Functional Materials 13, No.3 (2006) © 2006 — Institute for Single Crystals

VUV stimulated solid-phase reactions on the surface of Ni nano-layers on Si substrate

I.F.Mikhailov, S.V.Malykhin, S.S.Borisova, L.P.Fomina

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

Received April 26, 2006

Using X-ray reflectometry method, the kinetics of solid state reactions at the surface of layered thin film nickel/Si_{sub} system (effective nickel thickness 15 and 45 nm) under VUV irradiation of $8 \le h\nu \le 1.8$ eV energy was studied. Nickel and nickel oxide layers have shown no changes both in thickness and density. As a result of VUV stimulated silicon diffusion from the substrate and of its reaction with nitrogen, a new layer of silicon nitride with of (3.2...3.4) $g \cdot cm^{-3}$ density is formed at the nickel film surface. The silicon nitride formation reaction, where nickel acts as a catalyst, is of zero order typical of radiation-(photo)-chemical processes and stops at the layer thickness about 1.5 nm. After aging in air, the surface layer density decreases down to 2.3 $g \cdot cm^{-3}$ and thickness increases to about 25 nm due to oxidation. Repeated cycles of irradiation and oxidation result in degradation of the film-substrate system due to breaking the film adhesion.

Методом рентгеновской рефлектометрии исследована кинетика твердофазных реакций, протекающих на поверхности слоистой тонкопленочной системы никель/Si_{sub} (с эффективной толщиной слоя никеля 15 и 45 нм) под действием ВУФ — излучения с энергией $8 \le h\nu \le 11{,}8$ эВ. Слои никеля и его оксида не изменяются ни по толщине, ни по плотности. В результате ВУФ стимулированной диффузии кремния из подложки и соединения кремния с азотом на поверхности никелевой пленки формируется слой силицида кремния плотностью (3,2...3,4) $г \cdot см^{-3}$. Реакция образования нитрида кремния, в которой никель участвует в качестве катализатора, кинетически имеет нулевой порядок, характерный для радиационно-(фото-)химических процессов, и прекращается при достижении толщины ≈1,5 нм. При выдерживании на воздухе происходит уменьшение плотности поверхностного слоя до 2,3 $г \cdot см^{-3}$ и увеличение толщины слоя до ≈25 нм в результате реакции окисления. Повторные циклы облучения и окисления приводят к деградации системы пленка-подложка из-за нарушения адгезии пленки.

Two possible results of VUV effect on metal surface layers are under discussion: (i) radiation-stimulated chemical reactions with adsorbed atoms [1–5], and (ii) radiation-stimulated structure defect formation according to sub-threshold mechanism followed by acceleration of diffusion and dislocation reactions [6–8]. The phase and structure transformations in nano-sized layers result in variations of their thickness and density. In our previous work, the possibility was proved to determine thickness and density of nickel nano-layers on silicon substrates by reflectivity angle dependence $R(\theta)$ of X-rays with $\lambda = 0.154$ nm wavelength [12]. Using two VUV spectra in different wavelength ranges, we tuned to resonance excitation of either nitrogen ($8 \le h\nu \le 11.8$ eV, Ar lamp) or oxygen atoms ($6.2 \le h\nu \le 8.4$ eV, Xe lamp) [13]. After short-term VUV exposure, a new dense layer of nanometer thickness has been revealed at the nickel film surface; in the first case, we got a silicon nitride layer, while in the second case, a silicon oxide one. No variations both in nickel layer and its surface oxide have been

Table. Variations of the surface third layer parameters during VUV exposure and in air aging

No	Total VUV exposure, min. Air aging, days	Third layer thickness, *t*, nm	Reflectivity index $2\delta\cdot10^5$	Density ρ, $g\cdot cm^{-3}$
Sample Ni15	10	1.45	2.15	3.35
	1 day aging	1.95	1.80	2.70
	20	2.15	1.85	2.80
	2 days aging	2.35	1.77	2.65
	40	2.40	1.80	2.70
	80	2.20	1.79	2.67
	160	2.40	1.76	2.66
	1 day aging	2.55	1.70	2.60
	340	2.25	1.89	2.90
	1 day aging	2.75	1.75	2.63
Sample Ni45	15	1.48	1.97	3.30
	7 days aging	1.90	1.3	2.15
	30	1.76	1.62	2.70
	60	1.70	1.73	2.85
	160	1.78	1.80	2.95
	225	1.95	1.87	3.05
	1 day aging	2.25	1.72	2.75
	435	2.10	1.72	2.75
	780	2.03	1.80	2.90
	1 day aging	2.50	1.65	2.70
	3 days aging	2.50	1.57	2.60
	7 days aging	2.20	1.13	1.80

found. A possibility of photochemical reaction of atmosphere atoms (N, O) with silicon from the substrate was concluded. However, the mechanism of silicon delivery to nickel film surface under VUV irradiation as well as the kinetic of solid state reactions and stability of the system under natural aging remain unclear. The aim of this work was to study the mechanisms and kinetics of photochemical solid state reactions on the surface of the nickel film-silicon substrate system under VUV irradiation and aging.

The investigation objects were nickel films on silicon substrates prepared by magnetron rf-sputtering in SPUTRON-II installation (Baltzers Company) (see [14, 15] for details). The film growth morphology and crystalline structure were described before [16]. These films were shown to be polycrystalline, continuous, and stable under aging in laboratory atmosphere. For this investigation, two kinds of the samples Ni15 и Ni45 (about 15 and 45 nm nickel layer thickness, respectively) were chosen. Such choice allows to estimate the role of diffusion delivery of the components to chemical reaction zone. As the vacuum ultraviolet source, an Ar barrier lamp (BAr) with continuous spectrum $\lambda \geq 120$ nm and quantum flow density about 10^{15} $cm^{-2}s^{-1}$ was used [13]. The samples were exposed to VUV directly on the reflectometer table, the lamp window being pressed against the sample. The first exposure time was 15 min, while each following exposure duration was doubled as compared to the previous one. In order to analyze decomposition processes, several intervals (from 1 to 7 days) for aging in air were done between successive exposures. The total exposure and aging times for each sample are given in Table. Before and after each VUV exposure, X-ray reflectivity angle dependences $R(\theta)$ were measured in the range $\theta = 0...1.75°$ of Cu–K_α grazing incident beam [12]. For simulation $R(\theta)$ curves, the fitting parameters were layer thickness (t), and real part of refraction index (δ) calculated taking into account the anomalous scattering correction [17, 18].

After VUV exposure, typical 'beatings' (showed by arrows to curves *2* in Fig. 1, 2) were observed in the curves of X-ray reflec-

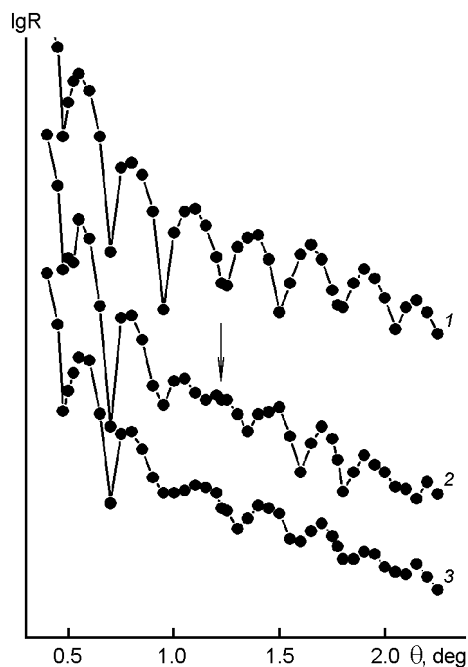


Fig. 1. Experimental curves of X-ray reflectivity angle dependence $R(\theta)$ for the system Ni/Si_{sub} with nickel film thickness 15 nm: *1* — initial state; *2* — after 15 min VUV exposure; *3* — after aging in air for 24 h. (Arrow indicates the beatings).

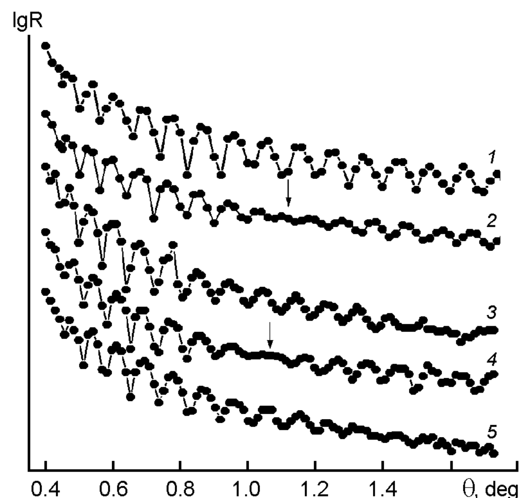


Fig. 2. Experimental curves of X-ray reflectivity angle dependence $R(\theta)$ for the system Ni/Si_{sub} with nickel film thickness 45 nm: *1* — initial state; *2* — after 15 min VUV exposure; *3* — after aging in air for 7 days; *4* — after next VUV irradiation (total exposure 30 min); *5* — after 13 h VUV exposure and following aging in air for 7 days. (Arrow indicates the beatings).

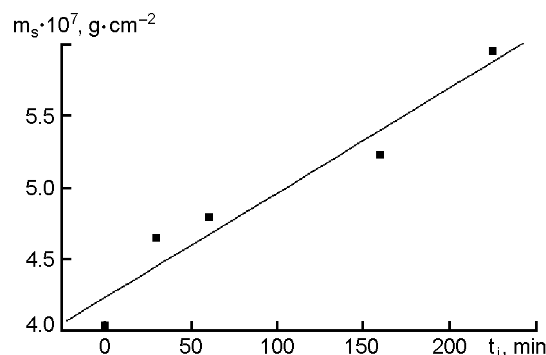


Fig. 3. Increase of the third layer mass-per-area m_S versus total VUV exposure time (in minutes) for the samples of Ni_{45}/Si_{sub} system.

tivity angle dependence $R(\theta)$. According to previous results [12], in both kinds of the samples, the surface layer formed just after the first VUV exposure have similar characteristics: ≈1.5 nm thickness and 3.2 to 3.4 g·cm^{-3} density (Table). In low-angle part of interference pattern, oscillation intensities do not drop, hence, thickness and density of the Ni and NiO_x layers as well as interface roughness remain unchanged.

Linear increase of surface layer mass per unit area m_S vs irradiation time (Fig. 3) is typical of photochemical reactions: the synthesized substance amount is proportional to absorbed dose [19, 20]. Under substance arrival, the third layer mass (but not thickness) increases due to rising density.

The features of interference patterns for both sample types after aging in air was found to be qualitatively similar: the beatings in interferential pattern become less pronounced (compare the curves *2* and *3* in Figs. 1 and 2). The surface layer density drops, while its thickness and mass change non-monotonically; at first, they rise a little, and then decrease (Fig. 4).

Repeated irradiation of the samples after aging results in partial restoration of the third layer initial density (Table). After repeated long-term irradiation and air aging exposures, the film degrades gradually. In the interference patterns, higher order peaks intensities drop (Fig. 1, curve *3*, and Fig. 2, curve *5*) that indicates the growing Ni/Si interface roughness. A net of cracks is observed on the sample surface, and after the longest exposures, the films are partially delaminated.

So, the following main experimental facts are revealed: (1) Under VUV irradiation, nickel-contained layers (Ni, NiO) remain unchanged both in thickness and den-

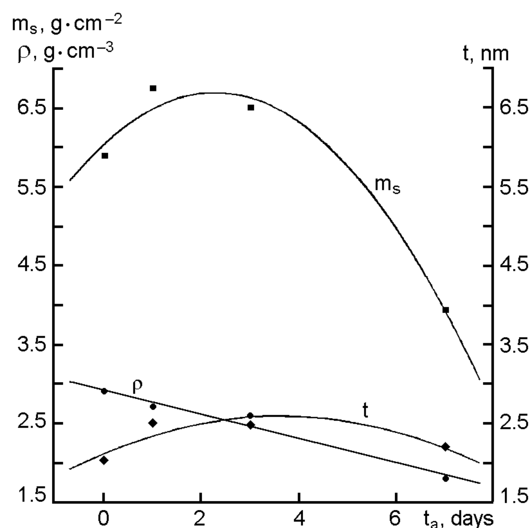
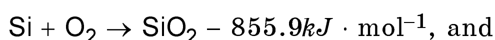


Fig. 4. Variations of mass-per-area m_S, density ρ, and thickness t of the third layer of VUV irradiated samples of Ni_{45}/Si_{sub} system after aging in air vs aging time (in days).

sity. Thes indicates, Ni might be involved in the photo-chemical reactions only as a catalyst. (2) After VUV-exposure with spectrum tuned for resonance absorption by atmosphere nitrogen, a new nano-layer of about 3.2÷3.4 g/cm^3 density grows on the sample surface which may correspond only to silicon nitride Si_xN_y for the system studied. (3) The mass increment of this nano-layer is proportional to absorbed dose that corresponds to zero-order reactions typical of a photo-chemical mechanism independent of reagent (silicon) arrival into reaction zone. (4) In the systems with different nickel film thickness, the reaction of new layer formation completes at the same its thickness of about 1.5 nm. (5) The aging in air is followed by the new nano-layer density drop down to 2.3 g·cm^{-3} which corresponds to the value for silicon oxide SiO_x, the layer thickness being increased.

We calculated the densities of all possible compounds of Ni, Si, O, C, and N to identify the surface layer. As no changes in Ni containing layers have been revealed, such high density values as ρ≈3.2 to 3.4 g·cm^{-3} might be caused by silicon compounds Si_xN_y or SiC, since the density of SiO_x doesn't exceed 2.65 g·cm^{-3}.

Under usual conditions, it is just the oxidation reaction that prevails of two possible reactions of silicon with oxigen and nitrogen:

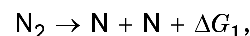


$$Si + O_2 \rightarrow SiO_2 - 855.9 kJ \cdot mol^{-1}, \text{ and}$$

$$3Si + 2N_2 \rightarrow Si_3N_4 - 642 kJ \cdot mol^{-1}.$$

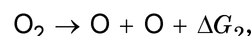
it is just the oxidation reaction that prevails. However, the energetics of these reactions may be substantially changed, if the gas molecular atomization is stimulated by VUV resonance absorption.

Thus, for the reaction



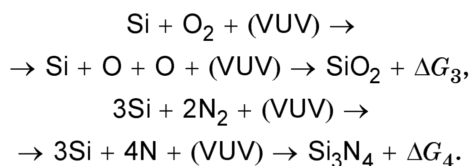
$$N_2 \rightarrow N + N + \Delta G_1,$$

the Gibbs energy expenditure ΔG_1 = 910.23 kJ·mol^{-1} (9.4 eV) is necessary which corresponds to quantum energy in spectral distribution of BAr lamp, while for the reaction



$$O_2 \rightarrow O + O + \Delta G_2,$$

ΔG_2 = 463.1 kJ·mol^{-1} (4.8 eV) is required. The latter value corresponds to the "tail" part of continuous spectrum, so, has a low intensity. For radiation emitted by BAr type lamps, there exists a "transparence window" in oxygen atmosphere, while nitrogen is resonance excited [5]. Due to delivered VUV energy, the reactions overcome the energy barrier and leave the metastability region, thus, become heterogeneous and spontaneous; their kinetics changes as well. Now, these reactions may be described as follows:



$$Si + O_2 + (VUV) \rightarrow$$
$$\rightarrow Si + O + O + (VUV) \rightarrow SiO_2 + \Delta G_3,$$
$$3Si + 2N_2 + (VUV) \rightarrow$$
$$\rightarrow 3Si + 4N + (VUV) \rightarrow Si_3N_4 + \Delta G_4.$$

Now the reactions of oxide and nitride formation have other initial states, and their thermal effects according to Hess law include atomization energies. On leaving the metastable region, nitride formation reaction gives a total Gibbs energy gain ΔG_4 = −2462.5 kJ·mol^{-1}, while oxidation reaction gives only ΔG_3 = −1087.4 kJ·mol^{-1}. This means that the nitride formation reaction has a higher reaction rate constant than for oxidation, hence, it runs first.

High rates of third layer formation in both types of films, its high thickness and density indicate the same nature of the surface layer in all the samples. This layer is formed due to interaction of VUV radiation with silicon substrate and to silicon diffusion to metal surface [12]. The effect of acceleration for reactions between gases and

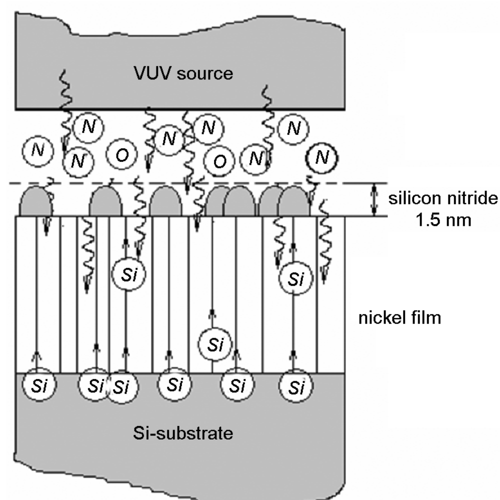


Fig. 5. Mechanism of Si–N layer formation on the surface of Ni/Si_{sub} system under VUV irradiation (schematic model).

thin oxide films formed on metal surface is well known. This was observed for copper, nickel and vanadium oxides interacted with CO and H_2 [19]. Such reactions are heterogeneous and named contact-catalytic, because the metal acts as a catalyst. In our case, the reaction of silicon with nitrogen is catalyzed by surface nickel atoms, the latter being not spent. In Fig. 3, linear character of kinetic dependence shows that the reaction rate is limited not by silicon atoms arrival to the surface, but by the reaction itself between silicon and active adsorbent atoms. The solid state reaction rate is found to be so high that the diffusion coefficient as high as D~10^{-16} $cm^2 \cdot s^{-1}$ would be necessary to provide it, which is characteristic to mechanism of rapid diffusion along grain boundaries. It is known that in nano-structured objects, diffusion is several orders higher than in bulk [21]. In fact, thin magnetron-sputtered metal films possess column substructure of the grains with nano-size in lateral direction and elongated along the normal to surface [22, 23]. Schematic model of silicon nitride layer formation on the surface of Ni/Si_{sub} system as a result of VUV irradiation is shown in Fig. 5.

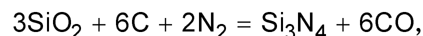
The stopping of the third layer growth at its thickness about 1.5 nm may be caused by two reasons: (i) silicon source exhaustion, or (ii) creation of diffusion-impermeable layer. In the first case, total film delamination from the substrate should be expected, as the only cause for ceasing the silicon arrival from the substrate. Though some delamination was observed after the largest doses of VUV exposure, it occupied less than 30 % of the film area. Thus, more probable is the barrier mechanism of nitride layer growth stopping (Fig. 5). The estimations show that in the stage of island nucleation, the nuclei centers are positioned in nickel grain boundaries, while an average distance between the islands is determined by nickel grain lateral size of about 3.5 nm. Thus, as the layer thickness attains about 1.5 nm, the islands coalesce, and a continuous nitride film forms which hinders further silicon diffusion into reaction zone.

Under aging in air, the density of the third layer drops and the thickness increases. Thermodynamically prevailing becomes the oxidation reaction of silicon nitride

$$Si_3N_4 + 3O_2 \rightarrow Si_xN_yO_z \rightarrow 3SiO_2 + 2N_2.$$

Isomorphic substitution of nitrogen by oxygen was observed before in silicon nitride [24, 25]. In the initial aging stage, nonlinear increase of specific mass m_s and thickness t of the surface layer is observed (Fig. 4) that indicates diffusion character of oxygen delivery to reaction zone [26]. As the aging time increases, the specific mass drops dramatically, while the density becomes even lower than the value for SiO_2 that is characteristic to open porosity development. A similar process with formation of blisters was revealed during oxidation of titanium pre-saturated by nitrogen [27].

The density increases a little after the next VUV exposure. This is explained by reduction reaction:



$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO,$$

which was observed in the presence of a catalyst [24]. The formation of silicon nitride on the nickel film is similar to gas-transport reactions of diamond-like film formation in the presence of metal [28].

Thus, during VUV exposure of nickel-containing nano-layers on silicon substrates, a nano-layer of 3.2 to 3.5 $g \cdot cm^{-3}$ density is formed by products of reaction between silicon and nitrogen according to a photochemical reaction mechanism with zero-order kinetics. Under aging in air, the decomposition processes take place caused by oxidation reaction running according to diffusion mechanism and are followed by the new layer density decreasing down to 2.3 $g \cdot cm^{-3}$.

References

1. Model of Outer Space, v.2, ed. by S.N.Vernov, MGU, Moscow (1973) [in Russian].
2. A.V.Mitrofanov, F.A.Pudonin, M.N.Filippov, *Surf. Invest.*, **14**, 85 (1998).
3. O.Masato, T.Jasuo, K.Kuo, *Appl. Surface Sci.*, **137**, 78 (1999).
4. Chang Sil Yang, Chi Kyu Choi, *Thin Solid Films*, **8**, 506 (2006).
5. Yu.I.Doroveyev, V.E.Skurat, Photochemical Processes under Vacuum Ultraviolet Radiation in: Results of Science and Technique NINITI AN SSSR, v.2: Radiation Chemistry, Photochemistry (1983) [in Russian].
6. Ch.B.Luschik, A.I.Luschik, Disintegration of Electronic Excitations with Formation of Defects in Solids, Nauka, Moscow (1989) [in Russian].
7. M.A.Aelango, Elemental Non-Elastic Radiation Processes, Nauka, Moscow (1988) [in Russian].
8. M.I.Klinger, Nucleation and Transformation of Defects under Electronic Excitation Relaxation in Solids (The Basic Theoretical Concepts) in: Readings in Mmemory A.F.Ioffe, Nauka, Leningrad (1984) [in Russian].
9. A.A.Kozma, S.V.Malykhin, L.P.Tischenko et al., *Fiz. Khim. Obr. Mat.*, **4**, 13 (1991).
10. L.S.Palatnik, S.V.Malykhin, A.A.Kozma et al., *DAN SSSR*, **298**, 102 (1988).
11. O.V.Sobol, A.A.Kozma, S.V.Malykhin et al., *Izv. RAN*, **56**, 182 (1992).
12. I.F.Mikhailov, S.S.Borisova, L.P.Fomina et al., *Functional Materials*, **13**, 85 (2006).
13. G.A.Volkova, N.N.Kirillova, E.N.Pavlovskaya et al., *Zh. Prikl. Spectr.*, **41**, 691 (1984).
14. I.F.Mikhailov, S.S.Borisova, L.P.Fomina et al., *Cryst. Res. Technol.*, **28**, 871 (1993).
15. I.F.Mikhailov, S.S.Borisova, L.P.Fomina et al., *Cryst. Res. Technol.*, **29**, 633 (1994).
16. I.F.Mikhailov, S.S.Borisova, L.P.Fomina et al., *Cryst. Res. Technol.*, **27**, 1061 (1992).
17. L.I.Mirkin, Reference Book on Structure Analysis of Polycrystals, Fiz.-Mat. Lit., Moscow (1961) [in Russian].
18. R.James, Optical Principles of X-Ray Diffraction, IL, Moscow (1950) [in Russian].
19. H.C.Taylor, Physical Chemistry, v.2, ONTI-KhimTeoret, Leningrad (1936) [in Russian].
20. V.A.Kireyev, Course of Physical Chemistry, Khimia, Moscow (1975) [in Russian].
21. H.Gleiter, *Nanostruct. Mater.*, **1**, 1 (1992).
22. D.W.Hoffman, *J. Vac. Sci. Technol.*, **A12**, 953 (1994).
23. V.P.Belevskiy, M.V.Belous, N.V.Gusev, *Poverkhnost:Fiz., Khim., Mekhan.*, No.9, 99 (1983).
24. I.N.Frantsevich, Superhard Materials, Naukova Dumka, Kiev (1980) [in Russian].
25. A.V.Ragulya, O.B.Zgalat-Lozynsky, M.Herrmann, *Silicates Ind.*, **69**, 143 (2004).
26. B.Delmon, Introduction a la Cinetique Heterogene, Editions Technip., Paris (1969).
27. A.S.Bay, D.I.Layner, E.N.Slesareva, M.I.Tsypin, Oxidation of Titanium and Its Alloys, Metallurgiya, Moscow (1970) [in Russian].
28. H.O.Pierson, Handbook of Carbon, Diamond and Fullerenes: Propeties, Processing and Appliccations, New Jersey, USA (1993).

Твердофазні реакції на поверхні наношарів нікелю, стимульовані ВУФ опроміненням

І.Ф.Михайлов, С.В.Малихін, С.С.Борисова, Л.П.Фоміна

Методом рентгенівської рефлектометрії досліджено кінетику твердофазних реакцій, які відбуваються на поверхні системи нікель/Si_{sub} (з ефективною товщиною нікелю 15 та 45 нм) під впливом ВУФ-опромінення з енергією $8 \le h\nu \le 11{,}8$ еВ. Шари нікелю та його оксиду не змінюються ні за товщиною, ні за густиною. У результаті ВУФ стимульованої дифузії кремнію з підкладки та сполучення кремнію з азотом на поверхні нікелевої плівки формується шар силіциду кремнію густиною (3,2...3,4) $г{\cdot}см^{-3}$ та товщиною ≈1,5 нм. Реакція формування нітриду кремнію, в якій нікель бере участь у якості каталізатора, кінетично має нульовий порядок, характерний для радіаційно-(фото-) хімічних процесів, та припиняється при досягненні товщини 1,5 нм. При витримці на повітрі має місце зменьшення густини поверхневого шару до 2,3 $г{\cdot}см^{-3}$ та збільшення товщини до ≈2,5 нм в результаті реакції окислення. Повторні цикли опромінення та окислення ведуть до деградації системи плівка-підкладка із-за порушення адгезії плівки.