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Structure changes in nickel on silicon nano-layers under vacuum ultraviolet irradiation

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The structure changes in nickel-on-silicon systems due to vacuum ultraviolet irradiation (VUV) have been studied using the X-ray reflectometry. An ultra-thin (1 to 2 nm) layer (of the density $\rho = 3.2$ to 3.4 g/cm^3 at VUV wavelength $\lambda = 120$ nm and 2.1 to 2.6 g/cm^3 at $\lambda = 180$ nm) has been revealed to be formed at the nickel film surface under irradiation. The nickel films themselves remain unchanged both in thickness and density after a short-time VUV irradiation. It has been supposed that the surface layer formation is a result of the VUV interaction with the silicon substrate, silicon nitride Si_3N_4 being formed at $\lambda = 120$ nm while oxide SiO_x at $\lambda = 180$ nm.

Методом рентгеновской рефлектометрии исследованы изменения структуры никелевых пленок различной толщины на кремниевых подложках при облучении вакуумным ультрафиолетом. Обнаружен тончайший (1–2 нм) слой (с плотностью $\rho = 3{,}2 \div 3{,}4$ г/см^3 при $\lambda = 120$ нм и $\rho = 2{,}1 \div 2{,}6$ г/см^3 при $\lambda = 180$ нм), возникающий на поверхности пленок никеля в результате ВУФ облучения. При этом слой никеля по плотности и толщине заметно не изменялся. Выдвинуто предположение, что образующийся на поверхности слой является результатом взаимодействия ВУФ с кремниевой подложкой, причем в случае ВУФ с $\lambda = 120$ нм образуется нитрид кремния Si_3N_4, а в случае $\lambda = 180$ нм образуется оксид кремния SiO_x.

Investigations on the structure transformation problem under vacuum ultraviolet irradiation demands to apply specific techniques for analysis of ultrathin surface layers commensurable to VUV effective penetration depths. It is just these layers where the changes caused by irradiation should be searched for first of all. In recent years, the methods of grazing X-ray beam are extensively used [1–6]. In particular, X-ray reflectometry method allows to define the mutual arrangement of layers of different densities in multilayer systems as well as to determine precisely the film system parameters, namely, thickness and density [1, 3–6]. The reflectometry results have been verified repeatedly by direct methods in the thickness ranges where the direct methods were applicable.

In our previous works, we used the X-ray reflectometry to study nickel, niobium, and titanium superthin films obtained by radio-frequency (rf) sputtering on silicon substrates [3–6]. The nickel films were shown to be smooth and continuous already at 3 nm thickness, with density close to "bulk" nickel value, while niobium and titanium films being considerably oxidized. Film elemental and phase composition were confirmed by independent methods of mass-spectrometry and grazing beam X-ray analysis [3–5]. Our experimental techniques of taking the curves of X-ray reflectivity angular dependences as well as calculating the reflectivity by Fresnel formulas for consequent fitting the film parameters have been found to be rather sensitive. So, the minimum revealed layer density variation was $\rho \cong 0.1$ g/cm^3 for a metal, and the minimum revealed layer thickness variation did not exceed 0.1 nm for 1 nm thick film. In this work, we apply the X-ray reflectometry to reveal the structure and phase changes in nano-layers of Ni/Si_{sub} system due to VUV irradiation.

The essence of the technique consists in determination of the real film parameters by interference effects occurring due to grazing X-ray beam reflection. The problem comprises two stages. The first stage includes the precision measurement of X-ray reflectivity angular dependences $R(\theta)$. We used the scheme of X-ray reflectometer with silicon monochromator in the incident beam of copper anode radiation [3]. The experimental curves $R(\theta)$ were taken in the angle range $\theta = 0 \div 1.75°$ by the technique described in details in [3–6]. At the second stage, the theoretical $R(\theta)$ curves were fitted using Fresnel functions in the model "n-layer film-substrate" with layer thickness and density as fitting parameters [4–6]. In going from the "single film-substrate" model to more complex cases of two- and three-layer film systems, the number of $R(\theta)$ fitting parameters increases that makes difficult not only the fitting process but as well unequivocal explanation of the results obtained. Thus, we followed the next rules when choosing the model: 1) the model should be extremely close to physical reality (all a priori information obtained using independent methods on the samples is taken into consideration); 2) the model is thought to be an adequate, if it describes the experimental curve with minimum number of variable fitting parameters.

In choosing the object, the following requirements were taken into consideration: 1) structure and composition of initial films should be studied in detail; 2) the objects are not oxidizable in usual conditions; 3) the films have a supersmooth surface (square root micro-roughness $\sigma \sim 1$ nm). As the samples, we used a series of nickel films (obtained by rf-sputtering on silicon substrates in Baltzer system), similar to those studied in our previous works [3, 6], of 80 nm (Ni80), 45 nm (Ni45), 15 nm (Ni15), 7.5 nm (Ni7.5), and 5 nm (Ni5) thickness. The thickness range was defined both by VUV penetration depth for chosen wavelength (~10 nm [7]), and by optimal registration conditions for interference patterns using X-ray beam of $\lambda = 0.154$ nm. As the vacuum ultraviolet sources, two barrier lamps were used, argon one (BAR, $\lambda = 120$ nm), and xenon one (BKS, $\lambda = 180$ nm). The lamps were attached to X-ray apparatus close to the sample surface to minimize radiation absorption in air gap. During the whole experiment, the sample was stationary attached to the goniometer table. The irradiation was done at room temperature. Exposure time was 15 min. The curves of X-ray reflectivity angular dependence were taken immediately before the irradiation and just after exposure for the same area of the sample.

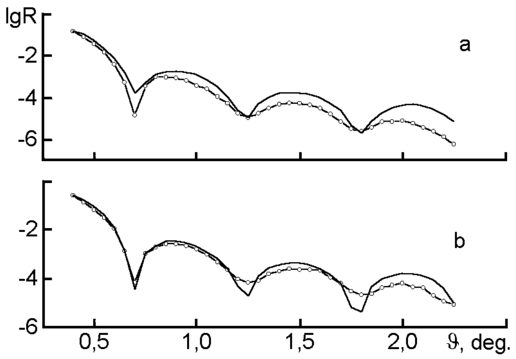

Fig. 1. Choosing an initial state simulating model for the sample Ni7.5: a) unsatisfactory fitting in the model of single-layer film $Ni(7.5\ nm)/Si_{sub}$; b) a satisfactory fitting in the model of two-layer film $NiO(1.2\ nm)/Ni(6.5\ nm)/Si_{sub}$.

First, we have identified the samples in initial state. The calculated $R(\theta)$ curve in the "film-substrate" Ni/Si_{sub} model at nickel bulk density ($\rho_{Ni} = 8.89$ g/cm^3) and initial film thickness was fitted roughly to determine more accurately the thickness and density of the basic film substance. In Fig. 1a, the result of calculated-to-experimental curve fitting for the Ni7.5 sample is shown. The minimum and maximum positions coincide well, i.e. the whole thickness and the average film density correspond to the preset parameters. However, as it is seen in the experimental curve, Fig. 1a, the intensity minimum in front of the first order peak is substantially deeper than that in the calculated curve. This effect was discussed in detail in previous works [4, 5] where thin metal oxide layer was found to be present, moreover, this layer was shown to exist just on the surface of metal film but not on the substrate-metal interface. Therefore, following to "physical considerations", we apply a model of two-layer $NiO/Ni/Si_{sub}$ film,

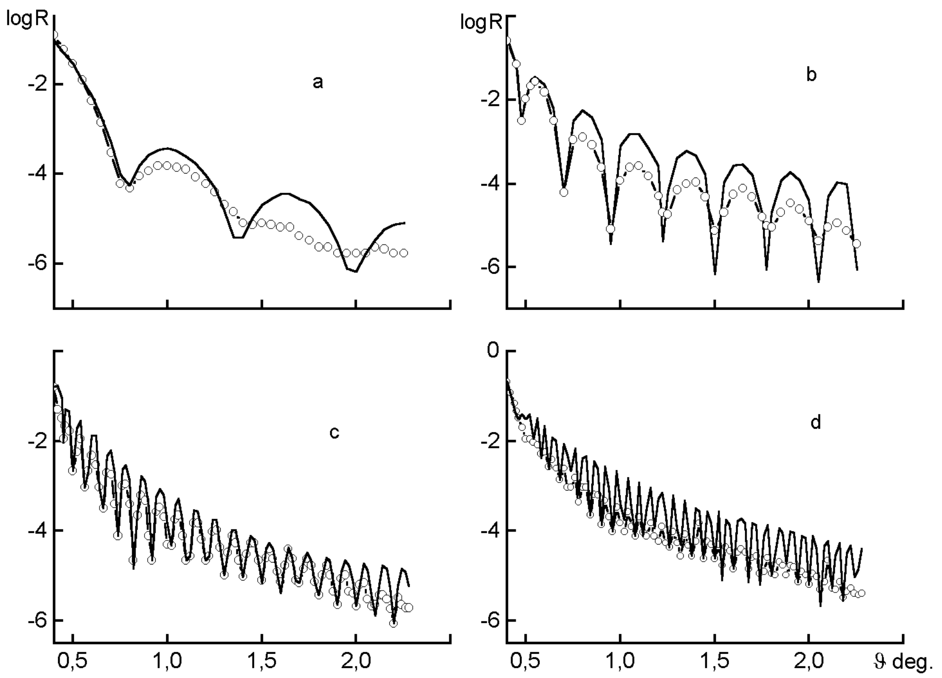

Fig. 2. Experimental X-ray reflectivity curves $R(\theta)$ and calculated fitting curves within the framework of the two-layer film/substrate model for the samples of various thickness in initial state: a) Ni5, model NiO(5.2 nm)/Si_{sub}; b) Ni15, model NiO(1 nm)/Ni(14.3 nm)/Si_{sub}; c) Ni45, model NiO(1.4 nm)/Ni(42 nm)/Si_{sub}; d) Ni80, model NiO(0.8 nm)/Ni(79.5 nm)/Si_{sub}.

involving an oxide layer NiO of 1 nm thickness and the bulk material density (ρ_{NiO} = 7.45 g/cm^3) that has improved the fitting quality (Fig. 1b).

The samples Ni80, Ni45, Ni15, and Ni7.5 in initial state were found to be well described by the same model chosen, moreover, the oxide layer thickness was almost similar for all the samples (Fig. 2 a–d). For the thinnest sample (Ni5), the experimental curve $R(\theta)$ contains only two orders of interferential maxima. The film X-ray optical thickness was 5.2±0.1 nm, while the density may be estimated as an average between ρ_{Ni} and ρ_{NiO} because, due to micro-roughness effect, the difference between fitting curves $R(\theta)$ for Ni and NiO is within error limits at such film thickness. Just the first VUV irradiation dose at wavelength $\lambda = 120$ nm during 15 min results in qualitative change of interference pattern for all the samples independently on film thickness (Fig. 3a–d): there appeared characteristic "beatings" observed for none of the samples in initial state. VUV irradiation at a longer wavelength ($\lambda = 180$ nm) results in similar change of interference curves $R(\theta)$ only for the films of ≤15 nm thickness (Fig. 4).

Under irradiation by 120 nm wavelength VUV during 15 min, all the films independently on the thickness have undergone the same changes which manifested themselves in the same interferential effect. The peak intensities and contrast as well as their number did not decrease after irradiation. If the changes on film surface would be caused by interaction of nickel with oxygen or adsorbents, we should observe decreasing of the peak contrast and their number due to damping of the higher interference orders, first of all, in the thinnest films. Hence, one should not speak about the processes connected with oxidation or degradation of nickel film. Using interference pattern calculations, we have verified several the most probable structure models.

An adsorbed layer of hydroxyls appeared under irradiation. This model does not provide a good coincidence between the experimental and calculated interference patterns: introducing the layer with $\rho \sim 1$ g/cm^3 and thickness 2–3 nm gives insufficient effect.

A layer on film-substrate interface. Introducing the interfacial layer between the substrate and the film also does not allow to fit the observed effect: due to substantial radiation absorption in nickel layer, the less dense layer on the substrate exerts a little influence on interference pattern [4, 5].

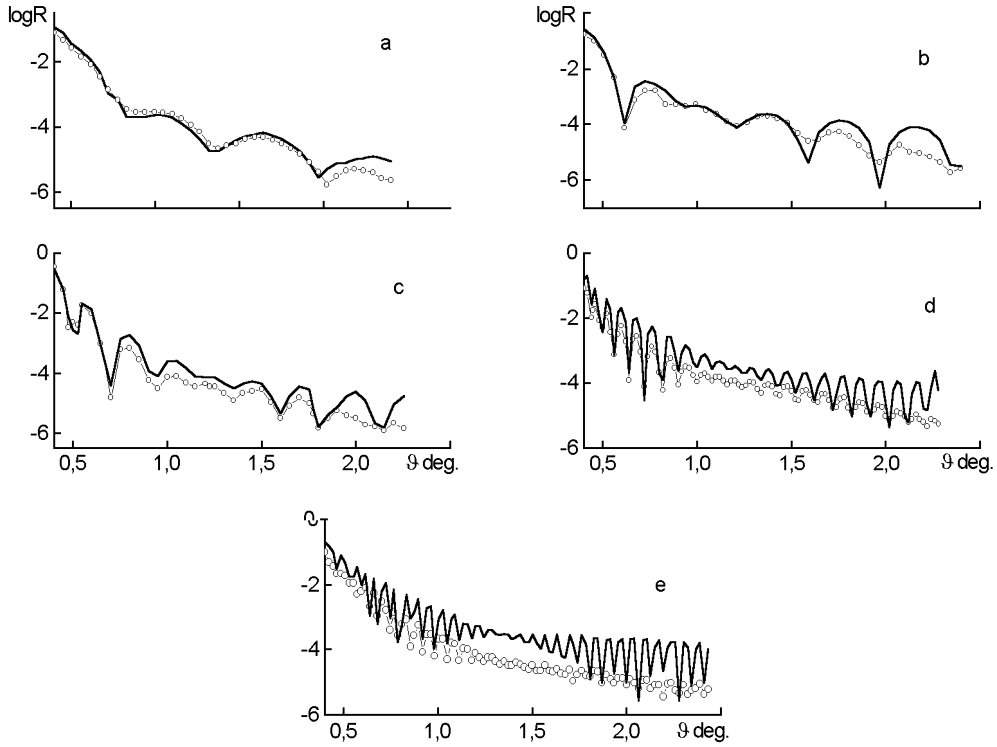

Fig. 3. Experimental X-ray reflectivity curves $R(\theta)$ and calculated fitting curves within the framework of the three-layer film/substrate model for the samples of various thickness after 15 min VUV irradiation at $\lambda = 120$ nm: a) Ni5; model X(1.6 nm) NiO(5.2 nm)/Si_{sub}; b) Ni7.5; model X(1.8 nm) NiO(1.2 nm)/ Ni(6.6 nm)/Si_{sub}; c) Ni15, model X(1.6 nm) NiO(1 nm)/ Ni(14.1 nm)/Si_{sub}; d) Ni45; model X(1.7 nm) NiO(1.2 nm)/ Ni(42.3 nm)/Si_{sub}; e) Ni80, model X(1.8 nm) NiO(0.8 nm)/ Ni(79.5 nm)/Si_{sub}, (X is a new surface layer formed during irradiation).

A dense layer on film surface. The satisfactory fitting appears to be possible for all experimental curves $R(\theta)$ in the model of three-layer plate. The initial thickness values of Ni and NiO layers remain unchanged, the third layer on the film surface is of 3.2 to 3.4 g/cm^3 density and 1.5 to 1.7 nm thickness. The fitting rasults are shown in Fig. 3 (a–e). Within the framework of the last model, we succeeded in fitting the interference patterns obtained after irradiation at the longer wavelength (180 nm). The thickness and density of Ni and NiO in this case were unchanged as well, while the third layer on the film surface was about 2 nm thick and 2.1 to 2.6 g/cm^3 dense, i.e. considerably less than in the previous case (Fig. 4a, b).

Let us consider the possible composition of the surface layer appeared due to the VUV irradiation. As none of thickness and density changes in Ni and NiO layers were observed after irradiation, nor interfaces were changed, so, the occurring some nickel compound on the surface is unlikely. An indirect confirmation of this statement is the similar thickness of the layer in different nickel films. Moreover, if the processes on nickel film surface would be caused by interaction of VUV with nickel, we should

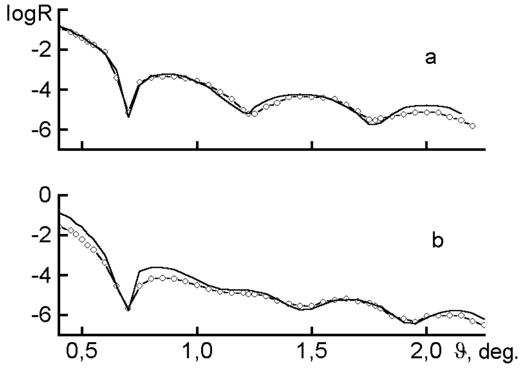

Fig. 4. Experimental X-ray reflectivity curves $R(\theta)$ and calculated fitting curves (a) for the sample Ni7.5 in initial state, model NiO(1.2 nm)/Ni(6.4 nm)/Si_{sub}; (b) in the frame of the three-layer film/substrate model for the sample Ni7.5 after 20 min VUV irradiation with $\lambda = 180$ nm: (Z/NiO/Ni/Si, Z is a new surface layer formed during irradiation).

observe the similar effects both on thin and thick films in the case of the longer VUV wavelength. Really, irradiation with longer wavelength (180 nm) resulted in noticeable effect only in the thinnest samples. The results obtained show that in the case λ = 120 nm, the interaction of VUV with silicon substrate took place in all the samples, while in the case λ = 180 nm, the VUV beam did not reach the substrate in the thickest samples.

It is worth to be noted that wavelength of argon lamp VUV radiation corresponds to nitrogen absorption jump, i.e. under irradiation, contained in air nitrogen molecules absorbing the energy may decompose into atoms and become active reagents. Xenon lamp wavelength corresponds to oxygen absorption jump, i.e. oxygen activity increase is possible under irradiation. Thus, using the chosen VUV wavelengths, the differences in observed effects should be expected. Indeed, we obtained different densities of surface layer formed under VUV irradiation at various wavelengths. The results obtained allow for an assumption about formation of silicon-nitrogen compounds (in the case λ = 120 nm), and silicon-oxygen compounds (in the case λ = 180 nm) on nickel film surface. The density ρ = 3.2 to 3.4 g/cm^3 is close to silicon nitride Si_3N_4, while ρ = 2.1 to 2.6 g/cm^3 corresponds to silicon oxides (SiO_x). The obtained effect is non-trivial and needs further studying.

Thus, using X-ray reflectometry method, an ultra-thin (1 to 2 nm) layer (of 3.2 to 3.4 g/cm^3 density at λ = 120 nm and 2.1 to 2.6 g/cm^3 at λ = 180 nm) has been revealed on the surface of nickel films after short-time VUV irradiation. The nickel films were found to remain unchanged. It has been assumed that this surface layer is a result of VUV irradiation interaction with silicon substrate; silicon nitride Si_3N_4 is formed in the case VUV at λ = 120 nm, and silicon oxide SiO_x at λ = 180 nm.

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Змінення структури наношарів нікелю на кремнії підчас опромінювання вакуумним ультрафіолетом

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Методом рентгенівської рефлектометрії досліджено змінення структури нікелевих плівок різної товщини на кремнійових підкладках підчас опромінювання вакуумним ультрафіолетом. Виявлений надтонкий (1–2 нм) шар (з густиною ρ = 3,2 ÷ 3,4 г/см^3 при λ = 120 нм та ρ = 2,1 ÷ 2,6 г/см^3 при λ = 180 нм), який утворюється на поверхні плівок нікелю в результаті ВУФ опромінення. При цьому шар нікелю за густиною і товщиною помітно не змінювався. Зроблено припущення, що шар, який утворюється на поверхні, є результатом взаємодії ВУФ з кремнійовою підкладкою, причому у випадку ВУФ з λ = 120 нм утворюється нітрид кремнію Si_3N_4, а у випадку λ = 180 нм створюється оксид кремнію SiO_x.