

Software Package Application for Self-consistent Processing of X-ray Measurement Data for Studying Structural Properties and Parameters of Objects

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Abstract: *The article presents the results of TiN diffusion-barrier layers studies on a silicon substrate, carried out with the use of the copyrighted software package. In this paper, it is proposed to use several methods for studying the structures and combine them in the form of an integrated approach, which allows not only to increase the calculation accuracy but also to solve most of the arisen problems. Based on this approach, an automated software package for X-ray spectral and X-ray structural analysis was developed to study the elemental and phase composition of the objects, including the analysis of ore minerals, which allows not only to obtain a more complete and detailed picture of the studied objects, but also to increase the sensitivity threshold detection of individual elements that are not detected by individual methods of analysis.*

Keywords: *automated system, X-ray research methods, nanoelectronics, X-ray reflectometry, refractometry, diffuse scattering.*

I. INTRODUCTION

In recent times, the structural properties study of various objects (e.g., extremely thin layer of nanoelectronic materials with an unknown density distribution in the layer or ore minerals) presents a difficult problem for traditionally used optical and photoacoustic research methods. In addition, the independent determination of thicknesses and densities of thin layers is required for the development of technological processes. X-ray reflectometry is currently considered as a standard and precision measurement method for studying thin-film structures and applied to the analysis of dimensional parameters, roughness and inhomogeneities of interfaces, and the density of individual layers with an accuracy of 1%. This accuracy is achieved due to the fact that the angles of X-ray reflection are fixed with an accuracy of 0.001° or less. The oscillation period on the reflectogram allows one to calculate the thicknesses of individual layers with an average absolute

error of 0.1 nm. Due to the fact that the refractive index for hard X-ray radiation is close to one, the thickness and density determination from reflectometry data does not depend on each other, in contrast to ellipsometry, which uses the visible radiation range. Another important measurement advantage of X-ray reflectometry is the ability to separate the contribution to the reflectogram from scattering at the rough edges of the external and internal interfaces. Moreover, the X-ray reflectometry is considered to be the basic method for independent study of thicknesses, layer densities in thin-film structures and roughness of interlayer interfaces without using benchmark standards. It investigates the specular reflection coefficient of multilayer thin-film structures of X-rays at normal incidence at grazing angles. Thus, the angular dependence of the reflection coefficient on the angle of incidence is recorded. However, carrying out a full technological cycle for nanoelectronic devices manufacture in practice is associated with difficulties in measuring the parameters of the manufactured structures, especially when switching to design standards or they are less than 90 nm. They include both the insufficient information content of certain standard techniques, the ambiguity of the models used, along with the use of incorrect assumptions on the structure and composition of the objects being created.

II. METHODOLOGY

As shown in the publications [1], [2], problems associated with disturbances in the relief and composition of the structure layers often arise during the process of thin-film samples study, consequently, the X-ray reflectometry method is not able to determine the values of the parameters of this structure with high accuracy. For example, such problems include incorrect determination of layers optical densities or the “density-roughness” ambiguity, where several profile variants of the electron density structure of a thin film can correspond to an unambiguous reflectometric dependence. To resolve the ambiguity, it is worth using additional methods, for example, to conduct a study of X-ray radiation diffuse scattering, which will reveal the most appropriate profile and correct the final parameters of the sample [3]. It is possible to use the X-ray refractometry method, which allows one to immediately calculate and correct the density of each layer, but when working with an

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X-ray source with a focus size of 20 μm , it is only possible to measure refraction in thin layers with a minimum possible thickness of 50-100 nm. For the case of studying diffusion-barrier structures with layer thicknesses of 5-10 nm, direct refraction observation turned out to be practically impossible due to a weak refractive signal, indistinguishable against the background of scattered radiation, therefore, the diffuse scattering method is more suitable for their additional study. The choice and development of an integrated approach system with the organization of control measurements is associated with the fact that the real technology of nanoelectronics faces many difficulties at the stage of new technological processes acquisition. They include unaccounted additional sublayers that could be formed in the fabricated structures or the parameters of the underlying functional layers could change during a multi-stage technological process [4].

Therefore, the developed integrated approach to the organization of multilayer thin-film nanostructures measurements (and implemented in the form of software) is primarily to ensure obtaining unambiguous and reliable research results through the use in a single cycle of mutually complementary research methods based on various physical principles and allowing to resolve arising ambiguities when solving inverse problems of the applied methods. The X-ray reflectometry method used in the measuring system is considered as a standard for the study of multilayer thin-film structures, however, the study of the X-ray reflection specular component alone does not allow separating the contribution to the reflectogram from the density gradient of the layer material, the roughness and inhomogeneities of the interfaces. In this regard, along with the method of relative reflectometry, X-ray refractometry and diffuse scattering of X-ray radiation were included in the complex of methods (Fig. 1).

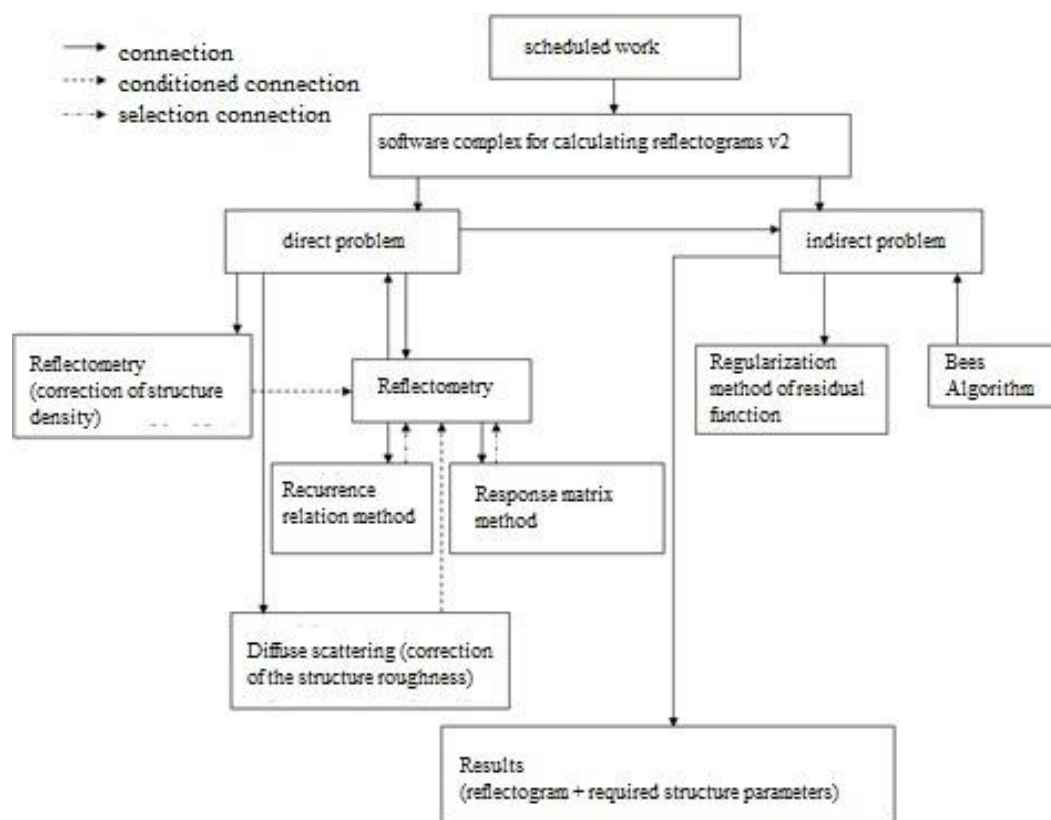


Fig. 1. Flow-diagram of a software package for modeling methods of reflectometry and refractometry.

The essence of the reflectogram experimental curves study and the reconstruction of the sample real structure using the above-described integrated approach may be summarized as follows: the input data are first processed in the refractometry and diffuse scattering units to further correct the densities and roughness of the structure layers, then it enters the reflectometry unit for further theoretical reflectogram construction and layer parameters determination by one of two methods (recurrence relations or characteristic matrix). After that, the reflectogram is processed by the bee algorithm. Using the method the comparison of the theoretical and experimental curves, it calculates the minimum of the residual function and reduces it to the minimum possible value by adjusting the layer parameters and fitting the theoretical curve to the experimental one. For the more

correct calculation of the minimum of the residual function, it is possible to use the regularization block of this function additionally. Based on the above-described approach, an automated complex for processing the results of the X-ray measurements was developed, which as the result makes it possible to analyze a wide range of objects from various fields of engineering and technologies, including the study of ore and mineral samples, using complementary methods of X-ray analysis and absorption spectroscopy within one measuring platform without involving a wide range of measuring equipment.

The system will allow not only to get a more detailed understanding of the qualitative and quantitative elemental composition, phase of the objects under study but also to significantly increase the accuracy of the analysis performed and the processing speed of the results obtained, which will reduce the cost of the research.

In this work, using this software package, we studied the diffusion-barrier of the TiN layers on a silicon substrate. The process of forming the structure consists of chemical vapor deposition (CVD) of the TiN layer. There is no single CVD deposition method for the TiN, but the N₂ / H₂ plasma treatment with thermal decomposition of TDMAT and TDEAT is most suitable. This is described in more detail in the publication [5].

However, during the process of the TiN structures formation, there is often a problem associated with the formation of several layers with the same chemical compound and with different densities that deviate from the standard value. The X-ray reflectometry method is able to calculate the densities of these layers; however, due to the occurrence of the “density-roughness” ambiguity, the analysis of the structure by this method may turn out to be difficult. To resolve this ambiguity, instead of the refractometry method,

the method of diffuse scattering of X-ray radiation is used, since, due to the small thickness of the film, refractometry in this case does not allow one to obtain distinguishable refraction peaks. Thus, after studying the film using the CompleXRay equipment, the data obtained were simultaneously processed using the developed software package.

Fig. 2 shows the reflectometric dependence measured and calculated in the software package (a) for the diffusion-barrier TiN structures, and it also shows the dependence (b) of the ratio of the reflection coefficients of two wavelengths (CuK β / CuK α) on the angle of the beam incidence. At shallow angles, a complex structure of diffraction maxima is observed: in the region of the critical angle, there are two close maxima, and the third one is deformed, which indicates the presence of at least one additionally formed layer in the structure under study and / or the existence of an inhomogeneous optical density distribution inward the sample. At the same time, it can be seen from the graphs that the layer roughness is not very high, however, due to the “density-roughness” ambiguity it is impossible to accurately determine this.

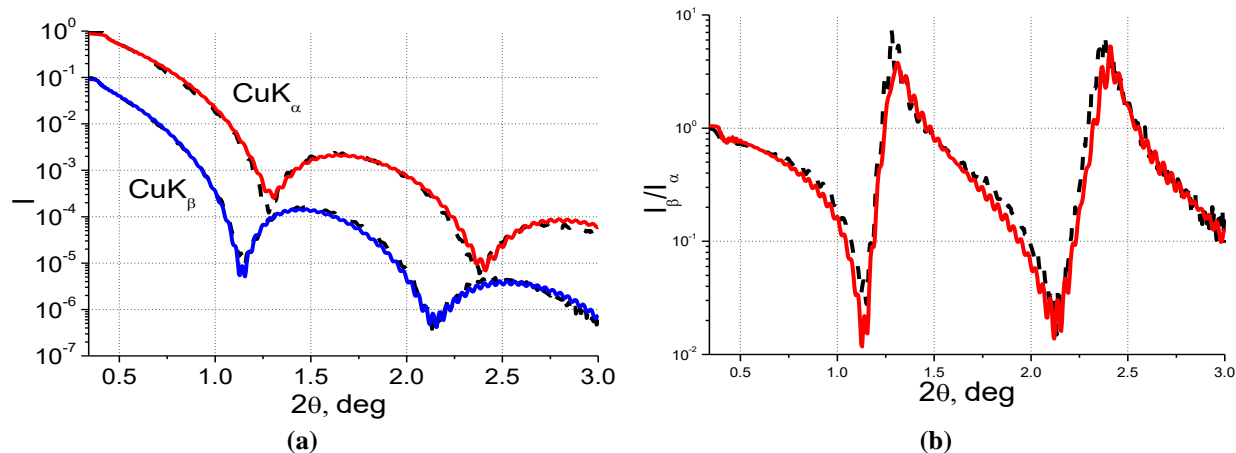


Fig. 2. The X-ray reflectogram at the two wavelengths CuK α and CuK β , constructed using the software package (a), and the reflectogram of the intensity ratio of the wavelengths CuK β / CuK α (b) for the diffusion-barrier TiN structure (5 nm) on silicon. The experimental curves are shown with dashed lines.

To resolve the ambiguity, the diffuse scattering of X-ray radiation was studied. It makes no sense to use the X-ray refractometry in this case, since the film thickness in the sample is not more than 10 nm, and as a result, refraction peaks will not be detected. Fig. 3 shows a scattering diagram of these structures, constructed using the software package. The results showed the minimal effect of layer roughness, which indicates the presence of several sublayers of different densities. The construction of the diagram using an integrated approach was carried out with the simultaneous data processing with the methods of the X-ray reflectometry and the diffuse scattering of X-ray radiation.

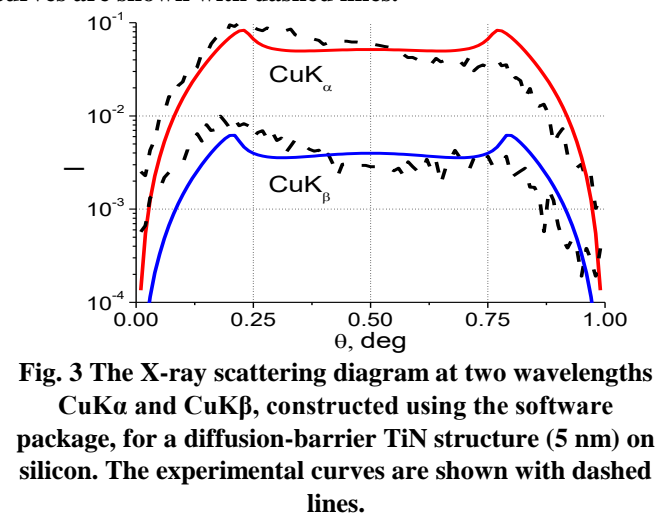


Fig. 3 The X-ray scattering diagram at two wavelengths CuK α and CuK β , constructed using the software package, for a diffusion-barrier TiN structure (5 nm) on silicon. The experimental curves are shown with dashed lines.

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The results of the software package data processing are summarized in tables 1-2:

Table 1. The reflectometry results for TiN (5 nm)

Parameters	z, nm	ρ , g/cm ³	σ , nm
TiNO _x	4,4	3,48	1,6
TiN (crystl.)	3,1	4,8	0,9
TiN (amorph.)	2,1	1,67	0,4
SiO ₂	191,5	2,2	0,3
Si (substrate)	∞	2,33	0,6

Table 2. The diffuse scattering results for TiN (5 nm)

Parameters	ρ , g/cm ³	σ , nm	ξ , nm	H
TiNO _x	3,45	0,6	167	0,5
TiN (crystl.)	4,8	0,9	-	-
TiN (amorph.)	1,67	0,4	-	-
SiO ₂	2,2	0,3	-	-
Si (substrate)	2,33	0,6	-	-

Summarizing the data on the phase composition, density, roughness, and features of the film deposition processes in the studied structure, the sublayers in the TiN film were identified. As shown in the tables 1 and 2 (TiN with the thickness of 5 nm), a thin amorphous layer between TiN and SiO₂ with a density of ≈ 1.67 g/cm³ and the thickness of ≈ 2.2 nm is a loose TDMAT film that is not completely compacted and crystallized by processing in a dense plasma environment. A thin amorphous layer with a density of ≈ 3.45 g/cm³ on the DBL surface was titanium nitride oxidized in the air due to the absence of an upper protective layer and the presence of a residual charge in the near-surface region after plasma treatment. The large thickness of this layer (more than 4 nm) is associated with its long-term oxidation.

III. RESULTS AND DISCUSSION

As the results of the study showed, for the analysis of the thin films basic parameters, a single method is not sufficient to obtain reliable information about the structure of the object and the subsequent adjustment of these parameters in accordance with the requirements of the technological process. This is due to the following: firstly, the accuracy of the procedure and the physical limitations that have arisen in the study of an object do not in all cases allow one or another method to be applied; Secondly, when using a particular method, various problems may arise related to the application of a particular technique, for example, for the X-ray reflectometry it is the presence of density-roughness ambiguities, for the refractometry it involves the problem of detecting nanosized objects on a structure or defects. Often, the above-mentioned problems arise when studying nanoscale structures or the presence of such objects on thin-film samples. Therefore, within the framework of this work, it was proposed to use several methods for studying structures and combine them in the form of an integrated approach, which allows not only to improve the accuracy of the calculations, but also to solve most of the problems that arise in this case.

This approach was implemented in the form of a software package, which was successfully tested and validated within the framework of this work when processing the results of

studying the diffusion-barrier TiN layer. In addition, based on this approach, an automated complex for the X-ray spectral and X-ray structural analysis was developed for studying the elemental and phase composition of objects, including for the analysis of ore minerals, which allows not only obtaining a more complete and detailed picture of the objects under study but also increasing sensitivity threshold detection of individual elements that are not detected by individual analysis methods.

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REFERENCES

1. S.A. Aprelov. *Mnogovolnovaya rentgenovskaya reflektometriya dlya analiza mnogokomponentnykh prostranstvenno uporyadochennykh struktur*. Dis. kand. fiz.-mat. nauk po special'nosti 01.04.10. – M.: MIET, 2007. – 123 p. [eng. translation of the title: Multi-wavelength X-ray Reflectometry for the Analysis of Multicomponent Three-dimensional-ordered Structures].
2. D.I. Smirnov, R.M. Giniyatullin, I. U. Zylkov. *Problemy izmereniya parametrov elementov i struktur sovremennoy mikro- i nanoelektroniki na primere diffuzionno-bar'ernykh struktur TiN/Ti // Pisma v JTF – 2013. – T. 39. – № 14. – pp. 34–42.* [eng. translation of the title: Problems of Measuring Parameters of Elements and Structures of Modern Micro- and Nanoelectronics on the Example of Diffusion-Barrier Structures TiN / Ti].
3. Smirnov D.I., Gerasimenko N.N., Petrakov D.S., Volokhovskiy A.D. *Characterization of surfaces and interfaces of nanoelectronic and nanophotonic thin-film structures by combined two-wavelength diffuse x-ray scattering and x-ray reflectometry // Book of abstracts The 6-th International School For Young Researchers «Smart Nanomaterials» – Rostov-on-Don, Russia. – 2017. – P. 69.*
4. A.D. Volokhovskiy, N.N. Gerasimenko, D.S. Petrakov *Primenenie kombinirovannoy metodiki opticheskoy skatterometrii dlya kontrolya processa travleniya shchelevoj izolyatsii // Izvestiya vuzov. Elektronika – 2017. – T. 22. – № 4. – pp. 331–340.* [eng. translation of the title: Combined Optical Scatterometry Technique Application for Monitoring the Pickling Process of Slotted Insulation].
5. Leng J. M., Chen J., Fanton J., Senko M., Ritz K., and Opsal J. *Characterization of titanium nitride (TiN) films on various substrates using spectrophotometry, beam profile reflectometry, beam profile ellipsometry and spectroscopic beam profile ellipsometry // Thin Solid Films. – 1998. – Vol. 313–314. – P. 308–313.*

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