National Research University Higher School of Economics

as a manuscript

Monakhov Ivan Sergeevich

X-ray reflectometry study of the formation, morphology and growth kinetics of metallic and semiconductor nanoscale films

PhD Dissertation summary

for the purpose of obtaining academic degree

Doctor of Philosophy in Engineering HSE

Academic supervisor:

Doctor of Physical and Mathematical Sciences

Bondarenko Gennady Germanovich

Moscow - 2019

Formulation of the problem

Continuous improvement of research methods for nanomaterials and nanostructures is due to the need to solve pressing problems of materials science of low - dimensional systems and is a global trend. Methods based on the phenomena of reflection and scattering of X-rays incident on a smooth surface at a glancing angle have a unique combination of capabilities and a very high sensitivity to the state of the interfaces. The development of X-ray optics and X-ray detection devices opens up new perspectives in the in situ monitoring of the parameters of nanotechnology products. The development and creation of diagnostic equipment for monitoring technological processes of applying ultrathin films of various materials in real time is an important task and requires the development of metrological support for the applied methods. In particular, test samples are developed and manufactured on an industrial basis for certification of electronic, probe microscopes and X-ray reflectometers.

The deposition of nanoscale films and the creation of multilayer structures is one of the basic processes of many modern technologies. In modern nanoelectronics, films are used whose thickness does not exceed several periods of the crystal lattice and amounts to units of nanometers. These objects differ significantly from bulk materials in structure and physical properties. Despite the growing number of studies in this direction, some issues remain poorly understood. These are, first of all, the initial stages of film formation, which correspond to layer thicknesses of up to 3 nm, at which the boundary effects are manifested to the greatest extent.

Thus, the creation of new and the development of existing in situ methods for controlling the growth processes of nanoscale films, as well as the study of their formation, growth kinetics and morphology, is an urgent task, the solution of which is currently the subject of close attention of domestic and foreign scientists.

The relevance of research

Nanoscale film structures are widely used in many fields of science and technology (nanoelectronics, plasmonics, optics, etc.). The boundary, dimensional, and quantum effects inherent in these physical objects attract the increased interest of researchers and open up promising prospects for the development of a number of technologies.

Thin films of metals are widely used in integrated circuits to create interconnects, transparent contacts for optoelectronic devices, periodic film structures are the basis of multilayer interference x-ray mirrors. Islet gold films capable of selectively transmitting light are used in optics. Germanium films and other semiconductor materials are used in the micro- and optoelectronic devices on the quantum dots. Magnetron sputtering produces nanosized films of amorphous silicon having a porous structure. Selection of optimal conditions for the deposition process allows you to vary their porosity in a fairly wide range and to obtain multilayer structures with alternating layers of different densities used in elements of x-ray optics.

The development of technologies for producing film coatings and multilayer compositions requires continuous improvement of methods for studying their morphology, structure and physical properties, as well as monitoring a number of other important parameters: thickness, growth rate, density and roughness. In this case, often there is a need to obtain information about the processes occurring in the hidden layers of multilayer structures and at the interfaces between them. The development of the in situ X-ray reflectometry method, which allows continuous monitoring of the parameters of growing films during the technological process, opens up special prospects in this direction. At present, experimental data on the growth processes of nanoscale films obtained in situ are not enough. The relevance of the topic of this dissertation is determined by the in situ method of obtaining new data on the processes of formation, morphology, and growth kinetics of nanoscale films.

Degree of problem development

Currently, there is a wide range of well-developed x-ray methods for studying thin films and phase interfaces. Widely used are methods with unique capabilities due to the use of synchrotron X-ray sources. Among them, it should be noted such in situ methods as GISAXS and reflectometry at a constant angle of incidence, based on the concepts of the sequential buildup of atomic layers of a forming film.

The in situ X-ray reflectometry method is, to a certain extent, an X-ray analogue of the known fast electron diffraction method. When studying the dynamic processes of growth, etching and modification of films, it can be considered as an alternative to classical reflectometry .

The in situ method of X-ray reflectometry abroad began to be applied at the end of the twentieth century. Around the same time, a group of researchers was involved in the development of this method in Russia, which included: I.S. Smirnov, E.G. Novoselova, A.M. Baranov. New data on the growth processes of carbon diamond-like films and multilayer structures based on them, intended for use as promising electronic devices as interference mirrors in the X-ray range and heterostructures, formed the basis for a number of articles and patents.

In the field of theoretical research, the work of I.V. Kozhevnikov dedicated to solving the phase problem of x-ray reflectometry. The inverse problem of X-ray reflectometry is to find the electron density profile of a layered system. The ambiguity leading to the existence of many electron density profiles, which the experimental reflection coefficient curve can correspond to, prevents this problem from being solved. The essence of the phase problem is the inevitable loss of information about the phase of the X-ray reflection coefficient when the detectors register the intensity of the reflected radiation, and not its amplitude. This is the reason for the occurrence of ambiguity.

The in situ method of X-ray reflectometry still remains a popular research method for studying the physicochemical processes that occur at the phase boundaries. However, in our opinion, the capabilities of this method have not been fully realized. In particular, a study of the formation of films carried out directly in the process of their deposition (in situ) allows one to obtain information on the kinetics of growth with a parallel measurement of thickness, starting with angstrom units, i.e. from almost two or three atomic layers. This work was the first to conduct in situ studies of this kind. New data on the formation, morphology, and growth kinetics of metallic and semiconductor nanoscale films were obtained using the advanced capabilities of the in situ X-ray reflectometry method modified in this work.

The purpose and objectives of the study

The aim of the study was to develop methods of X-ray reflectometry to determine the physical parameters of nanoscale films and to control the technological process of their preparation, to find technical solutions to implement these methods, to establish the laws of formation, morphology and growth kinetics of metal and semiconductor nanoscale films.

Research Objectives:

- development of an experimental equipment for in situ - studying the behavior of nanoscale films during their growth;
- improvement of the in situ method of X-ray reflectometry ;
- expanding the capabilities of the in situ method of x-ray reflectometry , achieved through the use of a new x-ray optical scheme;
- obtaining films of silicon and germanium, as well as films of Ti, W, Ta, Nb, Au, Cu ;
- a study of the morphology and kinetics of the growth of metal and semiconductor nanoscale films based on an analysis of the time and angular dependences of the X-ray reflection coefficient, density, roughness, thickness and growth rate of films;
- using research results to build new and develop existing models for the growth of nanoscale films.

The object of research is the growth processes of nanoscale films. The subject of this study is the morphology and kinetics of the formation of nanoscale metal (W, Ti , Au , Cu) films, as well as films of semiconductor materials of group IV of the periodic system — silicon and germanium.

Theoretical and practical significance of the work

Based on the experimental results, the growth mechanisms of metal, as well as silicon and germanium nanoscale films are identified. The data obtained expand the existing understanding of the initial stages of the formation of films of these materials.

The practical significance of the work is determined by the effectiveness of the application of the developed methods demonstrated in the dissertation to determine various characteristics of nanosized films: thickness, density, surface roughness, as well as parameters describing the growth kinetics: growth rate and roughness growth rate. The technical solutions found and the methods created are intended for use in scientific research of the problems of physics and material science of nanoscale films, as well as in the development of control systems for technological processes for producing thin films in such industries as optics, micro- o and nanoelectronics, plasmonics, microsystem technology.

Methodological base of the study

The following research methods were used in the dissertation:

- X-ray reflectometry method , including its in situ version modified during the dissertation ;
- X-ray method based on measuring the angular distribution of the intensity of diffuse scattered radiation to obtain data on the surface roughness at the atomic level;
- Methods of atomic force and scanning electron microscopy.

Key points to protect

- The design of a vacuum-technological complex for in situ study of the processes of nanoscale films formation and an improved X-ray optical scheme of the in situ X-ray reflectometry method ;
- The method of identification of the growth mechanisms realized in the process of film formation, based on the analysis of the time dependence of the density and surface roughness of the growing film;
- The results of studies of the kinetics of growth of Ti , Cu , Au , W metal films , as well as Si films obtained by magnetron sputtering on single-crystal silicon substrates;
- Experimental results describing the kinetics of the growth of a Ge film on a silicon substrate, obtained using a position-sensitive X-ray detector;
- The results of a study of formation laws of metal films of Cu, Au, and W on metal substrates.

The scientific novelty of the study

- The X-ray optical scheme of the in situ X-ray reflectometry method has been improved due to the use of a multilayer interference focusing mirror in the primary X-ray beam former, and in the recording system, a linear position-sensitive detector. As a result, the intensity of the primary X-ray beam increased by an order of magnitude, which made it possible to conduct in situ measurements of the angular distribution of the intensity of the reflected and scattered X-ray radiation, increase the sensitivity of the method and expand its field of application.
- An experimental X-ray reflectometry technique is proposed that allows in situ studies of the kinetics of film growth and is distinguished by the joint registration of specularly reflected and diffuse scattered radiation. Using this technique, it is possible to simultaneously and continuously perform an analysis of the morphology of a growing film and control its thickness;
- For the first time, experimental data were obtained on the kinetics of the growth of Cu, Au, W, Ti, Si, Ge films on silicon substrates, as well

as Cu, Au, and W films on Nb and Ta substrates, respectively. It is shown that when copper and gold films are deposited on substrates of refractory metals, the growth proceeds according to the Volmer- Weber mechanism, and tungsten films by the layer-by-layer mechanism.

- When conducting in situ measurements of specularly reflected and diffusely scattered X-ray radiation from a growing germanium film on a silicon substrate, it was found that the film was grown by the Volmer- Weber mechanism, and the thickness corresponding to the percolation threshold of the film was determined.

Personal contribution of the author

In the dissertation, the author owns the improvement of the X-ray optical scheme of the in situ method of X-ray reflectometry; development and creation of a vacuum-technological complex for studying the processes of formation and growth of nanoscale films in real time and controlling their parameters by X-ray reflectometry (patent obtained). The author proposed an original method for determining the temperatures of phase transitions in films and hidden layers of multilayer structures of the nanometer range of thicknesses (a patent for the invention was obtained); took part in the development of a device for determining the dew point temperature (patent obtained).

Using the developed vacuum-technological complex, the author personally carried out studies of the formation, morphology and growth kinetics of metal and semiconductor (Ti , W, Cu , Au , Si, and Ge) nanoscale films on substrates of single-crystal silicon, as well as metal films of Cu , Au , W on substrates of refractory metals - Nb and Ta , experimental results were obtained, laws of growth processes of the studied films were established, a method for identifying the film growth mechanism based on an analysis of the aggregate of time dependences of the density and surface roughness of the growing film; conducted (in co-authorship) analysis of the results obtained, conclusions are formulated on the thesis.

Reliability level and approbation of results

The reliability of the experimental results presented in the thesis is confirmed by their reproducibility, as well as the use of modern experimental equipment, additional independent research methods: scanning electron and scanning probe microscopy. The interpretation of the obtained data is based on modern ideas about the processes of formation and mechanisms of film growth. The developed technical solutions were patented: five patents of the Russian Federation for a utility model and one patent for an invention were issued.

The main results of the work were reported at the International and All-Russian conferences:

1. XXII International Conference "Radiation Physics of Solids", Sevastopol, July 9-14, 2012, report on "The X-ray reflectometry in situ conservation. Opportunities and limitations”;
2. IX International Conference and VIII School of Young Scientists "Silicon 2012", g. St. Petersburg, July 9–13, 2012, report “Application of the in situ X-ray reflectometry method for determining the parameters of nanoscale silicon films”;
3. Conference "X-ray Optics - 2012", Chernogolovka, October 1-4, 2012, the report "Possibilities and limitations of the in situ method of X-ray reflectometry for determining the parameters of growing films";
4. VI of the International Conference "New advanced materials and production technologies - 2014", Volgograd, 16-18 September 2014, reports " Rentgenoreflektometricheskoe porosity nano- dimensional films" and " control parameters of nanoscale films in real time of their formation" ;
5. XXVII International Conference “Radiation Solid State Physics”, Sevastopol, July 10-15, 2017, report “Determination of the percolation threshold in metal-containing nanocomposite films based on polymethylphenylsiloxane”.

General findings of the study

In this dissertation research, X-ray reflectometry methods were developed to determine the physical parameters of nanosized films and to control the technological process of their production, technical solutions were found for implementing these methods, and the regularities of the formation, morphology, and growth kinetics of metal and semiconductor nanoscale films were established .

The following tasks (1-4) were solved:

1. A vacuum-technological complex was created, equipped with an integrated X-ray reflectometric system for in situ study of the growth processes of nanoscale films with the possibility of continuous monitoring of their parameters (roughness, density, thickness and growth rate) at the nanoscale. This complex provides thickness control with an accuracy of at least 1 nm and an angular resolution of 9 arc seconds. Its application allows experiments to modify films, multilayer structures, and also surfaces of solids both in high vacuum and during ion-plasma and gas-phase technological processes under the control of an X-ray reflectometric system;
2. An experimental X-ray reflectance technique is proposed that allows in situ studies of the kinetics of film growth and is distinguished by the joint recording of specularly reflected and diffusely scattered X-ray radiation. Using this technique, it is possible to carry out simultaneous and continuous analysis of the morphology of a growing film, as well as control of its thickness;
3. The in situ method of X-ray reflectometry was improved: a new X-ray optical scheme of an in situ reflectometer with a multilayer Goebel mirror in the incident X-ray beam former was created. As a result, the intensity of the primary X-ray beam increased by an order of magnitude, which made it possible to increase the sensitivity of the method and expand its application field.
4. An original in situ X-ray method for determining the temperature of the phase transition from solid to liquid in films and hidden layers of multilayer structures of the nanometer range of thicknesses has been proposed and developed , which has several advantages compared to existing methods: the ability to determine the

melting temperature of the film, as well as individual layers of multilayer structures, the thickness of which lie in the nanometer range, to estimate the film density changes during melting and the absence of restrictions related to layers structure (amorphous or crystalline).

Listed in pp. 1-4 intellectual property objects are protected by patents of the Russian Federation.

. When conducting research using the developed vacuum-technological complex, the following results were obtained (5-7):

5. Thin films of titanium, copper, gold, tungsten, tantalum, niobium, silicon, and germanium were obtained by magnetron sputtering with continuous in situ thickness control at the nanoscale level. In the process of film deposition, continuous monitoring was carried out to obtain data on the thickness, growth rate, density and root mean square surface roughness of the formed films;
6. claim When analyzing the experimental time and the angular dependence of the intensity of the reflected X-ray, density, roughness and thickness of the film growth rate, in particular, found that the growth kinetics of the investigated films obey a power law with the exponent respectively: Ti-0.55, W-0.35, Cu-0.31, Au-0.43, Ge-0.23.
7. X-ray reflectometry study determines forming laws, the morphology and the kinetics of growth of metallic and semiconducting nanoscale films: the growth of tungsten films is by Frank and van der Merwe layer-mechanism, and films of copper, gold and germanium - on island mechanism Volmer -Veber. The deposition of titanium and silicon on Si (100) substrates leads to the formation of films with a reduced density (by 30% and 10%, respectively), which is due to their developed porous structure. It has been established that the growth of nanoscale films of copper and gold upon deposition onto substrates of refractory metals (niobium and tantalum, respectively) follows the islet Volmer-Weber mechanism. In this case, the discontinuity of copper films was manifested up to a thickness of 14 Å, and of gold films up to 12 Å. Unlike Cu and Au films,

the growth of a tungsten film on a tantalum substrate proceeds by a layer-by-layer mechanism. An analysis of the established laws has led to the conclusion that the kinetics of growth of the studied metal and semiconductor films is satisfactorily described by the scaling model of the development of the surface relief.

The obtained island films of copper, gold, and germanium, in our opinion, have a good prospect of using nanophotonics in devices (satisfactory surface roughness in combination with nanoscale thickness, etc.). Titanium films are promising as buffer layers of plasmonics structures , and tungsten films are promising materials for metallization in integrated circuits (due to the thermal expansion coefficients close to silicon and the low electromigration mobility of atoms compared to aluminum).

Further development of the topic of dissertation may include research:

- the effect of substrate temperature on the kinetics and growth mechanisms of nanoscale films;
- the effect of the substrate material on the growth pattern of films of a given composition;
- the dependence of the kinetics of growth on the deposition rate of the films;
- morphology, kinetics, and mechanisms of film growth obtained using other methods of deposition (vacuum-thermal evaporation, epitaxy, plasma-chemical processes);
- growth features of films of various compositions and structures: solid solutions, chemical compounds, compositions of immiscible components.

The main results of the dissertation are reflected in the following works:

Article published by the author in peer-reviewed scientific journals, included in the international abstract database and citation system Scopus:

1. Smirnov I.S, Novoselova E.G., Monakhov I.S., Egorov A.A. Applying the in situ X-ray reflectometry method to define the nanodimensional silicon film parameters. Russian Microelectronics. 2014, Vol. 43, No. 8, p. 587-589.

Article published by the author in the leading peer-reviewed scientific journals and publications recommended by the HSE:

2. Monakhov I.S. , Bondarenko G.G. Kinetics of the growth of a nanoscale germanium film deposited on the Si (001) surface by magnetron sputtering . Perspektivnye Materialy. 2019, No 2, p. 14-22.

Other publications:

3. Shupegin M.L., Monakhov I.S., Smirnov I.S., Novoselova E.G., Determination of the percolation threshold in metal-containing nanocomposite films based on polymethylphenylsiloxane. Proceedings of the XXVIII International Conference Radiation Solid State Physics. M.: RIAMT, 2017, p. 381-388.
4. Smirnov I.S., Novoselova E.G., Monakhov I.S. Control of the parameters of nanoscale films in real time of their formation. Collection of scientific papers of the VI International Conference "New Advanced Materials and Technologies for Their Production". Volgograd, 2014, p. 270-271.
5. Egorov A.A., Monakhov I.S., Novoselova E.G., Smirnov I.S. Possibilities and limitations of the in situ X-ray reflectometry method for determining the parameters of growing films. Reports of the conference " X-ray Optics- 2012" , Chernogolovka, 2012. p. 112-114.
6. X-ray reflectometry in situ. Features and limitations. Proceedings of the XX II International Conference "Radiation Solid State Physics". M.: RIAMT, 2012, p. 354 - 366 .
7. Novoselova E.G., Smirnov I.S., Egorov A.A., Monakhov I.S. The use of in-situ X-ray reflectometry to determine the parameters of nanoscale silicon films. Proceedings of the IX International Conference and VIII School of Young Scientists and Specialists on Actual Problems of Physics, Materials Science, Technology and Diagnostics of Silicon, Nanoscale Structures and Devices Based on It “SILICON-2012”, St. Petersburg , 2012, p. 304.

8. I. S. Monakhov Investigation of the growth mechanism of nanoscale copper films in the process of magnetron deposition by in-situ X-ray reflectometry. Proceedings of the 1st All-Russian School-Seminar for Students, Graduate Students and Young Scientists "Functional nanomaterials for space technology". M.: MIEM, 2010, p. 188-191.

Intellectual property:

1. Kulomzin E.K., Monakhov I.S., Novoselova E.G., Smirnov I.S., Vasilievsky V.V. A control system for the parameters of film coatings and surfaces in vacuum in the process of their modification. Utility model patent No 54191, 10.06.2006.
2. Monakhov I.S., Novoselova E.G., Smirnov I.S., Egorov A.A. Device for determining the dew point temperature. Utility model patent No 103001, 20.03.2011.
3. Monakhov I.S., Novoselova E.G., Smirnov I.S., Egorov A.A. Device for determining the dew point temperature. Utility model patent No 126138, 20.03.2013.
4. Novoselova E.G. Monakhov I.S., Gurinov D.E., Smirnov I.S. Test sample for the calibration of measuring equipment for the thickness of nanoscale films. Utility model patent No 74213, 20.06.2008.
5. Novoselova E.G., Smirnov I.S., Monakhov I.S. A device for forming thin film coatings. Utility model patent No 92015, 10.03.2010.
6. Monakhov I.S., Novoselova E.G., Smirnov I.S. A method for determining the temperatures of phase transitions in films and hidden layers of multilayer structures of the nanometer range of thicknesses. Patent for invention No 2657330, 13.06.2018.