

## Original articles

Brief review

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## Solid wetting layer, interphase formation, and thin-film nanomaterials. Brief review

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### Abstract

A review of the results on the formation of the interface between 3d metals and silicon silicides under identical conditions for various parameters of the deposited vapor, crystallographic orientation and substrate temperature is presented. A generalization of the results has been carried out, which consists of the fact that during the process of deposition of hot vapor on a colder substrate, the transition from the surface phase to the bulk phase occurs through a solid wetting layer (SWL). A classification of substrate-stabilized phases, including SWL, is proposed. It has been shown that SWL has an electronic density different from bulk phases, a smooth or nanostructured morphology, optical, electrical, and magnetic properties, and plays an important role in the formation of interfaces between bulk phases, their epitaxial films and multilayer nanostructures. These studies suggest the promise of SWL as a new nanotechnology object for the creation of thin-film nanomaterials.

The studied problem is the formation of interfaces in thin-film nanomaterials. The purpose of the article is to substantiate the discovery of nonequilibrium solid wetting layers, their uniqueness and their role in the formation of the above-mentioned interfaces. This is important research for nanomaterial technologies.

A review and generalization of the results of the study of the metal–silicon interface obtained under identical conditions was carried out. The review shows the detection a new type of transition state of the film under nonequilibrium conditions, a solid wetting layer, and the generalization justifies its role in the formation of the interface. Solid wetting layers are important as a new concept for the development of the theory of thin film growth, as well as a new object of nanotechnology for the production of thin-film nanomaterials.


**Keywords:** Solid wetting layers, Growth, Electronic and atomic structure, Nanomaterials, metal, Silicon

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## 1. Introduction

It is known that the capillary theory of the nucleation and growth of a thin film is based on the relationship between the energy of surface tension and the “tension” energies of the interface and the bulk of the wetting layer as the parent phase. In this case, if the wetting layer is frozen to a sufficiently low temperature, then a solid-phase wetting layer (SWL) is formed, in which mass transfer is absent. In this case, the start of nucleation is provided only by the deposition of atoms on the SWL.

Moreover, since the temperature of the SWL is significantly lower than the temperature of atomic vapor, the deposition of atoms on it is accompanied by a short-term release of thermal energy, its dissipation over the surface and into the bulk, and at a certain thickness, when the stability of the SWL decreases to a critical level, activation of the transition of the SWL to a more non-bulk or bulk equilibrium state, when its electronic structure approaches the electronic structure of the bulk phase of the adsorbate [1, 2].

In this work, TSL is understood as a layer with a thickness ranging from a monolayer (MLs) to several MLs of adsorbate (equivalent by the number of atoms of MLs substrate), in which the density of atoms, their position and the type of their packaging is determined by its adaptation to the substrate under the influence of minimization of the free energy of the adsorbate-substrate system [3]. In this case, SWL is formed by spreading over the surface of the substrate or by diffusion of a layer of adsorbate atoms deposited from hot vapor and its freezing to a solid aggregate state under the influence of a colder substrate.

In the case of an adsorbate–substrate system, foreign in structure and density, such as metal–silicon, the SWL is weakly subject to the orienting influence of the substrate. The availability of the SWL for the emergence of a solid bulk phase (BP) in it when a small amount of heat appears from the outside is limited by a critical thickness  $d^*$ , determined by the interatomic interaction forces (“tension”) in the film, on its surface and at the interface between the film and the substrate. In this case, the  $d^*$  value is determined by the minimum free energy of the system. The near thickness  $d^*$  atoms in the SWL acquire a three-dimensional environment, and the forces of collective interaction of their outer electrons begin

to dominate. These forces destabilize the SWL, and it becomes ready for the transition into BP depending on the amount of heat released during the deposition of the adsorbate on the surface. With a small amount of heat  $d^*$  may be more than 3 MLs. At the same time, when there is conjugation of the adsorbate and substrate lattices, the SWL can be ordered, which further stabilizes the SWL and delays its transition into BP. For example, at the Cr–Si(111) interface, where mixing occurs at moderate deposition or annealing temperatures, an epitaxially oriented and ordered silicide SWL is formed. This occurs due to the fact that in this system the silicides have a small mismatch with the silicon lattice and grow epitaxially on it [4, 5].

In the literature, there is no concept of SWL as a frozen wetting layer formed at the vapor-substrate interface, especially in such a non-isostructural solid-state adsorbate-substrate system as metal-silicon. Only recently information on the SWL of water (ice) on a nanotube, in which freezing occurs at room temperature due to interaction forces with a solid substrate appeared [6]. However, there is a lot of information on pseudomorphic solid layers on a crystal. In particular, we can mention the foreign study of Ge on silicon [7] and the work of domestic authors on Ge on Si(111) and Si(001) [8–10].

The SWL was actually mentioned as an atomic-like [1, 2], surface [11], thin-film [12–14] phase (nanophase) and as a nanophase wetting layer [15–17] for the transitional  $3d$  metal – silicon system (see also [18–24]). At the same time, the concept of SWL as a frozen layer formed from hot vapor introduced here most accurately reflects the nature of this layer and the method of its production.

This article substantiates and carries out a classification of solid phases stabilized by a substrate, including SWL as a phase distinct from submonolayer surface phases. The analysis of the results on SWL in the Cr, Co, Fe, Cu–Si(111), and Si(001) systems is provided. For these systems, the similarity of the obtained SWL according to features of their atomic and electronic structure, morphology and the mechanism of their transition to bulk phases is shown.

## 2. Classification of phases stabilized by a substrate

An important role in the development of the physics of interphases belongs to the concept of

solid surface phases (SP) as “two-dimensional layers in thermodynamic equilibrium with the bulk of the substrate” [11] or phases that have come into thermal equilibrium at the vapor-solid interface with the volume of the substrate heated to a certain temperature. SP usually considered as pseudo-equilibrium surface (with the thickness less than MLs) layers, formed during the deposition of the adsorbate and its diffusion over the surface of the substrate at a temperature below the threshold of desorption and melting of the adsorbate. Moreover, “surface phase transitions involve changes in the arrangement of atoms in the outermost layers of the solid, but not in the atoms inside the bulk of the material” [26]. Taking this into account, SP diagrams are plotted in the coordinates “temperature – thickness or surface concentration” (see, for example, [27, 28]). However, in nature there are other solid phases stabilized by a substrate. They are less stable and form at lower temperatures, but they usually reach a higher thickness. These phases were not considered, since the problem of structural identification of such phases as non-bulk phases had not previously been solved. Usually they were considered as bulk-like phases or some kind of “interface” compounds of small thickness. At the same time, there was essentially no classification of them, which made it difficult to understand the nature of these phases and their identification.

Let us consider the classification of solid phases stabilized by a substrate (films of massive or bulk phases, including metastable bulk phases, are not considered). Let us first turn to the surface phases.

The phases of “something” as separate parts of the entire system, are a thermodynamic concept, and their appearance is determined by the state in which this “something”, together with the entire system, is characterized by minimum of free energy. It is generally accepted that surface phases are two-dimensional layers with a number of atoms per unit area of less than one ML, stabilized by the substrate, i.e., adapted to it in accordance with the minimum free energy.

It is known, that interatomic interaction at the thin film–substrate interface depends on the distance between the atoms on it and the type of their electronic shells. Therefore, if we do not consider the degree of hybridization of their electronic shells (associated with chemical interaction with the substrate), then the phases (non-bulk) stabilized by the substrate can be arranged according to the strength of interatomic interaction (from weak to strong), or according to the degree of their proximity to surfaces, or according to the depth of their immersion into the surface.

From this point of view, we can distinguish (Fig. 1) types of solid phases stabilized by a substrate with a thickness less than MLs or electron screening lengths – surface phases, and phases with a thickness higher than MLs – wetting layers. Among the surface phases the following phases can be distinguished: 1) phases with weak interaction – the surface phase, 2) phases with physical interaction – physisorbed phase, 3) phases with chemical interaction – chemadsorbed phase, 4) phases

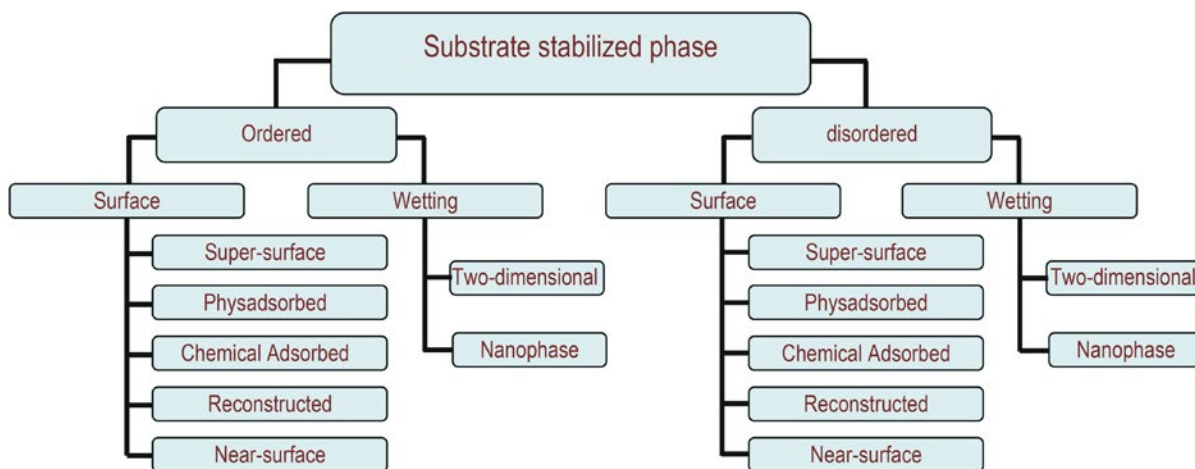


Fig. 1. Classification of phases stabilized by substrate

with rearrangement of the substrate surface – reconstructed phase and 5) phases with its own non-bulk structure – near-surface phase (compound). Moreover, with an increase in the strength of interatomic interaction with the substrate in these surface phases, the temperature of their existence increases.

Phases stabilized by the substrate, related to SWL with a number of atoms equal to or greater than MLs (up to several MLs) can be divided into two classes: 1) SWL in which there is no three-dimensional environment of atoms – two-dimensional (2D-SWL) and 2) SWL in which there is three-dimensional environment of atoms (3D-SWL). The 3D environment appears within a certain two-dimensional ensemble of clusters (domains). We will also call the second type of SWL nanophase SWL (using a similar name for BP, consisting of nanograins).

In addition, the division of all phases stabilized by the substrate into types reflects their degree of order: 1) disordered (or frozen) and 2) ordered (pseudo-equilibrium). The corresponding classification scheme is shown in Fig. 1.

### 3. Analysis and generalization of results

The discovery of metal SWL started in 1984 with the discovery of non-bulk (“atomically-like”) electron density in thin (with the thickness of ~4–6 Å) Cr films deposited almost simultaneously and equally on Si(111) and SiO<sub>x</sub> at room temperature. In this case, the composition and thickness of the films were determined using Auger electron spectroscopy - AES, and their electron density was determined using characteristic electron energy loss spectroscopy – EELS [1, 2]. Later, attention was drawn to the fact that the composition of the films in these studies was close to pure Cr due to the very fast (high deposition rate) spraying of Cr.

The review provided in [2] showed that the transition from the SWL (“atomic-like” phase) of pure metal (Cr and Pd) to bulk metal silicide occurs at approximately the same thickness as the transition of this SWL to the bulk metal on a non-reactive substrate (SiO<sub>x</sub>, – in the case of Cr, and ZnO, – in the case of Pd). This indicated that a possible reason for readiness of SWL to transition into BP silicide is the appearance of a collective valence band in the metal film.

By that time, it was believed that the transition metal «mixed» with the silicon substrate («mixed» in this case indicated diffusion activated by a chemical reaction at the interface) and formed a silicide. The vapor deposition rate and other vapor parameters (temperature, kinetic energy) were not taken into account. Thus, in an earlier study, during annealing of Cr film on Si(111), obtained with a low deposition rate, a transition to the  $\sqrt{3}\times\sqrt{3}$  surface structure and the transition of this structure to epitaxial CrSi<sub>2</sub> was discovered [11]. The composition and atomic density of the  $\sqrt{3}\times\sqrt{3}$  structure were not known at that time, but the incorrect assumption that the nucleation of CrSi<sub>2</sub> occurs from bulk CrSi formed as a result of “mixing” was made.

The recognition of the discovery of SWL required that the detected phase: 1) did not have the properties of a bulk phase (at least according to electron density), 2) had simultaneously identified composition and density, 3) was structurally adapted to the substrate (at least in terms of atomic density), 4) behave as a nonequilibrium phase (frozen layer) and had a composition dependence on the kinetics (deposition rate) and energy (temperature and kinetic energy of vapor) of deposition.

Therefore, in order to obtain evidence of the existence of SWL, studies in the Cr–Si(111) system were continued, but these studies were conducted under stable and identical deposition conditions in one chamber at low rate (an original effusion cell was manufactured for this purpose – see [29]), as well as at different substrate temperatures and vapor parameters.

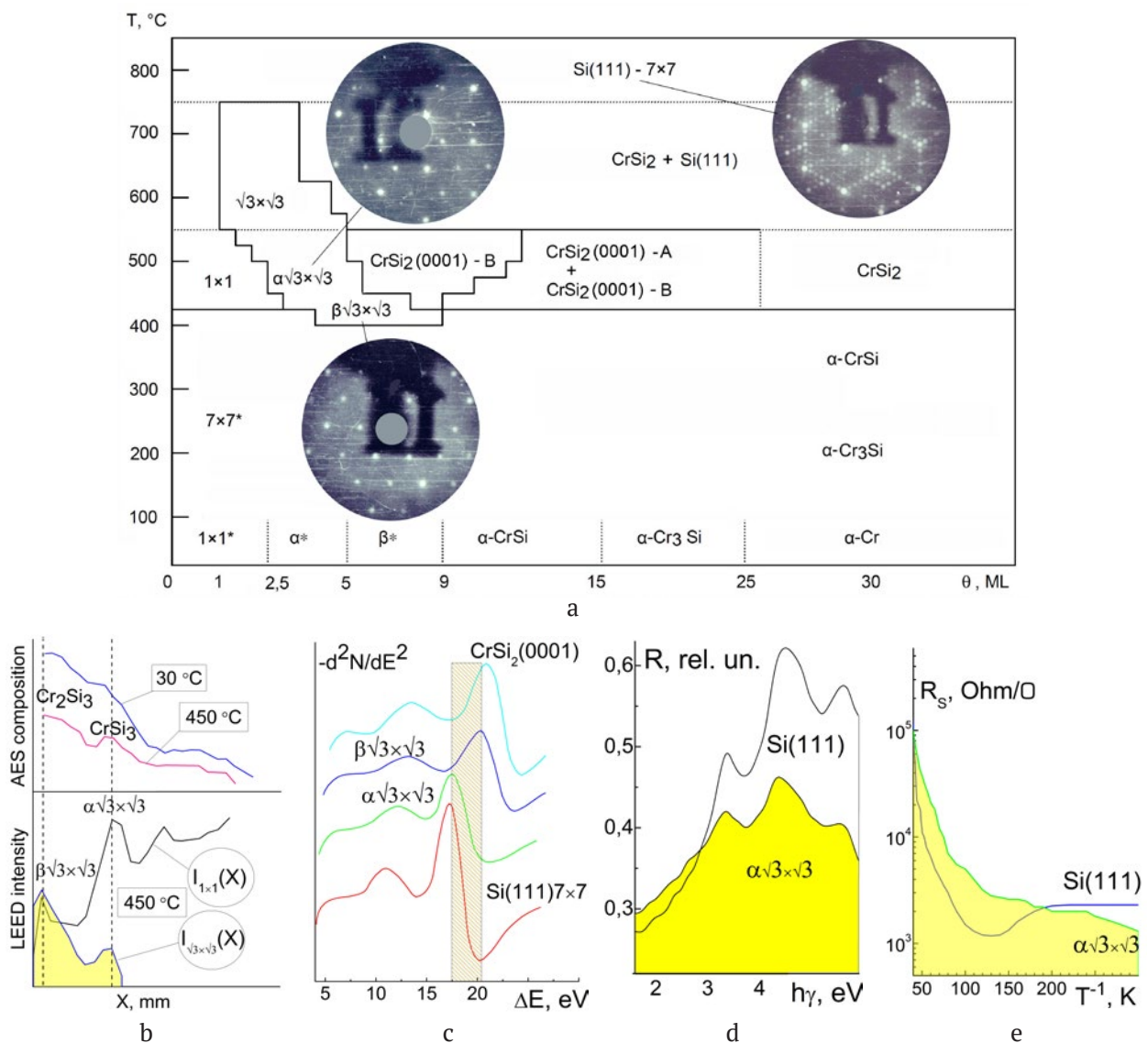
Unfortunately, the choice of a low deposition rate at high vapor temperatures led to silicide formation and then complicated the task of identification of phases as SWL based on electron density. However, Cr layers mixed with Si were discovered both at room temperature (frozen – amorphously like) and during annealing (ordered into various structures), and the influence of these mixed phases on the growth of silicides and their type was discovered [29, 30, 31]. In addition, using the results of [11, 29–31], an ordered 2D phase  $\sqrt{3}\times\sqrt{3}$  was grown, and conductivity and its temperature dependence were measured [32]. The specific conductivity of this phase increased exponentially with temperature and at 300 K it was



more than 4 times higher than that of bulk CrSi. Although this finding was not discussed in [32], in [33] it was noted that this fact cannot be explained within the framework of existing theories of the metal-insulator transition and localization.

Subsequently, systematic studies showed the role of the SWL of the metal and silicide in the formation of Cr and CrSi<sub>2</sub> on Si(111) [34], as well as the role of various types of SWL silicide in the epitaxy of the CrSi<sub>2</sub> seed layer-template of different orientations [29, 35]. In subsequent studies [13, 36], the analysis of the 2D-SWL

1×1-Cr and  $\alpha\sqrt{3}\times\sqrt{3}$ -Cr crystal structure and 3D-SWL  $\beta\sqrt{3}\times\sqrt{3}$ -Cr<sub>x</sub>Si (X = 0.6-1), as well as their thickness using the dependences of EELS on the energy of the primary beam was made. The absence of the Si(111) framework in the 3D-SWL  $\beta\sqrt{3}\times\sqrt{3}$ -Cr<sub>x</sub>Si was proven and its thickness, which reached 9 MLs was determined. It was proven that its electron density is significantly lower than in epitaxial CrSi, to which this phase was unprovenly assigned [37], and even lower than in CrSi<sub>2</sub> (see Fig. 2c). All this showed the non-bulk structure of the studied SWL and their difference from bulk



**Fig. 2.** Data on ordered TCC  $\alpha\sqrt{3}\times\sqrt{3}$  and  $\beta\sqrt{3}\times\sqrt{3}$  in the Cr - Si(111) system: (a) regions of their formation on the phase diagram with LEED pictures; (b) AES Cr concentration (top) and LEED reflex intensity (bottom); (c) loss intensity in EELS; (d) reflection coefficient and (e) layer resistance, respectively, depending on: thickness and temperature (a), coordinates of the film with a monotonically decreasing thickness (b), electron loss energy (c), energy of light quanta (d) and temperature (d)

phases, as well as the fact that the thickness of the 3D-SWL can reach 9 MLs.

The final discovery of the ordered SWL  $\beta\text{-}\sqrt{3}\times\sqrt{3}\text{-Cr}_x\text{Si}$  was comprehensively substantiated in studies [13, 29–31, 35, 36]. An entire paragraph was dedicated to it in the study [13] (pp. 244–248 – “5.2. Thin-film phase  $\beta\text{-}\sqrt{3}\times\sqrt{3}\text{-Cr}$  on Si(111) and its transition to CrSi during layered growth and annealing”). Data from AES, EELS, low energy electron diffraction (LEED), transmission microscopy (TEM) and microdiffraction (TMD) showed that before and during the transition to the bulk phase, at  $d = 9 \text{ \AA}$ , non-monotone-stepped changes of following parameters occur with increasing film thickness: 1) width, intensity, and energy position of AES, EELS peaks, 2) width and intensity of LEED reflections, and 3) morphology on TEM images. This is illustrated by the diagram in Fig. 2a [35].

As can be seen from Fig. 2a–c, SWL differ from each other and from bulk phases by structure (a, b), composition (b), electronic and, accordingly, atomic density (c). In addition, 2D-SWL with the  $\alpha\text{-}\sqrt{3}\times\sqrt{3}$  structure has anomalously high IR reflectance (Fig. 2d) and conductivity at room temperature (Fig. 2e).

Subsequently, the kinetic mechanisms (taking into account the deposition rate) of Si growth on  $\text{CrSi}_2(0001)$  as well as Cr and Co growth on Si(111) were studied experimentally and theoretically [13]. The concepts of SWL developed for metal on silicon were extended to silicon on silicide. Results obtained on 2D-SWL of silicon on single-crystal  $\text{CrSi}_2$  are still unique and open up new possible prospects for nanoelectronics.

Under other growth conditions and in other systems, Cr, Co, and Si SWL new at that time were discovered [13, 14, 34, 37, 38]. In the Co – Si(111) system [38], where Co deposition was carried out at room temperature of the substrate with a high vapor temperature and low deposition rate, mixing of Co with Si(111), depending on the deposition rate, and two types of  $\text{Co}_x\text{Si}$  SWL were discovered: at 1–2 MLs (2D-SWL) and 3 (3D-SWL) MLs. In addition, a transition from 3D-SWL to  $\text{CoSi}_2$  was discovered at a thickness of 4 MLs, and from it, to  $\text{CoSi}$  and from  $\text{CoSi}$  to  $\text{Co}_2\text{Si}$  at thicknesses of: 6–11 MLs and 13–30 MLs respectively. It was found that a high heating temperature of the W-helix of the Co source leads

to agglomeration of the first phase after 3D-SWL ( $\text{CoSi}_2$ ).

In the Cr – Si(111) system at room temperature of the substrate, the growth of Cr was studied at different deposition rates and Cr vapor temperatures [37]. For the first time, the formation of 3D-SWL of pure Cr at a thickness of 3 Å and then the transition to Cr islands with a layer of 3D-SWL of Cr between them was discovered and proven. In this Cr SWL, a very low resistivity was found – 9–18  $\mu\Omega \text{ cm}$  at concentration of a metallic carrier of  $p$ -type –  $(0.9\text{--}1.8)\cdot 10^{22} \text{ cm}^{-3}$  and high mobility for metal – 38  $\text{V/cm}^2\cdot\text{sec}$ . In addition, epitaxial growth of ultra-thin (Cr thickness of 6 Å) and continuous  $\text{CrSi}_2$  films of A-type during pulsed deposition of Cr with simultaneous pulsed heating of the substrate was performed [14].

The resulting  $\text{CrSi}_2$  films of A-type had high conductivity – 180–360  $\mu\text{Ohm}\cdot\text{cm}$  with high carrier concentration and mobility, respectively  $(0.5\text{--}1.0)\cdot 10^{20} \text{ cm}^{-3}$  and 480  $\text{V/cm}^2\cdot\text{sec}$ . This shows that such films, in terms of their parameters, are of interest as a silicide channel of a silicon spin transistor, regardless of whether these parameters relate to the  $\text{CrSi}_2$  film or to the Si substrate layer adjacent to it.

Moreover, by lowering the temperature of Cr and Co vapor and the time of its pulsed deposition, their pseudo layered growth on Si(111) was carried out, and it was found that Cr 3D-SWL with a thickness of 3.3 Å has a conductivity significantly higher than conductivity of bulk Cr [14]. In addition, it was shown that all the films obtained are characterized by conductivity anisotropy, which is most likely associated with equally-directed steps on the surface of the substrates.

As a result, a technology for growing SWL of metal on silicon was developed: with a low vapor temperature, a high deposition rate in one small portion, and a low average deposition rate during repeated deposition in small portions. Subsequently, this technology was protected by a number of patents according to methods for producing thin films, nanomaterials, metamaterials, and dispersed particles - see [39]. Using the developed technology, a pseudo layer-by-layer growth of super smooth Co layers on silicon was obtained up to a thickness of 28 Å [34]. In Co 2D-SWL with a thickness of 1–2 Å, a resistance minimum was discovered, which correlates with a

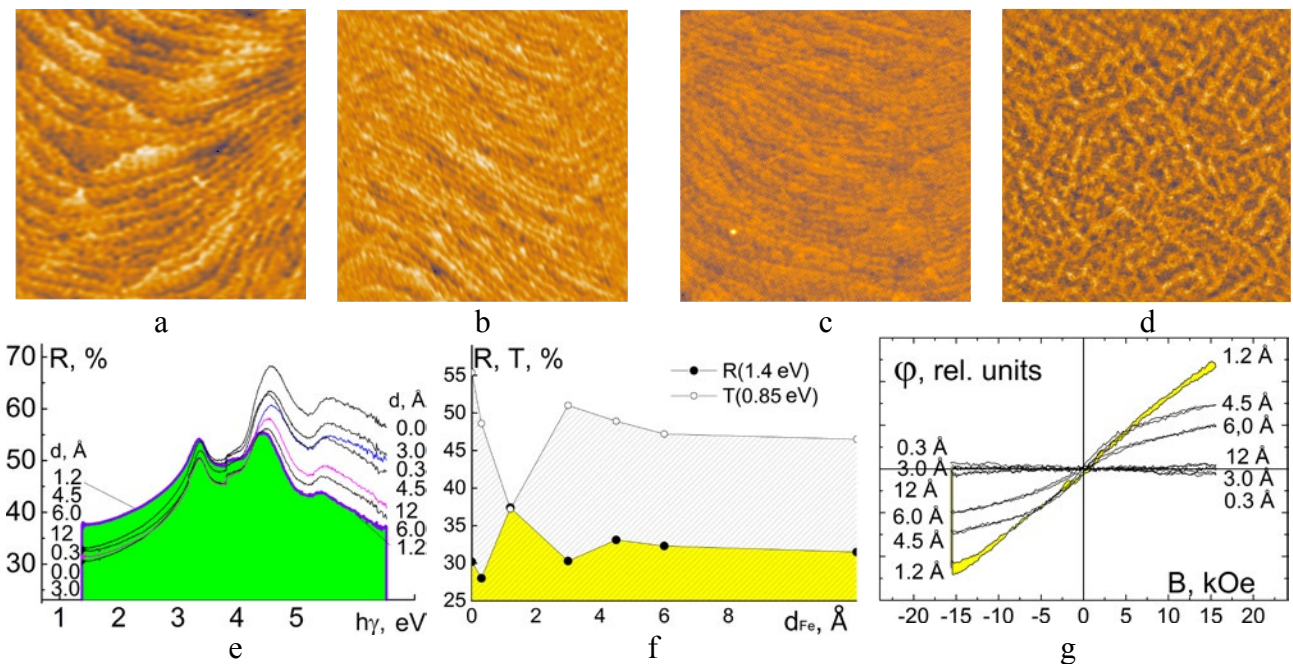
change in the concentration of valence electrons in the Si boundary layer. The reliability of the results of this experiment is beyond doubt, since in it, as in the experiments [14, 37], a joint AES-EELS analysis at the same probing depth comparable to the SWL thickness of 3 MLs was used [13]. Subsequently, similar properties of SWL as non-bulk 2D and 3D phases and their transition to the bulk phase were found in other systems: Fe and Cu – Si(111)/Si(001) [12, 40, 41]. Experimental evidence of the nature of SWL for other metals, under other conditions and on different orientations of the substrate makes the discovery of SWL in 3d metal-silicon system complete.

The morphology (a–d) and properties (e–g) of a smooth (relief height 0.2–0.3 nm) SWL Fe (1.2–6 nm) and fairly smooth (relief height 1.2 nm) Fe nanofilm (thickness 12 nm) is shown in Fig. 3: IR transmittance (e), reflectance spectra (f) and magnetization curves - MOKE (g). Anomalous properties of Fe 2D-SWL were discovered: high IR reflectance (Figs. 3e and 3f), strong quenching (due to absorption and reflection) of UV reflection (Fig. 3e) and a high degree of superparamagnetism (Fig. 3g). Obviously, these properties are mainly due to the nanostructured silicon interfacial layer under the 2D-SWL. They

characterize the structure of the 2D-SWL Fe – Si(001) substrate system.

Overall, the results obtained clarify the role of deposition kinetics and energetics in the formation of SWL. In addition, they allow to develop phenomenological models of both the growth process and the structure of the SWL [23, 24]. Further research will reveal the possible applications of SWL more completely. Dendritic, a currently relevant application is the formation of epitaxial nanofilms of iron and its silicides from SWL Fe. The possibilities of such application are discussed in [17]. It demonstrates the formation of an intermediate  $\text{FeSi}_2$  layer from annealed SWL and subsequent growth of a layered (stratified) film of  $\text{Fe}/\text{Fe}_3\text{Si}/\text{FeSi}_2$  composition. It was noted that the results obtained can be used for the development of epitaxy methods of ultrathin  $\text{FeSi}_2$ ,  $\text{FeSi}$ , and  $\text{Fe}$  films on Si(001).

In accordance with established ideas, freezing of the wetting layer occurs at room temperature of the substrate, which is significantly lower than the melting point of the adsorbate and the temperature (for the metals under consideration 1100 K and higher) of its vapor phase from which it is deposited. In this case, the SWL has a thickness from one to several MLs and stable



**Fig. 3.** Surface morphology on AFM images –  $2 \times 2 \mu\text{m}$  (a – Si(100); b – 2D-TCC Fe 1.5 ML; c – 3D-TCC  $\text{Fe}_3\text{Si}$  7.5 ML; d – Fe 15 ML) and properties of TCC Fe 3–7.5 ML and Fe nanofilms 12 ML after annealing at  $250^\circ\text{C}$  (e – IR transmission, f – reflection spectra and g – magnetization curves according to MOKE)



up to critical thickness  $d^*$ , the value of which is determined by the force of the influence of the substrate on the SWL, as well as the temperatures of its formation and freezing.

At  $d > d^*$  in 3D-SWL there is an LD-3D transition from a low-dimensional (LD) state to a volumetric (3D) state [31]. Moreover, with severe freezing (in the limit at a temperature of  $-0$  K), the LD-3D transition begins when the first atom (or layer of atoms) appears in the 3D-SWL, which has a 3D environment and is shielded by neighboring atoms from influence of both the substrate and vacuum. It is known that  $d^* = 3$  MLs for close-packed atoms is close to 3 Fermi screening radii [31] and is confirmed theoretically and experimentally [10]. However, with weak freezing, the SWL can also have a higher thickness due to the possibility of epitaxial ordering, which increases its interaction with the substrate and stability.

Subsequently, the discovery of SWL in various systems was supported by phenomenological models [23, 24]. According to these models, the methods of mutual adaptation of SWL structure and the substrate can be different. The SWL and the substrate can be adapted to each other not only due to elastic stresses and lattice deformations, but also due to the presence of interstitial atoms, defects and/or vacancies. In addition, with sufficiently strong freezing and proximity to the critical thickness (3D-SWL), this adaptation can be carried out by dividing the SWL into clusters (domains), and the boundary layer of the substrate into antiphase domains, resulting in the formation of SWL with a nanophase (two-dimensional-cluster) structure. It is also possible to adapt the SWL structure to the substrate due to the segregation of substrate atoms on the SWL surface.

The metal in SWL, despite the absolute mismatch of its lattice parameter with the lattice of the semiconductor (which can differ by more than 1.5 times), is well adapted in structure to the substrate both due to its nanophase structure and due to the structural-phase rearrangement of the boundary layer of the substrate [24, 25]. In contrast, the known pseudomorphic adsorbate layer on a substrate, which has a small (<5%) mismatch of crystal lattice parameters with the substrate, is adapted to the substrate only due to elastic deformations and mismatch

dislocations. At the same time, it does not rebuild the substrate and retains its properties. Therefore, the nanophase 3D-SWL of a metal on a semiconductor with structural rearrangement of the boundary layer of the substrate is an exclusively new object in the physics of thin films.

At the same time, the adaptation of 3D-SWL to the substrate weakens with increasing its thickness, and after a critical thickness an LD-3D transition occurs, during which certain metastable and stable 3D phases are formed in it in the form of film grains or its islands consisting of 3D phases.

Thus, SWL plays an important role in the processes of growth of thin films from gas, vapor, or liquid phases. Its presence or absence, its tense state, as well as the release of latent energy in it changes the film growth mechanism according to one out of three options: 1) layer-by-layer (Frank Van Der Merwe growth), 2) layer-island (Stranski-Krastanov growth) and 3) island (Vollmer-Weber growth). In the case of Stranski-Krastanov growth, the released energy from the SWL can determine the size, density, composition and structure of the islands. In this case, at the interface between the film and the substrate, reactive-activated diffusion (activated by the release of latent energy) is possible, followed by the freezing of the diffusion layer (the so-called “mixing”).

SWL is characterized by a significant amount of latent stress energy. The use of this energy during the LD-3D transition to a film of subnanoscale or nanoscale thickness allows to control the structure of this film, its morphology, topography, and physical properties [42]. Due to this, continuous and relatively smooth films of metals and silicides of extremely small thickness with record conductive and other properties can be obtained on a semiconductor or dielectric substrate.

Thus, SWL Fe, as well as nanofilms of Fe, Cu, and Co silicide with a thickness (respectively 1.2 MLs, 12 MLs; 14 MLs and 28 MLs.) and average relief height (respectively 0.2, 0.5, 0.9 and 0.7 nm) were obtained [42, 23]. In the Fe film on Si(001), Fe 2D and 3D-SWL with different properties at different thicknesses were discovered [12, 40]: at 2 MLs – with a smooth 2D structure and at 3 MLs – with a nanophase structure. The unique



properties of the listed films were revealed. Thus, Fe 2D-SWL on Si(001) with a thickness of 2 MLs had anomalously high IR reflection and UV light scattering, associated with the restructuring of the boundary layer of the silicon substrate, as well as a high degree of superparamagnetism with almost zero coercivity [42]. The same 2D-SWL turned out to be stable to oxidation at room temperature in air and stable up to a temperature of 500 °C in vacuum.

Atomic-force microscope imaging studies have shown that Fe 2D-SWL follows the relief of the substrate surface steps [12]. The presence of these steps, which appear in the image as a set of parallel curved stripes, indicates the adaptation of Fe 2D-SWL to the substrate in structure and relief. With a higher thickness of Fe, when the height of the Fe film relief reaches 0.5–0.9 nm, a Fe 3D-SWL is formed, which in structure and relief does not adapt to the substrate and therefore hides its stepped relief. With a further increase in thickness, segregation of Si, nanograins of Fe film, and its roughness form a completely new film surface relief.

For the production of SWL of metals on silicon, a special belt source of metal with oversputtering was developed [13, 38]. This source due to the higher area and small distance to the substrate, expanded the range of deposition rates towards its increase, as well as the range of temperature and kinetic energy of the vapor towards it decrease. At the Advanced Institute for Materials Research of Tohoku University (Japan), this source was used for the epitaxy of single-crystal Ir and Pt films as substrates for diamond films (see joint articles with Professor S. Kono for 2005–2007 [43]).

The use of a similar source for Cu deposition at low temperature and kinetic energy of vapor allowed obtaining record-breaking thin continuous SWL  $\text{Cu}_2\text{Si}$  [41]. Moreover, in these SWL, using an atomic-force microscope, a nanosquare was drawn as a product of a probe pressure-activated chemical reaction of mixing the SWL with air and the lower layers of silicon [15]. This effect demonstrated the feasibility of using SWL for direct maskless nanolithography.

In recent years, during deposition from a developed source, SWL and multilayer nanostructures with nanofilms of ferromagnetic (Fe, Co) metal and two-dimensional layers

(1–5 MLs) of non-magnetic metal (Cu) on silicon have been grown [16]. These nanostructures showed unique magnetic properties and their applicability as the drain and source of a silicon spin-field transistor. Indeed, an important stage in the creation of spin transistors is the formation of electrical and spin contacts based on ultrathin conducting and ferromagnetic layers, as well as multilayer nanofilms of ferromagnetic and non-magnetic metals. The lateral size of these contacts can reach 22 nm or less, and their nanolithography will require a proportional reduction in their thickness to nanometers and their interface to subnanometers. The use of SWL metal as a mother phase with latent energy for the formation of these silicide contacts, as well as nanolithography, will solve this problem.

#### 4. Conclusions

A review and generalization of the results of studying the metal–silicon interface obtained under identical conditions was performed. The discovery of a new, general type of transition state of the coating - a solid wetting layer, which is formed under nonequilibrium conditions and which plays a key role in the formation of the interface was substantiated. Solid wetting layers are important as a new concept for the development of thin film growth theory, as well as a new nanotechnology object for the production of thin film nanomaterials.

#### Conflict of interests

The author declares that they has no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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