Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 2, April - June 2017, p. 265 - 272

NEUTRON AND X-RAY REFLECTOMETRY FOR THE INVESTIGATION OF NANO-SCALE HARD MULTILAYERS

X. M. DU[a*], K. F. ZHENG[a], Y. WANG[b], X. X. LI[b], M. P. WANG[a], G. ZHANG[a], E. D. WU[c]

[a]*School of Materials Science and Engineering, Shenyang Ligong University, Shenyang 110159, China;*

[b]*Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900;*

[c]*Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China)*

Neutron and X-ray reflectometry are two non destructive techniques which provide a wealth of information on thickness, structure and interfacial properties in nanometer length scale. Combination of neutron and X-ray reflectometry is well suited for obtaining physical parameters of nanostructured thin films and superlattices. In the present work nanostructured multilayers of CrAlN/TiN with different repeated bilayer thickness were fabricated by reactive magnetron sputtering. Neutron and X-ray reflectometry methods were used to study interfacial structures of multilayers. The real space information, such as scattering length density (SLD), film thickness and interfical roughness, are extracted by fitting neutron and X-ray reflectivity data to a model for the structure of the multilayer samples in reflectometry experiments. The results show that the SLD and individual thickness in the repeated bilayers are closer to the nominal values of multilayers for neutron reflectometry than X-ray reflectometry. The interface roughness however is smaller for X-ray reflectometry than neutron reflectometry. X-ray reflectometry is thus complementary to neutron reflectometry which provide a different contrast between the elements than X-rays.

(Received January 16, 2017; Accepted April 5, 2017)

Keywords: Hard multilayer, neutron and X-ray reflectometry, interfacial structures

1. Introduction

The characterization of the surfaces and interfaces for hard multilayers is important for many application like protective coatings for cutting tools used in machining or for molds used in cold forming and hot forming of metals. The structure and properties of the surfaces and interfaces of the multilayer directly determine its mechanical properties and service life. Many researches indicated that nanolayered ceramic multilayers, also known as superlattices, exhibit exotic mechanical properties [1,2]. For example, a microscopic hardness of greater than 30 GPa has been reported for TiN/VC and AlN/NbN superlattices with a modulation periodicity of 30-85 Å [3,4]. Apart from high hardness, the ceramic multilayers also exhibit high strength, wear resistance and high temperature oxidation resistance [5-7]. These excellent properties are closely related to the characteristics with the nano-scale modulated periodic thickness for multilayers. However, the characterization of the surface and interface structures of nano-scale ceramic multilayers is still presently a big challenge due to the complexity of these thin films.

Neutron and X-ray reflectometry are very sensitive tools for the measurements of interfaces [8, 9]. The most advantageous feature is their high spatial resolution normal to the film

*Corresponding author: du511@163.com

surface which is of the order of some Angstroms and that the information on the vertical structure, such as distribution of density and thickness, can be obtained through the reflectivity of the surface (or interface) [10-12]. It should also be noted that the investigated sample is not damaged during the measurement. This high sensitivity makes reflectometry methods ideal for investigation of width and shape of hard multilayer interfaces. Compared with the X-ray, the neutron reflectometry has a unique potential for application. Neutrons can go deeply into the inner regions of common materials because neutrons physically interact not with electrons but with atomic nuclei. Neutrons can also detect even light atoms such as nitrogen in this work, in contrast to X-ray, making the neutron beam suitable for studies on TiN/CrAlN mutilayers.

For transition metal nitride multilayers, researchers have obtained periodic thickness of multilayers, such as TiAlN/TiB_2 [13,14], TiAlN/TiB [15] and TiAlN/Al_2O_3 [16], by X-ray reflectometry method. Dyadkina et al. [17] investigated the amorphous multilayer nanostructure $[(Co_{45}Fe_{45}Zr_{10})_x(Al_2O_3)_{100-x}/a\text{-}Si:H]_m$ by polarized neutron reflectometry. The critical thickness of the amorphous layer is estimated in the level less than 3 nm. Gibaud et al. [18] measured the structure along to the surface normal for ceramic-metal thin films of Pt/Al_2O_3 by neutron reflectometry, and obtained a certain periodicity which consists of blocks of Pt 28 Å thick separated by an average distance of 53 Å. For most of the ceramic multilayers, the characterization of the interfacial structures is rarely preformed by neutron reflectometry so far.

In this work, CrAlN/TiN multilayers with different repeated bilayer thickness were synthesized by magnetron sputtering. Neutron and X-ray reflectometry were used to investigate the thickness, interfacial roughness and the density along with the depth for multilayers. The effect of the repeated bilayer thickness in multilayers on the density and interfacial roughness is discussed. Moreover, the comparsion of the results obtained from neutron and X-ray reflectometry is also discussed.

2. Experimental details

CrAlN/TiN multilayers with different repeated bilayer thickness and constant modulation ratios (t_{CrAlN}: t_{TiN} =1) were deposited on Si (100) substrate with the size of 50×50 mm and thickness of 3 mm at a fixed substrate bias of -200 V by magnetron sputtering. High purity Ti (99.999%), Al (99.999%) and Cr (99.98%) targets were, respectively connected to RF source sputter guns, which were installed with the horizontal plane. The experimental details of magnetron sputtering have been reported in previous work [19]. The designed structure of the multilayer samples can be represented as: Si(100)/ TiN/CrAlN, as shown in Table 1.

Table 1 The designed samples in experiment

Sample	Bilayer thickness	Total thickness (nm)	
		Neutron	X-ray
CrAlN/TiN	8 nm/8 nm	240	144
CrAlN/TiN	10 nm/10 nm	240	140
CrAlN/TiN	15 nm/15 nm	240	150
CrAlN/TiN	20 nm/20 nm	240	120

Non-polarized neutron reflectivity, *R* (the ratio between the reflected and the incident intensity), was obtained on a time-of-flight polarized neutron reflectometer (TPNR) with horizontal scattering plane over the *Q* range 0.01 $Å^{-1}$<*Q*<0.1 $Å^{-1}$, where $Q = 4\pi \sin\theta / \lambda$ is the momentum transfer and θ is the angle of incidence/ reflection, at the China Mianyang Research Reactor (CMRR). The available wavelengths for TPNR studies at CMRR are λ = 2.5-12.5 Å. The detailed structure and parameters of the TPNR on CMRR can be found in [20]. X-ray reflectivity (XRR) measurements were carried out using a diffractometer (Vltima IV, Rigaku Co. Ltd.) with a

rotating Cu anode X-ray source (λ=1.5406 Å), operating at 40 kV, 40 mA. The incident and reflected beams were collimated with slits of 0.05 mm in width and 2 mrh in height and the reflection intensity was measured by a scintillation counter. The specular X-ray reflectivity, *R*, was measured over the *Q* range 0.02 $Å^{-1}<Q<0.14$ $Å^{-1}$. The specular reflectivity curves were recorded with a ω-2*θ* scan.

We used Parratt 32 fitting software from HZB Berlin for modeling the data [21]. The software is based on Parratt's recursive fitting algorithm [22] which allows to calculate reflectivity data for layered model systems built up from a set of well-defined layers of homogeneous refractive index and interface roughness. By independently fitting the experimental reflectivity data from neutron and X-ray reflectivity measurements through a theoretical model as a series of layers, scattering length density (SLD) profiles were generated as a function of depth in the sample. Detailed structural information for the layers and the interfaces were obtained in terms of three characteristic parameters: thickness of the layers, scattering length density as a function of depth and interface roughness. Errors of the parameters obtained from the fits were found to be within the range of 1.3-8.0%.

3. Results and discussion

XRR pattern recorded as a function of wave vector transfer *Q* for the all samples are shown in Fig. 1. The open circles correspond to the experimental data and the continuous line is the fit results. To obtain the best fit, we suppose that the structures are periodic, and thickness of the layers, scattering length densities, interface roughness are the same for all CrAlN layers in a given multilayer sample. Similar assumptions have been adopted for all TiN layers during fitting. The parameters extracted from the fit to XRR data, such as thickness of the layers, the scattering length densities and interface roughness for all studied samples, were summarized in Table 2.

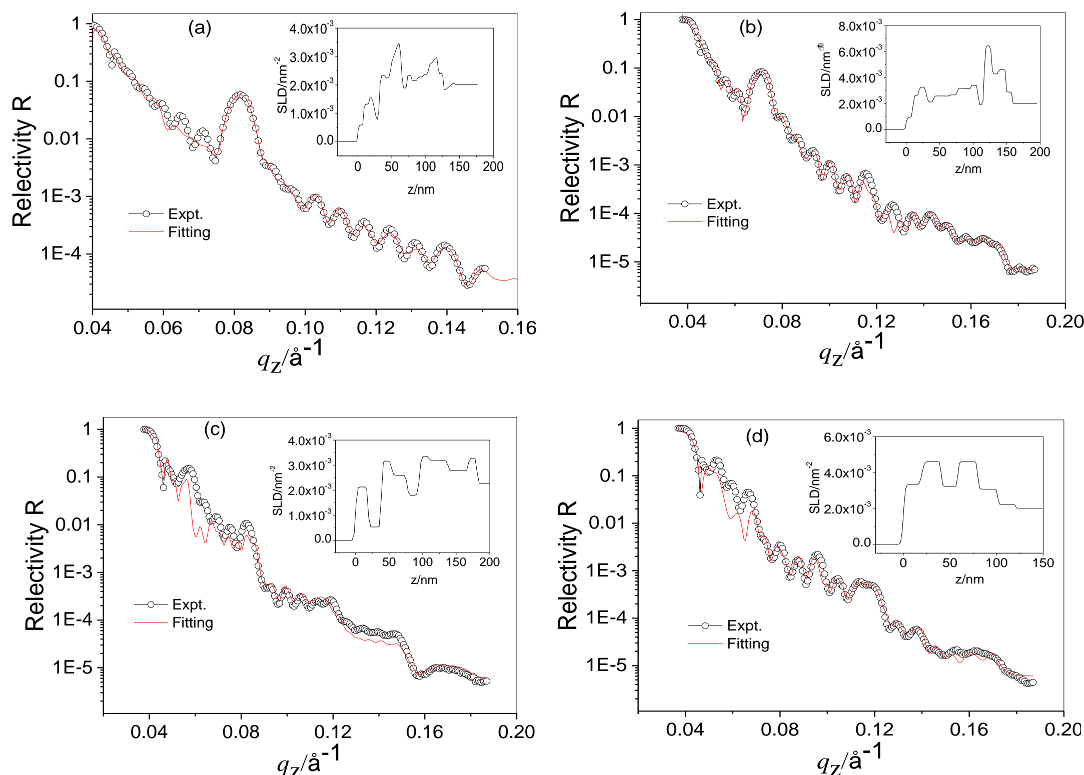

Fig. 1. X-ray reflectivity curves of CrAlN/TiN multilayers, (a) 8 nm/8 nm, (b) 10 nm/ 10nm, (c) 15 nm/15 nm, (d) 20 nm/20 nm

Table 2. Average film thickness, roughness, scattering length density of CrAlN/TiN multilayers as determined by neutron and X-ray reflectometry

	8 nm/8 nm		10 nm/10 nm		15 nm/15 nm		20 nm/20 nm	
	CrAlN	TiN	CrAlN	TiN	CrAlN	TiN	CrAlN	TiN
film thickness (nm)								
X-ray reflectometry	7.70	8.29	9.56	10.4	14.3	15.4	21.6	21.4
neutron reflectometry	7.89	7.73	9.65	9.77	14.6	14.4	18.8	18.9
scattering length density								
X-ray reflectometry (10^3nm^{-2})	-	-	-	-	-	-	4.61	3.22
neutron reflectometry (10^4nm^{-2})	5.18	3.09	5.48	2.83	5.49	3.41	5.66	3.62
roughness (nm)								
X-ray reflectometry	2.51	1.58	1.75	1.15	2.02	1.34	2.04	1.60
neutron reflectometry	3.72	1.82	2.54	2.25	2.28	2.14	2.55	2.32

In generally, the periodic repetition of the bilayer gives rise to so-called "Bragg peaks" in the reflected intensity, similar to the diffraction peaks arising from atomic periodicity in crystal lattices. The oscillations in intensity between two Bragg peaks are due to the interference of electron waves, reflected from the top and bottom the film. These are called "Kiessig oscillations" and are signatures of total thickness of the film. As shown in Fig. 1, X-ray reflectivity curves are characterized by the total reflection plateau with critical edge Q_{cr} and Kiessig oscillations with period dQ =0.004-0.0054 Å^{-1} caused by interference on the layer of CrAlN (or TiN) layer with total thickness $d\approx 2\pi/dQ$=116-157nm for different thickness of the bilayer (Fig. 1 (a)-(d)). It is found that the experimental data is in close agreement with the simulations, displaying the theory and models of multilayer are reasonable in this work.

From Table 1 and Table 2, the average deviation between the nominal thickness and fitted thickness for individual films in repeated bilayer decreases as the thickness of the repeated bilayer in mutilayers decreases. The fitted values of interface roughness for four samples are also listed in Table 2. The error of the fitting of the roughness is under 1.0 Å. It is found that the interface roughness of CrAlN on TiN (or TiN on CrAlN) interface is between 1-3nm. The corresponding electron SLD profiles, from which the composition and density gradient in a layered structure can be extracted, of the four films are displayed in the insets of Fig. 1. These insets provide a real space representation of the film. It is found that electron SLD profiles of CrAlN/TiN multilayers with the smaller thickness of the repeated bilayer, i.e. 8 nm/8 nm and 10 nm/10 nm, show an irregular change trend (Fig.1 (a) and (b)). Whereas the periodic alternation of TiN and CrAlN on electron SLD profile appears under the condition of large thickness of the repeated bilayer, i.e. 20 nm/20 nm multilayers (Fig.1 (d)). It is indicated that X-ray reflectometry is not sensitive to the films with thickness of several nanometers.

Unpolarized neutron reflectometry curves on the CrAlN/TiN multilayer samples with the different repeated bilayer thickness are shown in Fig. 2. Open circles and solid line are the measured neutron reflectivity data and fit to measured data, respectively. Similar to XRR curves, the "Bragg peaks" which occur at positions corresponding to the superlattice periodicity and "Kiessig oscillations" are very clear on neutron reflectometry curves, showing CrAlN/TiN multilayers are superlattice films. The first-order superlattice Bragg peak in Fig. 2 shifted to low Q space with the increase of the repeated bilayer thickness for CrAlN/TiN multilayers. The trend accords with the change rule that the first-order Bragg peak position is inversely proportional to the thickness of repeated bilayer. The analysis of neutron reflectivity requires getting the structure of thin film sample in terms of layer thickness, physical density, interface composition and interface roughness from the experimental data in 'Q' space. Ideally, it is through a Fourier inversion from momentum

space (‘Q’) one can get the structure (magnetic or physical) in real space (‘R’). In reality we can collect data only over a limited momentum ‘Q’ or angular range and direct Fourier transformation is not possible. We also take a ‘model-fitting’ where we start with an assumed structure of the thin film sample and generate a reflectivity pattern corresponding to this structure, as is similar to X-ray reflectometry. The fitted results of four samples are shown in Fig. 2. It is found that the agreement between experimental and calculated reflectivity is good in all cases, and that the oscillation spacing and amplitude of Kiessig oscillations are theoretically reappeared. The parameters extracted from the fit to neutron reflectivity data, such as thickness of the layers, neutron SLD and interface roughness for all studied samples, were summarized in Table 2. The deviation between the nominal thickness and fitted thickness for individual films in repeated bilayer is between 1% and 6% and which is less than that in X-ray reflectometry. Moreover, the fit of the multilayer model to the experimental data is best for 8 nm/8 nm CrAlN/TiN sample, as also shown in Fig.2 (a). These results indicate that the thickness of films measured by neutron reflectometry is more accurate for thinner films. This is not comparable to X-ray reflectometry.

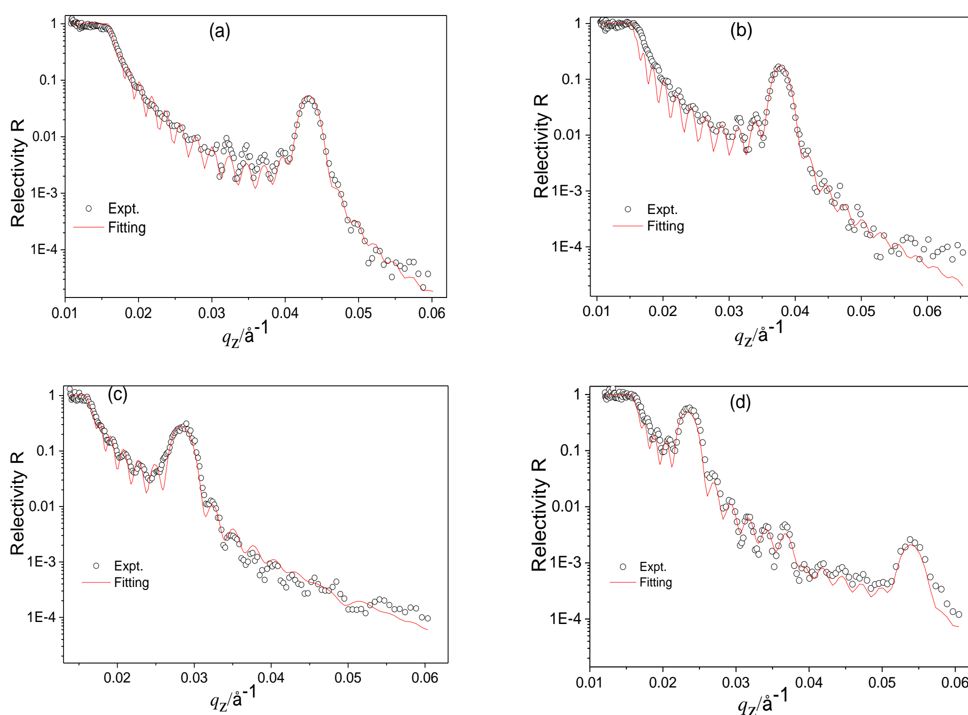

Fig. 2 Neutron reflectivity curves on CrAlN/TiN multilayer (a) 8 nm/8 nm, (b) 10 nm/ 10nm, (c) 15 nm/15 nm, (d) 20 nm/20 nm

The effect of roughness between CrAlN and TiN films on the specularly reflected intensity is considered Névot-Croce factor described in Ref.[23]. The fitted values of interface roughness for four samples are listed in Table 2. The error of the fitting of the roughness is under 1.0 Å. It is found that the interface roughness of CrAlN on TiN interface is larger than that of TiN on CrAlN interface, in the case of every sample. This phenomenon has been explained in our previous works [19, 24]. Moreover, it is also found that the interface roughness obtained from neutron reflectometry is larger than X-ray reflectometry for all samples.

The SLD profiles of the multilayers extracted from the neutron reflectivity data fit are shown in Fig. 3 as a solid line. It is found that the four multilayers have typically periodic structure in the z-direction, which is different from X-ray reflectometry. The fitting values of neutron SLD of the multilayers are listed in Table 2, which are relevant to the bulk densities of multilayers. The values of the neutron SLD corresponding to CrAlN and TiN layers are in the range of

5.18-5.66×10^{-4} nm^{-2} and 2.83-3.62×10^{-4} nm^{-2}, respectively. Moreover, there exists diffuse interface between CrAlN and TiN layers, especially for multilayers with smaller thickness of repeated bilayer. It is explained that CrAlN and TiN are both face-centered cubic crystalline structure, and lattice constants are close to each other. It is possible that two kinds of film show mixed growth mode in the small thickness range. However, the interfaces become more and more sharp as the thickness of repeated bilayer increases.

Neutron SLD can also be theoretically calculated by using following expression for the compound A_xB_y.

$$SLD = \rho N_A \frac{b_A N_x + b_B N_y}{N_x u_x + N_y u_y} \quad (1)$$

where ρ is the bulk density of the film. N_A is the Avogadro constant. b_A and b_B is the coherent nuclear scattering length for the elements A and B, respectively. N_x and N_y is the molar content of the elements A and B in compound A_xB_y, respectively. u_x and u_y is the molar weights of the elements A and B, respectively. In the present work, TiN and CrAlN films is referred to the full atomic composition of TiN and CrAlN, respectively. The available data is as following [25]: b_{Ti}=-3.438 fm, b_{Al}=3.449 fm, b_N=9.36 fm, b_{Cr}=3.635 fm. The bulk density is 5.37 g·cm^{-3} and 5.32 g·cm^{-3} for TiN and CrAlN layers, respectively. The calculated result is 3.088×10^{-4} nm^{-2} and 5.67×10^{-4} nm^{-2} for TiN and CrAlN layers, respectively, as also shown in Fig. 3. It is found that the calculated values of neutron SLD for CrAlN and TiN layers deviate to some exten from the experimental values for all samples. This is because the bulk density of the films is not a single value in the experiment, which is affected by the change of the density of the diffuse interface layer. Even then, the periodic structures of multilayer with small repeated bilayer thickness can be also clearly demonstrated by the neutron SLD depth profile. This indicates that the chemical composition of films measured by neutron reflectometry is more accurate for thinner films.

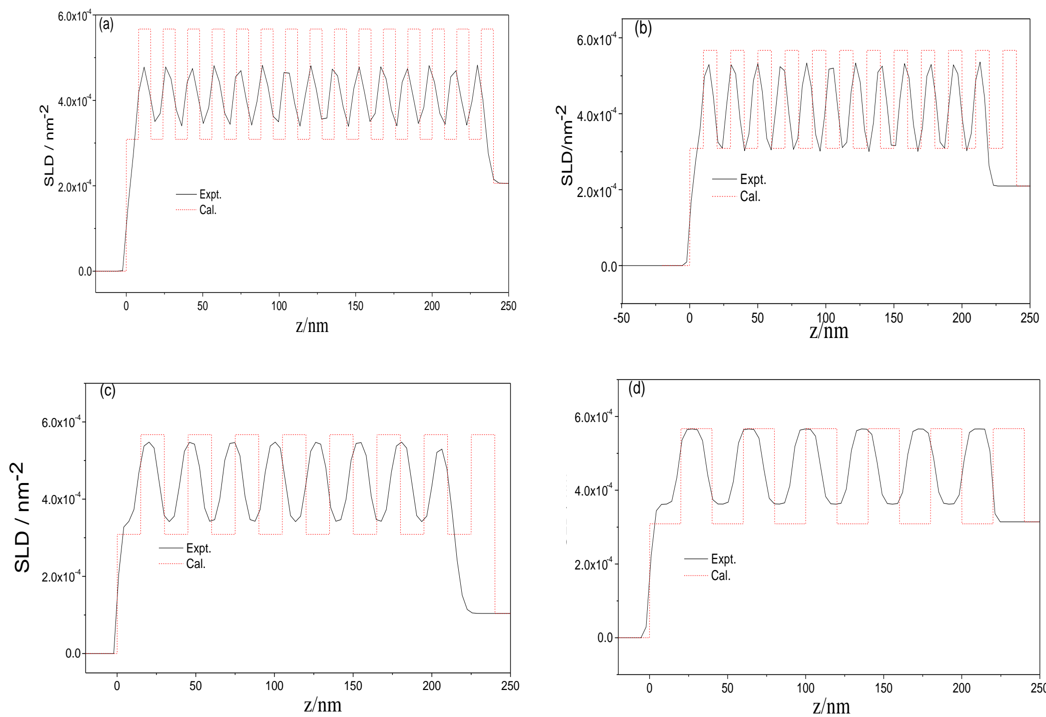

Fig. 3 The neutron SLD depth profile corresponding to the fit shown in Fig 2, (a) 8nm /8nm, (b) 10nm /10nm, (c)15 nm /15nm, (d) 20nm /20nm. The solid line denotes the fitting values and the dashed line denotes the calculated values from Eq.(1).

4. Conclusions

In the present work nanostructured multilayers of CrAlN/TiN with different repeated bilayer thickness were fabricated by reactive magnetron sputtering. Neutron and X-ray reflectometry methods were used to study interfacial structures of multilayers. The interfacial structure parameters such as the thicknesses, the scattering length densities and interface roughness for all studied samples, were obtained by fitting experimental data to a multilayer model. The results show that the agreement between neutron and X-ray experimental reflectivity and calculated reflectivity is excellent in all cases.

The neutron SLD and individual thickness in the repeated bilayers are closer to the nominal values of multilayers for neutron reflectometry than X-ray reflectometry. The interface roughness however is smaller for X-ray reflectometry than neutron reflectometry. The asymmetric interface roughness on CrAlN-TiN-Si interfaces causes the interface roughness of CrAlN on TiN interface is larger than that of TiN on CrAlN interface for X-ray and neutron reflectometry, in the case of every sample. X-ray reflectometry is thus complementary to neutron reflectometry which provide a different contrast between the elements than X-rays.

Acknowledgements

The authors gratefully acknowledge the financial support by NPL, CAEP (Key Laboratory of Neutron Physics, Chinese Academy of Engineering Physics) (2014BB05) and the Research Foundation of Education Bureau of Liaoning Province, China (LG201620).

References

[1] P. C.Yashar, W. D. Sproul, Vacuum **55**, 179 (1999).
[2] S. Barnett, A. Madan, Phys. World **11**, 45 (1998).
[3] J. L. Yue, W. Shi, G. Y. Li, Appl. Mechan. Mater. **184-185**, 1080 (2012).
[4] M. Wen, H. Hao, K. Zhang, Q. N. Meng, X. Li, L. W. Kong, C. Q. Hu, W. T. Zheng, Surf. Coat. Techn. 235, **367** (2013).
[5] Y. M. Zhou, R. Asaki, K. Higashi, W. H. Soe, R. Yamamoto, Surf. Coat. Tech. **130**, 9 (2000).
[6] H. Ljungcrantz, E. Engstrom, L. Hultman, M. Olsson, X. Chu, M. S. Wong, W. D. Sproul, J. Vac. Sci. Technol. A **16**, 3104 (1998).
[7] W. Li, P. Liu, Y. S. Zhao, F. C. Ma, X. K. Liu, X. H. Chen, D. H. He, J. Alloys Compd. **562**, 5 (2013).
[8] M. L. Fernandez, J. S. Higgins, J. Penfold, R. C. Ward, C. Shackleton, D. J. Walsh, Polymer **29**, 1923 (1988).
[9] T. P. Russell, A. Karim, A. Mansour, G. P. Felcher, Macromolecules **21**,1890 (1988).
[10] C. E. Miller, J. Majewski, T. Gog, T. L. Kuhl, Phys. Rev. Lett. **94**, 238104 (2005).
[11] T. Charitat, E. Bellet-Amalric, G. Fragneto, F. Graner, Eur. Phys. J. **8**, 583 (1999).
[12] R. Steitz, T. Gutberlet, T. Hauss, B. Liosgen, R. Krastev, S. Schemmel, Langmuir **19**, 2409 (2003).
[13] Y. D. Sun, J. Y. Yan, S. Zhang, F. Y. Xue, G. Q. Liu, D. J. Li, Vacuum **86**, 949 (2012).
[14] S. P. Liu, Y. B. Kang, H. Wang, Q. Li, L. Dong, X. Y. Deng, D. J. Li, Materials Letters **62**, 3536 (2008).
[15] A. Rizzo, L. Mirenghi, M. Massaro, U. Galietti, L. Capodieci, R. Terzi, L. Tapfer, D. Valerini, Surf. Coat. Technol. **235**, 475 (2013).
[16] C. K. Gao, J. Y. Yan, L. Dong, D. J. Li, Appl. Surf. Sci. **285**, 287 (2013).
[17] E. A. Dyadkina, S. V. Grigoriev, D. Lott, A. V. Sitnikov, Y. E. Kalinin, Physica B **406**, 2397 (2011).

[18] A. Gibaud, C. Sella, M. Maaza, L. Sung, J. A. Dura, S. K. Satija, Thin Solid Films **340**, 153 (1999).
[19] X. M. Du, M. P. Wang, Y. Wang, X. X. Li, Z. Zhang, G. Zhang, C. Q. Huang, E. D. Wu, Surf. Interface Anal. **48**, 1012 (2016).
[20] X. X. Li, C. Q. Huang, Y. Wang, B. Chen, G. A. Sun, Y. G. Liu, J. Gong, W. Kang, H. G. Liu, Eur. Phys. J. Plus **131**, 407 (2016).
[21] C. Braun, Parratt32 Software (ver.1.6), HMI, Berlin, 2002.
[22] L. G. Parratt, Phys. Rev. **95**, 359 (1954).
[23] L. Nevot, P. Croce, Revue de Physiquée **15**, 761 (1980).
[24] X. M. Du, M. P. Wang, Y. Wang, X. X. Li, Z. Zhang, C. Q. Huang, MRS Communications **6,** 408 (2016).
[25] http://www.ncnr.nist.gov/resources/n-lengths/.