]. To enhance the adsorption of nanoparticles or polymers, the substrate surface is covered with a special binding anchor layer [12]. In electrochemical reflectometry, in cells with metal anodes contacting liquid electrolytes, a thin metal film, which is used as a working electrode, is sputtered on the substrate surface. From the experimentally measured specular reflection curve as a function of the momentum transfer projection on the normal to the interface plane (z-direction), a neutron scattering length density depth profile is obtained along the normal.

The presence of sharp boundaries between components on the substrate in many cases makes it possible to present the neutron scattering length density

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profile as a layered structure. The objective of the experiment is to detect and analyze the changes of such profile, showing the structural evolution of the interface. Often, the corresponding changes in specular reflection curves are rather small, which leads to the problem of optimizing the initial configuration of the interface to enhance these changes appeared as a response to slight deviations of the interface from its initial state [13]. Despite the fact that any reflectivity curve is an implicit function of many parameters, including the mean neutron and X-Ray scattering length densities of the layers, the thicknesses of the layers and the parameters of the roughness of the interlayered boundaries, the initial scattering length density profile structure is well known, so that just few parameters of the new layers are responsible for the changes under discussion.

Recent applications of the neutron reflectometry to electrochemical interfaces with liquid electrolytes (see reviews [14–16]) demonstrate the advantages of the method for exploring the hidden interfaces, in particular, related to lithium power sources. In situ experiments make it possible to follow the formation of solid electrolyte interphase and lithiation of planar metal electrodes [17–20]. These days, power storage devices with metallic electrodes are still considered as one of the promising energy sources with a significantly higher (as compared to common Li-ion batteries with lithium percolation into electrodes) capacitive characteristics. Among the problems for this type of sources which requires the systematic studies of the processes at electrochemical interfaces, is the control over the formation of the regulating and protective electrode coating, solid electrolyte interphase, including its composition, homogeneity, and porosity. Another problem concerns the conditions of the uniform lithium plating on metal electrodes with a special accent on the initial stages, when nanoscaled deposition layers are formed. The general consideration of the optimization of the neutron reflectometry experiment for these purposes [21, 22] shows that characteristic relations between neutron scattering length densities of the components of the initial interface should be realized to determine the structure of the lithium-enriched layers at the electrode surface. The scattering length density contrasts between the components of the electrochemical interface of such kind can be changed by varying the neutron scattering length density of the liquid phase in the electrolyte using the isotopic D/H substitution. Still there are limits on the neuron scattering length density variations, which can be extended by using another potential possibility – a change in the electrode neutron scattering length density. This option can be realized by the deposition of quasi-homogeneous structures based on low-period multilayers. The idea is based on the fact that the practical $q_z$-resolution of the neutron reflectometry experiment is limited. Especially, this concerns in situ measurements, when a series of reflectivity curves is to be obtained under identical conditions and with sufficiently high statistics in a certain time interval. For low-period multilayers, the peaks in the initial part of the reflectivity curve covered in the neutron reflectometry experiment are mostly from a homogenous structure of the multilayers corresponding to its mean neutron scattering length density. In this case, an effective model neutron scattering length density profile with a reduced number of parameters can be used as a starting profile of the initial interface before the deposition of a new small layer. As compared to time-consuming high-resolution neutron reflectometry experiments in which the fine structure of electrochemically deposited layers (see, e.g., [17]) is analyzed, the task of the experiment in this case is to obtain the reflectivity curves with sufficient statistics in a reduced $q_z$-range, which can be treated well in the frame of a simple effective model. A lost in resolution is compensated by the possibility to increase the sensitivity of the neutron reflectometry experiment to the new thin layer by varying the neutron scattering length density of the electrode. The mean scattering length density of such kind of structures can be varied by regulating the relative thicknesses of sublayers. The proper candidates for this are Ti/Ni multilayers, in which the Ti- and Ni-sublayers exhibit the limiting in neutron scattering length density values. This makes it possible to cover a wide scattering length density range for metal electrode layer from $-1.93 \times 10^{-6}$ Å$^{-2}$ (Ti) to $9.41 \times 10^{-6}$ Å$^{-2}$ (Ni). Ti/Ni multilayers obtained by the magnetron spattering are widely used in the production of neutron supermirrors [23]. These materials show a good adhesion regarding silicon and quartz, which determines a good quality and stability of the practical multilayered structures together with their comparatively low production cost. The use of two independent Ni- and Ti-targets in the sputtering procedure provides somewhat a fine regulation of the neutron and X-Ray scattering length densities of the electrode film as compared to the synthesis of a single Ni/Ti compound with proper composition. The use of the magnetron sputtering is essential, since comparatively large (several tens of $cm^2$) areas of deposition are involved. This idea can be extended for other kinds of interfaces, where metal layers are essential components of the interface. Examples are ultra-thin metallized polymers [24], adsorption of proteins on metal surface [25], corrosion of metals [26], and lipid membranes on special heterostructures [27]. In each case, one needs to consider a specific interface structure and investigate to what extent this approach can be applied.

The goal of this work is to experimentally test the practical realization of the quasi-homogeneous approach regarding Ti/Ni-multilayers with different ratios of the thicknesses of the Ti- and Ni-sublayers in the bilayer. The usage of such films could prompt the optimization of the sample initial interface for the purpose to maximally enhance the reflectometry signal from the layers under study. The ferromagnetic structure of Ni opens additional possibilities for using the interference of nuclear and magnetic scatterings in varying the relative scattering contrasts between interface components. For this, a polarized neutron beam and a magnetization of the thin film under study are required. As the first stage, we consider a simpler case, in which the magnetic scattering contribution is eliminated by using, instead of pure Ni, the proper non-magnetic NiMo compound (fraction of Mo is about 16.8 wt%) with still high neutron scattering length density. The task is to study how a decrease in the thicknesses of the sublayers down to the limits of the magnetron sputtering method affects the quality of the specular reflectivity curves regarding the homogeneous approximation. The extended diagnostics of the films is performed by the specular X-ray reflectivity in a wide $q_z$-range covering, in the real space, the subnanometer scale. The analysis of the high-resolution X-ray reflectometry curves allows us to explicitly mark out a $q_z$-range, where the homogeneous approximation can be applied. Despite the difference in the interaction of neutrons and X-ray radiation with the matter, the general reflectometry theory slightly varies. Therefore, it is thought that the neutron reflectometry curves will show the same tendency, but with a different $q_z$-range, where the homogeneous approximation can be applied.

## 2. Experimental Part

Two thin films of multilayered structures (20 Ti/NiMo bilayers) were provided by Mirrotron Ltd. (Hungary) [28]. The films were prepared at the T1 research PVD DC magnetron sputtering system (coating area <0.2 $m^2$; the base pressure $10^{-6}$ Torr; two single rectangular planar magnetrons with direct water cooling, vertical position; constant sputtering power; glow discharge cleaning in the load lock chamber). The single crystal silicon substrates ($40 \times 40 \times 0.5$ mm, surface plane orientation $\langle 111 \rangle$, nominal roughness <0.5 nm) were purchased from Holm GmbH (Germany). Dust cleaning (acetone) and surface activation procedures were done before the sputtering. Films were deposited on one side of the single silicon substrate; nominal parameters are Si (crystal)/[Ti 7 Å/NiMo 7 Å]$_{20}$, Si (crystal)/[Ti 5 Å/NiMo 10 Å]$_{20}$. The layer thicknesses were regulated by the speed of substrate carrier calibrated before the final deposition by test depositions using a float glass as substrate. The NiMo target with the compound containing 16.8 wt % Mo was used.

The samples were characterized by X-ray specular reflectometry. X-ray reflectometry experiments were carried out on the Empyrean Malvern Panalytical instrument. Measurements were made in air at room temperature with a fixed wavelength of X-ray radiation of 1.54 Å (K-alpha line of the Cu cathode tube) in the interval of the grazing angle 0.16–3.5 dg., corresponding interval of the projection of the momentum transfer vector ($q_z$) is 0.023–0.5 Å$^{-1}$.

The reflectivity curves in both cases were processed within the Parrat formalism using the Motofit package for the IGOR Pro software [29].

## 3. Results and Discussion

X-ray specular reflectivity curves obtained for the two multilayered systems are shown in Figs. 1–4. First, they are treated as multilayers (Figs. 1 and 3). To experimentally estimate a $q_z$-range, where quasi-homogeneous approximation works well, the X-ray reflectometry curves were also fitted with the homogeneous monolayer model (Figs. 2 and 4).

The stable fits were obtained in the restricted $q_z$-range up to 0.2 Å$^{-1}$. The fitting failed in a wider $q_z$-range because of the influence of the diffraction peak ($q_z \sim 0.4$ Å$^{-1}$). The reflectivity curves corresponding to the homogeneous monolayer model are plotted in

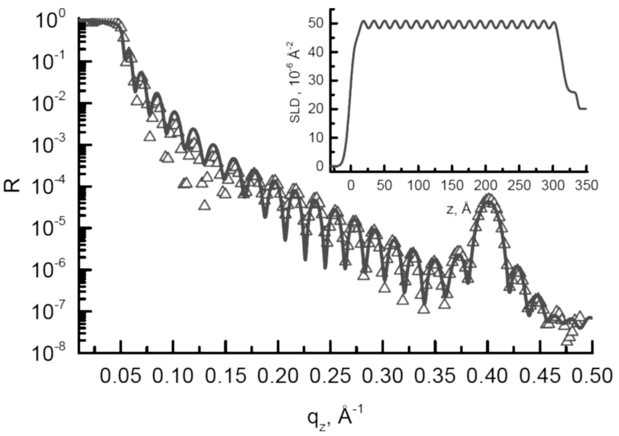


***Fig. 1.*** Experimental X-ray specular reflectivity curves R($q_z$) (points) and approximations (solid lines) for the two multilayered structures on the Si substrate: Ti 5Å/NiMo 10Å with 20 repetitions. Data were fitted with a multilayer model. X-ray scattering length density profile is represented on the inserted graph

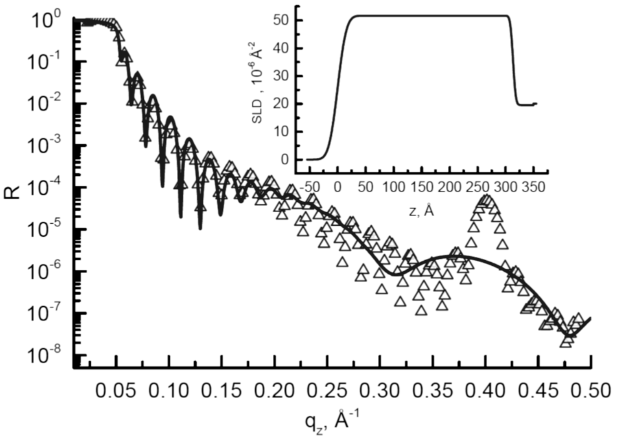


***Fig. 2.*** Experimental X-ray specular reflectivity curves R($q_z$) (points) and approximations (solid lines) for the two multilayered structures on the Si substrate: Ti 5Å/NiMo 10Å with 20 repetitions. Data were fitted with a quasi-homogeneous model. X-ray scattering length density profile is represented on the inserted graph

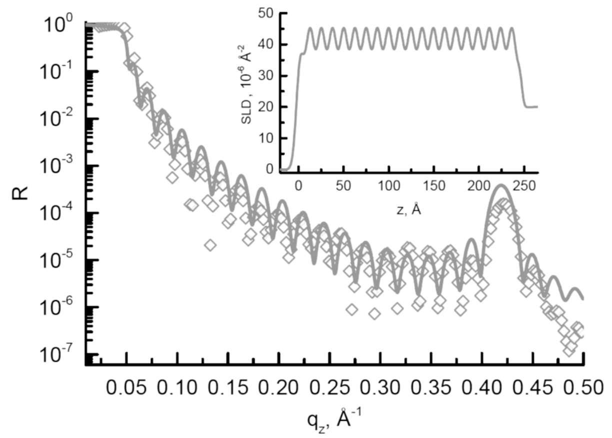


***Fig. 3.*** Experimental X-ray specular reflectivity curves R($q_z$) (points) and approximations (solid lines) for the two multilayered structures on the Si substrate: Ti 7Å/NiMo 7Å with 20 repetitions. Data were fitted with a multilayer model. X-ray scattering length density profile is represented on the inserted graph

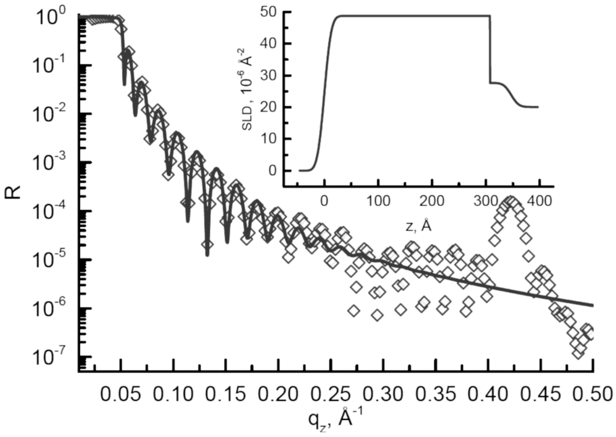


***Fig. 4.*** Experimental X-ray specular reflectivity curves R($q_z$) (points) and approximations (solid lines) for the two multilayered structures on the Si substrate: Ti 7Å/NiMo 7Å with 20 repetitions. Data were fitted with a quasi-homogeneous model. X-ray scattering length density profile is represented on the inserted graph

Figs. 2 and 4 in the whole experimental $q_z$-range to follow the deviation with increasing $q_z$. As is seen, it shows a good consistency with the experimental X-ray reflectometry curves up to $q_z \sim 0.17$ Å$^{-1}$.

As is expected, the homogeneous approximation extrapolated to the positions of the Bragg peaks of the layered structures (Figs. 1 and 3) "sees" no periodicity (with the period at subnanoscale).

In this case, the peak presence is a parasitic effect; so, the idea is to place it beyond the measuring window in the neutron reflectometry experiment (by using a short period of the Ti/NiMo layers), which is reduced as compared to that in the X-ray reflectometry experiment. The situation is opposite to the cases when long-period structures are designed so that the Bragg peaks are specially placed in the measuring

*Table 1.* **The parameters are obtained from the results of fitting the experimental X-ray reflectometry curves for [Ti 5Å/NiMo 10Å]$_{20}$ multilayer systems using two models: The multilayer system and the homogeneous approximation. SLD and ISLD are real and imaginary components of X-ray scattering length density, respectively**

| [Ti 5Å/NiMo 10Å]$_{20}$ | | | | |
|---|---|---|---|---|
| Layer | Thickness, Å | SLD × ×$10^{-6}$Å$^{-2}$ | iSLD × ×$10^{-6}$Å$^{-2}$ | Roughness, Å |
| Multilayer | | | | |
| Si | – | 20.07 | 0.46 | 1.85 |
| $SiO_2$ | 21.34 | 25.9 | 1 | 4.49 |
| Ti × 20 | 6.28 | 38.6 | 3 | 8.17 |
| Inter | 2.99 | 49.8 | 2 | 3.65 |
| Ni × 20 | 6.5 | 60.2 | 2 | 6.74 |
| Air | – | 0 | 0 | – |
| $\chi^2$ | Full range | 0.544 | To 0.2 Å$^{-2}$ | 0.112 |
| Homogeneous monolayer | | | | |
| Si | – | 20.07 | 0.46 | 0.01 |
| $SiO_2$ | 36.46 | 19.6 | 9 | 3.95 |
| Mono | 313.31 | 51.7 | 3 | 12.33 |
| Air | – | 0 | 0 | – |
| $\chi^2$ | Full range | – | To 0.2 Å$^{-2}$ | 0.186 |

*Table 2.* **The parameters are obtained from the results of fitting the experimental X-ray reflectometry curves for [Ti 7Å/NiMo 7Å]$_{20}$ multilayer systems using two models: the multilayer system and the homogeneous approximation. SLD and ISLD are real and imaginary components of X-ray scattering length density, respectively**

| [Ti 7Å/NiMo 7Å]$_{20}$ | | | | |
|---|---|---|---|---|
| Layer | Thickness, Å | SLD × ×$10^{-6}$Å$^{-2}$ | iSLD × ×$10^{-6}$Å$^{-2}$ | Roughness, Å |
| Multilayer | | | | |
| Si | – | 20.07 | 0.46 | 33.81 |
| $SiO_2$ | 7.62 | 22.1 | 5 | 3.39 |
| Ti × 20 | 8.12 | 35.8 | 2 | 1.45 |
| Inter | 1.23 | 38.2 | 3 | 3.43 |
| Ni × 20 | 5.72 | 64.0 | 5 | 4.99 |
| Air | – | 0 | 0 | – |
| $\chi^2$ | Full range | 0.137 | To 0.2 Å$^{-2}$ | 0.149 |
| Homogeneous monolayer | | | | |
| Si | – | 20.07 | 0.46 | 11.11 |
| $SiO_2$ | 39.41 | 27.6 | 0.5 | 0.01 |
| Mono | 307.72 | 48.8 | 0.5 | 10.20 |
| Air | – | 0 | 0 | – |
| $\chi^2$ | Full range | – | To 0.2 Å$^{-2}$ | 0.008 |

window of the neutron reflectometry experiment (e.g., supermirrors [23, 30], GISANS [31, 32]). The deviations of the model curves from experimental ones on Figs. 1 and 3 are indicative of a more significant effect of the interlayer roughness, than it is assumed in the modeling. The simplified model uses one set of the parameters for the intermediate layers and interlayer roughness for all NiMo/Ti bilayers in each periodic structure. It is also supported by the fact that the homogeneous approximation describes better the first fringes of the reflectivity curve (Figs. 2 and 4), than the "exact" model (Figs. 1 and 3). In this connection, the homogeneous approximation is helpful in the treatment of the potential evolution of the reflectivity curves, since there is an average model which effectively describes the experimental data referred to the initial interface. For this, one needs to be sure that the initial interface does not change, and the variation in the reflectivity is caused only by the appearance of a new small layer, which is true in the design of the reflection experiment under consideration. The application of a better resolution for the multilayers requires a more complicated model to describe exactly their fine structure, which is practically insoluble problem because of a large number of multilayers.

The results of the fits are collected in Tables 1 and 2. It is difficult to obtain consistent fits with experimental curves over the whole $q_z$-range covered, since X-ray reflectometry is rather sensitive to the transitional layers because of a high resolution. In this regard, the additional diffusion layer between NiMo- and Ti-sublayers is introduced; the parameters of roughness become comparable with the thicknesses of the sublayers, and the resulting increase in the effective thickness of the whole layer. The systematic difference between X-ray and neutron reflectometry measurements for metal bilayers with the Ti component deposited on the silicon substrate was recently discussed in [17]. It is proved to be a result of the consideration of the intermediate diffusion layers in order to improve the fitting of high-resolution X-ray reflectometry curves. The contrast sensitivity of neutron and X-ray reflectometries to this kind of layers are different, which explains the observed shifts in the parameters of the interface. It is affected also by a potential oxide layer on the silicon substrate. It is difficult to separate two effects in practice. So, one has to talk about an effective model of the initial interface which describes well the reflectivity curve. It is not changed, when the evolution of the interface is due to the electrochemical deposition of a new layer.

## 4. Conclusions

The paper presents a method of increasing the sensitivity of the X-ray or neutron reflectometry technique in the study of near-surface layers of liquid systems. For this purpose, test multilayer homogeneous systems with a small period (∼1 nm), for which a quasi-homogeneous approach is applicable, are investigated. The use of Ni/Ti multilayers of such kind makes it possible to vary, in a wide range, the effective scattering length density of thin films in X-ray or neutron reflectometry experiments, in particular, with electrochemical interfaces containing metal electrodes, by changing the thicknesses of the sublayer. All that allowed the use of the quasi-homogeneous approximation for the analysis of X-ray or neutron reflectometry curves while optimizing the initial interface in order to maximize the reflectometry signal from investigated layers.

In the conducted X-ray reflectometry experiment, on two multilayer systems, the agreement of the data with an error of 5% with the quasi-homogeneous approximation model is observed for the range of scattering vectors up to 0.17 $Å^{-1}$. In the case of neutron reflectometry, the value of the limit of the practically applicable range of the scattering vectors is expected to be less, which is due to the difference between neutron and X-ray reflectometries.

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*Є. Косячкін, Л.А. Булавін, П. Копчанський*

## РОЗВИТОК НЕЙТРОННОЇ РЕФЛЕКТОМЕТРІЇ ПОВЕРХНЕВИХ ШАРІВ РІДИННИХ СИСТЕМ

З метою розвитку методів нейтронної та рентґенівської рефлектометрії для дослідження поверхневих шарів рідинних систем запропоновано метод збільшення чутливості рефлектометричного експерименту до появи та еволюції приповерхневих шарів. У зв'язку з цим, проведено тестування багатошарових гетероструктур Ni/Ti щодо практичного застосування квазиоднорідного підходу зі зміною ефективної густини довжини розсіяння рентґенівського випромінювання тонких (товщиною до 100 нм) металевих плівок в рентґенівських рефлектометричних експериментах на прикладі електрохімічних інтерфейсів. Структури з надзвичайно малою товщиною двошарової системи Ni/Ti та різним співвідношенням товщин підшарів нікелю та титану були синтезовані методом магнетронного напилення. Проаналізовано дзеркальну відбивну здатність рентґенівського випромінювання від поверхні гетероструктур для визначення межі можливості використання квазиоднорідного наближення.

*Ключові слова*: тонкі плівки, багатошарові структури, нейтронна рефлектометрія, рентґенівська рефлектометрія, електрохімічні інтерфейси, оптимізація сигналу.